VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ……………………………………………………………..

CT GROUP ……………………………..

CHEMISTRY 9729/03

Paper 3 Free Response **19 September 2022**

Candidates answer on the Question Paper. **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.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

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.

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

For Examiner's Use		
Section A	**1**	**/ 18**
	2	**/ 22**
	3	**/ 20**
Section B	**4 OR 5**	**/ 20**
Total		**/ 80**

This document consists of **26** printed pages.

Section A

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

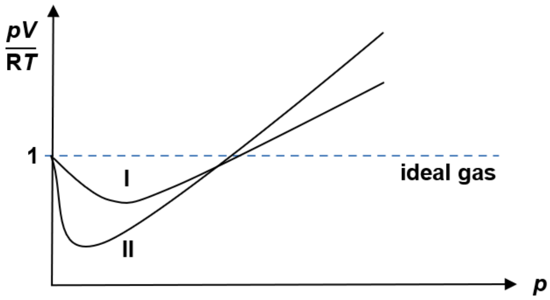
1 **(a)** **(i)** Under what conditions of temperature and pressure would you expect the behaviour of a real gas to be most like that of an ideal gas? [1]

(ii) Barium ethanedioate, BaC_2O_4, decomposes on heating to produce a mixture of two different gases, **A** and **B**, and an oxide only.

Neither gas **A** nor gas **B** is an ideal gas. They have the following boiling points.

gas	boiling point / °C
A	–191.5
B	–78.5

The graph below shows the variation of $\frac{pV}{RT}$ with pressure, p, for 1 mol each of gas **A** and gas **B** at constant temperature. Identify the graph that corresponds to gas **A** and explain your choice.



[2]

(iii) Free volume, V, refers to the volume of space between gas molecules. For an ideal gas, the free volume is essentially the same as the volume of the container. This can be calculated using the ideal gas equation, $pV = nRT$.

The pressure of a 72 g gaseous sample containing gas **A** and gas **B** in a container of volume 400 cm^3 is measured to be 3.36×10^7 Pa at 527 °C.

Using the ideal gas equation, calculate the free volume of this gaseous sample in cm^3. Assume the gaseous sample has an average M_r = 36. [2]

(iv) Explain why the volume you have calculated in **(a)(iii)** differs from that of the volume of the container. [1]

(v) An impure sample of barium ethanedioate, BaC_2O_4, of mass 0.500 g, is added to 50.0 cm^3 of 0.0200 mol dm^{-3} acidified MnO_4^-(aq) and heated. A redox reaction takes place and all BaC_2O_4 are reacted. The resulting solution is titrated with Fe^{2+}(aq). The end-point is reached when 30.40 cm^3 of 0.0500 mol dm^{-3} Fe^{2+}(aq) has been added.

$$C_2O_4^{2-} \rightleftharpoons 2CO_2 + 2e^-$$
$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$
$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

Calculate the percentage by mass of BaC_2O_4 in the 0.500 g impure sample. Show your working. [M_r: BaC_2O_4, 225.3] [4]

(b) The elements of Group 14 can form monoxides and dioxides. The monoxides are unstable and will disproportionate into their element and dioxide. The equations for the disproportionation reactions are given in **Table 1.1**, together with some thermodynamic data for the reactions.

Table 1.1

disproportionation equation	$\Delta S^{\ominus}$ / J mol^{-1} K^{-1}	$\Delta H^{\ominus}$ / kJ mol^{-1}	$\Delta G^{\ominus}$ / kJ mol^{-1}
$2CO(g) \rightarrow C(s) + CO_2(g)$	–176	–173	–120
$2SiO(g) \rightarrow Si(s) + SiO_2(s)$	–363	–712	–603
$2GeO(s) \rightarrow Ge(s) + GeO_2(s)$	–13.6	–127	–123
$2SnO(s) \rightarrow Sn(s) + SnO_2(s)$	–9.20	–9.10	–6.36
$2PbO(s) \rightarrow Pb(s) + PbO_2(s)$	–4.00	+157	+158

(i) Explain why the entropy change for the disproportionation of SiO(g) is much more negative than that for CO(g). [1]

(ii) Explain why the entropy change for the disproportionation of PbO(s) is close to zero. [1]

(iii) Use data from Table 1.1 to deduce the temperature above which the disproportionation of CO(g) becomes unfavourable. [1]

(iv) Explain why CO(g) does not spontaneously disproportionate at room temperature. [2]

(v) Carbon monoxide, CO, is a gas at room temperature and pressure. It contains a coordinate bond. Explain what is meant by a *coordinate bond*. [1]

(vi) Dicarbon monoxide, C_2O, is extremely reactive and is not encountered in everyday life. It is found in dust clouds in space and analysis has shown that the central atom is carbon with no unpaired electrons while the other carbon atom has a lone pair of electrons.
Draw the structure of dicarbon monoxide, stating its shape and bond angle. [2]

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[Total: 18]

2 **(a)** Alanine, $CH_3CH(NH_2)CO_2H$, is an amino acid that is used to make proteins. Its pK_a values are 2.34 and 9.87.

(i) Sketch a graph to show how the pH of the solution would change during the gradual addition of 25.0 cm^3 of 0.100 mol dm^{-3} NaOH to 10.0 cm^3 of 0.100 mol dm^{-3} fully protonated alanine. Label the pK_a values in your sketch. [2]

(ii) From the following list of indicators, suggest an indicator that could be used to detect the first end–point of the titration. Explain your answer.

indicator	pH at which colour changes
malachite green	0 – 1
thymol blue	1 – 2
bromophenol blue	3 – 4.6
thymolphthalein	9 – 10

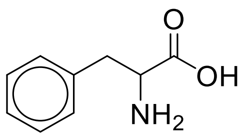
[2]

Alanine can be synthesised by a general reaction shown below.

$$CH_3CHO \xrightarrow{NaCN\ +\ NH_4Cl} \textbf{E}\ (C_3H_6N_2) \xrightarrow[\text{2. neutralise}]{\text{1. } H_3O^+\text{, heat}} \underset{\text{alanine}}{CH_3CH(NH_2)CO_2H}$$

(iii) Suggest the structure of compound **E**. [1]

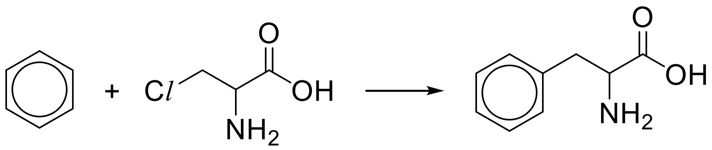
(iv) Suggest the structure of the starting material needed to synthesise phenylalanine by the above general reaction.



phenylalanine

[1]

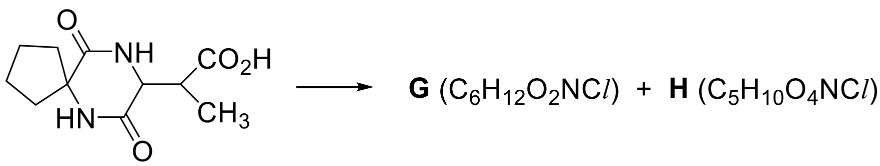
(v) Phenylalanine can also be synthesised by reacting benzene and a halogen derivative, $ClCH_2CH(NH_2)CO_2H$, in the presence of aluminium chloride. Suggest the mechanism for this reaction. Show all charges and the movement of electron pairs using curly arrows.



phenylalanine

[3]

(vi) Compound **F** undergoes a reaction when heated in aqueous hydrochloric acid to produce two compounds, **G** and **H**.



F

Suggest the type of reaction that has occurred. Draw the structures of compounds **G** and **H**. [3]

(b) An electric cell was set up using a $Ag^+(aq)|Ag(s)$ half-cell and a $\mathbf{M}^{2+}(aq)|\mathbf{M}(s)$ half-cell where **M** is an unknown metal. The standard cell potential, $E^{\ominus}_{cell}$, was found to be +1.96 V. The silver electrode in this cell was the positive electrode.

(i) Draw the experimental set-up of the above cell, label clearly the species in each cell and the direction of the electron flow. [2]

(ii) Use data from the *Data Booklet* to calculate the standard electrode potential of the $\mathbf{M}^{2+}(aq)|\mathbf{M}(s)$ half-cell. [1]

(iii) State and explain how the E_{cell} value measured would change when 200 cm^3 of water is added to the $Ag^+(aq)|Ag(s)$ half–cell. [2]

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(c) Silver chloride, Ag*Cl*, is sparingly soluble in water. The numerical value of the solubility product, K_{sp}, for silver chloride is 1.80×10^{-10} mol^2 dm^{-6} at 25 °C.

(i) Solid Ag*Cl* is stirred at 25 °C with 5.00×10^{-3} mol dm^{-3} $AgNO_3$ until no more Ag*Cl* dissolves. Calculate the concentration of chloride ions in this solution. [1]

(ii) Silver ions and thiosulfate ions react in a molar ratio 1:2 to form a soluble complex in aqueous solution. Explain, with the aid of relevant equations, how the solubility of silver chloride would be affected when solid sodium thiosulfate is added to an aqueous solution of silver chloride at 25 °C. [2]

(iii) 7.00×10^{-5} mol of solid silver chloride is added to 2.50 dm^3 of aqueous sodium thiosulfate. 1.88×10^{-5} mol of silver chloride remained undissolved after equilibrium has been established. Determine the concentration of silver ions that has been used to form the silver-thiosulfate complex in the solution. [2]

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[Total: 22]

3 **(a)** Compound **A** has a molecular formula of $C_{12}H_{16}O$.

Ozone can be used to convert a C=C bond into two C=O bonds. Under certain conditions, ketones and/or carboxylic acids are formed, as shown in **Figure 3.1**. Ozone has **no** reaction with benzene.

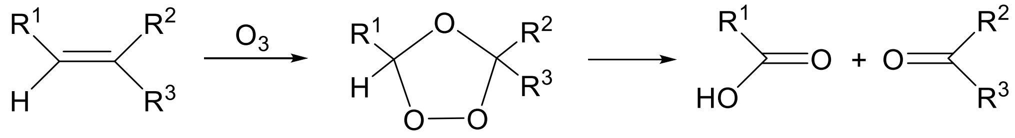

Figure 3.1

Compound **A** reacts with an excess of ozone under similar conditions to form two organic compounds, **B**, $C_9H_{10}O$, and **C**, $C_3H_6O_3$.

Compounds **A**, **B** and **C** form a yellow precipitate with alkaline aqueous iodine but only compound **B** forms an orange precipitate with 2,4-dinitrophenylhydrazine.

When compound **B** is reacted with concentrated HNO_3 and concentrated H_2SO_4, two possible mono-nitro compounds can be formed but only **D** is formed in practice.

Compound **C** has a chiral centre and effervesces with aqueous sodium carbonate. When warmed with concentrated H_2SO_4, **C** forms **E**, $C_6H_8O_4$.

(i) Explain what is meant by a *chiral centre*. [1]

(ii) Suggest possible structures of **A**, **B**, **C**, **D** and **E**. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional groups present in each compound. [9]

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(b) (i) When white anhydrous $CuSO_4$ is dissolved in liquid ammonia at –40 °C, a deep blue solution **F** is formed.

Solid NaOH is then added to solution **F**, and the ammonia solvent is allowed to evaporate leaving behind a solid residue. Heating the residue to 220 °C produces a mixture of two solids. When water is added to this mixture, one of the solids remains as a black solid **G**.

Solid **G** dissolves in HNO_3(aq) on warming without the evolution of gas to give a pale blue solution.

Suggest the chemical formulae of the compounds **F and G**. [2]

(ii) When water is added to the white anhydrous $CuSO_4$, the solid dissolves to give a blue solution. The solution changes to a yellow-green colour when concentrated NH_4Cl is added to it. Concentrating the solution produces green crystals of an ammonium salt with the empirical formula $CuN_2H_8Cl_4$.

State the type of reaction occurring and give the chemical formula of the ammonium salt formed. Explain these observations with the aid of an equation. [3]

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(c) **Figure 3.2** shows the octahedral geometry of a transition metal complex with six monodentate ligands, **L**.

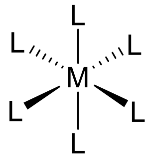

Figure 3.2

With reference to an octahedral complex, the *cis-trans* configuration is defined as follows:

Cis configuration:
Same groups of atoms are on the same side of the central metal atom, i.e. 90° from each other.

Trans configuration:
Same groups of atoms are on directly opposite sides of the central metal atom i.e. 180° from each other.

$[Co(NH_3)_4Cl_2]^+$ is an octahedral complex. Similar to organic molecules, this complex can exist as a pair of *cis-trans* isomers.

Using the information above, draw the 3-dimensional structures of the *cis-trans* isomers of $[Co(NH_3)_4Cl_2]^+$ and label the configuration. [2]

(d) Radium was discovered in the ore, pitchblende, by Marie Curie in 1898. The metal was first isolated in 1910.

The metal was obtained by first reacting the radium present in the pitchblende to form insoluble radium sulfate which was converted into aqueous radium bromide. This solution was then electrolysed using a mercury cathode and a carbon anode. The radium formed react vigorously with water to form an alkaline solution.

(i) Write an equation, with state symbols, for the reaction of radium with water. [1]

(ii) State and explain if the reaction will be more or less vigorous than the reaction of barium with water. [2]

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[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** With reference to $E^{\ominus}(X_2|X^-)$ values from the *Data Booklet, d*escribe the relative reactivity of the halogens Cl_2, Br_2 and I_2 as oxidising agents. [2]

(b) Lactic acid, $CH_3CH(OH)CO_2H$, was first isolated in sour milk. It is also formed in our body during anaerobic respiration.

(i) Lactic acid exhibits stereoisomerism. State the type of stereoisomerism and draw the pair of stereoisomers. [2]

Lactic acid can be synthesised from ethanol as shown below.

$$CH_3CH_2OH \xrightarrow{\text{step 1}} CH_3CHO \xrightarrow{\text{step 2}} CH_3CH(OH)CN \xrightarrow{\text{step 3}} CH_3CH(OH)CO_2H$$

(ii) State the reagents and conditions for steps 1 and 2. [2]

(iii) Describe the reaction mechanism for step 2. Show all relevant charges, dipoles, lone pairs and electron movement using curly arrows. [2]

(iv) State and explain how K_a of lactic acid would compare to that of propanoic acid. [2]

(c) Lactic acid undergoes dimerisation by forming two hydrogen bonds between two molecules.

$$2CH_3CH(OH)CO_2H(g) \rightleftharpoons (CH_3CH(OH)CO_2H)_2(g)$$
dimer

In a container, 6.65 bar of lactic acid undergoes dimerisation at 127 °C. The total pressure of the gas mixture at equilibrium is found to be 3.52 bar.

(i) Calculate the partial pressures of lactic acid and its dimer, in bar, at equilibrium. [2]

(ii) Write the K_p expression for this equilibrium and calculate its value in bar^{-1}. [2]

The Gibbs free energy change for this reaction is related to K_p by the following equation.

$$\Delta G = -RT\ln K_p$$

In the above equation, ΔG is in J mol^{-1}, T is in K and K_p is in bar^{-1}.

(iii) Calculate the Gibbs free energy change of the dimerisation [1]

(iv) The entropy change for the dimerisation is –30.0 J K^{-1} mol^{-1}.

Calculate the enthalpy change of the dimerisation. Hence, estimate the strength of hydrogen bond in the dimer in kJ mol^{-1}. [2]

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(d) The K_a value of lactic acid is 1.4×10^{-4} while the K_{a1} and K_{a2} values of carbonic acid, H_2CO_3, are 4.5×10^{-7} and 4.7×10^{-11}.

(i) Estimate the K_c value for the reaction between lactic acid and hydrogencarbonate ion. [2]

(ii) A student claims that the reaction between lactic acid and hydrogencarbonate ion is negligible as it is a reaction between a weak acid and a weak base. Do you agree with this claim? Explain your answer. [1]

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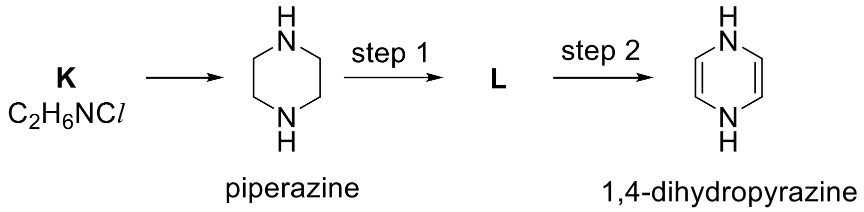
5 **(a)** Piperazine, $C_4H_{10}N_2$ was used as an anti-parasites drug in the early 20th century. It can be synthesised from an organic compound **K**, C_2H_6NCl under suitable conditions. Piperazine can be used to prepare 1,4-dihydropyrazine via a two-step pathway as shown below.



(i) Suggest and explain if 1,4-dihydropyrazine can exhibit *cis-trans* isomerism. [1]

(ii) Suggest the structures of compounds **K** and **L**. [2]

(iii) State the reagents and conditions for steps 1 and 2. [2]

(iv) The preparation of 1,4-dihydropyrazine from piperazine in the above pathway gives a very low yield. Suggest which step in the pathway contributed to this low yield. Explain your answer. [1]

(v) State and explain how the K_b of piperazine would compare to that of diethylamine, $(CH_3CH_2)_2NH$. [2]

(vi) The two pK_b values of piperazine are 5.35 and 9.73 respectively.

A buffer solution is prepared by adding 11.2 g of piperazine into 100 cm^3 of 1.00 mol dm^{-3} hydrochloric acid solution.

Calculate the pH of this buffer solution. [3]

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(b) In order to function properly, the human body needs to maintain a blood pH between 7.35 and 7.45. Large deviations from this pH range are extremely dangerous. pH values greater than 7.8 or less than 6.8 often result in death. Blood contains large amounts of carbonic acid and hydrogencarbonate which help to maintain the blood pH. Describe, with the aid of equations, how the pH of blood is controlled by carbonic acid and hydrogencarbonate. [2]

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(c) The reaction between NO_2 and SO_2 is a key stage in the formation of acid rain.

$$NO_2(g) + SO_2(g) \rightarrow NO(g) + SO_3(g)$$

The initial rate of this reaction was measured for different concentrations of reactants and the rate equation was obtained as shown.

$$\text{rate} = k[NO_2][SO_2]^2$$

(i) Explain if the reaction between NO_2 and SO_2 is an elementary step reaction. [1]

(ii) NO_2 is produced in the car engine when the temperature of the engine is very high. Write an equation to show how NO_2 is removed by the catalytic converter. [1]

(iii) The catalyst in the catalytic converter functions as a heterogeneous catalyst. Outline the mode of action of the heterogeneous catalyst. [2]

(iv) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect of catalyst on the rate constant of a reaction. [3]

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Additional answer space

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