NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **15 September 2017**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Writing Paper

READ THESE INSTRUCTIONS:

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. Marks [60]

Section B

Answer **one** question. Marks [20]

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

A Data Booklet is provided.

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.

This document consists of **14** printed pages (including this page).

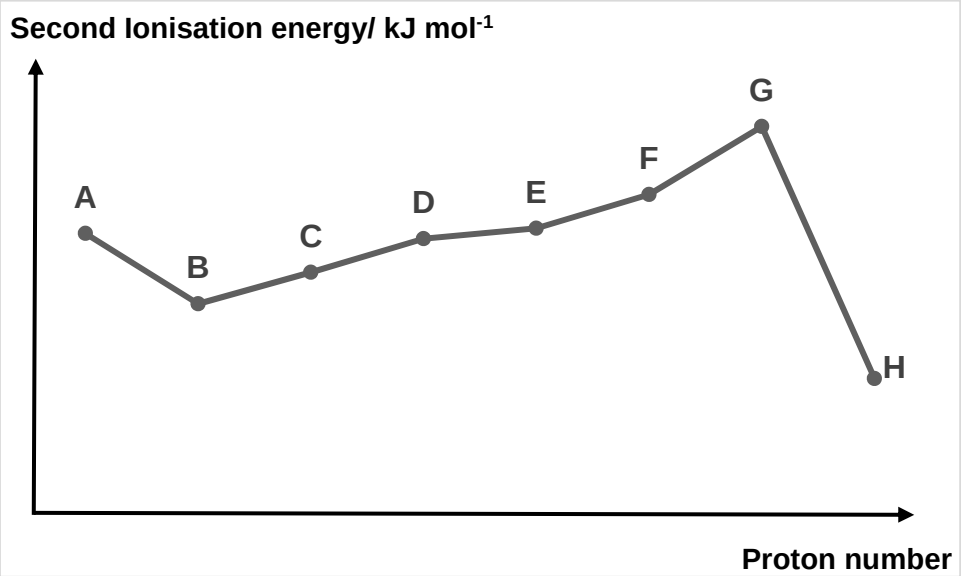
Section A

Answer **all** the questions in this section.

1 (a) Iodine is a lustrous purple-black solid at standard conditions that sublimes readily to form a violet gas.

(i) Give the equation that represents the *second ionisation energy* of *iodine*. [1]

(ii) The graph below shows the second ionisation energies of eight elements with consecutive atomic number. [2]



Which of the above elements, **A** to **H**, is iodine? Explain your answer.

(iii) Explain the trend in second ionisation energies from elements **A** to **G**, including the irregularity for element **B**. [4]

(iv) Suggest, with reason, which of the above elements, **A** to **H**, can form an amphoteric oxide. [2]

Hence, write an equation to show the reaction of this amphoteric oxide with hydrochloric acid. (You are not required to provide the identity of the element in the equation.)

1 (b) Hydrogen peroxide reacts with acidified iodide ions to liberate iodine, according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

The rate of reaction can be measured by the increase in the concentration of iodine formed over time. The reaction was determined to be zero order with respect to $[H^+]$.

The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

Expt	Initial $[H_2O_2(aq)]$ / mol dm^{-3}	Initial $[I^-(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.020	0.040	1.2×10^{-4}
2	0.020	0.050	1.5×10^{-4}
3	0.050	0.040	3.0×10^{-4}
4	0.020	0.500	1.5×10^{-3}
5	0.050	1.000	7.5×10^{-3}

(i) What is understood by the terms *order of reaction* and *half-life*. [2]

(ii) Determine the order of the reaction with respect to $[H_2O_2]$ and $[I^-]$ and hence suggest the units of the rate constant of this reaction. [3]

(iii) The half-life of hydrogen peroxide in experiment 4 was 9.24 min. Predict the half-life of hydrogen peroxide in experiment 5. [1]

To investigate the rate of the above reaction, a teacher suggested titrating the iodine formed with sodium thiosulfate solution at specified time intervals.

(iv) Write an equation for the reaction between iodine and thiosulfate. [1]

1 (b) (v) Suggest how the reaction can be quenched at specified time intervals. [1]

(vi) With reference to the *Data Booklet*, explain why hydrochloric acid is not a suitable acid used for the reaction between hydrogen peroxide and iodide. [2]

[Total:19]

2 Metals have been used widely since ancient times.

(a) An electrochemical cell is constructed using solutions of $NaHSO_4$, H_2SO_3, and $MnSO_4$ with suitable electrodes.

The relevant half reactions are:

$HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O \quad E^\ominus = +0.17\ V$

$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s) \quad E^\ominus = -1.18\ V$

(i) Draw a fully labelled diagram of the above electrochemical cell to measure the cell potential under standard conditions, indicating clearly the direction of the electron flow in the external circuit. [3]

(ii) Write a balanced equation for the reaction that would take place if the electrodes of the cell were connected together by an external circuit. [1]

(iii) Calculate the standard cell potential for this cell [1]

(iv) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the cell above. [1]

(v) Suggest, with reasons, what happens to the $E^\ominus_{cell}$ when the following are done to the electrochemical cell above. [4]

1) The pH of the HSO_4^-/H_2SO_3 half−cell is increased.

2) A solution of sodium hydroxide to the Mn^{2+}/Mn half−cell.

2 **(b)** In an electrolytic cell, a current of 0.250 A is passed through a concentrated solution of a chloride of iron, producing iron metal and gas, **Y**.

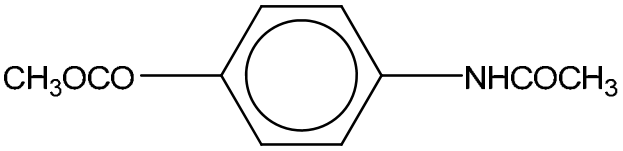
(i) Write the equation for the half-reaction take occurs at the anode. [1]

(ii) When the cell operates for 2 hours, 0.521 g of iron is deposited at one of the electrodes. Determine the formula of the chloride of iron in the original solution. [2]

(iii) Write a balanced equation for the overall reaction that occurs in the cell. [1]

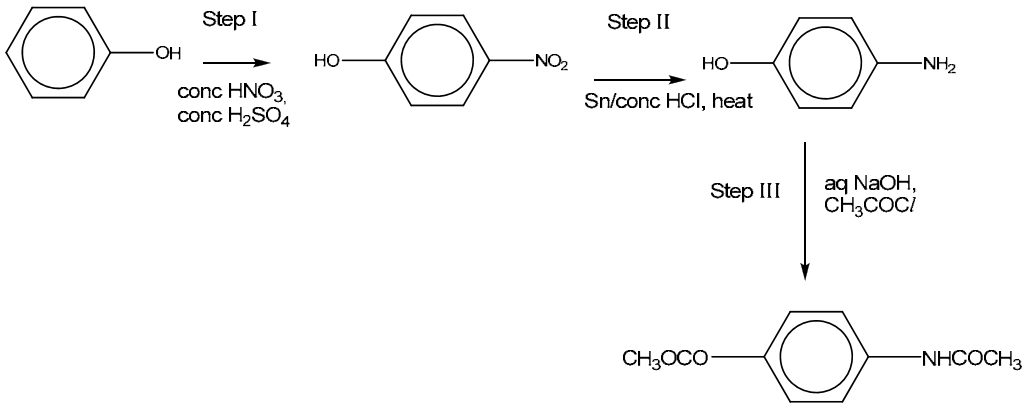
(iv) Calculate the current that would produce the gas **Y** from the solution at a rate of 2.50 g per hour. [2]

(c) Metals are also used as catalysts in organic synthesis. The derivative of acetaminophene is investigated for the treatment of headaches.

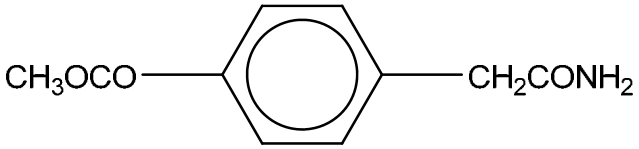


Derivative of acetaminophene

(i) A student suggested a flawed synthesis of the derivative of acetaminophene starting from phenol. Identify and explain the error in each step. [3]



2 (c) (ii) Compound **Z** is an isomer of the derivative of acetaminophene. Suggest a simple chemical test to distinguish between the derivative of acetaminophene and compound **Z**. [2]



compound **Z**

[Total:21]

3 (a) Blood obtains its colour from its respiratory proteins which occur as octahedral metal complexes. It is different in different organisms.

Protein	Source	Metal per subunit	De-oxygenated colour	Oxygenated colour
Haemoglobin	Mammals, birds, fish, reptiles, insects	1 Fe	red-purple	red
Haemocyanin	mollusks, crustaceans, spiders	2 Cu	colourless	blue

(i) Explain why oxygenated haemoglobin and haemocyanin are coloured. [3]

(ii) Using the Cartesian axes, like those shown in Figure 3.1, draw **fully labelled** diagrams of the following. [2]

- One of the d-orbitals at the lower energy level in an octahedral complex. Label the diagram “lower”.
- One of the d-orbtials at the upper energy level in an octahdral complex. Label this diagram “upper”.

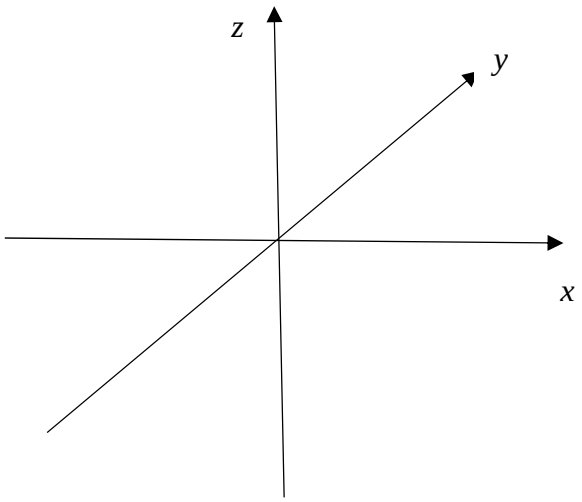
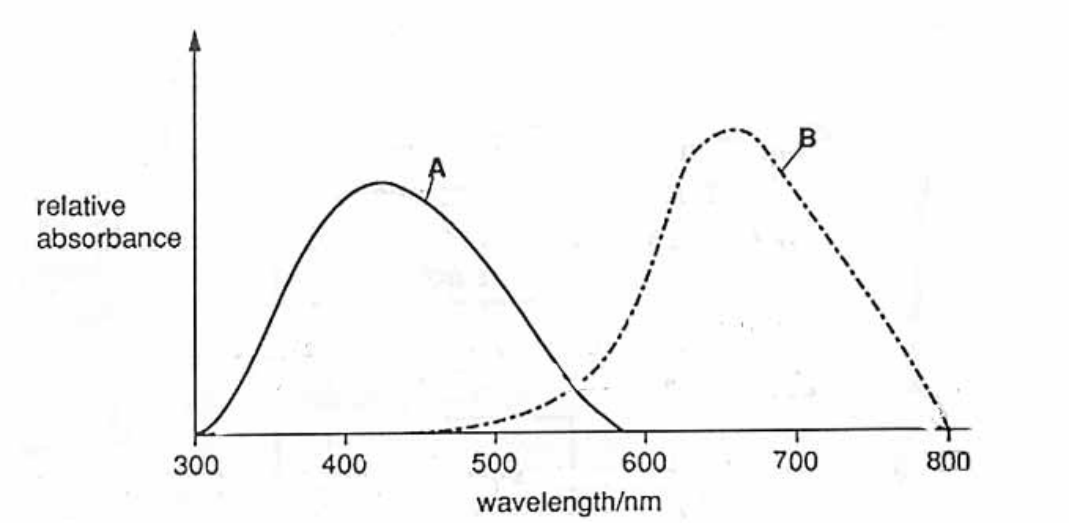


Figure 3.1

(iii) Explain why the splitting of the d subshell occurs in an octahedral complex using your answer in **(a)(ii)**. [2]

3 (b) Oxygenated haemoglobin and haemocyanin were analysed and the absorption spectrum was observed.



Colour	Wavelength (nm)	Colour	Wavelength (nm)
Violet	380 – 400	**Yellow**	560 – 580
Blue	400 – 490	**Orange**	580 – 620
Green	490 – 560	**Red**	620 – 800

(i) Which graph represents the absorption spectrum of oxygenated haemocyanin? Explain your answer. [2]

(ii) Which oxygenated blood (haemoglobin or haemocyanin) has a larger energy gap between the d subshells after splitting? Explain your answer. [2]

(iii) The deoxygenated haemocyanin has a Cu^+ central ion. State the electronic configuration of Cu^+. Hence, suggest why the deoxygenated haemocyanin is colourless? [2]

3 (c) Carbon monoxide, chlorine and phosgene are the best known toxic gases. Many of these gases are assigned an NFPA 704 health rating of 4 (may be lethal) or 3 (may cause serious or permanent injury).

Toxic Gas	Chemical formula	Colour	Odour	NFPA 704 Health Rating
carbon monoxide	CO	colourless	No	3
chlorine	Cl_2	green	Yes	4
phosgene	CCl_2O	colourless	No	4

(i) Describe, in terms of bonding, what happens when carbon monoxide is absorbed in the human blood and hence, explain why it is given a NFPA 704 health rating of 3. [2]

(ii) Chlorine was widely used as a chemical warfare in World War I. However, it was replaced by phosgene as a more effective chemical warfare. Suggest one possible reason why chlorine was replaced by phosgene. [1]

(d) Phosgene reacts with water to release hydrogen chloride and carbon dioxide gas.

$$CCl_2O + H_2O \rightarrow CO_2 + 2HCl \quad \text{----------Reaction } \mathbf{1}$$

(i) Draw the dot-and-cross diagram of phosgene and suggest its bond angle. [2]

(ii) Suggest the type of reaction involved in Reaction **1**. [1]

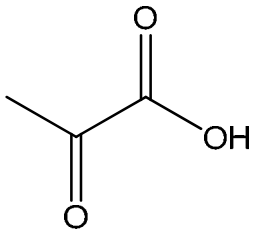
(iii) Gaseous spills of phosgene can be removed using ammonia. The reaction is similar to Reaction **1**. Suggest how phosgene reacts with ammonia, using a chemical equation . [1]

[Total:20]

Section B

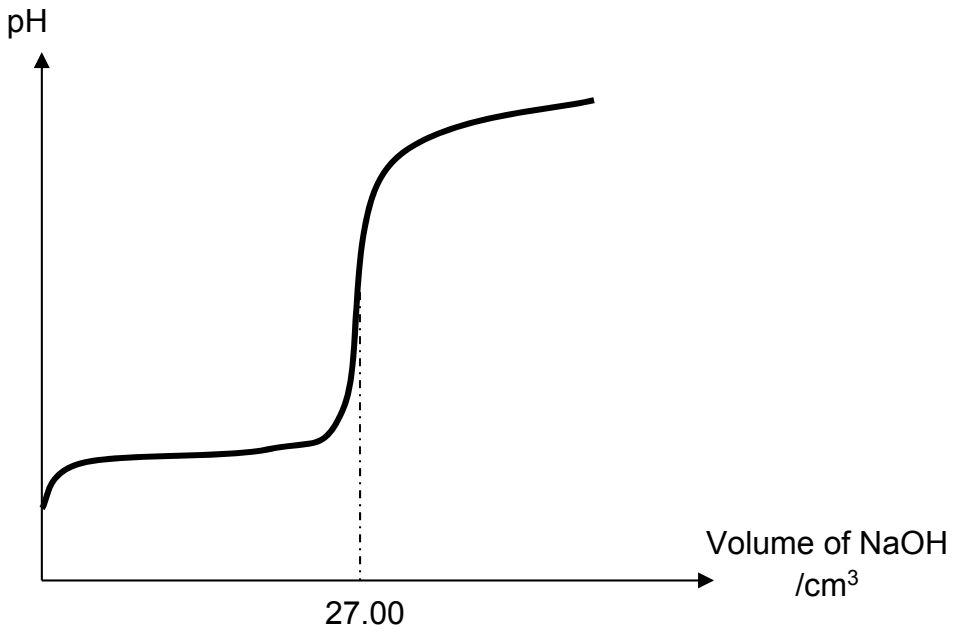
Answer **one** question from this section.

4. Pyruvic acid is an important component in the human body. It is involved in various processes such as the Krebs Cycle.



Pyruvic acid

(a) 30.0 cm^3 of pyruvic acid was titrated against 0.15 mol dm^{-3} of NaOH. The following titration curve was obtained.



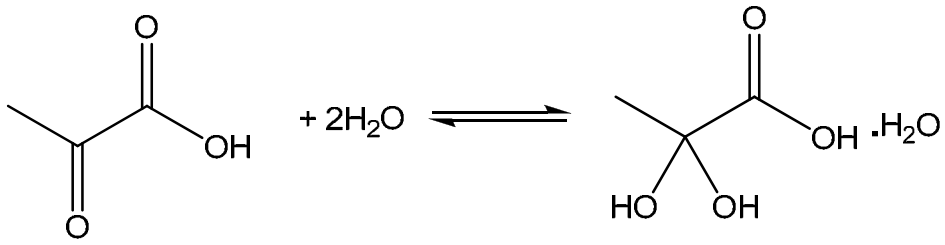
(i) Given that the solution of pyruvic acid is only 15.3 % dissociated, calculate the value of K_a for pyruvic acid, stating clearly its units. [2]

(ii) Calculate the volume of NaOH added to obtain a solution of pH 12. [2]

(iii) Suggest a suitable indicator for this titration. [1]

4 (a) (iv) Blood has a working pH of 7.35 to 7.45. Suggest why pyruvic acid is found in trace amounts in blood. Hence, draw the major species of pyruvic acid in blood. [2]

(b) An experiment to study the equilibrium between pyruvic acid and its hydrated form was done by Y. Pocker in 1969. The following data was obtained.



pyruvate hydrate

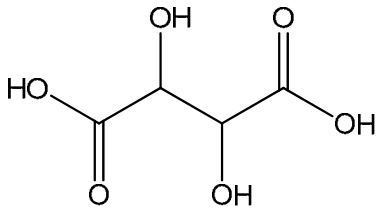
Temperature/ K	$\frac{[\text{pyruvate hydrate}]}{[\text{pyruvic acid}]}$
278	3.47
294	1.75
304	1.06
324	0.47

(i) Deduce whether the hydration of pyruvic acid is an endothermic or exothermic reaction. [2]

(ii) The pyruvate hydrate has a higher pK_a value than pyruvic acid. Explain. [2]

(c) Suggest a 2-step synthesis for the formation of carbon dioxide from pyruvic acid. [3]

4 (d) Pyruvic acid was first synthesised in the laboratory through the distillation of tartaric acid with potassium hydrogen sulfate. The structure of tartaric acid is shown below.



Tartaric acid

(i) Suggest why tartaric acid has a much higher melting point than pyruvic acid. [2]

(ii) There are three stereoisomers present in tartaric acid. Two of them rotate plane of polarised light in opposite direction, whereas one has no effect on plane of polarised light. [4]

Draw **all** the stereoisomers of tartaric acid and explain why one of the stereoisomers does not rotate the plane of polarised light.

[Total: 20]

5 (a) Thallium(I) chromate, Tl_2CrO_4, has a solubility product of 8.67×10^{-13} mol^3 dm^{-9} at 25 ^oC.

(i) Calculate the solubility of Tl_2CrO_4 in 0.05 mol dm^{-3} K_2CrO_4. [2]

(ii) Given that the numerical K_{sp} value of $BaCrO_4$ is 1.17×10^{-10}, deduce which precipitate will be formed first if K_2CrO_4 was added slowly into a solution containing 0.015 mol dm^{-3} of Ba^{2+} and 0.015 mol dm^{-3} Tl^+. [2]

(b) Transition elements are known to form coloured complexes. Chromium is one of the common transition element used today.

(i) An equilibrium exists between chromate(VI) ion and dichromate(VI) ions. [2]

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Explain why changes in pH will cause changes in the colour of the solution.

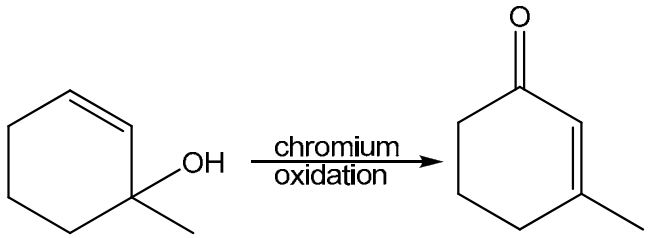
(ii) When gallium, Ga, is added to an acidified $Na_2Cr_2O_7$ solution, a series of colour changes takes place until a blue solution is obtained. [3]

Using relevant data from the *Data Booklet* and the data given below, explain the observation of the colour changes.

$$Ga^{3+} + 3e^- \rightleftharpoons Ga \qquad E^\ominus = -0.53V$$

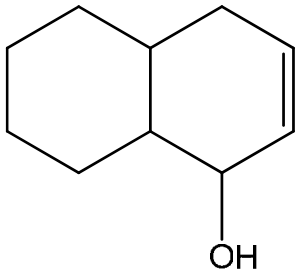
(iii) Suggest why the blue solution slowly changes to a green solution when it is left standing in air. [1]

(c) Chromium oxidation is a special type of reaction in which oxidation and a rearrangement takes place. An example of a chromium oxidation is as shown.



1-methylcyclohex-2-enol 3-methylcyclohex-2-enone

(i) Draw the structure of the product when the following compound undergoes chromium oxidation. [1]



(ii) Suggest a simple chemical test to distinguish between 1-methylcyclohex-2-enol and 3-methylcyclohex-2-enone. [2]

5 (d) Compound **F**, $C_4H_9O_3N$, is a neutral and chiral compound which is soluble in water. When compound **F** is heated with dilute sulfuric acid and potassium dichromate(VI), compound **G**, $C_4H_6O_5$, is formed. 1 mol of compound **G** reacts with aqueous sodium carbonate to produce 1 mol of CO_2. If compound **F** is heated with concentrated sulfuric acid and potassium dichromate(VI), compound **H**, $C_4H_4O_4$, is formed instead. When compound **F** reacts with $LiAlH_4$ in dry ether, a compound **J** which is no longer neutral is formed. [7]

Deduce the structures of compounds **F**, **G H** and **J**, and explain the reactions involved.

[Total: 20]

~END OF PAPER~