## ADVANCED MATRICULATION LEVEL

 2022 SECOND SESSION```
SUBJECT:
PAPER NUMBER:
DATE:
TIME: 9:00 a.m. to 12:05 p.m.
Required Data: \(\quad\) Universal Gas constant \((R)=8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}\). RAM: \(\mathrm{H}=1 ; \mathrm{C}=12 ; \mathrm{O}=16 ; \mathrm{Cl}=35.5\)
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## Answer ALL questions

1. This question is about atomic structure.
a) i) Identify and write the electronic configuration using the $s$ and $p$ notation of the element with an atomic number of 11 .
ii) Write the electronic configuration of $\mathrm{Zn}^{2+}$.
$\qquad$
b) The first ionisation energy of carbon is $1086 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Would you expect the first ionisation energy of silicon to be greater or less than this amount? Explain.
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$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
c) Complete the following table.

| Hybridisation | Molecular geometry |
| :---: | :---: |
| $\mathrm{sp}^{3}$ |  |
|  | trigonal planar |

d) Using the electron box notation, describe the hybridisation of the carbon atoms in ethyne
$\qquad$
$\qquad$
$\qquad$
e) Give the systematic name of the hydrocarbon shown below and state the hybridisation of the carbon atoms labelled $\mathbf{a}$ and $\mathbf{b}$.

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2. This question is about bonding.
a) Use the valence shell electron pair repulsion (VSEPR) theory to draw the structure of the $\mathrm{I}_{3}{ }^{+}$ion. Show your working.
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$\qquad$
b) Solid sodium sulfate, which has a melting point of $884^{\circ} \mathrm{C}$, does not conduct electricity, but molten sodium sulfate and aqueous solutions of sodium sulfate conduct electricity. Explain.
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$\qquad$
$\qquad$ (3)
c) With the aid of a diagram, use HF to explain intermolecular hydrogen bonding.
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d) Ice melts upon increasing pressure at a constant temperature. Explain this in terms of the structure of solid water.
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$\qquad$
$\qquad$ (3)
(Total: 11 marks)

Please turn the page.
3. This question is about periodicity.
a) Consider the elements of period 3 .
i) Explain why the electrical conductivity increases from Na to Al .
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$\qquad$
$\qquad$
$\qquad$
$\qquad$ (2)
ii) Explain why silicon has a high melting point.
$\qquad$
$\qquad$ (2)
b) Consider the hydrides formed by elements lithium to fluorine.
i) Give an example of a hydride having the following structures:

Ionic $\qquad$

Polymeric covalent $\qquad$

Simple covalent
ii) Give the equation for the reaction (if any) of the hydrides of the elements with atomic numbers 6, 7 and 9, with water.
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$\qquad$
$\qquad$
4. a) In a mixture of gases, each component exerts its partial pressure.
i) Explain what is meant by partial pressure.
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$\qquad$
$\qquad$
$\qquad$
ii) State Dalton's law of partial pressures.
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$\qquad$
iii) Gases can undergo diffusion and effusion. Distinguish between the two processes.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
iv) State which states of matter can undergo diffusion and effusion.
$\qquad$
$\qquad$ (2)
b) A mixture of neon and argon in a $0.20 \mathrm{dm}^{3}$ container had a pressure of 760 kPa . The mixture was transferred to a $1.0 \mathrm{dm}^{3}$ container at a constant temperature. Calculate the partial pressure of neon in the $1.0 \mathrm{dm}^{3}$ container if the mole fraction of argon is 0.34 .
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5. a) Calculate the osmotic pressure (in kPa ) of a solution containing 13.6 g of sucrose $\left(\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}\right)$ in $250 \mathrm{~cm}^{3}$ of solution at $25^{\circ} \mathrm{C}$.
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$\qquad$
b) The vapour pressure of trichloromethane and dichloromethane at 298 K is 200 mm Hg and 415 mm Hg , respectively. Calculate the vapour pressure of the ideal mixture prepared by mixing 25.5 g of trichloromethane and 40.0 g of dichloromethane at 298 K .
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6. a) The plot below gives the experimental values for the initial rate of reaction against the molar concentration of $A$, for a reaction $A \rightarrow B+C$.

Initial rate of reaction against [A]

i) Use the graph to determine the order of reaction with respect to A .
$\qquad$
$\qquad$
$\qquad$
$\qquad$ (3)
ii) Give the rate expression and calculate the rate constant.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$ (2)

Please turn the page.
iii) Comment on the half-life of the reaction.
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$\qquad$
$\qquad$
$\qquad$
b) Consider the following reaction mechanism:

Step 1: $A_{2}+B_{2} \rightarrow R+C$ (slow step)
Step 2: $A_{2}+R \rightarrow C$ (fast step)
i) Write the overall equation for this chemical reaction.
$\qquad$
$\qquad$
ii) Identify any intermediates in the reaction mechanism.
iii) What is the order with respect to each reactant? Explain your answer.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
iv) Write the rate law for this reaction.
$\qquad$
$\qquad$
7) Consider the following reaction scheme involving propan-1-ol.

a) Give the reagent/s and conditions for reactions:
(i) $\qquad$
(ii) $\qquad$
(iii) $\qquad$
(iv) $\qquad$
(v) $\qquad$
(vi) $\qquad$
(vii)
b) Give the structural formula for the organic compounds $\mathbf{P}, \mathbf{R}, \mathbf{T}, \mathbf{X}$ and $\mathbf{Y}$.

| $\mathbf{P}$ | $\mathbf{R}$ |
| :--- | :--- |
| $\mathbf{T}$ | $\mathbf{X}$ |
| $\mathbf{Y}$ |  |

8) This question is about alcohols and carbonyl compounds.
a) Figure 1 presents a laboratory set-up for the preparation of butanal, starting with butan-1-ol. The boiling point of butanal is $75^{\circ} \mathrm{C}$, while that of butan-1-ol is $118{ }^{\circ} \mathrm{C}$.


Figure 1
i) Continue the following sentence by filling in the blanks:

A1 and A2 are both $\qquad$ but A1 is set to carry out the process of
$\qquad$ while A2 is set to carry out the process of
$\qquad$
ii) Name the apparatus labelled B, C, D.

B $\qquad$

C $\qquad$

D
iii) Give the contents of vessels $\mathbf{B}$ and $\mathbf{C}$ before the reaction starts.

B $\qquad$

C $\qquad$
iv) In Figure 1, the inlet water temperature of $\mathbf{A 1}$ is set at $80^{\circ} \mathrm{C}$, while the inlet water temperature of $\mathbf{A 2}$ is set to cold $\left(<5^{\circ} \mathrm{C}\right)$. Suggest why the water inlet temperatures of A1 and A2 are set in this way.
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$\qquad$
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$\qquad$
v) Why is it important to closely monitor the temperature inside the still head labelled $\mathbf{E}$ ?
$\qquad$
$\qquad$ (1)
b) After the reaction is over, a few grams of anhydrous calcium chloride are added to the butanal collected in $\mathbf{D}$. The calcium chloride is then filtered out, and the butanal is re-distilled. Suggest ONE reason for:
i) the addition of anhydrous calcium chloride;
$\qquad$
$\qquad$
ii) the re-distillation of the aldehyde.
$\qquad$
$\qquad$
9) Complete the following table by writing suitable structural formulae of organic compounds or properties of the organic compound in the spaces provided as required.

| Organic substance | Product of reaction or property of the organic <br> compound |  |
| :--- | :--- | :--- |
| a) |  | Draw the molecular structure of the sublimed product that <br> is collected after heating this substance. |
| b) |  | Draw and name the structure of each of the two <br> geometrical isomers of this substance. |
| c) |  | But-2-ene-1,4-dioic acid  |
|  |  | Give the structural formula of the product of reaction <br> obtained when an equimolar amount of $\mathrm{Cl}_{2}$ is bubbled <br> through the boiling substance in the presence of trace <br> quantities of red phosphorus. |


| e) | Draw the molecular structure of the organic product of the <br> mononitration of this substance. |
| :--- | :--- |
| (2) (Total: 11 marks) |  |

(Total: 11 marks)

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| SUBJECT: | Chemistry |
| :--- | :--- |
| PAPER NUMBER: | II |
| DATE: | $30^{\text {th }}$ August 2022 |
| TIME: | $9: 00$ a.m. to $12: 05$ p.m. |

A Periodic Table is provided.
$K_{w}=1.0 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6}$

## Answer TWO questions from each section and ANY other question.

## SECTION A

1. This question is about transition metals.
a) i) Write the electronic configurations for Cu and $\mathrm{Cu}^{2+}$.
ii) Explain why copper is considered a transition metal but zinc is not.
iii) Give an example of a complex ion of copper which clearly shows a typical property of transition metals.
iv) Identify and give the electronic configuration of another d-block element in period 4 that is not considered a transition element.
b) Define the following terms: ligand, complex ion and chelate. Give suitable examples for each term.
c) Explain how potassium thiocyanate, KSCN, can be used to test for the presence of iron(III) ions.
d) Chromate and dichromate ions exist in equilibrium in an aqueous solution. Write an equation for this equilibrium and comment on the effect of adding acid or alkali on the equilibrium.
(Total: 20 marks)
2. This question is about elements in group 7.
a) Explain, with the help of a labelled diagram, how you would safely prepare chlorine in the laboratory. Give the chemical equation for the reaction involved, including the state symbols. State and explain how you would test for chlorine.
b) Explain why bromine can be easily prepared in the laboratory by oxidation of bromide ions by a halogen. Include a chemical equation to support your answer.
c) Freon-12, $\mathrm{CCl}_{2} \mathrm{~F}_{2}$, is prepared by reaction of $\mathrm{CCl}_{4}$ with HF . The other product of this reaction is HCl . Determine the percentage yield if $12.5 \mathrm{~g} \mathrm{CCl}_{2} \mathrm{~F}_{2}$ is produced from $32.9 \mathrm{~g} \mathrm{CCl}_{4}$. (4)
d) An iodimetric titration was carried out to determine the amount of copper in an unknown copper(II) salt. A 0.10 g sample of the salt was weighed out and treated with excess potassium iodide solution. The liberated iodine was titrated against $0.0120 \mathrm{~mol} \mathrm{dm}{ }^{-3}$ sodium thiosulfate solution. A volume of $32.50 \mathrm{~cm}^{3}$ of sodium thiosulfate solution was needed to react with the iodine. Calculate the percentage by mass of copper in the unknown copper(II) salt. State any assumptions made.
e) Explain why aqueous HF is a weak acid.
(Total: $\mathbf{2 0}$ marks)
3. This question is about chemical equilibria.
a) An aliquot of $100 \mathrm{~cm}^{3}$ of $0.150 \mathrm{~mol}_{\mathrm{dm}}{ }^{-3}$ solution of aqueous propan-1-amine was shaken in a separating funnel with $50.0 \mathrm{~cm}^{3}$ of an organic solvent at $25^{\circ} \mathrm{C}$. The system was allowed to reach equilibrium. At this point, $50.0 \mathrm{~cm}^{3}$ of the aqueous layer was run off, and on titration, it needed $14.1 \mathrm{~cm}^{3}$ of $0.225 \mathrm{~mol} \mathrm{dm}^{-3}$ hydrochloric acid for complete neutralisation.
i) Calculate the partition coefficient of propan-1-amine between the organic solvent and water.
ii) Use your answer to part (a) (i) to explain in which phase, water or the organic solvent, is propan-1-amine more soluble.
iii) Primary amines can be converted into alcohols. Give an equation including reagents and conditions for the conversion of propan-1-amine into an alcohol.
b) Calculate how much propan-1-amine is extracted from the same volume of $0.150 \mathrm{~mol} \mathrm{dm}^{-3}$ solution if two consecutive extractions using $25.0 \mathrm{~cm}^{3}$ aliquots of organic solvent at $25^{\circ} \mathrm{C}$ are employed. Which of the two techniques provides the higher yield of amine, and by how much? Quote your answer in moles of amine.
(Total: $\mathbf{2 0}$ marks)
4. Kevlar ${ }^{R}$ is a man-made fibre material used in the manufacture of bullet-proof vests and other shock-resistant materials. The fibres may be formed by the poly-condensation of the monomers $\mathbf{X}$ and $\mathbf{Y}$. The structure of monomer $\mathbf{Y}$ is given below, while that of monomer $\mathbf{X}$ is given in part (c).

a) Give an equation to show how molecules $\mathbf{X}$ and $\mathbf{Y}$ polymerise to produce Kevlar ${ }^{R}$.
b) Suggest the main type of intermolecular forces acting between the polymer chains of Kevlar ${ }^{R}$ and identify the functional group responsible for such interactions.
c) A synthetic route for monomer $\mathbf{X}$ starting with phenylamine is given below.

i) Identify the reagents and reaction conditions in steps 1, 2, $\mathbf{3}$ and 4, and give the structure of the intermediate $\mathbf{W}$.
ii) In what way does intermediate $\mathbf{V}$ aid in the preparation of monemer $\mathbf{X}$ ?
d) Give a reaction scheme to show how monomer $\mathbf{Y}$ presented above can be synthesised from 1,4-dimethylbenzene.

## SECTION B

5. The addition of hydrogen bromide to ethene proceeds by electrophilic addition across the double bond and the formation of a carbocation. The polymerisation of ethene occurs by a free radical addition process.
a) Show the mechanism of the reaction of hydrogen bromide with ethene, identifying clearly the electrophile and the intermediate involved. Suggest a step in the mechanism that likely serves as the rate-determining step and give a reason for your answer.
b) The addition of hydrogen bromide to propene gives rise to two products, a major product and a minor one. Identify these two products, giving their respective structural formulae and stating which of them forms in major amount. Explain why the formation of the major product is preferred in terms of carbocation stability.
c) The high-pressure polymerisation of ethene occurs in three steps, a chain initiation process that leads to chain propagation and growth. The growth of the polymer chain ends with a chain termination step. Describe the mechanism of polymerisation of ethene when the chain initiation step involves use of benzoyl peroxide, which breaks down into free radicals as follows:

d) The following represents a segment of an addition-type water-soluble polymer:

i) Deduce the structural formula of the monomer.
ii) Suggest a reason for the good water-solubility of the polymer.
iii) Explain why the polymer cannot be made directly from its monomer.
(Total: $\mathbf{2 0}$ marks)
6. This question is about energetics.
a) Consider the following thermochemical information:

| Enthalpy change of atomisation of Mg | $+148 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| :--- | :--- |
| First electron affinity for O | $-141 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| First ionisation energy for Mg | $+738 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| Second ionisation energy for Mg | $+1450 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| Bond dissociation enthalpy for $\mathrm{O}_{2}$ | $+498 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| Second electron affinity for O | $+798 \mathrm{~kJ} \mathrm{mo}^{-1}$ |
| Lattice enthalpy for $\mathrm{MgO}(\mathrm{s})$ | $-3845 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |

Given the above information for magnesium, oxygen, and magnesium oxide, construct a Born-Haber cycle and calculate the enthalpy change of formation of magnesium oxide.
b) i) Consider the following reaction:

$$
4 \mathrm{NH}_{3}(\mathrm{~g})+7 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 4 \mathrm{NO}_{2}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

The enthalpy change for the reaction is -1135 kJ . Given that the bond enthalpy terms for $\mathrm{N}-\mathrm{H}, \mathrm{O}=\mathrm{O}$ and $\mathrm{O}-\mathrm{H}$ are $389 \mathrm{~kJ} \mathrm{~mol}^{-1}, 498 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $464 \mathrm{~kJ} \mathrm{~mol}^{-1}$, respectively, find the bond enthalpy term for the nitrogen-oxygen bonds in $\mathrm{NO}_{2}$.
ii) Given that the bond enthalpy terms for $\mathrm{N}-\mathrm{O}$ and $\mathrm{N}=\mathrm{O}$ are $222 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $590 \mathrm{~kJ} \mathrm{~mol}^{-1}$, respectively and considering the result of part (b) (i), what can you conclude about the bonding between nitrogen and oxygen in the $\mathrm{NO}_{2}$ molecule?
(Total: 20 marks)
7. This question is about ionic equilibria.
a) Given that the $\mathrm{p} K_{\mathrm{a}}$ of ethanoic acid is 4.76 at $25^{\circ} \mathrm{C}$, what is the pH of a solution prepared by dissolving $5.0 \times 10^{-3}$ moles of ethanoic acid in water to give $250 \mathrm{~cm}^{3}$ of solution at this temperature.
b) Give an expression for the equilibrium constant, $K_{b}$, for the equilibrium reaction between the ethanoate ion and water, in terms of the $K_{a}$ of ethanoic acid and $K_{\mathrm{w}}$.
c) Find the pH of the solution prepared in part (a) if $5.0 \times 10^{-3}$ moles of sodium hydroxide are added to the solution. Ignore any changes in volume due to the addition of sodium hydroxide.
(Total: $\mathbf{2 0}$ marks)
Please turn the page.
8. Explain the following observations as fully as you can, giving relevant chemical equations and chemical structures where appropriate.
a) Primary, secondary and tertiary alcohols can be distinguished on the basis of their reaction with oxidising agents.
b) A substance with molecular formula $\mathrm{C}_{6} \mathrm{H}_{10}$ reacts with ozone at low temperature in tetrachloromethane solvent to produce an oily product. Mild acid hydrolysis in the presence of Zn dust produces a single product.
c) Alkenes are most effectively hydrogenated in the presence of finely divided metallic powders such as Ni, Pt or Pd. With the aid of a labelled diagram, describe the mechanism of heterogeneous catalysis of alkenes. Explain why these catalysts are used as finely divided powders.

## ADVANCED MATRICULATION LEVEL 2022 SECOND SESSION

| SUBJECT: | Chemistry |
| :--- | :--- |
| PAPER NUMBER: | III - Practical |
| DATE: | $26^{\text {th }}$ August 2022 |
| TIME: | $9: 00$ a.m. to $11: 05$ a.m. |

1. You are provided with three solutions as follows:
i) Potassium manganate(VII), labeled $\mathbf{N}_{\mathbf{n}}$;
ii) ethanedioic acid, of concentration $0.0500 \mathrm{~mol} \mathrm{dm}^{-3}$, labelled $\mathbf{A}$;
iii) A solution of iron(II) sulfate-7-water, labelled $\mathbf{U}$, made by dissolving 30.0 g of a low-grade sample of the iron(II) salt in $1.00 \mathrm{dm}^{3}$ water.
iv) Dilute sulfuric acid.

In this experiment, you are required to:
i) determine the molar concentration of solution $\mathbf{N}_{\mathbf{n}}$;
ii) determine the concentration of the iron(II) solution, $\mathbf{U}$.
iii) determine the percentage purity of the solid used to make solution $\mathbf{U}$.
a) Record the value of your laboratory number, $\mathbf{n}$ (found on solution $\mathbf{N}$ ), on your answer book in the following box.
$\qquad$

## Determination of the molar concentration of solution $\mathbf{N}_{\mathbf{n}}$

b) Fill your burette with solution $\mathbf{N}_{\mathrm{n}}$. Into each of three conical flasks, pipette a $25.0 \mathrm{~cm}^{3}$ aliquot of solution A. Add $20 \mathrm{~cm}^{3}$ of dilute sulfuric acid. Heat each flask to approximately $60^{\circ} \mathrm{C}$ and titrate with solution $\mathbf{N}_{\mathrm{n}}$ to the first permanent pink end-point. Record your results in the table below.

|  | $1^{\text {st }}$ Titration | $2^{\text {nd }}$ Titration | 3rd Titration |
| :--- | :--- | :--- | :--- |
| Final burette reading |  |  |  |
| Initial burette reading |  |  |  |
| Titre $\left(\mathrm{cm}^{3}\right)$ |  |  |  |

Mean titre: $\qquad$ $\mathrm{cm}^{3}$ of solution $\mathbf{N}_{\mathrm{n}}$.
c) Oxalic acid and manganate(VII) react according to the equation

$$
2 \mathrm{MnO}_{4}^{-}(\mathrm{aq})+5(\mathrm{COOH})_{2}(\mathrm{aq})+6 \mathrm{H}^{+}(\mathrm{aq}) \rightarrow 2 \mathrm{Mn}^{2+}(\mathrm{aq})+10 \mathrm{CO}_{2}(\mathrm{~g})+8 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

Using the data obtained above, determine the molar concentration of solution $\mathbf{N}_{\mathbf{n}}$.
$\qquad$
$\qquad$
$\qquad$
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$\qquad$
$\qquad$

Determination of the percentage purity of the iron(II) solution.
d) Transfer a $25.0 \mathrm{~cm}^{3}$ aliquot of solution $\mathbf{U}$ into each of 3 conical flasks and acidify with $20 \mathrm{~cm}^{3}$ dilute sulfuric acid. Titrate each flask with solution $\mathbf{N}_{\mathbf{n}}$ to the first permanent pink end-point, and record your data in the table below.

|  | $1^{\text {st }}$ Titration | $2^{\text {nd }}$ Titration | 3rd Titration |
| :--- | :--- | :--- | :--- |
| Final burette reading |  |  |  |
| Initial burette reading |  |  |  |
| Titre |  |  |  |

Mean titre: $\qquad$ $\mathrm{cm}^{3}$ of solution $\mathbf{N}_{\mathrm{n}}$.
e) Iron(II) ions and manganate(VII) react according to the equation

$$
\mathrm{MnO}_{4}^{-}(\mathrm{aq})+5 \mathrm{Fe}^{2+}(\mathrm{aq})+8 \mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{Mn}^{2+}(\mathrm{aq})+5 \mathrm{Fe}^{3+}(\mathrm{aq})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

Use the data above to calculate the concentration of solution $\mathbf{U}$ in $\mathrm{g} \mathrm{dm}^{-3}$.
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DO NOT WRITE ABOVE THIS LINE
f) Determine the percentage purity of the solid used to make solution $\mathbf{U}$.
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$\qquad$
$\qquad$
$\qquad$

