# Candidate Name:



millennia institute

## **H2 CHEMISTRY**

Paper 2 Structured Questions

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

9729/02 28 June 2024 2 hours

Class Adm No

## Answer **all** questions.

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.

For Examiners' Use

compound	M <sub>r</sub>	melting point / °C	solubility in water / g dm <sup>-3</sup>	solubility in ethanol / g dm <sup>-3</sup>	density / g cm <sup>-3</sup>
HO ibuprofen (C <sub>13</sub> H <sub>18</sub> O <sub>2</sub> )	206.0	75	0.021	1.2	1.03
$HO \qquad O \qquad$	180.0	135	3.0	80	1.40
HO Paracetamol (C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub> )	151.0	169	12.8	130	1.26
phenol (C <sub>6</sub> H <sub>6</sub> O)	94.0	40.5	84.2	highly soluble	1.07
Cl ethanoyl chloride (C <sub>2</sub> H <sub>3</sub> OC <i>l</i> )	78.5	-112	_	_	1.10

## Table 1.1

For Examiners' Use

[1]

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.

(a) (i) Define the term relative molecular mass,  $M_{\rm r}$ .

The weighted average mass of one molecule relative to the  $\frac{1}{12}$  the mass of a <sup>12</sup>C atom.

Marker's comment: - Poorly done, many students wrote C<sup>12</sup>

(ii) Suggest, briefly, two reasons for the difference in solubilities between ibuprofen and paracetamol in water. [2]

<u>Stronger instantaneous dipole-induced dipole forces of attraction between ibuprofen</u> <u>molecules</u> due to the <u>larger electron cloud size</u> (Mr = 202.0) than paracetamol molecules (Mr = 151.0) OR <u>longer</u> non-polar <u>alkyl chain</u>;

Paracetamol molecules form <u>more extensive hydrogen bonding with water molecules</u> (due to greater number of electronegative O, N atoms and lone pairs available) than ibuprofen molecules. ;

Marker's comment:

- Very poorly done, with many students only giving one reason

- Many students did not make mention to main keyword of electron cloud size / no. of electrons

- Students who counted the no. of H-bonds did not correctly identify the number

(iii) Suggest the reagents and conditions, stating the observations, for the two simple chemical tests used to distinguish between ibuprofen, aspirin, and paracetamol. [4]

To 1 cm<sup>3</sup> of each solution, add neutral FeC*l*<sub>3</sub>(aq). ; Paracetamol will give a dark / violet colouration. For aspirin and ibuprofen, no dark / violet colouration OR neutral FeC*l*<sub>3</sub>(aq) remains yellow / orange. ; **OR** To 1 cm<sup>3</sup> of each solution, add Br<sub>2</sub>(aq). ; For paracetamol, orange Br<sub>2</sub>(aq) decolourises (and white ppt forms). For aspirin and ibuprofen, Br<sub>2</sub>(aq) remains orange. ; **OR** To 1 cm<sup>3</sup> of each solution, add Na<sub>2</sub>CO<sub>3</sub>(s). ; For aspirin and ibuprofen, effervescence of a gas that forms white ppt in Ca(OH)<sub>2</sub>(aq).

For paracetamol, no effervescence is observed.

To another 1 cm<sup>3</sup> of each solution, add KMnO<sub>4</sub>(aq) in H<sub>2</sub>SO<sub>4</sub>(aq), heat/warm. ; For ibuprofen, purple KMnO<sub>4</sub>(aq) decolourised (and effervescence which produces white ppt in limewater).

For aspirin and paracetamol KMnO<sub>4</sub>(aq) remains purple.

Marker's comment:

- Many students were still unable to identify the functional groups successfully (e.g. confused between ketone/aldehyde/ester/acid).

(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.



[1]

[1]

[1]

For



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.

step 1: AIC $l_3$  or FeC $l_3$  catalyst (can accept AIB $r_3$  or FeB $r_3$ );

(ii) Draw the structure of the intermediate A.





Marker's comment:

- Some students could not appreciate that the question asked for a "reaction intermediate" (stable structure) and not a "mechanism intermediate" (not so stable structure).

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

step 2:  $I_2$  NaOH, warm, followed by dilute acid ;

(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] amount of phenol used =  $4.00 \div 94.0 = 0.04255$  mol ; mass of ethanoyl chloride required =  $0.04255 \times 2 \times 78.5 = 6.68$  g ;

volume of ethanoyl chloride required =  $6.68 \div 1.10 = 6.07 \text{ cm}^3 (3 \text{ s.f.})$ ;

Marker's comment:

- Many students did not identify the data that was relevant from the table (e.g. Mr, notice units of density was g cm<sup>-3</sup>).

- A significant number of students still multiplied amount by 24.0, not recognising that the formula only applies for gases since the volume of 1 mol of gas at rtp is 24.0 dm<sup>3</sup>.

(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]

Theoretical mass of aspirin =  $0.04255 \times 180.0 = 7.66$  g [no marks, LO tested in **(b)(ii)**] % yield =  $(5.57 \div 7.66) \times 100\% = 72.7\%$ ;

Marker's comment: - Generally well done.

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

[1]

Ethanoyl chloride <u>reacts readily</u> with <u>both water and ethanol</u>; (in a nucleophilic acyl substitution reaction to form ethanoic acid and ethyl ethanoate respectively, and HC*l*).

#### Marker's comment:

- Many students did not recall that ethanoyl chloride reacts vigorously with water, choosing to talk about how it is insoluble instead (ethanoyl chloride is able to form H-bonds with water). An insoluble substance would still have a value for solubility, either a very very small number, or at the extreme end, "0". A "--" implies something else entirely. Students should also note that liquids and gases have solubility values associated to them as well.

- Some students recognised the above, but did not talk about ethanol, which is required by the question ("value<u>s</u>").

[Total: 15]

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



[4]

(weakest base)  $CH_3CONH_2 < C_6H_5-NH_2 < CH_3CH_2NH_2$  (strongest base) ;

 $CH_3CONH_2$  is neutral (not basic) as the <u>lone pair on N is delocalised due to p-orbital overlap</u> with the  $\pi$  electron cloud across the C=O. As <u>O is highly electronegative</u>, the <u>lone pair on N</u> is not available for donation (to H<sup>+</sup> usually).

 $C_6H_5$ -NH<sub>2</sub> (phenylamine): Lone pair on N is delocalised due to partial p-orbital overlap of N with  $\pi$  electron cloud of the benzene ring, hence less available for donation and weaker base ;

compared to CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> which has an <u>electron-donating alkyl group</u>, <u>increases the electron</u> density and hence availability of lone pair on N for donation, hence stronger base ;

### Marker's comment:

- Answers of many students have substance but lack keywords required.

- Students are advised to use inequality arrows for 'ranking' questions.
- (b) Ethylamine, CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>, can be formed from ethane, CH<sub>3</sub>CH<sub>3</sub>, 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]

Initiation



**Propagation** 



**Termination** 

Marker's comment:

- Not required for students to draw the half-arrows in propagation and termination steps (but aids in understanding)

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

Excess concentrated ethanolic NH<sub>3</sub>, heat in sealed tube

(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.
 [4]

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Step 1:
Electrophilic substitution
Concentrated HNO<sub>3</sub>, concentrated H<sub>2</sub>SO<sub>4</sub>, heat under reflux
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Step 2:
Reduction
Sn, concentrated HCl, heat under reflux
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#### Marker's comment:

A significant number of students tried to go via chlorobenzene as the reaction intermediate, not realising that it cannot undergo N.S..
Many students still wrote (aq) together with conc, but (aq) implies dilute.

(ii) After step 2, a colourless solution containing phenylammonium ions, C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>, was obtained. Upon addition of NaOH(aq), solid crystals of phenylamine, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, precipitated out of the colourless solution.

Explain the observations in terms of the interactions between particles.

[2]

For

Examiners Use

[1]

<u>Energy released</u> from the <u>ion-dipole interactions between the phenylammonium ion and</u> <u>water</u> was sufficient to overcome the ionic bonding (strong electrostatic forces between oppositely charged ions) in phenylammonium chloride (and the hydrogen bonding between water molecules). ;

However, the <u>energy released from the formation of hydrogen bonding between</u> <u>phenylamine and water</u> was <u>insufficient to overcome the extensive instantaneous</u> <u>dipole-induced dipole forces of attraction between phenylamine molecules</u> (and the hydrogen bonding between water molecules). ;

## Marker's comment:

- Many students did not recognise that the "observation" referred to precipitation of the solid.

The Hofmann degradation is an organic rearrangement reaction of a primary amide to a (d) Examiners Use 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

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



[1]

#### Marker's comment:

- Many students drew the correct answer but wrote "H<sub>3</sub>C" or bonded to wrong C atom



[1] [Total: 16]

For

For 3 (a) Use of the Data Booklet is relevant for this question. Examiners Use (i) Define the term *first electron affinity* of fluorine. [1] The enthalpy change (energy released) when one mole of gaseous F atoms accepts one mole of electrons to form one mole of gaseous F-ions. Marker's comment: - Poorly done. (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 -561 kJ mol-1 enthalpy change of formation,  $\Delta H_{f}$ , for KF(s) enthalpy change of atomisation of potassium, K(s) +90 kJ mol-1 -328 kJ mol<sup>-1</sup> first electron affinity of fluorine [5] Energy / kJ mol<sup>-1</sup>  $K^{+}(g) + F(g) + e^{-}$ -328 K⁺(g) + ½F₂(g) + <mark>e⁻</mark>  $K^{+}(g) + F^{-}(g)$ /<sub>2</sub>(+158) +418  $K(g) + \frac{1}{2}F_2(g)$ Lattice Energy +90  $K(s) + \frac{1}{2}F_2(g)$ 0  $\Delta H_{\rm f}$ KF(s) [1m for each highlighted component] ;,;;  $\Delta H_{\rm f} = -561 = +90 + (+418) + \frac{1}{2}(+158) + (-328) + L.E.$ L.E. =  $-561 - (+90) - (+418) - \frac{1}{2}(+158) - (-328) = -820 \text{ kJ mol}^{-1}$ ; (sign and ans) Marker's comment: - Most students still forgot to include the e<sup>-</sup> / did not draw energy level lower for negative ΔH value

For (iii) Explain how the magnitude of lattice energy of MgF<sub>2</sub> will compare to that of KF. [2] Examiners Use Charge of Mg<sup>2+</sup> is higher and ionic radius of Mg<sup>2+</sup> is smaller than K<sup>+</sup> Anion is the same ; Since  $|L.E.| \propto \left| \frac{q^+ \cdot q^-}{r^+ + r^-} \right|$  (required) L.E. for MgF<sub>2</sub> is larger than that of KF. ; Marker's comment: Many candidates are able to apply the correct concept, but left out the comparison of the anions. (iv) The enthalpy change of atomisation for calcium is +178 kJ mol<sup>-1</sup>. Account for the difference in enthalpy change of atomisation between potassium and calcium and explain it in terms of structure and bonding. [2] Both have giant metallic (lattice) structures. • Calcium has higher charge and • more delocalised electrons per atom than potassium, • more energy required to overcome the stronger metallic bonds. More endothermic enthalpy change of atomisation for calcium /OR/ • More exothermic enthalpy change of atomisation for potassium. 5pts: 2m 2-4pts: 1m 0-1pts: 0m Marker's comment: Many candidates did not attempt this question or are unable to apply the correct concept. Some of the candidates who applied the correct concept used 'enthalpy change of atomisation for calcium increases' instead of 'more endothermic'. (b) You are provided with the following additional information. For Examiners Use Table 3.2

enthalpy change of hydration of fluoride ions, F <sup>-</sup> (g)	–504 kJ mol⁻¹
enthalpy change of solution of potassium fluoride, KF(s)	–15 kJ mol <sup>–1</sup>

(i) Use your answer in (a)(ii) and the information in Table 3.2 to calculate the enthalpy change of hydration of K<sup>+</sup>(g).

[If you did not obtain a value in **(a)(ii)**, use the value of lattice energy for KF(s) to be  $-1739 \text{ kJ mol}^{-1}$ . This is not the answer for **(a)(ii)**.] [2]

Lattice Energy +  $\Delta H_{\text{solution}} = \Delta H_{\text{hyd}} (\text{K}^+(\text{g})) + \Delta H_{\text{hyd}} (\text{F}^-(\text{g}))$  $\Delta H_{\text{hyd}} (\text{K}^+(\text{g})) = \text{Lattice Energy} + \Delta H_{\text{solution}} - \Delta H_{\text{hyd}} (\text{F}^-(\text{g}))$ 

Using -820 answer from **(a)(ii)**,  $\Delta H_{hyd} (K^+(g)) = -820 + (-15) - (-504) = -331 \text{ kJ mol}^{-1}$ If using -1739,  $\Delta H_{hyd} (K^+(g)) = -1739 + (-15) - (-504) = -1250 \text{ kJ mol}^{-1}$ 

(1m for the relationship between the terms / substitution, 1m for final answer with sign). Marker's comment:

Weaker candidates were not able to show the correct relationship to calculate enthalpy change of hydration.

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

[1]

Formation of ion-dipole attractions between gaseous ions and water molecules <u>releases</u> <u>energy</u>. Since there is <u>no bond-breaking</u>, the enthalpy change of hydration of an ion is always exothermic.

Marker's comment:

This question proved to be demanding. Candidates who applied the correct concept did not mention the lack of bond-breaking.

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

[2]

[Total: 15]

Down Group 17, the H–X bond becomes <u>weaker</u> Due to <u>increasing</u> atomic radius of the halogen atom X /OR/ <u>longer</u> H–X bond, <u>less effective orbital overlap</u> between H and X. ;

**less energy** to break H–X bond /OR/ thermal stability of HX molecule decreases. order of thermal stability: (lowest) HBr(g) < HCl(g) < HF(g) (highest) ;

Marker's comment:

Candidates confused the explanation for thermal stability of hydrogen halides with thermal stability of Group 2 metal carbonates/oxides/nitrates.

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.

	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

Table 4.1

\*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.



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

For (i) Draw a well-labelled diagram to illustrate the set-up for a sodium-ion battery, indicating (a) Examiners' Use the direction of electron-flow during the **discharging** process. [3]

Labels + drawing +,cathode, anode direction of electron flow identity of both electrodes electrolyte membrane + voltmeter / load (6pts: 3m, 4-5pts: 2m, 2-3pts: 1m, 0-1pts: 0m) Suggested diagram Anode **Cathode** Graphite Prussian White / Na<sub>2</sub>Fe[Fe(CN)<sub>6</sub>] membrane diglyme Also accept:



Marker's comment:

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Many candidates are able to identify the correct electrodes with correct signs and electron flow. Only some candidates included membrane as part of the set-up.

(ii) Given that the complex ion in Prussian White is [Fe(CN)<sub>6</sub>]<sup>3-</sup>, 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.

+0.5

Marker's comment: Majority of the candidates did well in this question.

(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,  $E^{\Theta}$ , value. [2]

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\begin{array}{ll} [Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-} & E^{\Theta} = +0.36 \text{ V} \\ \text{OR} \\ Fe^{2+} + 2e^- \rightarrow Fe & E^{-\Theta} = -0.44 \text{ V} \end{array}
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Marker's comment:

This question proved to be challenging. Some candidates gave  $Fe^{3+} + e^- \rightarrow Fe^{2+}$ 

(iv) Define the term standard conditions.

Temperature of 298 K, Pressure of 1 bar for any gases, Concentration of 1 mol dm<sup>-3</sup> for any aqueous species.

Marker's comment:

Majority of the candidates left out the 'concentration of 1 mol dm<sup>-3</sup> for any aqueous species'.

[1]

[1]

- (v) Suggest why an aqueous electrolyte should not be used.
  - During charging, electrolysis of water would occur instead / redox reactions involving water would interfere in the charging process OR
  - Sodium metal would not be produced in aqueous electrolytes OR
  - Sodium reacts vigorously / in a highly exothermic reaction with water

Marker's comment: Many of the candidates gave vague answers.

(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.
For Examiners Use

(i) Write the ion-electron equations for the discharging process of a lead-acid battery, and hence construct the overall balanced equation. [3]

 $\begin{array}{l} \label{eq:constraint} [O]: Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^- \\ [R]: PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O \\ (accept PbO_2 + 2H^+ + \underline{H_2SO_4} + 2e^- \rightarrow PbSO_4 + 2H_2O) \\ Overall: Pb + PbO_2 + 2SO_4^{2-} + 4H^+ \rightarrow 2PbSO_4 + 2H_2O \\ (accept Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O) \end{array}$ 

## OR

[accept if left out SO<sub>4</sub><sup>2-</sup> spectator ion: but max 2m] [O]: Pb  $\rightarrow$  Pb<sup>2+</sup> + 2e<sup>-</sup> [R]: PbO<sub>2</sub> + 4H<sup>+</sup> + 2e<sup>-</sup> $\rightarrow$  Pb<sup>2+</sup> + 2H<sub>2</sub>O Overall: Pb + PbO<sub>2</sub> + 4H<sup>+</sup>  $\rightarrow$  2Pb<sup>2+</sup> + 2H<sub>2</sub>O

## Marker's comment:

This question proves to be challenging. Some candidates were able to identify the correct ion-electron equation for oxidation but left out  $SO_4^{2^-}$  spectator ion. Very few candidates were able to identify the ion-electron equation for reduction. Weaker candidates used reversible arrows for the equations.

(ii) Explain, in terms of oxidation numbers, why the reverse reaction (the charging process) of a lead-acid battery is a *disproportionation* reaction. [2]

Oxidation number of <u>Pb in PbSO<sub>4</sub></u> is <u>increased</u> from <u>+2</u> to <u>+4</u> in <u>PbO<sub>2</sub></u> (oxidation) and simultaneously <u>decreased</u> to <u>0</u> in <u>Pb</u>. Since a <u>single species</u> PbSO<sub>4</sub> was <u>simultaneously oxidised and reduced</u>, disproportionation has occurred.

Marker's comment:

Many candidates were able to apply the concept but did not include the species after stating the oxidation state of the element in that species.

(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. [3]

[Total: 16]

## SIBs (max 3m)

- Cheapest to manufacture compared to LIBs and LABs (as sodium is a readily available resource / in large supply.)
- Lowest environmental impact to manufacture as sodium is an abundant resource.
- Higher temperature range of operation for SIBs than LIBs

(Do not look at cycling stability as both are high)

LIBs (max 3m)

- Lithium is most lightweight / lowest density / lower mass per unit volume
- LIBs has highest energy density / stores more energy per unit mass than SIBs & LABs / longer range
- Longest lifespan / maintains capacity at >80% for the largest number of cycles.

LABs (max 3m)

- Lowest risk of (chemical) fire / safest compared to sodium or lithium leaks
- Higher temperature range of operation for LABs than LIBs
- (to award 3m, student must have justified safety as the top most concern then the 3<sup>rd</sup> reason will be the materials for manufacture are quite readily available, if not, do not accept this reason.)

### Marker's comment:

Weaker candidates did not compare the chosen rechargeable battery with the other two batteries.

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

$$HOCN \rightleftharpoons H^+ + OCN \quad pK_a = 3.48$$

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



[Turn over

For

Examiners Use Marker's comment:

Majority of the candidates did well in this question. Weaker candidates did not include the correct labelling and wrong identification of the volume at maximum buffer capacity.

(b) (i) Write down the expression for 
$$K_{a}$$
, stating its units. [2]

$$K_{a} = \frac{\left[H^{+}\right]\left[-OCN\right]}{\left[HOCN\right]} ; \text{ mol dm}^{-3} ;$$

Marker's comment: Almost all of the candidates were able to do this question.

(ii) Calculate a value for  $K_{a}$ .

 $K_{\rm a} = 10^{-3.48} = 3.311 \times 10^{-4}$ (do not penalise for units here)

Marker's comment: Many candidates know the relationship between  $K_a$  and  $pK_a$ .

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

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[2] Examiners
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For

[1]

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K_{a} = \frac{[H^{+}][ \text{ }^{-}\text{OCN}]}{[\text{HOCN}]} = \frac{[H^{+}]^{2}}{[\text{HOCN}]}
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 $[H^+] = \sqrt{(K_a \times [HOCN])}$ 

Since H<sub>3</sub>PO<sub>4</sub> is a weak acid, dissociation is to a very small extent, [HOCN]  $\approx$  [HOCN]<sub>initial</sub> [H<sup>+</sup>]  $\approx \sqrt{(K_{a1} \times [HOCN]_{initial})}$  $\approx \sqrt{(0.0003311 \times 0.100)}$ 

 $pH = -lg [H^+] = -lg 0.005754 = 2.24$ ;

shortcut method: initial pH =  $[pK_a + (-lg \ 0.1)] \div 2 = 2.24$ ;;

Marker's comment: Many of the candidates did not attempt this question.

(c) (i) Using your answer in (a)(i), calculate the concentration of the cyanate ions, [<sup>-</sup>OCN], at equivalence point.

At equivalence point, all HOCN has been completely reacted to form <sup>-</sup>OCN ions.

Amount of  $\neg OCN$  = amount of HOCN used = 0.100 × 0.0250 = 0.00250 mol [ $\neg OCN$ ] = 0.00250 ÷ (0.025 + 0.025) = 0.0500 mol dm<sup>-3</sup>;

Marker's comment:

Majority of the candidates who attempted this question did this correctly.

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

$$\begin{split} \mathcal{K}_{b} &= \mathcal{K}_{w} \div \mathcal{K}_{a} \\ &= 10^{-14} \div 10^{-3.48} \\ &= 10^{-10.52} \\ &= \underline{3.02 \times 10^{-11}} \text{ mol dm}^{-3} \quad ; \\ [OH^{-}] &= \sqrt{(\mathcal{K}_{b} \times [^{-}OCN])} \\ &= \sqrt{(3.02 \times 10^{-11} \times 0.0500)} \\ &= 1.229 \times 10^{-6} \text{ mol dm}^{-3} \quad ; \\ pH &= 14 - pOH \\ &= 14 - [-\lg (1.229 \times 10^{-6})] \\ &= 14 - 5.91 \\ &= \underline{8.09} \quad (3 \text{ s.f.}) \quad ; \end{split}$$

Marker's comment: Majority of the candidates did not attempt this question.

[Total: 13]

[3]

END