VICTORIA JUNIOR COLLEGE
JC 1 PROMOTIONAL EXAMINATION
Higher 2

CANDIDATE NAME .....

CT GROUP .....

CHEMISTRY **9729**

Paper 1 **2 hours**
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A: Answer all questions in the spaces provided on the Question Paper.
Section B: Answer all questions on college writing papers.
Begin each question on a fresh sheet of paper.

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

For Examiner's Use		
Section A	1	
	2	
	3	
Section B	1	
	2	
Total		

This document consists of 11 printed pages and 1 blank page.

Section A: Structured Questions [35 marks]

Answer **all** the questions in the spaces provided.

S1 A pure sample of $NO_2(g)$ is introduced into an evacuated vessel and the following equilibrium is established at a constant volume.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g) \qquad \Delta H > 0$$

(a) At 80 °C, 30% of NO_2 has dissociated at equilibrium and the total pressure is 3 atm. Calculate the mole fraction of NO_2, NO and O_2 in the equilibrium mixture.

[2]

(b) Calculate the value of K_p at 80 °C, giving its units.

[2]

(c) (i) Explain how an increase in temperature would affect the value of K_p.

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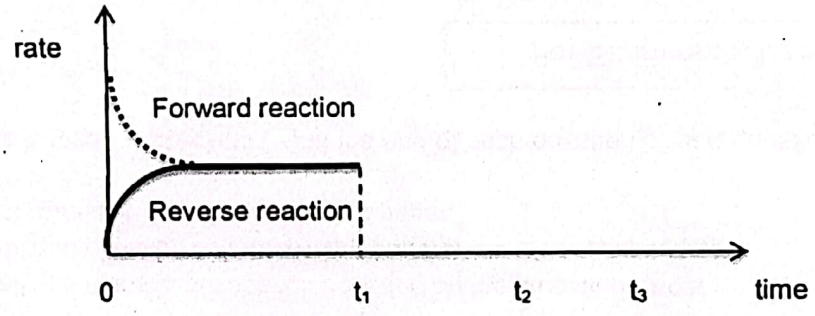
.....[2]

(ii) Temperature of the reaction is raised at time t_1 and a new equilibrium is established at time t_2 and maintained till time t_3.

Complete the graph below showing how the rates of the forward and reverse reactions change from time t_1 to t_3. Use dotted line for the forward reaction and solid line for the reverse reaction.



[2]

[Total:8]

S2 (a) On heating gaseous phosphorus pentachloride, the following equilibrium is set up:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

When 12.0 g of phosphorus pentachloride were put into a sealed evacuated vessel of capacity 1.00 dm^3, and heated to 300 °C, the pressure increased to 3.50×10^5 Pa.

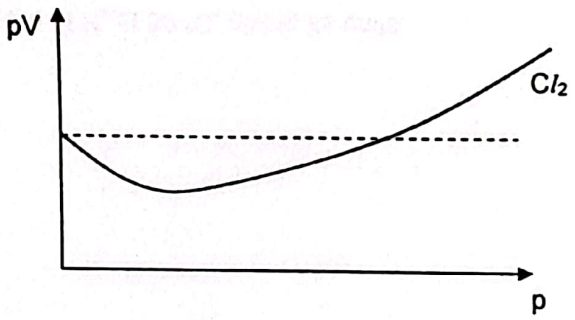
(i) Use the above data to calculate the average M_r of the gaseous mixture.

[2]

(ii) Hence, determine the percentage dissociation of PCl_5 in the mixture.

[2]

(iii) Sketch a graph to show how the value of the product pV changes with pressure for PCl_3 in the diagram below.



[1]

(b) (i) State the electronic configurations of phosphorus and sulfur.

phosporus:.....

sulfur: .....[2]

(ii) With reference to the *Data Booklet*, explain how the first ionisation energy of phosphorus is compared to that of silicon and sulfur.

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.....[3]

[Total: 10]

S3 (a) Dimethyl ether (DME), CH_3OCH_3, is a gas which can be synthesised from methanol, CH_3OH. Methanol can be obtained from biomass, such as plant waste from agriculture.

(i) Draw the shape of a molecule of dimethyl ether, CH_3OCH_3, showing the values of the bond angles about oxygen and carbon atoms.

[2]

(ii) Explain why dimethyl ether form a product with gaseous $AlCl_3$ when they react in a molar ratio of 1:2. Draw a diagram to illustrate the shape of the product formed about the oxygen atom.

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[2]

(iii) Explain why dimethyl ether is soluble in methanol.

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.....[2]

(iv) Explain why methanol has a lower boiling point than water.

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.....[1]

(v) Some bond energies are given in the table below.

Bond	Bond energy, kJ mol^{-1}
C=O	740
C–O	360
C–F	485

Given that the sizes of fluorine and oxygen are comparable, explain the relative strength of these bonds with reference to the bond energies given.

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.....[2]

(b) Potassium hydrogen tartrate, $KHC_4H_4O_6$ (KHT) is a sparingly soluble salt. In a saturated solution with undissolved solid KHT, the following equilibrium is established.

$$KHC_4H_4O_6(s) \rightleftharpoons K^+(aq) + HC_4H_4O_6^-(aq)$$

At 25 °C, the solubility of KHT in water is 0.032 mol dm^{-3}.

(i) Write an expression for the solubility product, K_{sp}, of KHT. Hence calculate the value of K_{sp}.

[2]

(ii) State the effect, if any, on the solubility and K_{sp} of KHT when solid potassium chloride is added to a saturated solution of KHT.

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.....[2]

(iii) The hydrogen tartrate ion, $HC_4H_4O_6^-$ (HT^-), is a weak monobasic acid and its concentration in the saturated solution of KHT can be determined by titration with a strong base like sodium hydroxide of known concentration.

In a titration experiment, 20.00 cm^3 of 0.0400 mol dm^{-3} aqueous sodium hydroxide was needed to neutralise a saturated solution of KHT at 25 °C.

Calculate the volume of saturated solution of KHT used in the titration.

[1]

500 cm^3 of 0.50 mol dm^{-3} potassium chloride is added to 500 cm^3 of saturated KHT solution to form a solution **A** at 25 °C.

(iv) Calculate the concentration of hydrogen tartrate ion, HT^-, in solution **A**.

[1]

(v) Calculate the mass of KHT precipitated.

[2]

[Total: 17]

Section B: Essay Questions [40 marks]

Answer **both** questions on the writing paper provided.
Begin each question on a **fresh** sheet of paper.

E1 **(a)** The sulfur-iodine cycle has been proposed as a means of producing hydrogen fuel more efficiently than by electrolysis.

At high temperatures, the sulfur-iodine cycle involves three gas-phase equilibria:

	Equation			$\Delta H_f°$/ kJ mol^{-1}
1	$I_2(g) + SO_2(g) + 2H_2O(g)$	→	$H_2SO_4(g) + 2HI(g)$	$\Delta H_1°$
2	$2H_2SO_4(g)$	→	$2SO_2(g) + 2H_2O(g) + O_2(g)$	+439
3	$2HI(g)$	→	$H_2(g) + I_2(g)$	+11

(i) Conditions are chosen so that the three equilibrium reactions above all proceed from left to right. Assuming that the products of reaction **1** are all consumed in reactions **2** and **3**, write an overall equation for the sulfur-iodine cycle. [1]

(ii) Standard enthalpy change of formation for $H_2O(g)$, $\Delta H_f°$ is –242 kJ mol^{-1}.

Using the data given, construct an energy cycle to determine $\Delta H_1°$. [3]

(b) Consider the reaction,

$$SF_6(g) + 4H_2O(g) \rightarrow H_2SO_4(g) + 6HF(g)$$

(i) State and explain the sign of ΔS for the reaction. [1]

(ii) Use the data on standard enthalpy change of formation below to calculate the standard enthalpy change for this reaction.

	$SF_6(g)$	$H_2O(g)$	$H_2SO_4(g)$	$HF(g)$
$\Delta H_f°$/ kJ mol^{-1}	–1210	–242	–735	–273

[2]

(iii) By considering the entropy and enthalpy changes, predict the spontaneity of the reaction of sulphur hexafluoride with water. [2]

(c) Hydrogen can be used to generate electricity in a fuel cell. The earliest hydrogen fuel cell used phosphoric acid, H_3PO_4, as an electrolyte. H_3PO_4 is a *weak Bronsted Acid* that is often used to form buffer solutions with near-physiological pH.

(i) Explain fully what is meant by the phrase ***weak Bronsted Acid***. [1]

A student purchased a bottle of concentrated phosphoric acid, H_3PO_4 from an online merchant. The following information regarding the H_3PO_4 purchased was provided by the merchant:

General description
In aqueous solutions, phosphoric acid, H_3PO_4 behaves as a triprotic acid. The triprotic acid has three ionisable hydrogen atoms, which can be lost sequentially.

Properties:
- Total volume: 1.00 dm^3
- Concentration: 14.7 mol dm^{-3}
- Relative Molecular Mass of H_3PO_4: 98.0
- $K_{a1} = 7.5 \times 10^{-3}$ mol dm^{-3}
- $K_{a2} = 6.2 \times 10^{-8}$ mol dm^{-3}
- $K_{a3} = 4.8 \times 10^{-13}$ mol dm^{-3}

(ii) Calculate the volume of water that needs to be added to dilute 10 cm^3 of the 14.7 mol dm^{-3} H_3PO_4 solution to a final concentration of 0.500 mol dm^{-3}. [1]

(iii) Write down the expression for K_{a2} of H_3PO_4 [1]

(d) The student plans to prepare a buffer solution that contains the species $H_2PO_4^-$ and HPO_4^{2-}.

(i) With the aid of equations, explain how this $H_2PO_4^-/HPO_4^{2-}$ buffer solution maintains a fairly constant pH when

- a small amount of acid is added
- a small amount of base is added [3]

(ii) To prepare the buffer solution, the student added 8.0 cm^3 of 1.00 mol dm^{-3} NaOH to 10.0 cm^3 of 0.500 mol dm^{-3} H_3PO_4.

Calculate the pH of the resultant buffer solution formed. [3]

(iii) Sketch the titration curve of pH against volume of NaOH when 10.0 cm^3 of 0.500 mol dm^{-3} H_3PO_4 is titrated against 20.00cm^3 of 0.500 mol dm^{-3} NaOH.

Label the co-ordinates corresponding to the points of maximum buffering capacity. [2]

[Total: 20]

E2 Alkenes are hydrocarbons that contain at least one carbon-carbon double bond. Dienes are hydrocarbons that contain two carbon-carbon double bonds and they display reactivity similar to alkenes.

(a) Compound **A** has the formula $CH_3CH{=}CHCH{=}CHCH_2Cl$. It is a diene which exhibit isomerism.

Draw all the possible stereoisomers of compound **A**. [2]

(b) Cyclohexene and cyclohexa-1,4-diene are cyclic alkenes.

cyclohexene

cyclohexa-1,4-diene

(i) State the total numbers of sigma and pi bonds in a molecule of cyclohexa-1,4-diene. [1]

(ii) State the type of hybridisation that carbon **1** undergoes and the shape around it. [2]

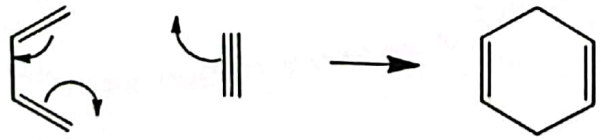
(iii) Cyclohexene undergoes hydrogenation to form cyclohexane.

Describe the mechanism for the bromination of cyclohexane to form bromocyclohexane. [3]

(iv) Bromocyclohexane undergoes further substitution to form 1,3-dibromocyclohexane.

State the probability of forming 1,3-dibromocyclohexane from bromocyclohexane. [1]

Cyclohexa-1,4-diene can be made by heating buta-1,3-diene with ethyne. The diagram below shows the movement of electron pairs, represented by curly arrows, needed to generate the cyclohexa-1,4-diene in a single step.



buta-1,3-diene ethyne

(v) In a similar type of reaction, cyclohexene can be formed from two alkenes.

Suggest the names of the two alkenes that would react to form cyclohexene in this type of reaction. [2]

(vi) In another similar reaction, penta-1,3-diene reacts with propene to form two products that are constitutional isomers. Draw the structures of these two isomers.

penta-1,3-diene [1]

(c) **B**, **C** and **D** are compounds with molecular formula C_6H_{12}.

B does not decolorise aqueous bromine but will decolourise bromine in sunlight.

C decolourises aqueous bromine and reacts with HBr to give $CH_3CHBrCH_2CH(CH_3)_2$. On oxidation with hot, acidified potassium manganate(VII), **C** gives **E**, $C_5H_{10}O_2$, as the only organic product.

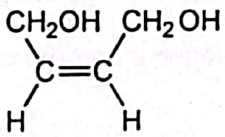
D undergoes oxidation with hot, acidified potassium manganate (VII) to give $CH_3CH_2CO_2H$ as the only organic product.

(i) Suggest the identities of the organic compounds **B**, **C**, **D** and **E** by giving their structural formulae. [4]

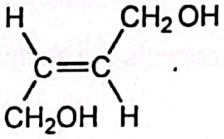
(ii) Write the balanced equation for the oxidation of **C** to **E**.
You may use [O] to represent the oxidation of **C**. [1]

(iii) Give the structural formula of the major product obtained when $CH_3CHBrCH_2CH(CH_3)_2$ reacts with hot alcoholic potassium hydroxide. [1]

(d) It was observed that the boiling point of cis-but-2-ene-1,4-diol is lower than that of the trans isomer. Suggest a reason for this observation.



cis-but-2-ene-1,4-diol



trans-but-2-ene-1,4-diol

[2]

[Total: 20]

END OF PAPER