NATIONAL JUNIOR COLLEGE

SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/03

Paper 3 Free Response

Monday 10 Sep 2018
2 hours

Candidates answer on separate paper.
Additional Materials: Data Booklet
Answer Paper

READ THESE INSTRUCTIONS FIRST

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

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

Section A
Answers **all** questions.

Section B
Answers **one** question.

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

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

Section A

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

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

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

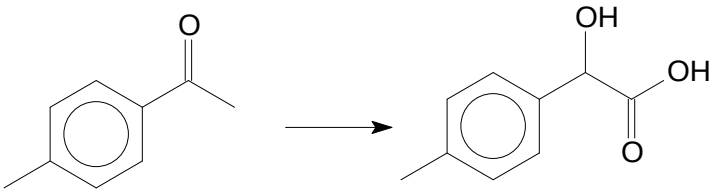
(i) Explain why the melting points of octan-1-ol and iodine are comparable. [2]

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

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

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

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



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

[5]

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

Carbon dioxide enters the water through equilibrium with the atmosphere.

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

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

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

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

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

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

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

Carbonic acid will further dissociate in the following reactions.

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

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

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

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

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

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

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

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

[4]

[Total:18]

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

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

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

[3]

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

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

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

[2]

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

[1]

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

[1]

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

[2]

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

Calculate its solubility product.

[2]

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

Table 1

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

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

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

[3]

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

[2]

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

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

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

[3]

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

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

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

[1]

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

[2]

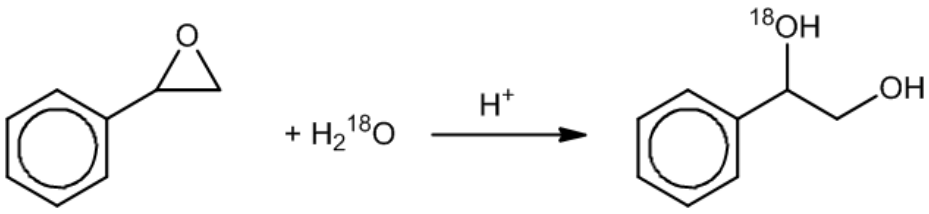
(iii) Hence calculate the melting point of $LiAlH_4$. [1]

[Total: 23]

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

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

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



styrene oxide styrene glycol

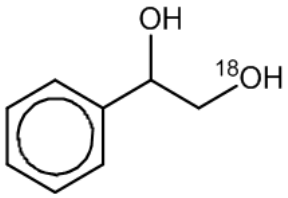
Some details of the mechanism are as given.

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

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

[3]

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



isotopic isomer **A**

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

[2]

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

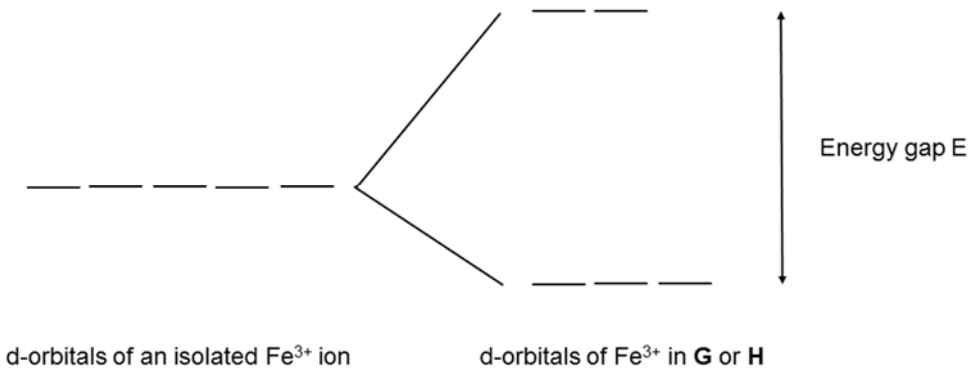
[1]

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

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

[3]

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



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

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

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

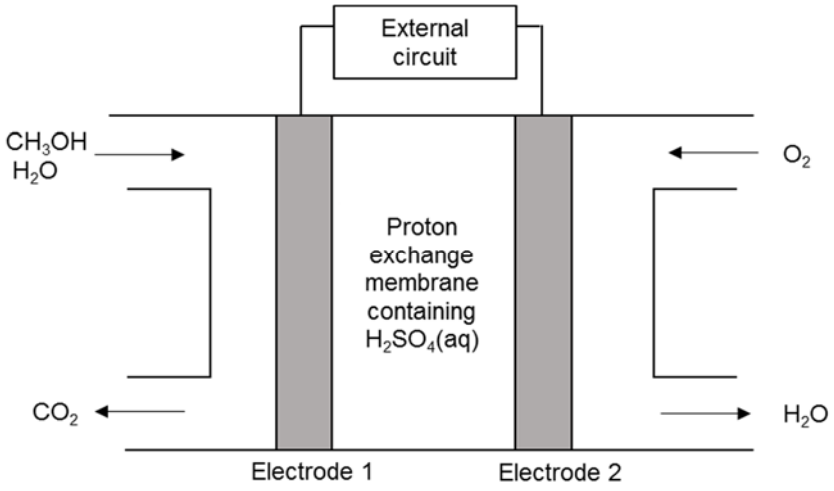
(ii) Use diagrams like the one above to show the electronic distribution of a Fe^{3+} ion in a high spin state, and in a low spin state.

[2]

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

[2]

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



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

[1]

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

[2]

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

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

[2]

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

[1]

[Total:19]

Section B

Answer **one** question from this section.

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

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

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

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

[2]

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

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

[2]

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

[2]

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

[1]

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

[3]

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

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

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

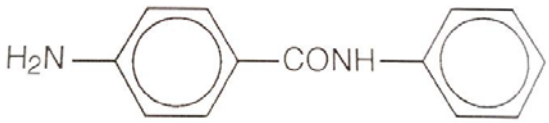
Compound **E** reacts with phosphorus pentachloride to give compound **F**, $C_8H_7NO_2$.

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

[10]

[Total:20]

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



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

[2]

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

[2]

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

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

[2]

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

[2]

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

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

[2]

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

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

J reacts with $LiAlH_4$ to form **K**, $C_5H_{12}O_2$. On heating with excess concentrated H_2SO_4, **K** forms **L**, C_5H_8. **L** does not exhibit cis-trans isomerism. When **L** is heated with acidified $KMnO_4$ solution, **M,** $C_3H_4O_3$ is formed.

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

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

[10]
[Total:20]

COVER PAGE

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PRELIM EXAMINATION

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