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Scholarship 2021
Chemistry

Time allowed: Three hours
Total score: 32

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

You should answer ALL the questions in this booklet.

Pull out Resource Booklet 93102R from the centre of this booklet.

Show ALL working.

If you need more room for any answer, use the extra space provided at the back of this booklet.

Check that this booklet has pages 2–20 in the correct order and that none of these pages is blank.

YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

Question	Score
ONE	
TWO	
THREE	
FOUR	
TOTAL	

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QUESTION ONE

(a) A small 0.185 g piece of calcium metal, Ca(*s*), was dropped into a large beaker containing 750.0 mL of distilled water at 25 °C. It spontaneously reacted, producing a colourless gas and a clear, colourless solution. When a further two pieces of calcium metal, with a combined mass of 0.396 g, were then added to the same beaker, they also spontaneously reacted to produce a colourless gas, but a cloudy white solid was observed forming in the solution as the metal pieces reacted. Addition of a small volume of dilute hydrochloric acid solution, HCl(*aq*), caused the solution to become clear.

Justify these observations with use of calculations, balanced chemical equations, and equilibrium principles.

$K_s(Ca(OH)_2) = 6.40 \times 10^{-6}$

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(b) A pale-blue, weakly acidic copper(II) chloride solution, $CuCl_2(aq)$, was prepared by sitting a piece of copper metal, $Cu(s)$, in a beaker containing chlorine water, $Cl_2(aq)$. When pieces of aluminium foil, $Al(s)$, were added to a sample of the solution, the pieces of foil slowly disappeared as a colourless gas and brown solid were produced. When potassium permanganate, $KMnO_4(s)$, was added to a separate sample of the solution, a brown solid and pale-green gas were produced.

Using the standard electrode potentials provided in the table below, justify the reactions described above with use of balanced chemical equations and cell potential calculations.

	E^o / V
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	–1.68
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(\ell)$	+1.23
$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(\ell)$	+1.69
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34

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(c) A buffer solution with pH = 10.00 was required for an experiment. The following procedure was used to prepare this solution.

A technician began by dissolving 0.1918 g of methylammonium chloride, $CH_3NH_3Cl(s)$, into 50.0 mL of 0.0250 mol L^{-1} methylamine solution, $CH_3NH_2(aq)$. However, when the pH of the solution was measured, it was found to be too high. To lower the pH, 10.0 mL of 0.0415 mol L^{-1} hydrochloric acid solution, HCl(*aq*), was added.

Calculate the pH of the initial and final buffer solutions, and decide whether the technician added a sufficient amount of hydrochloric acid to achieve the intended pH.

$M(CH_3NH_3Cl) = 67.5$ g mol^{-1} $\quad$ $pK_a(CH_3NH_3^+) = 10.64$

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QUESTION TWO

(a) A solution was prepared for a competition by mixing varying amounts of three compounds; ethanoic acid, $CH_3COOH(\ell)$, sodium chloride, $NaCl(s)$, and oxalic acid, $H_2C_2O_4(s)$, in a volume of water, $H_2O(\ell)$. There was no solid remaining in the final solution. Groups of students were each given 100.0 mL of the solution and were tasked with determining the mass of each of the three compounds in the sample provided.

One group of students carried out the following procedures in the laboratory.

First, the students diluted the solution by pipetting 20.00 mL into a 200.0 mL volumetric flask, and filling it to the mark with distilled water. The students then titrated 20.00 mL samples of the diluted solution with a standardised potassium permanganate solution, $KMnO_4(aq)$. The potassium permanganate solution had a concentration of 0.02960 mol L^{-1} and required an average titre of 18.93 mL to reach the end point.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Next, the students titrated further 20.00 mL samples of the diluted solution with a standardised sodium hydroxide solution, $NaOH(aq)$, using phenolphthalein as the indicator. The sodium hydroxide solution had a concentration of 0.4790 mol L^{-1} and required an average titre of 13.32 mL to reach the end point.

Finally, each student in the group pipetted 10.00 mL of the original undiluted solution into pre-weighed beakers. Each beaker was heated to evaporate all liquids, then the beakers and any solids remaining were weighed. The average mass of solids remaining was 2.130 g.

From these measurements, determine the final answers that the group should have submitted in the competition.

$M(NaCl) = 58.50$ g mol^{-1} $M(H_2C_2O_4) = 90.00$ g mol^{-1} $M(CH_3COOH) = 60.00$ g mol^{-1}

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(b) The enthalpy of solution, $\Delta_{sol}H$, is the enthalpy change that occurs when one mol of a solid dissolves to produce a solution. The $\Delta_{sol}H$ for calcium carbonate, $CaCO_3(s)$, in water is negative, while the $\Delta_{sol}H$ for sodium chloride, $NaCl(s)$, in water is positive.

Discuss the thermodynamic factors that affect the relative solubilities of $CaCO_3$ and NaCl, with consideration of enthalpy and entropy changes occurring within the solute, solvent and solution.

$K_s(CaCO_3) = 3.3 \times 10^{-9}$ $\qquad$ $K_s(NaCl) > 1.00$

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(c) (i) Draw all potential 3-dimensional structures for the $IF_2O_2^-$ ion.

(ii) In VSEPR theory, it is observed that a bond from the central atom to an atom of lower electronegativity occupies more space than the bond from the central atom to an atom of higher electronegativity. Double bonds have greater electron density and, thus, greater repulsion than single bonds.

Justify the most probable positional arrangement of atoms in the $IF_2O_2^-$ ion.

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QUESTION THREE

(a) (i) Use the following information to solve the molecular formula for Compound **X**.

- Elemental analysis of Compound **X** determined that it contained only the elements carbon, hydrogen, and oxygen.
- Mass spectrometry produced a molecular ion (M+) peak at 90 m/z for Compound **X**.
- Complete combustion of 4.388 g of Compound **X** produced 8.591 g of CO_2 and 4.410 g of H_2O.

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(ii) Compound **X** was produced following reaction of Compound **W** with H^+/MnO_4^-.

Draw all possible structures for Compounds **X** and **W**.

You do not need to name any of the structures.

(b) Compounds **E – H** are a group of alcohols that naturally occur in a mixture together. They are isomers with the molecular formula $C_4H_{10}O$. Addition of acidified potassium dichromate solution, $H^+/K_2Cr_2O_7(aq)$, to a sample of the mixture, followed by gentle heating, resulted in the formation of a variety of new organic compounds. In the conditions used, not all the compounds fully reacted, and the final mixture contained nine different organic compounds (**E – M**) with various functional groups. The mixture was then separated using distillation.

(i) Determine a structure for each of the nine compounds in the final mixture.

The order in which you assign the compounds does not matter. You do not need to name them.

E	**I**
F	**J**
G	**K**
H	**L**
	M

(ii) Using the labels given to your compounds above, discuss the chemistry involved in the separation of Compounds **E – M**.

You should explain the predicted order in which they would separate during distillation.

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(iii) Compound **N** can be synthesised using two of compounds **E**–**M** from part (i).

When analysed using ^{13}C NMR, only five peaks are detected in the spectra for this compound.

Determine the structure of Compound **N**, give the conditions required for the synthesis to occur, and explain the resulting ^{13}C NMR peaks of the product.

QUESTION FOUR

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(a) Solid sodium thiosulfate, $Na_2S_2O_3$, can react with both dilute hydrochloric acid, HCl(*aq*), and concentrated nitric acid, HNO_3(*conc*).

When it is reacted with dilute hydrochloric acid, HCl(*aq*), colourless sulfur dioxide gas, SO_2(*g*), is released from the mixture, and a yellow solid is slowly formed in the solution.

When it is reacted with concentrated nitric acid, HNO_3(*conc*), brown nitrogen dioxide gas, NO_2(*g*), is released from the mixture and the same yellow solid is again observed in the solution. This second solution additionally tests positive for the presence of sulfate ions, SO_4^{2-}(*aq*).

Account for the oxidation and reduction processes occurring in the reactions with HCl(*aq*) and HNO_3(*conc*).

You should write balanced equations, and use changes in oxidation numbers to justify the oxidant(s) and reductant(s) in the reactions.

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(b) Hess's law calculations use the known enthalpy changes of various reactions to calculate the enthalpy change for an overall reaction for which the enthalpy changes cannot be measured. For example, Hess's law can be used to determine lattice formation enthalpies. These are a measure of the enthalpy change when one mole of an ionic solid is formed from its ions in the gaseous state. Caesium(II) fluoride, $CsF_2(s)$, is an example of an ionic salt that does not exist, but the theoretical lattice formation enthalpy can be calculated using Hess's law and depicted as:

$Cs^{2+}(g) + 2F^{-}(g) \rightarrow CsF_2(s)$ $\Delta_{lat}H° = -2347$ kJ mol^{-1}

(i) Using the thermochemical information provided, calculate the theoretical enthalpy of formation, $\Delta_f H°$, for $CsF_2(s)$, and then justify why CsF_2 does not exist, but CsF does.

Consider the position of these elements in the periodic table in your answer.

$Cs(s) \rightarrow Cs(g)$	$\Delta_r H° = +76.0$ kJ mol^{-1}
$Cs(g) \rightarrow Cs^{+}(g) + e^{-}$	$\Delta_r H° = +382$ kJ mol^{-1}
$Cs^{+}(g) \rightarrow Cs^{2+}(g) + e^{-}$	$\Delta_r H° = +2430$ kJ mol^{-1}
$F_2(g) \rightarrow 2F(g)$	$\Delta_r H° = +158$ kJ mol^{-1}
$F(g) + e^{-} \rightarrow F^{-}(g)$	$\Delta_r H° = -334$ kJ mol^{-1}
$Cs(s) + \frac{1}{2}F_2(g) \rightarrow CsF(s)$	$\Delta_f H° = -554$ kJ mol^{-1}

(ii) Justify the differences in the lattice formation enthalpies for CsF and CsF_2.

$\Delta_{lat}H°(CsF(s)) = –757 \text{ kJ mol}^{-1}$

Question Four continues on the next page.

(c) Compounds **A**–**D** are constitutional isomers with a molar mass less than 100 g mol^{-1}.

^{13}C NMR and IR spectra for Compounds **A**–**D** are provided in the resource booklet.

Use the spectral data provided to determine the molecular formula for the isomers **A**–**D**, then determine, name, and justify ONE possible structure for each compound.

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Extra space if required.
Write the question number(s) if applicable.

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