Class Adm No

Class	Adm No

Candidate Name: ____________________

H

millennia institute

2024 Mid-Year Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **28 June 2024**

2 hours

Candidates answer on the Question paper.
Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST
Do not turn over this question paper until you are told to do so.
Write your name, class and admission number on all the work you hand in.
Write in dark 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.
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.

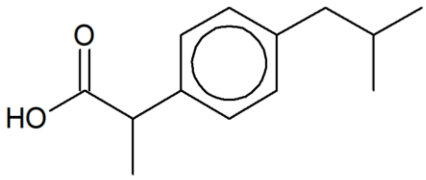
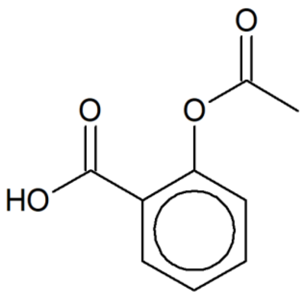
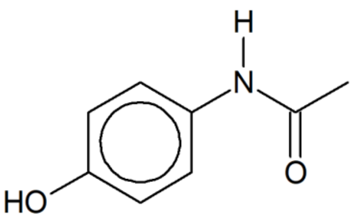
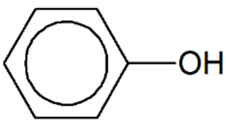
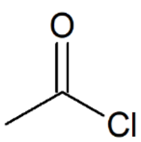
Question	**1**	**2**	**3**	**4**	**5**	Total
Marks	**15**	**16**	**15**	**16**	**13**	**75**

Answer **all** questions.

For Examiners' Use

1 Ibuprofen, aspirin, and paracetamol are commonly sold as over-the-counter painkillers that offer versatile relief for different forms of pain. Table 1.1 shows the physical properties of the painkillers and some organic compounds.

Table 1.1

compound	M_r	melting point / °C	solubility in water / g dm^{-3}	solubility in ethanol / g dm^{-3}	density / g cm^{-3}
 ibuprofen ($C_{13}H_{18}O_2$)	206.0	75	0.021	1.2	1.03
 aspirin ($C_9H_8O_4$)	180.0	135	3.0	80	1.40
 paracetamol ($C_8H_9NO_2$)	151.0	169	12.8	130	1.26
 phenol (C_6H_6O)	94.0	40.5	84.2	highly soluble	1.07
 ethanoyl chloride (C_2H_3OCl)	78.5	–112	–	–	1.10

A student was provided with three unlabelled tablets, one from each of the three different painkillers. To identify them, he crushed each of the tablets and dissolved them in ethanol. To a small portion of each solution, he conducted two simple chemical tests to distinguish between the painkillers.

For Examiners' Use

(a) **(i)** Define the term *relative molecular mass*, M_r.

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....

.... [1]

(ii) Suggest, briefly, two reasons for the difference in solubilities between ibuprofen and paracetamol in water.

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.... [2]

(iii) Suggest the reagents and conditions, stating the observations, for the two simple chemical tests used to distinguish between ibuprofen, aspirin, and paracetamol.

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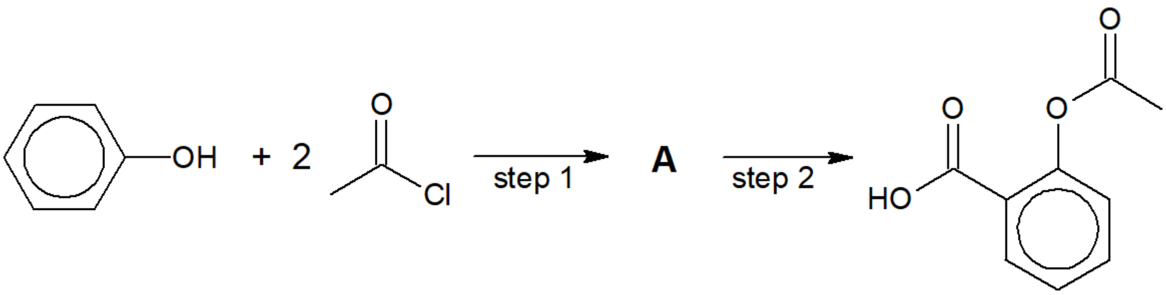
.... [4]

(b) The student planned to synthesise aspirin from phenol and ethanoyl chloride (in 1 : 2 molar ratio) via an acylation reaction to form an intermediate **A**, before turning it into aspirin under controlled conditions in step 2.



The liquid ethanoyl chloride was measured out using a graduated gas syringe and added to phenol in an inert solvent.

(i) Suggest a catalyst for step 1.

....[1]

(ii) Draw the structure of the intermediate **A**.

[1]

(iii) State the reagents and conditions for step 2.

....

....[1]

(iv) Calculate the volume of ethanoyl chloride that is needed to completely react with 4.00 g of phenol to form aspirin using the suggested synthetic pathway in **(b)(i)**.

[3]

For Examiners' Use

(v) The resultant aspirin product was washed, dried, and weighed. Given that 5.57 g of aspirin was formed, calculate the percentage yield of the reaction.

[1]

(vi) Suggest why there are no solubility values for ethanoyl chloride.

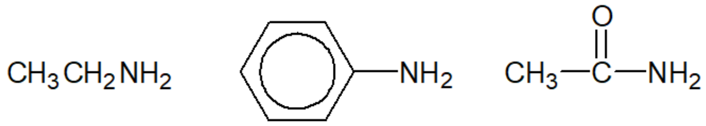
....

....[1]

[Total: 15]

For Examiners' Use

2 **(a)** Arrange the following molecules in increasing order of gas phase relative basic strength, explaining your answer.



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.... [4]

(b) Ethylamine, $CH_3CH_2NH_2$, can be formed from ethane, CH_3CH_3, via the following steps.

Step 1: Free radical substitution of ethane to form chloroethane.

Step 2: Nucleophilic substitution of chloroethane to ethylamine.

(i) Outline the mechanism for step 1. Draw curly arrows to show the movement of electrons.

[3]

For Examiners' Use

(ii) Suggest the reagents and conditions for step 2.

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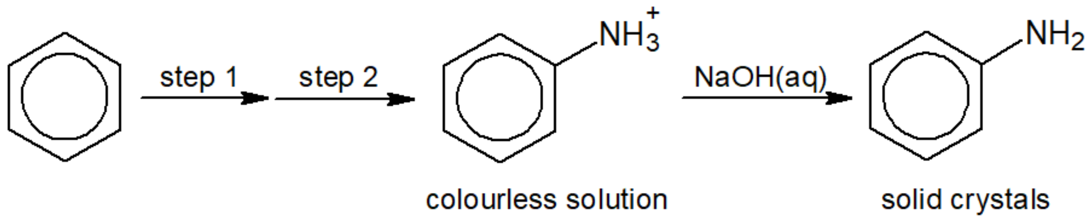
....[1]

(c) Phenylamine, $C_6H_5NH_2$, can be synthesised from benzene.



(i) Suggest the reagents and conditions for steps 1 and 2 and state the type of reaction in each step.

Step 1: ....

....

Step 2: ....

....[4]

(ii) After step 2, a colourless solution containing phenylammonium ions, $C_6H_5NH_3^+$, was obtained. Upon addition of NaOH(aq), solid crystals of phenylamine, $C_6H_5NH_2$, precipitated out of the colourless solution.

Explain the observations in terms of the interactions between particles.

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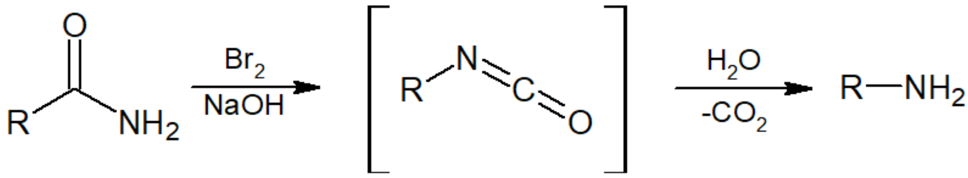
....[2]

For Examiners' Use

(d) The Hofmann degradation is an organic rearrangement reaction of a primary amide to a primary amine with the loss of one carbon atom. The reagent is heated under reflux with bromine in sodium hydroxide to transform the primary amide into an isocyanate intermediate, which is subsequently hydrolysed to a primary amine.

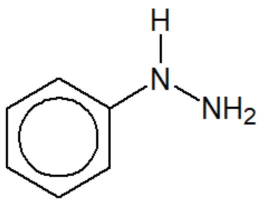


isocyanate intermediate

Suspect the amide used to produce the following products via the Hoffmann degradation.

(i) $\rightarrow$ $CH_3CH_2NH_2$

[1]

(ii) $\rightarrow$ 

[1]

[Total: 16]

3 **(a)** Use of the Data Booklet is relevant for this question.

(i) Define the term *first electron affinity* of fluorine.

....

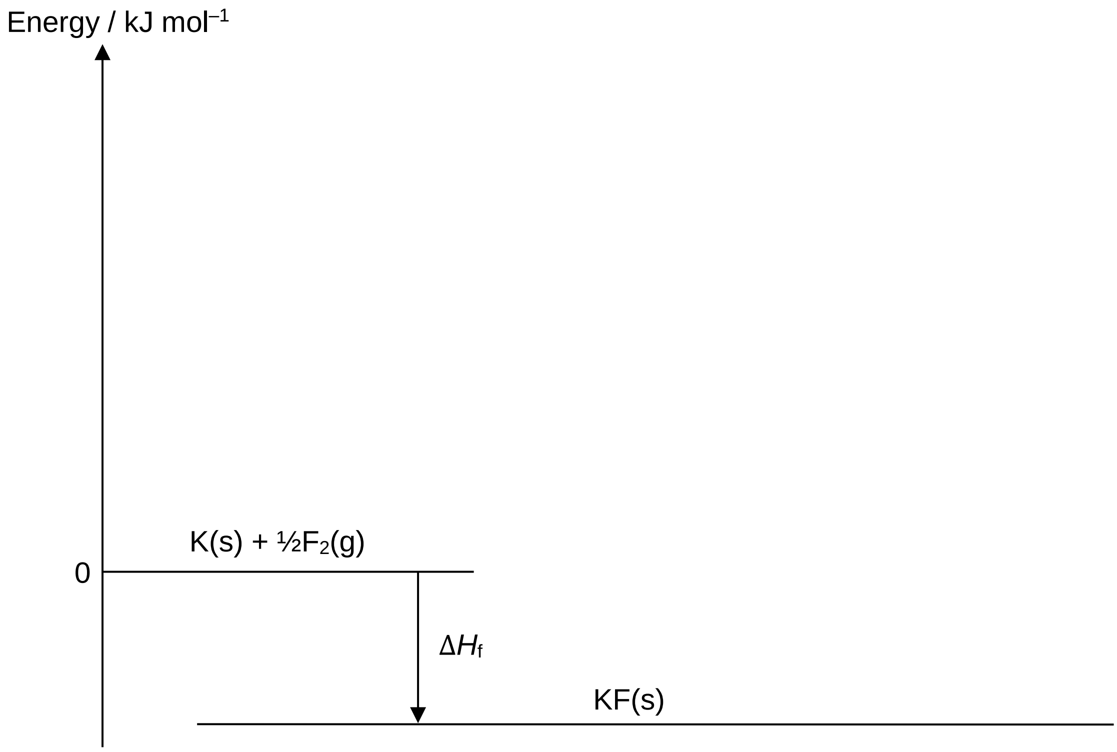
.... [1]

(ii) Potassium fluoride, KF, is a main source of fluoride ions for manufacturing and in chemistry. It is found in the mineral carobbiite.

Use the data in Table 3.1 and relevant bond energy values from the *Data Booklet* to complete the Born-Haber cycle below and hence calculate the lattice energy for KF(s).

Table 3.1

enthalpy change of formation, ΔH_f, for KF(s)	–561 kJ mol^{-1}
enthalpy change of atomisation of potassium, K(s)	+90 kJ mol^{-1}
first electron affinity of fluorine	–328 kJ mol^{-1}



[5]

For Examiners' Use

(iii) Explain how the magnitude of lattice energy of MgF_2 will compare to that of KF.

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....[2]

(iv) The enthalpy change of atomisation for calcium is +178 kJ mol^{-1}.

Account for the difference in enthalpy change of atomisation between potassium and calcium and explain it in terms of structure and bonding.

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....[2]

(b) You are provided with the following additional information.

For Examiners' Use

Table 3.2

enthalpy change of hydration of fluoride ions, $F^-(g)$	-504 kJ mol^{-1}
enthalpy change of solution of potassium fluoride, KF(s)	-15 kJ mol^{-1}

(i) Use your answer in **(a)(ii)** and the information in Table 3.2 to calculate the enthalpy change of hydration of $K^+(g)$.

[If you did not obtain a value in **(a)(ii)**, use the value of lattice energy for KF(s) to be -1739 kJ mol^{-1}. This is not the answer for **(a)(ii)**.]

[2]

(ii) Hence, or otherwise, explain the sign of the enthalpy change of hydration of $K^+(g)$.

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(c) Arrange the hydrogen halides HF, HC*l* and HBr in order of increasing thermal stability. Explain your answer.

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

[Total: 15]

4 In the automotive transformation to green and sustainable transportation options, rechargeable batteries play a significant role in determining the availability, cost, range, and safety of electric vehicles (EVs). Lithium-ion batteries (LIBs) are currently the most widely manufactured type of rechargeable battery. However, as the demand for LIBs has grown exponentially, lithium has become a limited resource. In addition, lithium mining generates undesirable environmental impacts such as air and water pollution, land degradation, and groundwater contamination.

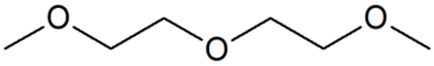
To overcome these challenges, sodium-ion batteries (SIBs) are being researched as a viable alternative. The table below shows a comparison of SIBs with common rechargeable batteries used in cars today.

Table 4.1

	sodium-ion battery	**lithium-ion battery**	**lead-acid battery**
cost per kilowatt-hour of capacity	\$40–77	\$137	\$100–300
energy density*	75–200 W·h/kg	120–260 W·h/kg	35–40 W·h/kg
no. of cycles before reaching 80% of initial capacity	300–1000	3500	900
materials	abundant	scarce	limited
safety	high risk	high risk	moderate risk
optimal temperature range for operation	−20 °C to 60 °C	15 °C to 35 °C	−20 °C to 60 °C

*Energy density is given in Watt-hour per kilogram (W·h/kg),
where 1 Watt = 1 Ampere × 1 Volt

The most promising cathode material for SIBs is Prussian White (PW), which has the formula $Na_2Fe[Fe(CN)_6]$, while the anode is typically graphite. The cathode and anode are separated by a porous membrane, with the electrolyte being diglyme.



diglyme

When the SIB is charged, sodium atoms in the PW electrode are oxidised to sodium ions, which flow past the membrane to the graphite electrode and before being reduced back to sodium atoms inside the layers of graphite. When the SIB is being discharged (i.e. being used to power appliances), the reverse process occurs.

For Examiners' Use

(a) **(i)** Draw a well-labelled diagram to illustrate the set-up for a sodium-ion battery, indicating the direction of electron-flow during the **discharging** process.

[3]

(ii) Given that the complex ion in Prussian White is $[Fe(CN)_6]^{3-}$, and that the oxidation number of the Fe ion *outside* of the complex is +2, state the average oxidation number of sodium in Prussian White.

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

(iii) During the discharging process, a potential (reversible) side reaction might occur in the Prussian White electrode.

Suggest an ion-electron equation for this side reaction, and state its standard electrode potential, $E^{\ominus}$, value.

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

(iv) Define the term *standard conditions*.

……………………………………………………………………………………………

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

(v) Suggest why an aqueous electrolyte should not be used.

……………………………………………………………………………………………

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

(b) The lead-acid battery consists of a lead metal electrode and a lead(IV) oxide electrode immersed in concentrated sulfuric acid. During discharging, both electrodes produce solid lead(II) sulfate which is coated on the surface of the electrodes.

(i) Write the ion-electron equations for the discharging process of a lead-acid battery, and hence construct the overall balanced equation.

[O]: ....

[R]: ....

Overall: .... [3]

(ii) Explain, in terms of oxidation numbers, why the reverse reaction (the charging process) of a lead-acid battery is a *disproportionation* reaction.

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....[2]

(c) Using the information presented and in Table 4.1, suggest which rechargeable battery an automotive manufacturer should adopt for use in EVs, explaining why it is preferred.

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.... [3]

[Total: 16]

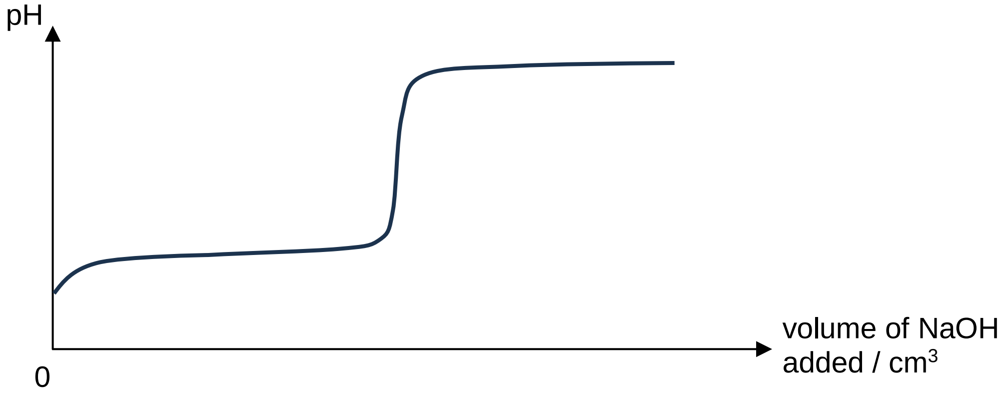
For Examiners' Use

5 Cyanic acid, HOCN, dissociates in water according to the following equation.

$$HOCN \rightleftharpoons H^+ + {}^-OCN \qquad pK_a = 3.48$$

When 25.0 cm^3 of 0.100 mol dm^{-3} cyanic acid was titrated against 0.100 mol dm^{-3} sodium hydroxide, the following pH curve was obtained. The experiment was conducted at 25 °C.

Fig. 5.1



(a) **(i)** Define the term *buffer*.

....

.... [1]

(ii) On the curve in Fig 5.1, mark out and state the numerical value of:

- the volume at equivalence point,
- the volume at maximum buffer capacity, and
- the pH at maximum buffer capacity. [3]

(b) **(i)** Write down the expression for K_a, stating its units

.... [2]

(ii) Calculate a value for K_a.

[1]

For Examiners' Use

(iii) Hence, or otherwise, calculate the initial pH of the cyanic acid solution before titration.

[2]

(c) **(i)** Calculate the concentration of the cyanate ions, [$^{-}$OCN], at equivalence point.

[1]

(ii) Hence, calculate the pH at the equivalence point.

[3]

[Total: 13]

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