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

Scholarship 2016 Chemistry

2.00 p.m. Monday 14 November 2016 Time allowed: Three hours Total marks: 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 Sheet 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 – 20 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.

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USE ONLY QUESTION ONE

- (a) A very dilute solution of sodium cyanide, NaCN, can be used to extract gold from its ore. Gold reacts with oxygen gas to form, in the presence of cyanide ions, the $[Au(CN)_2]$ [–] ion. This process is carried out at pH 10–11 in order to ensure that $CN⁻$ ions are not converted to toxic hydrogen cyanide gas, HCN. The gold is then recovered as a metal by reacting the solution with zinc, which is converted to $[Zn(CN)₄]^{2-}$. Sometimes the recovered gold also contains elemental silver as an impurity. This silver impurity can be removed from the gold by reacting the mixture with nitric acid.
	- (i) Discuss the chemistry occurring in the extraction process described above by identifying the oxidation-reduction processes that take place, using electrode potentials to explain why gold can be extracted in this way, including the use of nitric acid to separate gold and silver.

 Include balanced equations for each step in the procedure, and use the electrode potentials in the Resource Booklet to account for the reactivity observed.

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(ii) The stability of the complex ions $[Au(CN)_2]$ ⁻ is reflected in the size of the formation constant K_f , the equilibrium constant for the following equation:

 $Au^+ + 2CN^- \rightleftharpoons [Au(CN)_2]^-$ *K*_f = 4 × 10²⁸ (at 25°C)

Determine the concentration of sodium cyanide, NaCN (in mol L^{-1}) that is required to keep 99% of the soluble gold in solution as the complex ion (assume that all the soluble gold is $Au(I)$).

Comment on the pH dependence of the composition of the equilibrium mixture.

 $pK_a(HCN) = 9.5$

(b) Iron ore, $Fe₂O₃$, in a rock sample can be analysed by titration with acidified potassium dichromate solution, $K_2Cr_2O_7 /H^+$.

A 2.8351 g sample of haematite rock containing $Fe₂O₃$, was dissolved in hot concentrated hydrochloric acid, HCl, and the solution diluted to 250.0 mL in a volumetric flask.

20.00 mL samples were pipetted into conical flasks, and a small excess of tin(II) chloride solution was added to change the colour from yellow to pale green. A saturated solution of mercury(II) chloride was then added until a small amount of white precipitate appeared. A few drops of diphenylamine sulfonate indicator were added. The resulting mixture was titrated with a standard solution of potassium dichromate. The average titre value recorded was 18.56 mL.

The standard solution of potassium dichromate was made by dissolving 2.5077 g of $K_2Cr_3O_7$ in sufficient water to give 500.0 mL of solution.

(i) Calculate the % composition of $Fe₂O₃$ in the haematite sample.

ASSESSOR'S (ii) Explain why it is not appropriate to carry out this titration using potassium permanganate, $K MnO₄$, instead of potassium dichromate, as the oxidant.

USE ONLY QUESTION TWO

(a) Compound **A**, has the molecular formula $C_{10}H_{17}O_2Cl$ and has one chiral centre. Compound **A** does not decolourise bromine water. When Compound **A** is reacted with dilute acid solution, two products, Compound **B** and Compound **C**, are formed.

Compound **B** does not have a chiral centre. When subjected to mass spectrometry, it is found to have a molecular ion peak at $m/z = 114$.

Compound **C**, when subjected to mass spectrometry, is found to have a molecular ion peak at $m/z = 108$. There is also a M+2 peak present, and the ratio of the heights of the M and M+2 peaks is 3:1.

When Compound C is treated with thionyl chloride, $S OCl₂$, Compound D is produced.

The 13C NMR spectrum of all Compounds A to D are available in the Resource Booklet. The IR spectrum of Compound B is also available.

Determine the identity of Compounds **A** to **D**.

Justify your answers by linking your choices to the spectra provided and the information given above.

Compounds **A** to **D**:

(b) Nitrogen dioxide, NO₂, is a brown gas that is often a component of air pollution. It is in equilibrium with a dimeric species, dinitrogen tetroxide, N_2O_4 . Dinitrogen tetroxide is used as a rocket fuel in combination with hydrazine, N_2H_4 , and the products of the combustion reaction of this mixture are gaseous nitrogen and water.

Table 1: Selected thermochemical data

Table 2: Selected bond enthalpies (kJ mol–1)

(i) Discuss how enthalpy and entropy affect the dimerisation equilibrium.

ASSESSOR'S (ii) Discuss why a N_2O_4 / N_2H_4 mixture is suitable for use as a rocket fuel, linking assessore appropriate data from Tables 1 and 2 to molecular structures.

QUESTION THREE

(a) The pH titration curves for the following reactions are shown below.

20 mL of 0.5 mol L⁻¹ propanoic acid, CH₃CH₂COOH, titrated with 0.5 mol L⁻¹ sodium hydroxide (Graph One)

20 mL of 0.5 mol L⁻¹ propan-1-amine, CH₃CH₂CH₂NH₂, titrated with 0.5 mol L⁻¹ hydrochloric acid (Graph Two)

 pK_a (CH₃CH₂COOH) = 4.88 p K_a $(CH_3CH_2CH_2NH_3^+) = 10.71$

(i) Sketch the titration curve for the reaction of 20 mL of 0.5 mol L^{-1} propanoic acid, CH_3CH_2COOH , titrated with 0.5 mol L⁻¹ propan-1-amine, $CH_3CH_2CH_2NH_2$.

(ii) Aqueous solutions containing equal concentrations of propanoic acid and propan-1-amine are mixed.

 Complete the table below by giving the **dominant** species that would be present in the mixture at the given pH.

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Give reasons linked to the graphs, and show relevant equations.

(b) An organic nitro-compound, CH_3NO_2 , is reduced by electrolysis in an aqueous ethanoate buffer solution at pH 5.0. In the solution, the total ethanoate concentration, $[CH_3COOH] + [CH_3COO^-]$ is known to be 0.500 mol L^{-1} .

A 300 mL sample of the buffered solution contains 0.0100 mol L^{-1} CH₃NO₂ that has been completely reduced by the electrolytic process.

The reduction reaction is: $CH_3NO_2 + 4H^+ + 4e^- \rightarrow CH_3NHOH + H_2O$

(i) Calculate the pH of the solution after reduction of $CH₃NO₂$ is complete.

Assume that the effect of the hydrolysis of the methylhydroxylamine, $CH₃NHOH$, is negligible at this pH.

 K_a (CH₃COOH) = 1.75 × 10⁻⁵ p K_a $pK_{3}(CH_{3}COOH) = 4.76$

(ii) Evaluate the validity of the assumption that hydrolysis of methylhydroxylamine does not occur at this pH.

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K_a(CH<sub>3</sub>NH<sub>2</sub>OH<sup>+</sup>) = 1.09 × 10<sup>-6</sup> pK_apK_aCH_3NH_2OH^+) = 5.96
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QUESTION FOUR

The melting points of a selection of hydrides are given in the table below. The position of the hydrides in the table reflects the relative position of the non-hydrogen element in the Periodic Table.

(a) (i) Discuss the **variation** in the melting points of the hydrides of the elements of Period 3 $(SiH₄, PH₃, and H₂S).$

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(ii) Discuss the **trend** in the melting points of the hydrides of the elements of Group 15 $(NH_3$ to $SbH_3)$. **Question Four continues on the following page.**

(iii) The acidic properties of the non-metal hydrides increase left to right across a period, and down a group.

Account for these trends using the hydrides of Period 2 elements ($CH₄$ to HF) and those of Group 16 elements (H_2O to H_2Te).

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(b) The hydrides of the elements of Groups 1 and 2 are all solids at room temperature, but apart from LiH, which melts at 689ºC, the metallic hydrides decompose at temperatures around 250ºC. Because of this it is not possible to use melting points to compare the strength of the metal hydride bond. To compare the strength of these bonds, some enthalpy data is provided in the table below.

Note: Lattice enthalpy is the standard enthalpy change for the conversion of an ionic solid into a gas of ions.

Compare and contrast the expected strength of the metal hydride bonds of the Group 1 and 2 elements, and justify whether the lattice enthalpy data or the enthalpy of formation data is the better predictor of the expected trends in the strength of the metal hydride bonds.

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