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QUALIFY FOR THE FUTURE WORLD
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Scholarship 2019 Chemistry

9.30 a.m. Wednesday 27 November 2019

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.

Pull out Resource Booklet S–CHEMR from the centre of this booklet.

You should answer ALL the questions in this booklet.

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 2–24 in the correct order and that none of these pages is blank.

You are advised to spend approximately 45 minutes on each question.

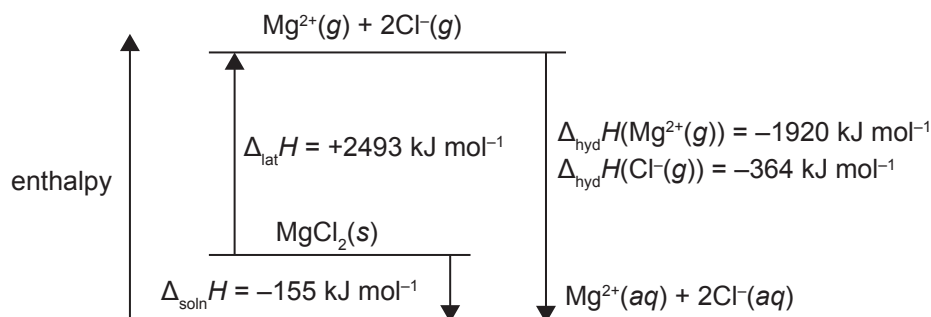
YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

Question	Score
ONE	
TWO	
THREE	
FOUR	
TOTAL	

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QUESTION ONE

- (a) The enthalpy change of solution, $\Delta_{\text{soln}}H$, is the enthalpy change when 1 mole of an ionic substance dissolves in water to give a solution. The enthalpy of solution can be calculated from the lattice enthalpy and hydration enthalpy values for the ions involved, as shown in the following Hess's Law diagram for MgCl_2 :



Single-use instant cold and hot packs often involve the dissolution of an ionic solid. Both types consist of a small plastic bag that contains a measured volume of water plus an anhydrous salt in the main compartment. Upon twisting, squeezing or striking the pack, the inner bag is ruptured, releasing the water and dissolving the salt. As the salt is dissolved, the temperature of the water can increase or decrease, depending on the composition of the pack. The processes occurring in each type of pack are thermodynamically favoured.

- (i) One such pack contains 115 mL of water and 39.0 g of ammonium nitrate, $\text{NH}_4\text{NO}_3(\text{s})$.

Calculate the temperature that the pack will theoretically reach when it is activated.

Assume that the pack is used at room temperature, 25 °C.

$$M(\text{NH}_4\text{NO}_3) = 80.0 \text{ g mol}^{-1} \quad c(\text{H}_2\text{O}) = 4.18 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$$

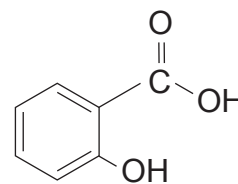
	Standard Enthalpy of Hydration/ kJ mol^{-1}
$\text{NH}_4^+(\text{g})$	-307
$\text{NO}_3^-(\text{g})$	-314

	Standard Lattice Enthalpy/ kJ mol^{-1}
$\text{NH}_4\text{NO}_3(\text{s})$	646

Use the total mass of the solution in your calculations. You may assume the specific heat capacity of the solution is the same as water.

- Justify this statement with consideration of the enthalpy and entropy of the processes occurring in **both** hot and cold packs.

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Salicylic acid

$M(\text{C}_7\text{H}_6\text{O}_3) = 138 \text{ g mol}^{-1}$
M.P: 159°C

Account for the difference in the melting points of the three compounds.

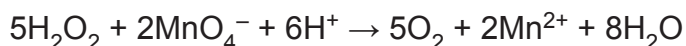
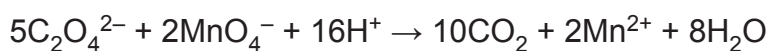
(a) Hydrogen peroxide solution, $\text{H}_2\text{O}_2(aq)$, can be purchased from the supermarket with a concentration given as “20 vol or 6%”. This represents 6 g of $\text{H}_2\text{O}_2(l)$ in 100 mL of solution. At this concentration the solution is useful as a bleaching agent for fabrics and hair.

A standard solution of sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4(aq)$, was prepared by dissolving 1.756 g of anhydrous $\text{Na}_2\text{C}_2\text{O}_4$ in sufficient distilled water to make 250.0 mL of solution.

www.lifepharmacy.co.nz/
globalassets/product-
images/gxh-11049862-0.
jpg

From the supermarket bottle, a 10.00 mL sample was extracted and diluted with distilled water to 100.0 mL in a volumetric flask. 10.00 mL samples of the diluted solution were mixed, in a conical flask, with 20 mL of 2 mol L⁻¹ H₂SO₄, and titrated against the KMnO₄ solution. The average titre value recorded was 13.43 mL.

The balanced equations for the two reactions in the procedure are:



- (i) Determine the mass of hydrogen peroxide per 100 mL in the bottle and use this to evaluate the extent of decomposition that has occurred since manufacture.

$$M(\text{Na}_2\text{C}_2\text{O}_4) = 134.0 \text{ g mol}^{-1} \quad M(\text{H}_2\text{O}_2) = 34.01 \text{ g mol}^{-1}$$

- standardisation of the KMnO_4 solution
- addition of H_2SO_4 solution to the reaction mixture
- heating the $\text{Na}_2\text{C}_2\text{O}_4$ solution prior to titration with the KMnO_4 solution.

- | | |
|-----------------------------|------------------------------|
| SF ₄ structures: | XeF ₄ structures: |
|-----------------------------|------------------------------|

- [illegible]

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(a) A wide variety of chlorine compounds exist, including oxoacids such as HClO , HClO_2 , HClO_3 , and HClO_4 , each containing chlorine atoms in different oxidation states.

The HClO is then believed to react in a second stage with any remaining HClO_2 to form ClO_2 and HCl. The reaction equation for the second stage can be balanced two possible ways, depending on which of HClO or HClO_2 is the oxidant.

Write the two possible balanced equations for the second stage of the decomposition and use the standard reduction potentials provided below to justify which of the two equations represents the reaction that is thermodynamically favoured.

$$\begin{array}{lll} E^\circ(\text{ClO}_2/\text{HClO}_2) = +1.18 \text{ V} & E^\circ(\text{HClO}/\text{HCl}) = +1.50 \text{ V} & E^\circ(\text{HClO}_2/\text{HCl}) = +1.58 \text{ V} \\ E^\circ(\text{ClO}_2/\text{HClO}) = +1.51 \text{ V} & E^\circ(\text{HClO}_2/\text{HClO}) = +1.67 \text{ V} & E^\circ(\text{ClO}_2/\text{HCl}) = +1.50 \text{ V} \end{array}$$

- (b) Compound **A**, with an unknown structure, was isolated from a reaction pathway and determined through high-resolution mass spectrometry to have a molecular formula of $C_6H_{13}OCl$.

In order to deduce the structure of Compound **A**, the following reactions were carried out.

Compound **A** was reacted with $NaOH(alc)$ to produce a single Compound **B**, which was then separated into two samples. The first sample was reacted with H_2/Pt to give Compound **C**, with the molecular formula $C_6H_{14}O$, which showed no optical activity.

The ^{13}C NMR spectra for Compounds **B** and **C** are provided in the resource booklet.

The second sample of Compound **B** was reacted with dilute H_2SO_4 , producing two products, Compounds **D** and **E**. After separation, each compound was analysed using mass spectrometry and both produced molecular ion peaks (M^+) at 118 m/z . Compounds **D** and **E** were each separately reacted with acidified potassium permanganate solution, H^+/MnO_4^- , to give Compounds **F** and **G** respectively. Analysis of Compounds **F** and **G** with mass spectrometry determined Compound **F** to have a greater molar mass than Compound **G**.

Compound **G** was miscible with water, but after treatment with $SOCl_2$, followed by reaction with an equimolar amount of methanol, formed Compound **H**, which was found to be immiscible with water.

- (i) Identify and give the structures of Compounds **A** to **H**.

Space for working:

Compounds A to H:

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- ¹³C NMR, MS, and IR spectra of Compound **K** are provided in the resource booklet.

Determine possible structure(s) for Compound **K**. Justify the structure(s) by integrating the spectroscopic data provided. Suggest any laboratory techniques that could be used to further narrow down the identity of Compound **K**.

-
- The graph displays a titration curve for a weak base being titrated with a strong acid (HBr). The x-axis represents the volume of HBr(aq) added in mL, ranging from 0 to 40. The y-axis represents the pH, ranging from 0 to 14. The curve starts at a high pH (approximately 11) and remains relatively flat until about 18 mL. It then drops sharply, passing through a pH of 7 at approximately 20.5 mL, and levels off at a low pH (approximately 1) after about 22 mL.

- Use these values and any other useful information to carefully sketch the remainder of the titration curve on the axes above.

- As the titration proceeds, a white precipitate slowly appears and then disappears. The greatest amount of precipitate is observed between 10–15 mL, and once the equivalence point has been reached, it has all completely disappeared.

No calculations are necessary.

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

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QUESTION
NUMBER

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