Class Adm No

Class	Adm No

Candidate Name: ____________________

H

millennia institute

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **18th Sept 2018**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Section A – Answer **all** questions.

Section B – Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

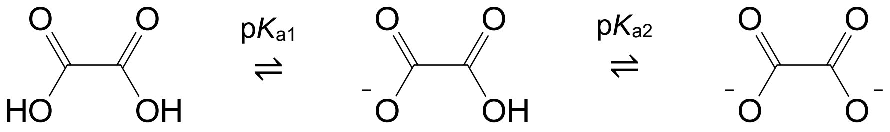
Question	**Section A**			**Section B**		Total
	1	**2**	**3**	**4**	**5**	
Marks	**23**	**20**	**17**	**20**	**20**	**80**

This question paper consists of **11** printed pages and **1** blank page.

Section A

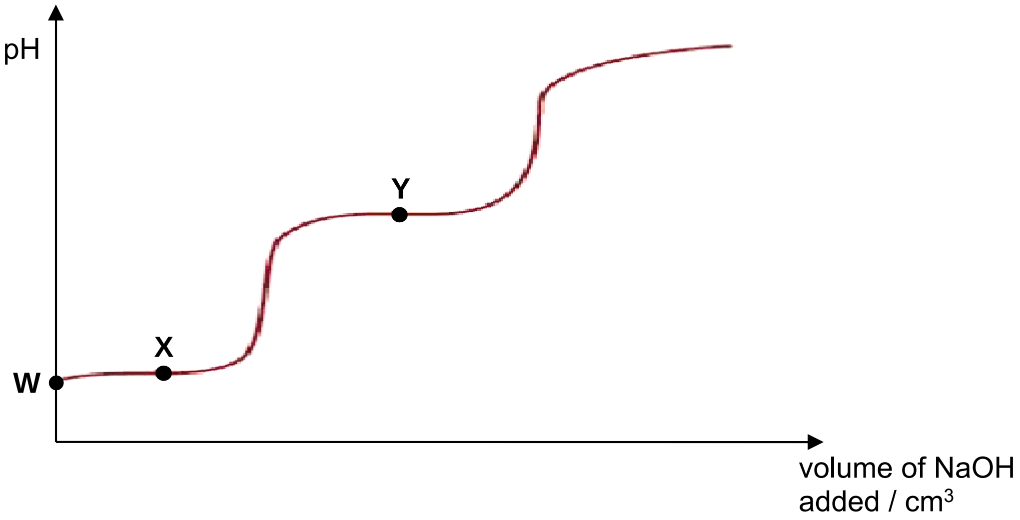
Answer **all** questions from this section.

1 Oxalic acid is a weak diprotic Brønsted acid with pK_{a1} and pK_{a2} values of 1.25 and 4.14 respectively.



25 cm^3 of 0.50 mol dm^{-3} oxalic acid was titrated against a solution of 1 mol dm^{-3} of sodium hydroxide. Only 1 to 2 drops of phenolphthalein indicator was used in this titration. It was found that the first colour change occurred at 19.40 cm^3.

A sketch (not drawn to scale) of the pH titration curve is shown below.



(a) Suggest why the value of pK_{a2} is larger than pK_{a1}. [2]

(b) **(i)** Calculate the value of pH at point **W**. [1]

(ii) Given that the pH at point **X** is 1.25, calculate the volume of NaOH added at point **X**. [2]

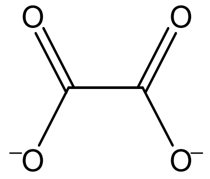
(c) **(i)** Define the term *buffer*. [1]

(ii) Write an equation to illustrate how the reaction mixture found at point **Y** can maintain the pH of a solution when a small amount of OH$^-$(aq) is added. [1]

(d) **(i)** Describe how you would recognise the end point of the titration described. [1]

(ii) Explain why only 1 or 2 drops of phenolphthalein indicator was used in the titration. [1]

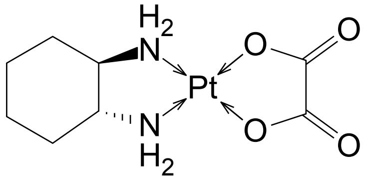
The oxalate ion, $C_2O_4^{2-}$, is known to form complexes with transition metal ions such as platinum(II). The structure of the oxalate ion is as follows.



(e) **(i)** It is observed that a solution of aqueous platinum(II) ions turns universal indicator orange.

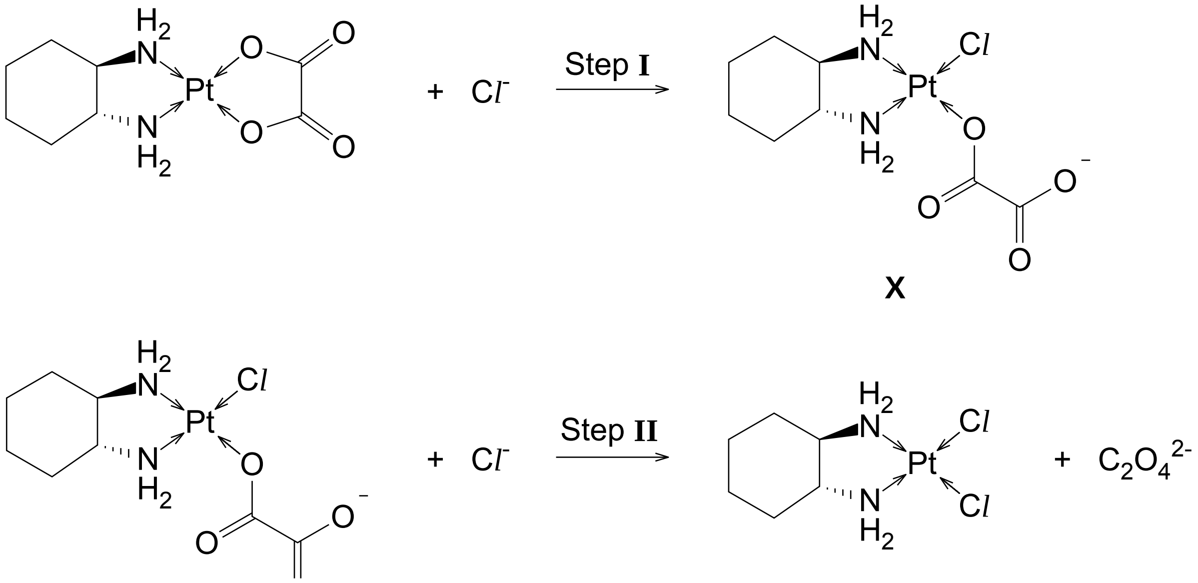
Given that platinum(II) is a transition metal ion known to form **square planar complexes**, explain the observation seen with the aid of a chemical equation. [3]

Oxaliplatin is a platinum(II) based anti-cancer drug used to treat colorectal cancer. It contains one $C_2O_4^{2-}$ ligand.



oxaliplatin

When a **concentrated** Cl^- solution is added to oxaliplatin, ligand exchange occurs and the Cl^- ligands take the place of $C_2O_4^{2-}$ in a two-step reaction.



(ii) By consideration of entropy changes, predict with explanation if Step **I** is likely to be **feasible** if diluted Cl^- solution was used instead. Assume that Cl^- and $C_2O_4^{2-}$ have the same ligand strength.

State the missing numerical data necessary to confirm your prediction. [2]

(iii) Determine if any the three complexes, oxaliplatin, **X** and/or **Y** can exhibit cis-trans isomerism. Explain your answer. [2]

(iv) Hydrated crystals of complex **Y** have the structural formula $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$.

When excess $AgNO_3$ solution was added to an aqueous solution containing 0.0094 mol of an isomer of $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$, 1.35 g of a white precipitate was obtained.

Determine the structural formula of this isomer. [3]

(f) **(i)** Determine the number of protons, neutrons and electrons in $^{52}Cr^{3+}$. [1]

(ii) State the full electronic configuration of $^{52}Cr^{3+}$. [1]

(iii) Draw and label the d orbitals in the valence shell of $^{52}Cr^{3+}$.

You are required to show the orientation of the orbitals with respect to the x, y and z axes. [2]

[Total: 23]

2 **(a)** State the relationship between the Faraday constant, *F*, the charge on the electron, *e*, and the Avogadro number, *L*. [1]

(b) Copper metal containing impurities such as zinc, iron, and silver can be purified via electrolysis.

(i) Draw a **well-labelled** diagram of a suitable set-up for purifying impure copper and state the reaction occurring at the cathode. [3]

A fixed current was passed through the cell for a duration of time to determine the experimental values of *F* and *L*. The following are the results obtained.

current passed through the cell = 0.500 A
duration of time = 30.0 min
change in mass of cathode = 0.299 g

(ii) Use the data above and relevant information from the *Data Booklet* to calculate a value of *L*. [3]

(c) Rechargeable lithium ion batteries have been developed in Japan.

The standard electromotive force of a rechargeable lithium ion battery is 3.70 V. During discharge, Li^+ ions flow from the anode to the cathode through the electrolyte.

During the **discharging** process, the ion-electron equation at the cathode is

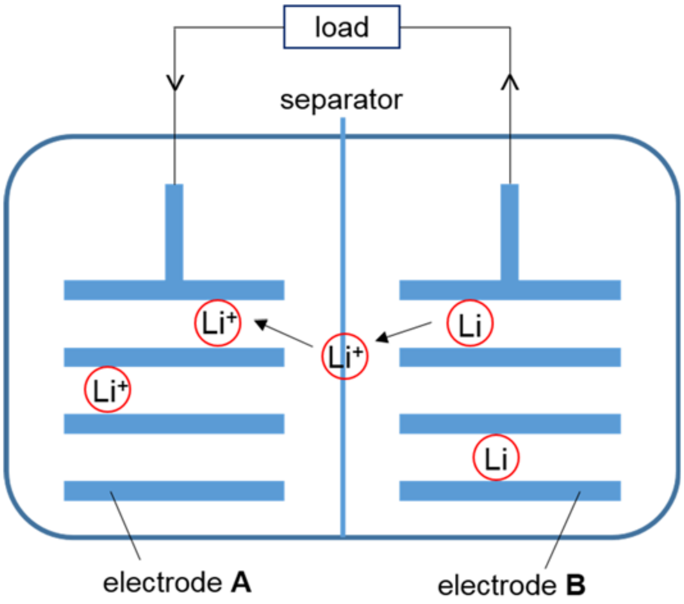
$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2,$$

and the ion-electron equation at the anode is

$$LiC_6 \rightarrow C_6 + Li^+ + e^-$$

where CoO_2 and graphite, C_6, are *layered* solid electrodes which can have Li^+ ions and Li atoms **embedded between their layers** respectively.

A schematic of the rechargeable lithium ion battery **during discharge** is shown below.



(i) By considering the overall equation of the battery during discharge, calculate a value for the standard Gibbs free energy of the reaction in kJ mol^{-1}. [1]

(ii) A fully charged battery cell starts with 10.0 g of CoO_2 and 10.0 g of LiC_6.

Calculate the mass of electrode **A** when this cell is fully **discharged**. [3]

(iii) The fully discharged cell is plugged into a power source to recharge it. During the charging process, the direction of electron-flow is reversed.

Determine the mass of electrode **B** when the cell is fully **charged**. [1]

(iv) Suggest **two** reasons why water cannot be used as the electrolyte solvent in rechargeable lithium ion batteries. [2]

(v) Rechargeable lithium ion batteries tend to perform poorly when used in cold countries. Suggest a reason for this. [1]

(d) Lithium oxide is a white solid that is used to lower the melting point of ceramic glazes.

(i) Write an equation, with state symbols, to represent the lattice energy of lithium oxide. [1]

(ii) Use the following data, together with appropriate data from the *Data Booklet*, to calculate a value for the lattice energy of lithium oxide.

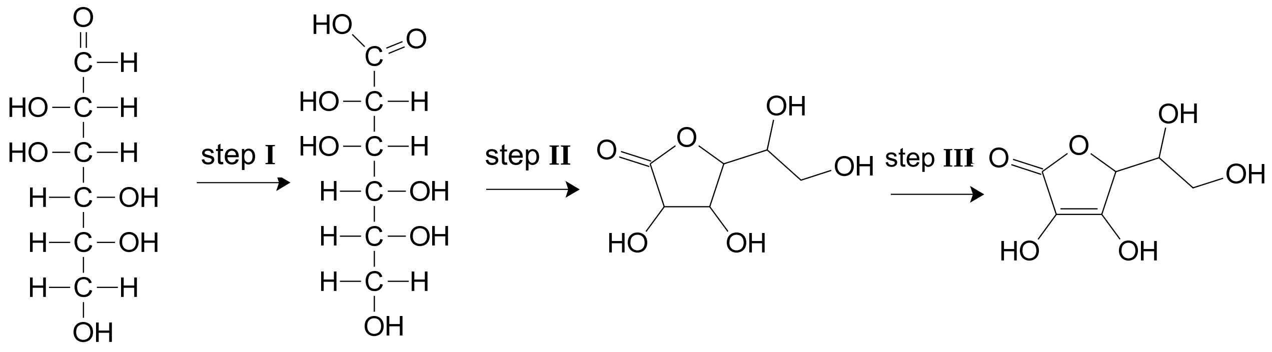
1st electron affinity of oxygen = -141.1 kJ mol^{-1}
2nd electron affinity of oxygen = +798 kJ mol^{-1}
enthalpy change of atomisation of lithium = +159.4 kJ mol^{-1}
enthalpy change of formation of lithium oxide = -597.9 kJ mol^{-1}

[4]

[Total: 20]

3 Ascorbic acid, also known as Vitamin C is required for the synthesis of collagen in humans. A vitamin C deficient diet leads to a disease called scurvy. Ascorbic acid is known to be water soluble and is commonly used as a food additive.

The building block for ascorbic acid is the glucose molecule. The following synthetic pathway for the formation of ascorbic acid was proposed.



Glucose **Intermediate A** **Intermediate B** **Ascorbic Acid**

(a) State the functional groups present in intermediate **B**. [2]

(b) State the reagent and conditions required for step **II**. [1]

(c) State the type of reaction for steps **I** and **II**. [2]

(d) Identify the type(s) of stereoisomerism shown by ascorbic acid. State the total number of possible stereoisomers. [2]

(e) Explain why ascorbic acid is water soluble. [2]

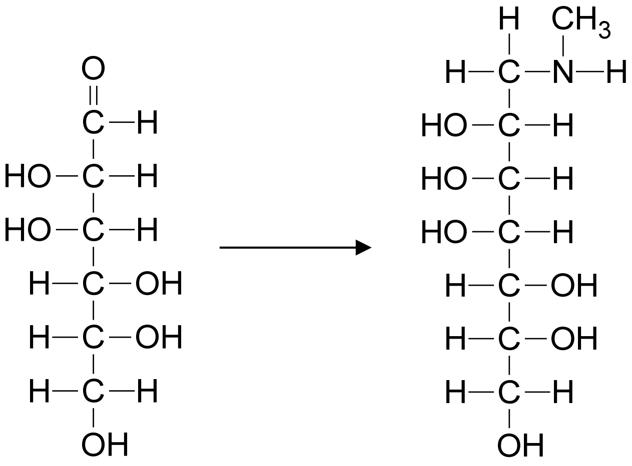
(f) Draw the structural formulae of all the organic products formed when ascorbic acid is treated with the following reagents. [3]

(i) PCl_5

(ii) excess hot acidified $K_2Cr_2O_7$

(iii) Na(s)

(g) Compound **L** can be formed from glucose.



glucose **L**

Suggest a synthetic route, involving *not more than three steps*, from **glucose** to **L**.

In your answer, suggest the reagents and conditions involved in each step and draw the structural formulae of the intermediate organic products. You may use R to represent the side chain of the compound that is not involved in the reaction. [5]

[Total: 17]

Section B

Answer **one** question from this section.

4 In the chlor-alkali industry, 19.8 g impure sample of NaC*l*(s) was dissolved in 150 cm^3 water to form sodium chloride solution. 50 cm^3 of the solution was electrolysed to produce chlorine, sodium hydroxide, and hydrogen.

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2$$

The pure chlorine gas reacts with hydrogen gas to produce 1.8 g of hydrogen chloride gas in the presence of ultraviolet light.

(a) **(i)** Write an equation to show the production of hydrogen chloride gas. [1]

(ii) Explain why ultraviolet light is required in the production of hydrogen chloride. [1]

(iii) State the type of mechanism for the reaction between chlorine gas and hydrogen gas. [1]

(iv) Calculate the number of hydrogen chloride molecules produced at room temperature and pressure. [1]

(v) Calculate the percentage of sodium chloride present in the impure solid, assuming that all of the chlorine gas and hydrogen gas had reacted. [3]

(b) Hydrogen chloride gas can also be produced by the reaction between concentrated sulfuric acid and dilute hydrochloric acid.

State the role of concentrated sulfuric acid. [1]

(c) Explain why hydrogen chloride has a lower boiling point than hydrogen bromide. [2]

(d) When an equimolar mixture of gaseous ammonia and gaseous hydrogen chloride at an initial total pressure of 2.5 atm was injected into a chamber maintained at 400 °C, white crystals of ammonium chloride were formed as shown in the following dynamic equilibrium:

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s) \qquad \Delta H > 0$$

It was found that 84% of the gases had dissociated at equilibrium.

(i) Define the term *dynamic equilibrium*. [1]

(ii) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

(iii) Calculate the value of K_p at 400 °C, giving its units. [2]

(iv) State and explain how the partial pressure of the gases and the value of K_p would change if the following changes were made separately:

I. the temperature of the chamber was halved to 200 °C
II. the volume of the chamber was increased (at constant temperature)
III. 2 atm of neon gas is inserted into the chamber [6]

[Total: 20]

5 **(a)** The reaction between propanone, CH_3COCH_3, and bromine, Br_2, in the presence of acid, H^+, is found to have an overall order of reaction of 2.

(i) Given that rate is independent of the bromine concentration, write **three** possible rate expressions for this reaction. [3]

(ii) Three separate experiments were carried out. In each experiment, the concentration of one of the three different reactants was doubled respectively.

Predict the effect of doubling the concentration of each reactant on the rate of reaction for the **first** rate expression you have written in **(a)(i)**. [2]

(iii) The table below shows how the concentration of propanone changes with time in a reaction.

Time / min	[propanone] / mol dm^{-3}
5.0	1.6
7.0	1.4
9.0	1.2
12.0	1.0
15.0	0.8
18.5	0.6
21.5	0.5
25.0	0.4
28.0	0.3
35.0	0.2

Without plotting a graph, use the data given in the table to confirm that the reaction is first order with respect to propanone. Show your working clearly. [2]

(iv) The overall reaction described in **(a)** is:

$$CH_3COCH_3(aq) + Br_2(aq) \xrightarrow{H^+} CH_3COCH_2Br(aq) + HBr(aq)$$

State **one** dependent variable that you can readily measure in order to follow the progress of the reaction. [1]

(v) State and explain the role of acid in this overall reaction. [2]

(b) Similar to bromine, halogens like fluorine and chlorine are not naturally found in their elemental form due to their high reactivity.

(i) State and explain the trend in atomic radius down the halogen group. [2]

(ii) By citing relevant values from the *Data Booklet*, deduce and explain the relative reactivity of the halogens as oxidising agents. [2]

(iii) Describe **one** chemical test to illustrate the relative reactivity of any two halogens as oxidising agents. Clearly state any observations seen. [1]

(iv) Chlorine reacts explosively with hydrogen to form the hydride of chlorine, hydrogen chloride.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Using your answer in **(b)(ii)** or otherwise, suggest a reason for the general reactivity of the halogens. [1]

(v) Describe and explain the trend in thermal stability of the halogen hydrides. [2]

(c) Chlorine is able to form an acidic oxide with the formula ClO_2. Another Period 3 element, magnesium, forms a basic oxide with the formula MgO.

(i) Write an equation to show how the oxide ion, O^{2-}, acts as a base in the reaction with water. [1]

(ii) Suggest why ClO_2 is not a basic oxide, unlike MgO. [1]

[Total: 20]

BLANK PAGE