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QUALIFY FOR THE FUTURE WORLD KIA NOHO TAKATŪ KI TŌ ĀMUA AO!

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.

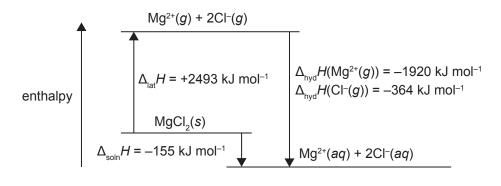
Check that this booklet has pages 2–24 in the correct order and that none of these pages is blank.

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	DIS USE ONLY

(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 MgCl₂:



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, $NH_4NO_3(s)$. Calculate the temperature that the pack will theoretically reach when it is activated.

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

$$M(NH_4NO_3) = 80.0 \text{ g mol}^{-1}$$
 $c(H_2O) = 4.18 \text{ J } ^{\circ}C^{-1}\text{ g}^{-1}$

	Standard Enthalpy of Hydration/kJ mol ⁻¹
$NH_4^+(g)$	-307
$NO_3^-(g)$	-314

	Standard Lattice Enthalpy/kJ mol ⁻¹
$NH_4NO_3(s)$	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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(b) Methyl salicylate (oil of wintergreen) and acetylsalicylic acid (aspirin) are two substances that can be synthesised industrially from salicylic acid. Both are used medicinally, with methyl salicylate used in skin creams such as Deep Heat^(TM) to treat muscle injury and pain, while aspirin is consumed orally in a tablet form to treat pain or reduce blood clotting.

Oil of wintergreen (methyl salicylate)

 $M(C_8H_8O_3) = 152 \text{ g mol}^{-1}$ M.P: -8 °C Aspirin (acetylsalicylic acid)

 $M(C_9H_8O_4) = 180 \text{ g mol}^{-1}$ M.P: 135 °C Salicylic acid

ОН

 $M(C_7H_6O_3) = 138 \text{ g mol}^{-1}$ M.P: 159 °C

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

ASSESSOR'S USE ONLY

(a) Hydrogen peroxide solution, $H_2O_2(aq)$, can be purchased from the supermarket with a concentration given as "20 vol or 6%". This represents 6 g of $H_2O_2(\ell)$ in 100 mL of solution. At this concentration the solution is useful as a bleaching agent for fabrics and hair.

To determine the percentage decomposition of hydrogen peroxide in a bottle purchased from the supermarket, the following procedure was carried out.

A standard solution of sodium oxalate, $Na_2C_2O_4(aq)$, was prepared by dissolving 1.756 g of anhydrous $Na_2C_2O_4$ in sufficient distilled water to make 250.0 mL of solution.

A solution of potassium permanganate, KMnO₄(aq), was prepared so that it was approximately 0.04 mol L⁻¹. To accurately determine the concentration of the solution, a 25.00 mL sample of the oxalate solution was pipetted into a conical flask and mixed with 20 mL of 2 mol L⁻¹ sulfuric acid, H₂SO₄(aq). The mixture was heated to 60–70 °C and titrated against the KMnO₄ solution until a faint pink colour appeared and was maintained for longer than 20 seconds. After repeats, the average titre value was 17.85 mL.

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

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 $\rm L^{-1}~H_2SO_4$, 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:

$$5C_2O_4^{2-} + 2MnO_4^{-} + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O_4^{-} + 2MnO_4^{-} + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O_4^{-}$$

(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.

$M(\text{Na}_2\text{C}_2\text{O}_4) = 134.0 \text{ g mol}^{-1}$	$M(H_2O_2) = 34.01 \text{ g mol}^{-1}$	

	e reasons for the following steps in the titration procedure, including justification of they improve the accuracy of the analysis:	ASSESS USE O
•	standardisation of the KMnO ₄ solution	
•	addition of H ₂ SO ₄ solution to the reaction mixture	
•	heating the Na ₂ C ₂ O ₄ solution prior to titration with the KMnO ₄ solution.	

SF ₄ structures:	XeF ₄ structures:
4	4
	shape , approximate bond angles, and polarity for each ew of the factors that contribute to these.

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QUESTION THREE

ASSESSOR'S USE ONLY

(a) A wide variety of chlorine compounds exist, including oxoacids such as HClO, HClO₂, HClO₃, and HClO₄, each containing chlorine atoms in different oxidation states.

Chlorine dioxide, ${\rm ClO_2}$, results from the spontaneous decomposition of one such oxoacid, ${\rm HClO_2}$. Studies indicate that the initial stage of the decomposition of ${\rm HClO_2}$ produces ${\rm HClO_3}$ and ${\rm HClO}$.

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.

In reactions that can proceed in more than one way, the pathway with the more positive E° value is thermodynamically favoured.

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.

$E^{\circ}(\text{ClO}_2/\text{HClO}_2) = +1.18 \text{ V}$ $E^{\circ}(\text{ClO}_2/\text{HClO}) = +1.51 \text{ V}$	$E^{\circ}(HClO/HCl) = +1.50 \text{ V}$ $E^{\circ}(HClO_2/HClO) = +1.67 \text{ V}$	$E^{\circ}(HClO_2/HCl) = +1.58 \text{ V}$ $E^{\circ}(ClO_2/HCl) = +1.50 \text{ V}$

(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 $C_6H_{13}OCl$.

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

The second sample of Compound **B** was reacted with dilute H₂SO₄, 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⁺/MnO₄⁻, 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 SOCl₂, 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:]	ASSESSOR'S USE ONLY
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n a different reaction pathway, Compound \mathbf{K} can be isolated. Based on its molar ma Compound \mathbf{K} is predicted to be a structural isomer of Compound \mathbf{B} .	.SS,
³ C 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 integration espectroscopic data provided. Suggest any laboratory techniques that could be use further narrow down the identity of Compound K .	
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ASSESSOR'S USE ONLY

(a) Gravimetric analysis of phosphate ions, PO_4^{3-} , in a solution can be achieved by following a procedure that precipitates the ions out as silver phosphate, $Ag_3PO_4(s)$.

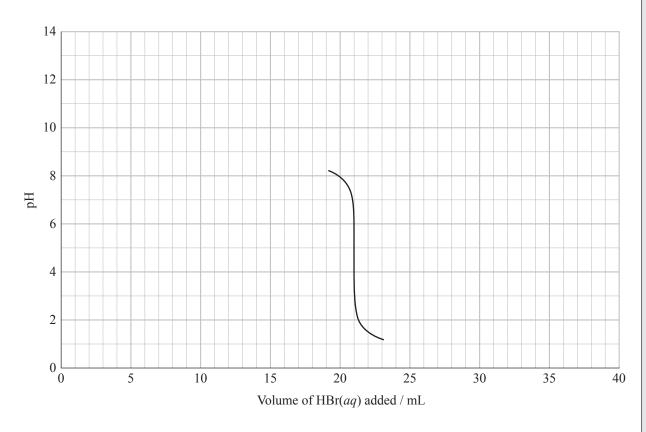
The procedure involves mixing the sample containing phosphate ions with an ammonia solution and adding silver nitrate dissolved in a solution of ammonia to bring the total volume up to 500 mL. The solution is then slowly heated at a low temperature, causing ammonia gas to be evaporated from the solution and the slow precipitation of silver phosphate. The heating is stopped once the pH drops below 7.5. The solution is cooled to 25 °C, and the precipitate is filtered, washed, dried, and weighed. The phosphate content can be determined from the mass of precipitate formed.

A sample containing phosphate ions is analysed using this procedure and produces 17.32 g of Ag_3PO_4 . Once the precipitate is filtered off, the concentration of silver ions, $[Ag^+]$, in the remaining 471.3 mL of solution is 5.017×10^{-5} mol L⁻¹.

Evaluate the efficiency of the procedure by determining the solubility product of silver phosphate, $K_s(Ag_3PO_4)$, and using it to calculate the percentage of phosphate ions not captured by the procedure.

$M(Ag_3PO_4) = 418.6 \text{ g mol}^{-1}$	$s(Ag_3PO_4)$ at 25 °C = 7.381 × 10 ⁻³ g L ⁻¹

(b) 15.00 mL of a dilute solution of ammonia, $NH_3(aq)$, is titrated with a standardised solution of 1.15 mol L⁻¹ HBr(aq). The pH is digitally monitored, and a portion of the titration curve is shown below.



(i) The pH at the equivalence point is 4.70.

Determine the p K_a for the conjugate acid of NH₃(aq), and calculate the pH at 0 mL, 3 mL, and after 35 mL of HBr(aq) has been added.

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

(ii)	A second titration is carried out with a small amount of solid zinc bromide, $\operatorname{ZnBr}_2(s)$, dissolved in the ammonia solution, $\operatorname{NH}_3(aq)$, before any hydrobromic acid, $\operatorname{HBr}(aq)$, is added. The solution is observed to be colourless.	ASSESSOR' USE ONLY
	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.	
	Give an account of the observations made, with reference to the species present in the solution.	
	No calculations are necessary.	

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

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

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