NAME ______________________________ CLASS **19S**

# JURONG PIONEER JUNIOR COLLEGE
## JC2 PRELIMINARY EXAMINATION 2020

# CHEMISTRY

**9729/02**

## Higher 2

Paper 2 Structured Questions

**17 September 2020**

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A *Data Booklet* is provided.

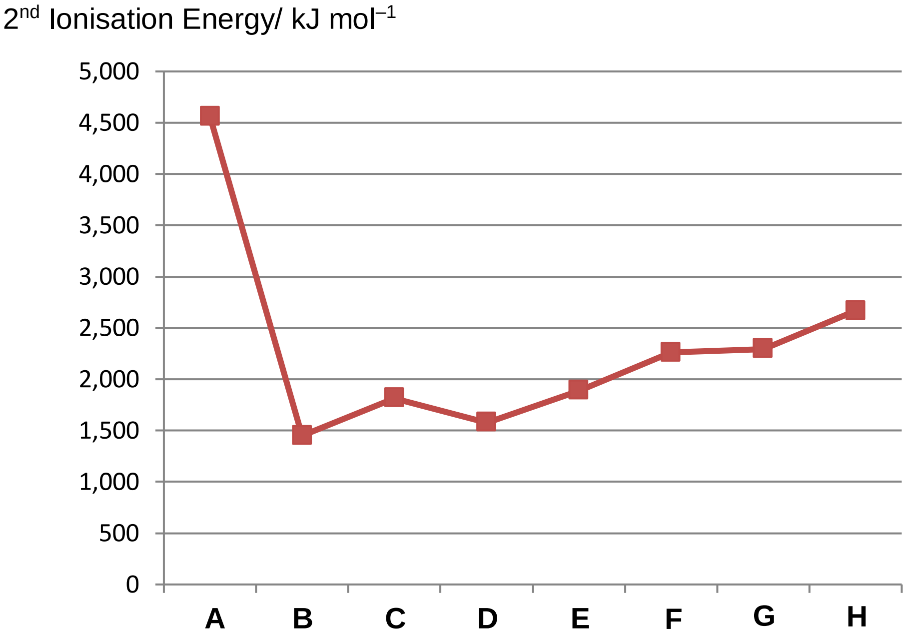
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

| | | |
|---|---|---|
| **For Examiner's Use** | | |
| **Paper** | **Question** | **Mark** |
| **2** | **1** | **13** |
| | ***2*** | **9** |
| | **3** | **14** |
| | **4** | **12** |
| | **5** | **6** |
| | **6** | **21** |
| **Penalty** (delete accordingly) | | |
| Lack **3sf** in final ans | | **–1 / NA** |
| Missing/wrong **units** in final ans | | **–1 / NA** |
| **Total** | | **75** |

This document consists of **21** printed pages.

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

**1** **(a)** The following graph below shows the **second** ionisation energies of Period 3 elements with consecutive proton number.



**(i)** Explain why the second ionisation energy generally increases from **B** to **H**.

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**(ii)** Which of the above elements, **A** to **H**, is aluminium?

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**(iii)** Explain the following:

- big drop in second ionisation energy from **A** to **B**
- slight drop in second ionisation energy from **C** to **D**

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**(b)** Among the elements of Group 14, those towards the top, carbon to germanium, have very different properties from those at the bottom, tin and lead. For example, the melting points show a marked change after germanium.

| element | C | Si | Ge | Sn | Pb |
|---|---|---|---|---|---|
| mp / °C | >3550 | 1410 | 937 | 232 | 327 |

Carbon, silicon and germanium each form a solid with the same type of structure.

**(i)** Explain why the melting points of these elements decrease from carbon to germanium.

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**(ii)** Carbon and silicon each form a tetrachloride. $CCl_4$ has no reaction with water; $SiCl_4$ reacts violently with water. Suggest an explanation for the inertness of $CCl_4$ to water.

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**(c)** The chalcogens are Group 16 elements which form compounds with carbon. The properties of some of these compounds, along with $CO_2$, are given in the Table 1 below.

**Table 1**

| **compound** | **structure** | **dipole moment** | **boiling point / °C** |
|---|---|---|---|
| $CO_2$ | O=C=O | 0 | sublimes |
| $CS_2$ | S=C=S | 0 | 46 |
| COS | S=C=O | 0.71 | –50 |
| COSe | Se=C=O | 0.73 | –22 |

**(i)** Explain, in terms of structure and bonding, the difference in the boiling point of $CS_2$ and COS.

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**(ii)** Explain why

- $CO_2$ has no overall dipole moment.
- COSe has a greater dipole moment than COS.

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…………………………………………………………………………………… [2]

**(d)** Chalcogens also form compounds with halogens known as chalcohalides. One such compound is selenium tetrafluoride, $SeF_4$, which is used as a fluorinating reagent in organic syntheses.

Draw a ‘dot-and-cross’ diagram showing the electrons (outer shell only) in a $SeF_4$ molecule. Use the VSEPR (valence shell electron pair repulsion) theory to predict its shape.

[2]

[Total:13]

**2** **(a)** The key reaction during the Contact process for the manufacture of sulfuric acid is as follows.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

A mixture of $SO_2$ and $O_2$ in a 2:1 molar ratio was introduced into a sealed vessel and heated to 450K.

At equilibrium it was found that the total pressure was 4.2 atm, and the mole fraction of $O_2$ was 0.0476.

**(i)** Write an expression for the equilibrium constant, $K_p$ for this reaction.

[1]

**(ii)** Calculate the equilibrium partial pressures of $O_2$, $SO_2$ and $SO_3$.

[2]

**(iii)** Calculate the value of $K_p$ for the reaction at 450K.

[1]

**(iv)** Explain clearly the effect on the yield of $SO_3$, when the volume of reaction mixture is reduced.

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…………………………………………………………………………………… [2]

**(b)** Due to the importance of the Contact process, the spontaneity of the reaction has been studied extensively.

**(i)** Predict the sign of the entropy change for the Contact process reaction. Explain your answer clearly.

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…………………………………………………………………………………… [2]

**(ii)** The enthalpy change for the Contact process is exothermic. Hence, using the answer in **(b)(i)**, explain why this reaction is only spontaneous at low temperature.

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[Total:9]

**3** **(a)** A sample of ground copper powder was contaminated with zinc powder. Treatment of the sample with an excess of hydrochloric acid produced 126 $cm^3$ of hydrogen gas, measured at a temperature of 300 K and a pressure of $1.00 \times 10^5$ Pa, by the reaction shown.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

The remaining copper was then reacted with acidified potassium manganate(VII), forming a blue solution containing $Cu^{2+}(aq)$.

It was found that 24.00 $cm^3$ of 0.2 mol $dm^{-3}$ of potassium manganate(VII) was required for complete oxidation of the copper.

**(i)** Calculate the mass of zinc present in the sample.

[2]

**(ii)** Write a balanced **ionic** equation for the reaction between acidified $MnO_4^-$ and Cu. Hence, calculate the percentage by mass of copper in the original sample.

[2]

**(b)** Zinc and copper can react to form zinc(II) sulfide, ZnS, and copper(II) sulfide, CuS, both of which are used as semi-conductors.

The values of the solubility products of ZnS and CuS are given below.

$$K_{sp}\text{ (ZnS)} = 1.6 \times 10^{-24}$$
$$K_{sp}\text{ (CuS)} = 6.3 \times 10^{-36}$$

**(i)** Write an expression for $K_{sp}$ for ZnS, giving its units.

[1]

**(ii)** Calculate the solubility of ZnS in mol dm$^{-3}$.

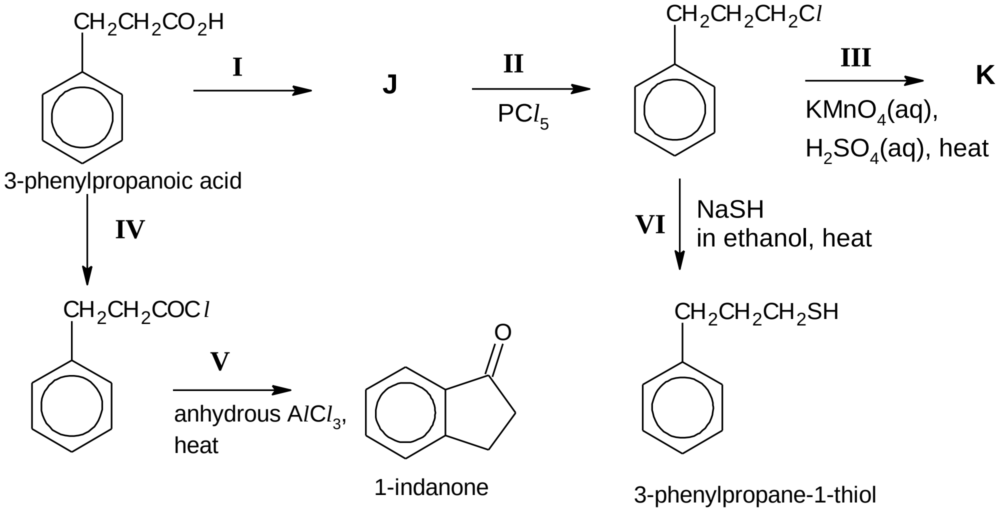
[1]

**(iii)** An experiment was carried out by a chemist in the laboratory involving these two sulfides. Solid ZnS was shaken with water thoroughly. The remaining solid was filtered off, leaving a saturated solution. Drops of aqueous copper nitrate were added to the saturated solution, until CuS just precipitated.

Determine the concentration of $Cu^{2+}$ when CuS just precipitated.

[1]

**(c)** The flow-scheme below outlines the routes from 3-phenylpropanoic acid to form 3-phenylpropane-1-thiol and 1-indanone, both of which are used to synthesise inhibitors for the treatment of rheumatoid arthritis and Alzheimer's disease.



**(i)** Draw the structure of Compound **K**.

[1]

**(ii)** Give the reagents and conditions for step **I**.

step **I** : ……………………………………………………… [1]

**(iii)** Suggest the role of $SH^-$ ion in step **VI.**

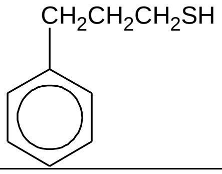
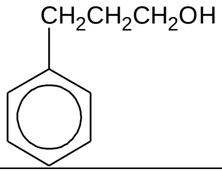
……………………………………………………… [1]

**(iv)** Name and draw the mechanism for step **V**.

[3]

**(v)** Suggest a reason why the p$K_a$ of 3-phenylpropane-1-thiol is lower than that of 3-phenylpropan-1-ol in Table 3 below.

**Table 3**

| **Name** | **structure** | **p$K_a$** |
|---|---|---|
| 3-phenylpropane-1-thiol |  | 10.2 |
| 3-phenylpropan-1-ol |  | 16.9 |

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[Total:14]

**4** **(a)** Copper is purified by electrolysis. When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with iron and silver as minor impurities. It contained no other metal. In order to purify it, this alloy was made the anode of an electrolysis cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.
After some time, copper was coated at the cathode and metal **X** was found at the bottom of anode.

**(i)** Write equations to show the reactions that have occurred at the anode and cathode.

equation at the anode:………………………………………………

equation at the cathode:………………………………………………

[2]

**(ii)** Identify metal **X**.

[1]

**(iii)** Given the following information,
surface area of cathode before electrolysis = 30 $cm^2$
density of copper = 8.96 g $cm^{-3}$

Calculate the minimum time, in hours, needed to coat a layer of 0.2 mm of pure copper on the cathode if a current of 3.0 A was used.

[2]

**(b)** Four different constitutional (structural) isomers, **L**, **M**, **N** and **P**, with molecular formula of $C_8H_8NOCl$, were tested in order to identify them.

Table 4 shows the results of the tests carried out on the four isomers.

**Table 4**

| | 2,4-DNPH | reaction with drops of water | Tollens' reagent | reaction with warm $AgNO_3$(aq) | Fehling's reagent |
|---|---|---|---|---|---|
| **L** | no precipitate | fumes which turn damp litmus paper blue to red | no silver mirror | white ppt formed immediately | no precipitate |
| **M** | orange precipitate | no change | silver mirror | white ppt formed after some time | no precipitate |
| **N** | orange precipitate | no change | silver mirror | no ppt | no precipitate |
| **P** | orange precipitate | no change | silver mirror | white ppt formed after some time | brick red precipitate |

**(i)** All four isomers decolourised orange aqueous bromine with white precipitate formed. One mole of each isomer reacts with two moles of aqueous bromine.

**None** of the four isomers **L**, **M**, **N** and **P** reacts with sodium metal.

Write an equation to show the reaction of the **functional group** of any one of the isomers, **L**, **M**, **N** or **P**, with aqueous bromine. You may use R to represent the rest of the molecule.

[1]

……………………………………………………………………………………

**(ii)** Draw the structure of **L**.

[1]

**(iii)** Explain the difference in observations when **M** and **N** react separately with warm $AgNO_3$(aq). Hence, deduce the structure of **N**.

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…………………………………………………………………………………

[2]

**(iv)** Compound **P** contains a chiral centre. Explain the chemistry of the reactions that **P** undergoes, and draw the structure of **P**.

[3]
[Total:12]

*For Examiner's Use*

**5** Many classes of organic compounds can undergo oxidation with potassium manganate(VIII). The structures of these organic compounds can then be elucidated though careful analysis of the oxidation products.

The following equation would enable you to deduce the structure of the **sweet-smelling** organic compound **R**, which contains **alkene** functional groups.

$$\underset{(C_{14}H_{16}O_2)}{\mathbf{R}} \xrightarrow{KMnO_4} \underset{(C_7H_6O_3)}{\mathbf{S}} + \underset{(C_2H_4O_2)}{\mathbf{T}} + \underset{(C_3H_6O)}{\mathbf{U}} + 2CO_2$$

**(a)** The following statements describe the reactions of compounds **S** and **T**.

- **S** reacts with neutral aqueous $FeCl_3(aq)$ to form a purple colouration.
- Both **S** and **T** effervesces with aqueous sodium carbonate, producing a gas that gives a white precipitate in limewater.

Suggest the structures for compounds **S** and **T**.

| | |
|---|---|
| **S** | **T** |

[2]

**(b)** Compound **U** gives yellow crystals when it is warmed with alkaline aqueous iodine.

State the type of reaction occurred. Suggest the structure for compound **U**.

............................................................................................ [2]

**(c)** What does the production of 2 mol of carbon dioxide gas from 1 mol of **R** reveal about the structure of **R**?

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

**(d)** You now have sufficient information to elucidate the structure of compound **R**. Give the structure of **R**.

[1]

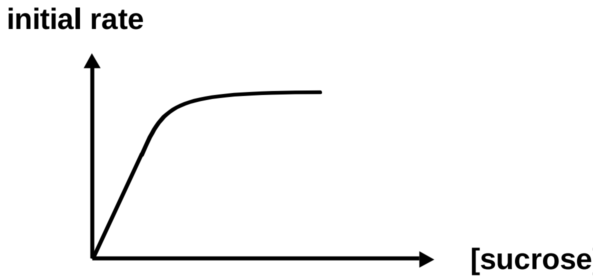
[Total:6]

**6** **(a)** Enzymes are special proteins that function as biological catalysts. They speed up the rate of chemical reactions in our body to help support life.

An example is the enzymatic hydrolysis of the complex sugar, sucrose, by the enzyme invertase to form simple sugars, fructose and glucose.

$$\text{sucrose} \xrightarrow{\text{invertase}} \text{fructose + glucose}$$

The graph below shows the initial rate of hydrolysis against [sucrose].



Explain the shape of the graph and determine the order of reaction with respect to [sucrose] when:

- concentration of sucrose is low;
- concentration of sucrose is high.

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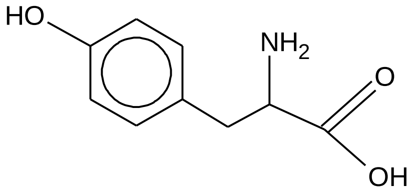
………………………………………………………………………………………… [2]

**(b)** Tyrosine is a non-essential amino acid that is present in the structure of almost every protein in the human body. It plays an important role in the production of neurotransmitters, which help nerve cells communicate and influence our mood.

The structure of a Tyrosine molecule is given below.



Some important information of Tyrosine is given below.

- Melting point: 343°C
- The p$K_a$ values associated with the amino acid are 2.20, 9.11 and 10.2.
- For fully protonated Tyrosine, $H_3N^+CH(CH_2C_6H_4OH)CO_2H$, it is known that the phenol group would be the last to lose a proton.

**(i)** Provide an explanation for the high melting point of Tyrosine amino acid.

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……………………………………………………………………………………… [1]

**(ii)** Give the structures of the major chemical species that would be present in solutions of Tyrosine at various pH values given below:

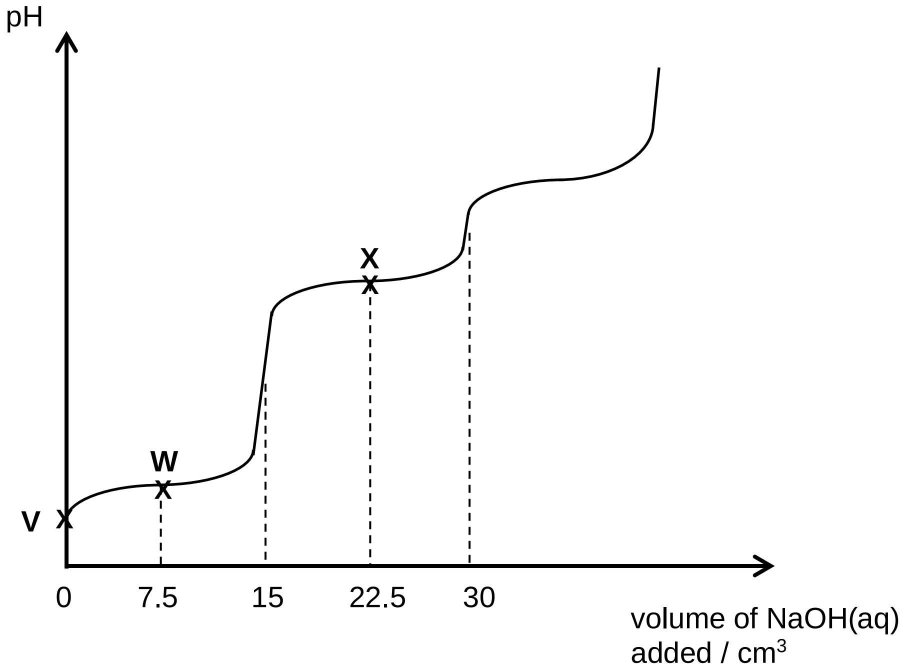
- pH = 9.5
- pH = 13

**structure at pH = 9.5**

**structure at pH = 13**

[2]

**(c)** The graph below is obtained when a solution containing 0.100 mol dm$^{-3}$ of fully protonated Tyrosine, $H_3N^+CH(CH_2C_6H_4OH)CO_2H$, is titrated with aqueous sodium hydroxide.



**(i)** Calculate the initial pH at point **V**. (ignore the effects of p$K_2$ and p$K_3$ of protonated Tyrosine on the pH)

[1]

**(ii)** The two major organic species present at point **W** are given below:
$H_3N^+CH(CH_2C_6H_4OH)CO_2H$ and $H_3N^+CH(CH_2C_6H_4OH)CO_2^-$.

Write equations to show how these organic species present help to resist pH changes when the following are added separately:

- HC*l* (aq)
- NaOH(aq)

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……………………………………………………………………………………… [2]

**(iii)** In light of your answer to **(c)(ii)** or otherwise, state the pH at point **W**.

pH at **W**: …………………………………………………………

[1]

**(iv)** From Table 6.1 below, suggest a suitable indicator that you would use to detect the first equivalence point. Briefly explain your choice.

**Table 6.1**

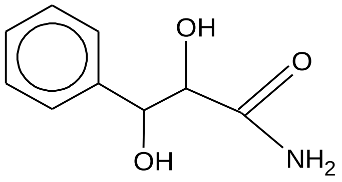
| **indicator** | **colour (lower pH)** | **pH range** | **colour (upper pH)** |
|---|---|---|---|
| dichlorofluorescein | colourless | 3.5 – 6.6 | green |
| alizarin yellow | yellow | 10.0 – 12.1 | red |

……………………………………………………………………………………

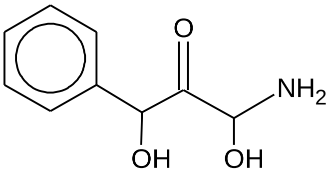
……………………………………………………………………………………

[1]

**(d)** The structures of compound **Y** and compound **Z**, $C_9H_{11}NO_3$, which are isomers of Tyrosine, are given below. **Y** and **Z** are used as plant fertilisers.



compound **Y**



compound **Z**

**(i)** Compare the base strength of the nitrogen-containing functional groups in compound **Y** and compound **Z**. Explain your answer.

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…………………………………………………………………………………… [2]

Compound **Y** is one of the many chemicals that can be found in a plant fertiliser.

A known mass of the fertiliser was boiled with an excess of dilute potassium hydroxide, KOH. $NH_3$ gas was evolved.

The $NH_3$ gas was absorbed in water and titrated with dilute sulfuric acid.

The equation for the reaction of compound **Y** with dilute KOH to produce $NH_3$ is given below.

$C_6H_5CH(OH)CH(OH)CONH_2 + OH^- \rightarrow C_6H_5CH(OH)CH(OH)COO^- + NH_3$

When 1.20 g of a fertiliser was subjected to this treatment, the resulting solution containing the $NH_3$ gas required 25.20 $cm^3$ of 0.100 mol $dm^{-3}$ $H_2SO_4$ for complete reaction.

**(ii)** Given that the molar mass of **Y** is 181 g $mol^{-1}$, determine the percentage of compound **Y** in this fertiliser.

[2]

**(e)** Due to its high reactivity towards nitrogen gas, lithium nitride is often used as an intermediate to “fix” nitrogen in the production of ammonia-based fertilisers.

$$N_2(g) \xrightarrow{+\text{ Li}} Li_3N \xrightarrow{+\text{ }H_2O} NH_3 + \text{ compound } \mathbf{U}$$

**(i)** Construct a balanced equation for the reaction between $Li_3N$ and water, identifying compound **U**.

………………………………………………………………………………… [1]

**(ii)** *Use of the Data Booklet is relevant to this part of the question.*
How would you expect the magnitude of the lattice energy of barium oxide, BaO to be compared with that of lithium nitride, $Li_3N$? Explain your answer.

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…………………………………………………………………………………

………………………………………………………………………………… [2]

…………………………………………………………………………………………

**(f)** Ammonia, $NH_3$, reacts with boron trifluoride, $BF_3$, to form a compound of the formula $H_3N.BF_3$. State and explain if $NH_3$ and $BF_3$ are behaving as Lewis acid or Lewis base in this reaction.

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………………………………………………………………………………………… [2]

**(g)** **(i)** Hydrazine ($N_2H_4$) is a colourless liquid with a slight odour like ammonia. However, the solubility of hydrazine in water is higher than that of ammonia.

Account for the difference in solubility of hydrazine and ammonia in water.

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

**(ii)** Table 6.2 lists the boiling points of hydrazine and hydrogen peroxide. Suggest a reason why the boiling point of $H_2O_2$ is significantly higher than that of $N_2H_4$.

**Table 6.2**

| Compound | $M_r$ | boiling point/ $^oC$ |
|---|---|---|
| $N_2H_4$ | 32.0 | 114 |
| $H_2O_2$ | 34.0 | 150 |

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[Total:21]

**End of paper**