Class | Adm No

Class	Adm No

Candidate Name: ____________________

H

millennia institute

2022 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **19 September 2022**

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 in the spaces at the top of this page.
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 in the spaces provided on the Question Paper. If additional space is required, you should use the page at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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	A				B	**Total**
	1	2	3	4	5 / 6	
Marks	16	12	18	14	20	**80**

Section A

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

1 (a) The Bunsen cell is an electrochemical cell built to provide electrical energy.

It consists of a zinc anode in dilute sulfuric acid, separated by a salt bridge from a carbon cathode in dilute nitric acid.

Nitrogen dioxide, NO_2, is the only gas formed from the reaction. At the anode, zinc decreases in size during the reaction.

(i) Draw a fully labelled diagram of the Bunsen cell. [3]

(ii) Use data from the *Data Booklet* to construct an overall equation for the reaction. [2]

(iii) Calculate the cell potential, E, for the reaction. [1]

(iv) The experimental E of the Bunsen cell is +1.9 V.

Use ideas about reversible reactions to suggest why the experimental E may differ from the calculated value in **(iii)**. [2]

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(b) Nitrogen dioxide, NO_2, and dinitrogen tetroxide, N_2O_4, exists at equilibrium as a mixture:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

(i) Draw the 'dot-and-cross' diagram for N_2O_4. [1]

(ii) The standard enthalpy changes of formation for these gases are shown.

gas	NO_2	N_2O_4
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	+33.2	+9.2

Calculate the standard enthalpy change for the reaction shown above. [1]

(iii) Explain why the sign of the value calculated in **(ii)** is as such. [1]

(iv) The standard entropy change for the reaction is –175.8 J mol^{-1} K^{-1}.

Explain why the value is negative. [2]

(v) Explain how the Gibbs free energy change, ΔG, of the reaction will vary with temperature. [2]

(vi) A sample of NO_2(g) was sealed in a container. Its initial pressure was 1.00 bar. After reaching equilibrium, 0.351 bar of N_2O_4(g) was formed.

Calculate the equilibrium constant, K_p, for this equilibrium. [1]

[Total: 16]

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2 **(a)** The copper(II) ion forms a coloured complex ion with six water molecules.

(i) Use your knowledge of VSEPR theory to name the shape of and state the bond angle in the complex. Explain your reasoning. [2]

(ii) Explain why the 3d orbitals of the copper(II) ion are split into 2 separate energy levels. [2]

The water molecules on the z-axis (axial ligands) can move further away from the copper(II) ion (Fig. 2.1), resulting in a further splitting of the orbitals into separate energy levels (Fig. 2.2). This is known as *Jahn–Teller distortion*.

As the new energy levels (Fig. 2.2) are close together, the electrons remain in their respective orbitals.

The complex is stabilised as the Cu^{2+} electrons now have a lower overall energy.

Jahn–Teller distortions will only be able to decrease the overall energy if the metal ion has an odd number of 3d electrons.

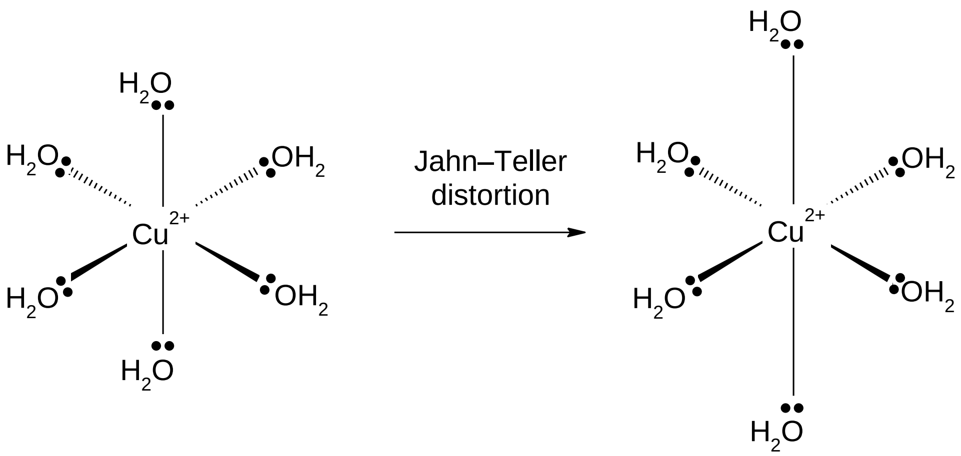

Fig. 2.1

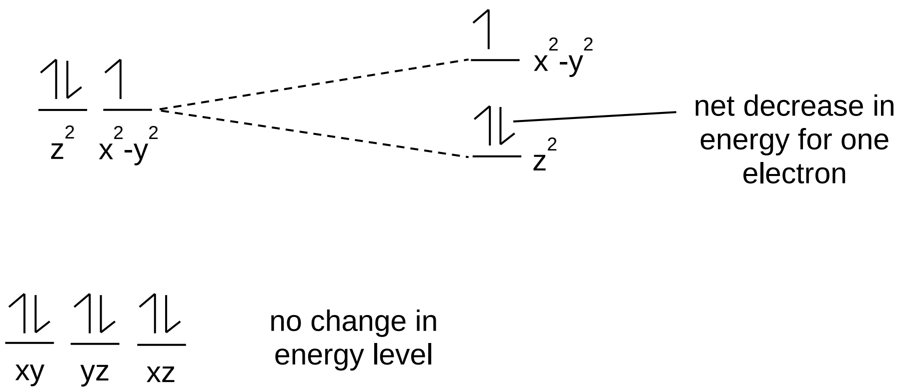

Fig. 2.2

(iii) Explain why the z^2 orbital is lower in energy after the further splitting. [1]

(iv) Predict if each of the ions will exhibit *Jahn–Teller distortion*:
1) Co^{2+}
2) Ni^{2+}.

Explain your reasoning. [2]

(v) Unlike complex ions of Cu^{2+}, complex ions of Cu^{+} are not coloured.
Write the electronic configuration of Cu^{+} and explain why its complex ions are not coloured. [2]

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(b) Use standard electrode potential data from the *Data Booklet* to calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the formation of the $[Cu(NH_3)_4]^{2+}$ complex ion from Cu^{2+}.

Hence, explain whether the reaction is feasible. [3]

[Total: 12]

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3 **(a)** Phosphate buffered saline (PBS) is a solution that mimics the solute ion concentration of biological human cells.

PBS is prepared by dissolving 2.00 g of potassium dihydrogen phosphate, KH_2PO_4 (M_r = 136.1) and 1.42 g of disodium hydrogen phosphate, Na_2HPO_4 (M_r = 142.0), into water, then making up to 1.00 dm^3.

(i) Define the term *buffer solution*. [1]

(ii) PBS contains the ions produced from the dissociation of phosphoric acid, H_3PO_4 (Fig. 3.1). The successive pK_a of H_3PO_4 are 2.14, 7.20, and 12.37 respectively.

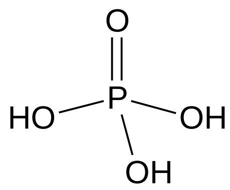

Fig. 3.1

Explain why the successive pK_a of H_3PO_4 increases. [1]

PBS contains the $H_2PO_4^-$(aq) and HPO_4^{2-}(aq) ions in equilibrium,

$$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq) \qquad pK_a = 7.20$$

(iii) Calculate the pH of PBS. [3]

(iv) Write an ionic equation to show how PBS reacts with KOH(aq) [1]

(v) 100.0 cm^3 of PBS was reacted with different volumes of 0.0100 mol dm^{-3} KOH(aq) in separate experiments.

Calculate the pH of the solution formed when the following volumes of KOH(aq) are added to 100.0 cm^3 of PBS.

I 10.0 cm^3
II 200.0 cm^3 [6]

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(b) 'Hard water' contains a high concentration of calcium ions. PBS prepared using 'hard water' may appear cloudy due to precipitate formation.

Na_2HPO_4 and NaH_2PO_4 may react in a condensation reaction. Fixed proportions of Na_2HPO_4 and NaH_2PO_4 may be heated together to form sodium triphosphate, $Na_5P_3O_{10}$. The structure of $P_3O_{10}^{5-}$ is shown in **Fig 3.2**.

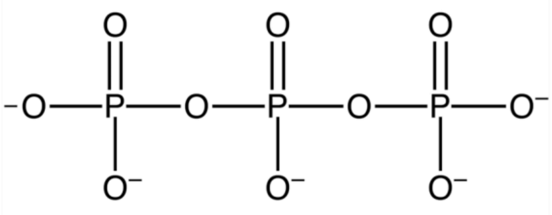

Fig 3.2

The $P_3O_{10}^{5-}$ ion consists of three phosphorus atoms linked together by oxygen atoms. It behaves as a tridentate ligand, binding to Ca^{2+} ions in a 1:1 ratio to form a soluble complex.

(i) Write a balanced chemical equation for the reaction to produce $Na_5P_3O_{10}$. [1]

(ii) State the shape of the $P_3O_{10}^{5-}$ ion about any of the P atoms. [1]

(iii) Draw the structure of the complex ion formed between the Ca^{2+} and $P_3O_{10}^{5-}$ ions. [1]

(iv) The numerical value of the K_{sp} of calcium phosphate is 2.07×10^{-33}. Since calcium phosphate is very insoluble in water, any small concentration of PO_4^{3-}(aq) present becomes significant.

The water used to prepare the PBS contains 5.06×10^{-5} g dm^{-3} of Ca^{2+}(aq).
The 1.00 dm^3 PBS contains 6.53×10^{-8} mol dm^{-3} of PO_4^{3-}(aq).

Calculate the minimum mass of $Na_5P_3O_{10}$ that must be dissolved into the 1.00 dm^3 PBS in order to prevent the precipitation of calcium phosphate. [3]

[Total: 18]

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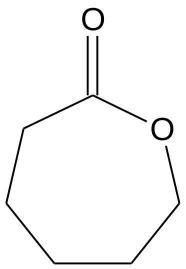
4 Potassium manganate(VII) is a potent oxidising agent that can take part in numerous reactions.

(a) **G** is a cyclic ester while **J** is a non-cyclic ester.



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$$\mathbf{G} \xrightarrow[\text{heat}]{KMnO_4(aq),\ H_2SO_4(aq)} \mathbf{I}\ (C_6H_{10}O_4) \xleftarrow[\text{heat}]{KMnO_4(aq),\ H_2SO_4(aq)} \mathbf{H}\ (C_6H_{10})$$

$$\mathbf{J}\ (C_6H_{12}O_2) \xrightarrow[\text{heat}]{H_2SO_4(aq)} \mathbf{K}\ (C_4H_{10}O) + \mathbf{L}\ (C_2H_4O_2)$$

$$\mathbf{K}\ (C_4H_{10}O) \xrightarrow[\text{heat}]{KMnO_4(aq),\ H_2SO_4(aq)} \text{no reaction}$$

Suggest the structures of compounds **H**, **I**, **J**, **K** and **L**. [5]

(b) **A**, $C_6H_{10}O_5$, is a chiral compound that has wide uses in the manufacture of polymers.

When 1 mol of **A** is reacted with excess solid sodium carbonate at room temperature and pressure, 24 dm^3 of CO_2 is formed. **A** does not react with hot acidified potassium dichromate(VI) but reacts with excess hot concentrated H_2SO_4 to form **B**, $C_6H_8O_4$.

1 mol of **B** reacts completely with 2 mol of NaOH(aq). When **B** is heated with acidified $KMnO_4$(aq), **C**, $C_3H_4O_3$, and **D**, $C_3H_4O_4$, are formed.

C gives a yellow precipitate with warm aqueous alkaline iodine. Both **C** and **D** reacts with magnesium to give effervescence.

Deduce the structures of compounds **A**, **B**, **C** and **D** explaining the reactions described. [9]

[Total: 14]

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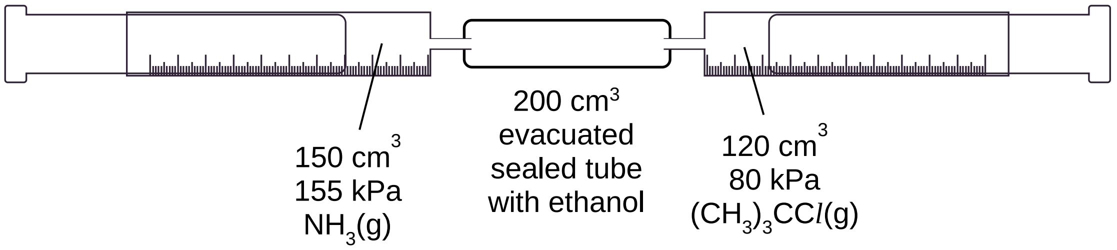
Section B

Answer **one** question from this section.

5 **(a)** The apparatus shown was used to produce 2-methylpropan-2-amine, $(CH_3)_3CNH_2$.



The volume occupied by the ethanol and its vapours can be taken to be insignificant.

(i) The two reactant gases were injected into the evacuated sealed tube at 293 K.

Calculate the total pressure after the two gases were mixed together.
Assume that there was no reaction taking place under these conditions. [2]

(ii) The reaction between NH_3(g) and $(CH_3)_3CCl$(g) would begin to take place when the system is subjected to heat.

Predict the predominant mechanism for the reaction.
Explain your reasoning. [2]

(iii) Outline the predominant mechanism for the reaction, showing clearly any lone pair, partial charges and the movement of electrons using curly arrows. [3]

(iv) Suggest a by-product of the reaction and how to minimise its formation. [2]

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(b) Fluorine gas is manufactured by electrolysing potassium hydrogen difluoride, KHF_2, dissolved in liquid hydrogen fluoride, HF, at –50°C and 1 atm.

(i) The HF_2^- ion further dissociates into two species.

A strong interaction forms between these two species.

Draw the two species, and label the interaction between them. [2]

(ii) Hydrogen fluoride can also dissociate, forming ions.

State and explain the *type* of acid-base behaviour exhibited by hydrogen fluoride. [1]

(iii) The only products of electrolysis were fluorine gas and hydrogen gas.

Write two half-equations to describe the discharge of ions at each electrode.
The electrodes can be taken to be inert. [1]

(iv) In one experiment, 355 g of KHF_2 and 145 g of HF were electrolysed.

Calculate the volumes of fluorine gas and hydrogen gas produced under the reaction conditions. [3]

(v) Explain which gas, fluorine gas or hydrogen gas, would have a more accurately calculated volume. [2]

(vi) Draw labelled diagrams to show the orbital overlaps in:
1) H_2
2) F_2
3) HF. [2]

[Total: 20]

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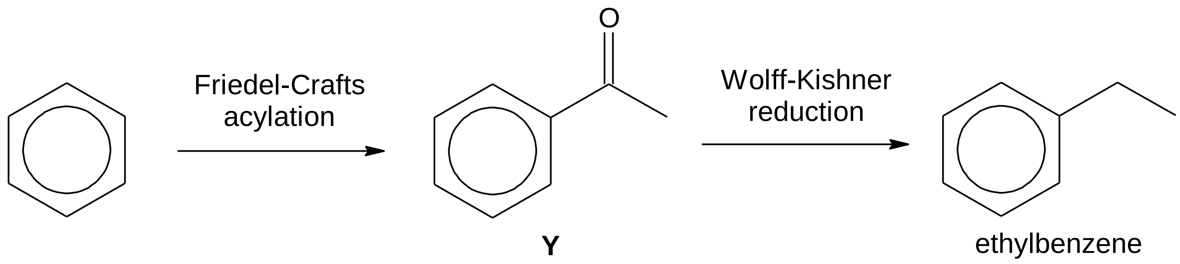
6 **(a)** Ethylbenzene can be produced from benzene using two consecutive reactions.



(i) The mechanism of Friedel-Crafts acylation in the first reaction shown above is the same as Friedel-Crafts alkylation using chloroethane as the reactant.

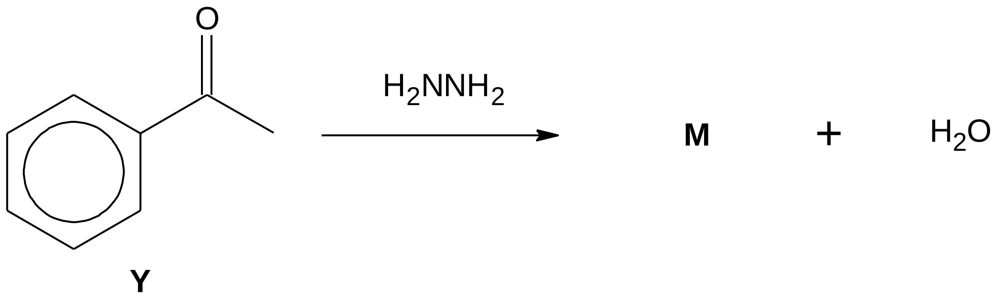
Outline the mechanism of Friedel-Crafts acylation to form **Y** above, showing clearly any lone pair, partial charges and the movement of electrons using curly arrows. [3]

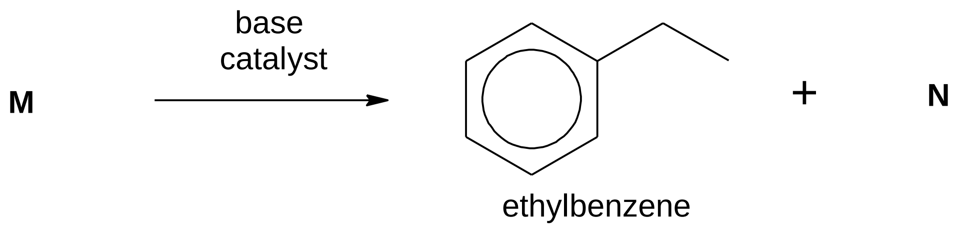
(ii) One advantage of Friedel-Crafts acylation over Friedel-Crafts alkylation is a higher percentage purity of the product. Whereas Friedel-Crafts alkylation often results in multi-substituted benzene rings, Friedel-Crafts acylation predominantly yields mono-substituted benzene rings.

Explain why Friedel-Crafts alkylation often results in multi-substituted benzene rings. [2]

(iii) The Wolff-Kishner reduction occurs in two steps.

In the first step, hydrazine, H_2NNH_2, reacts with **Y** in the same way as 2,4-dinitrophenylhydrazine.





Suggest the identity of **M** and **N** respectively. [2]

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(b) **(i)** State and explain the trend of atomic radii down the Group 2 elements. [2]

(ii) State and explain the trend of thermal stability of the Group 2 carbonates. [2]

(iii) 1.02 g of an unknown Group 2 carbonate, **X**CO_3, was strongly heated until a white solid of constant mass 0.505 g remained.

Determine the unknown element **X**. [3]

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(c) Uranium oxide, UO_2, reacts with hydrogen fluoride, HF, to form UF_4.
On adding fluorine, F_2, uranium fluoride, UF_6, is formed.

(i) Construct a balanced chemical equation for the overall reaction. [2]

(ii) Explain, using oxidation numbers, why the reaction is a redox reaction. [2]

There are two isotopes of uranium, ^{235}U and ^{238}U. While ^{238}U is much more abundant, only ^{235}U can be used to generate nuclear power.

Only samples of UF_6 containing at least 2% $^{235}UF_6$ can be used in nuclear reactors.

A sample of UF_6 has an average M_r of 351.95.

(iii) Calculate the percentage $^{235}UF_6$ in the sample. [1]

(iv) Hence determine if the sample can be used in nuclear reactors to generate power. [1]

[Total: 20]

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