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 **25** 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]

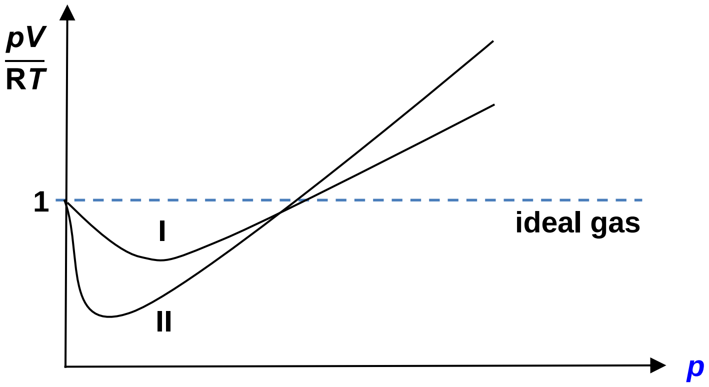
- **High temperature and low pressure**

(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]

- **Graph I corresponds to gas A.**
- **Gas A has lower boiling point than B, hence, it has weaker intermolecular forces of attraction leading to less deviation from ideality.**

(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]

$n = 72 / 36 = 2.00$ **mol**

$pV = nRT$

- $V = \frac{2.00 \times 8.31 \times (527+273)}{3.36 \times 10^7}$
  $= 3.96 \times 10^{-4}\ m^3$
- $= 396\ cm^3$

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

The gaseous sample behaves non–ideally and the volume calculated in (a)(iii) is smaller than the volume of the container.

- **Under high pressure, the <u>volume of the gaseous molecules is not negligible / significant</u>. Hence, the <u>actual free volume</u> between the gas molecules is <u>smaller</u>.**

(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]

- **Initial total amount of MnO_4^- = 0.0200 × 50.0 × 10^{-3} = 1.00 × 10^{-3} mol**
  Amount of Fe^{2+} used = 0.0500 × 30.40 × 10^{-3} = 1.52 × 10^{-3} mol

  $5Fe^{2+} \equiv MnO_4^-$
- **Amount of MnO_4^- unreacted with $C_2O_4^{2-}$ = 1.52 × 10^{-3} / 5 = 3.04 × 10^{-4} mol**
  Amount of MnO_4^- reacted with $C_2O_4^{2-}$ = 1.00 × 10^{-3} – 3.04 × 10^{-4} = 6.96 × 10^{-4} mol

- **Amount of $C_2O_4^{2-}$ reacted = 6.96 × 10^{-4} × 5/2 = 1.74 × 10^{-3} mol**

- **Mass of BaC_2O_4 reacted = 1.74 × 10^{-3} × 225.3 = 0.392 g**
  Percentage by mass of BaC_2O_4 = $\frac{0.392}{0.500}$ × 100% = 78.4%

(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]

- **The disproportionation of SiO(g) leads to a <u>larger decrease in the amount of gas</u> than that for the disproportionation of CO(g). Thus, there are <u>less ways of arrangement</u>, leading to a <u>greater decrease in disorderliness</u> and hence a much more negative entropy change.**

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

- **The disproportionation of PbO(s) only involves the <u>same amount of solid reactants and solid products</u>. Thus, there is <u>very little change in disorderliness</u> and hence a close to zero entropy change.**

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

When disproportionation of CO(g) becomes unfavourable,
$\Delta G > 0$
$\Delta H - T\Delta S > 0$
$-173 - T(-176 \times 10^{-3}) > 0$
$T > 983$ K

- **When T is greater than <u>983 K</u>, the disproportionation of CO(g) becomes unfavourable.**

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

CO contains <u>strong C≡O bond (or triple bond)</u> which requires a lot of energy to be broken. The <u>activation energy is high</u> and the reaction is <u>kinetically not feasible</u> at room temperature.

(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]

- **A coordinate bond is a <u>covalent</u> bond in which <u>both electrons</u> come from <u>only one of the atoms</u> in the bond.**

(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.

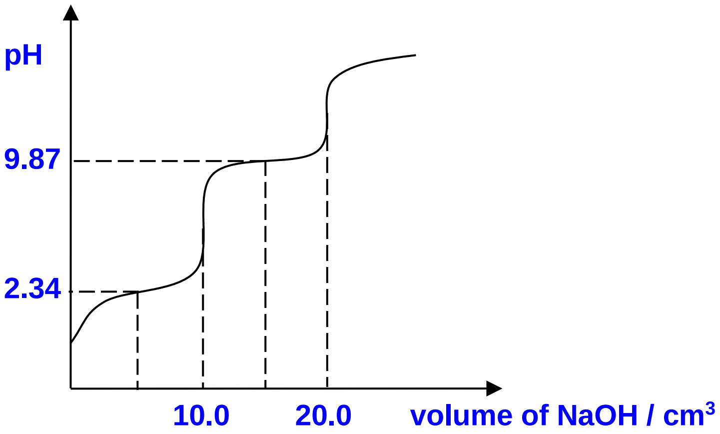
Draw the structure of dicarbon monoxide, stating its shape and bond angle. [2]

- **C=C=O**
- **Shape: linear, bond angle: 180°**

[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]

- **Indicator: bromophenol blue**
- **The working pH range of bromophenol blue lies within the rapid pH change at the first equivalence point.**

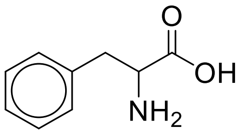
Alanine can be synthesised by a general reaction shown below.

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

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

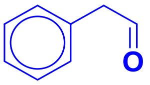
- **$CH_3CH(NH_2)CN$**

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

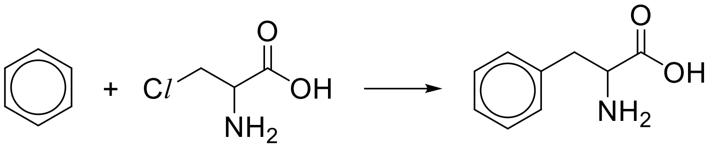


phenylalanine

[1]

- 

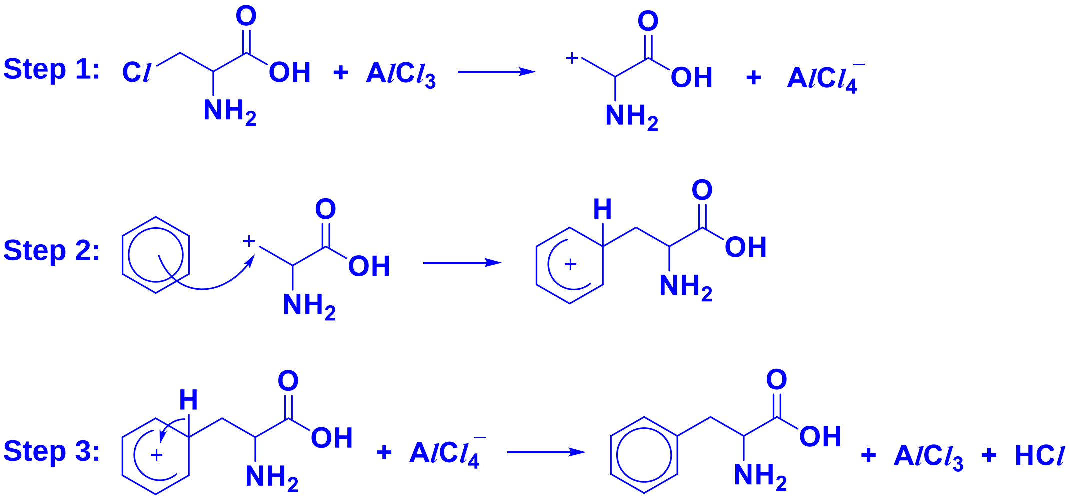
(v) Phenylalanine can also be synthesised by reacting benzene and a halogen derivative, $C\mathit{l}CH_2CH(NH_2)CO_2H$, in the presence of aluminium chloride. Suggest the mechanism for this reaction. Show all charges and the movement of electron pairs using curly arrows.



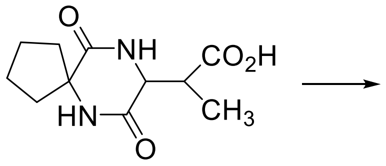
phenylalanine

[3]

Mechanism: electrophilic substitution



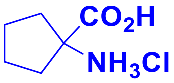
(vi) Compound **F** undergoes a reaction when heated in aqueous hydrochloric acid to produce two compounds, **G** and **H**.

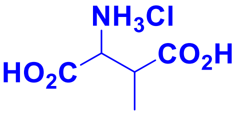
 **G** ($C_6H_{12}O_2NC\mathit{l}$) + **H** ($C_5H_{10}O_4NC\mathit{l}$)

F

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

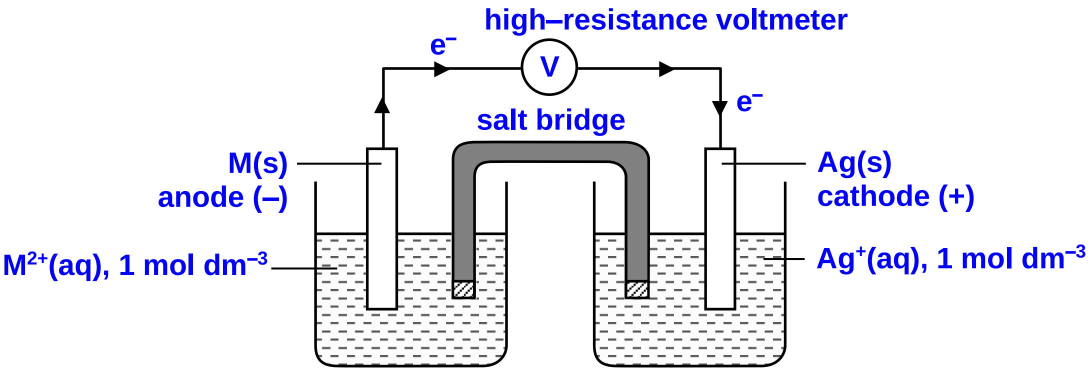
- **Type of reaction: hydrolysis**

- **G:** 

- **H:** 

(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]

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$

$+1.96 = E^\ominus(Ag^+|Ag) - E^\ominus(M^{2+}|M)$

$E^\ominus(M^{2+}|M) = +0.80 - 1.96$

$= -1.16$ V

(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]

- **When water is added to the $Ag^+(aq)|Ag(s)$ half–cell, $[Ag^+]$ decreases. The equilibrium position of $Ag^+ + e^- \rightleftharpoons Ag$ shifts to the left to increase $[Ag^+]$. Hence, $E(Ag^+|Ag)$ is less positive.**

- **The E_{cell} value measured becomes less positive.**

(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]

Let *s* be the solubility of Ag*Cl* in the given $AgNO_3$ solution.

$K_{sp} = [Ag^+][Cl^-] = 1.80 \times 10^{-10}$
$(s + 5.00 \times 10^{-3})(s) = 1.80 \times 10^{-10}$
Assuming $s << 5.00 \times 10^{-3}$,
$s = 3.60 \times 10^{-8}$ mol dm^{-3}

- **Hence, $[Cl^-] = 3.60 \times 10^{-8}$ mol dm^{-3}**

(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 two equations, how the solubility of silver chloride is affected when solid sodium thiosulfate is added to an aqueous solution of silver chloride at 25 °C. [2]

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ (1)
$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq)$ (2)

When solid sodium thiosulfate is added, soluble silver complex is formed. $[Ag^+]$ decreases in the solution, causing ionic product of Ag*Cl* to fall below its K_{sp}. By Le Chatelier's principle, equilibrium position of (1) shifts right, and so increases the solubility of Ag*Cl* .

(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]

Amount of Ag*Cl* dissolved
$= (7.00 - 1.88) \times 10^{-5}$
$= 5.12 \times 10^{-5}$ mol

Amount of Ag^+ ions in solution
$= [1.8 \times 10^{-10} / (5.12 \times 10^{-5}/2.5)] \times 2.5$
$= 2.20 \times 10^{-5}$ mol

Amount of Ag^+ ions involved in forming the complex
$= 5.12 \times 10^{-5} - 2.20 \times 10^{-5}$
$= 2.92 \times 10^{-5}$ mol

Concentration of Ag^+ ions involved in forming the complex
$= 2.92 \times 10^{-5} / 2.50$
$= 1.17 \times 10^{-5}$ mol dm^{-3}

[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.

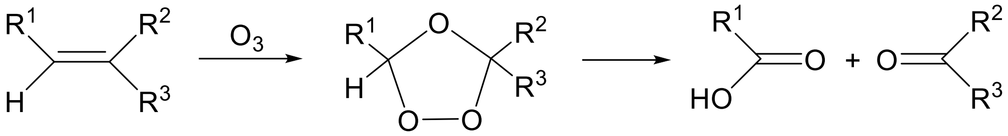


Figure 3.1

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.

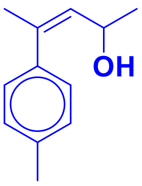
When compound **B** is reacted with concentrated HNO_3 and concentrated H_2SO_4, two possible mono-nitro compounds can be formed but only **D** is formed in practice.

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

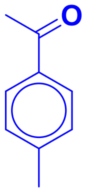
(i) Explain what is meant by a *chiral centre*. [1]

- **A chiral centre is a carbon atom bonded to four different groups or atoms.**

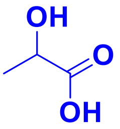
(ii) Suggest possible structures of **A**, **B**, **C**, **D** and **E**. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional groups present in each compound. [9]



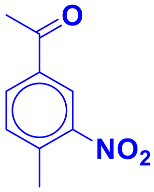
A



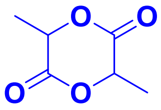
B



C



D



E

- **A undergoes oxidation with ozone to form B and C. Thus, A is an alkene.**
- **A, B and C undergo oxidative cleavage (or oxidation) with alkaline aqueous iodine. They have either $CH_3CO–$ or $CH_3CH(OH)–$ structures.**
- **B undergoes condensation with 2,4-DNPH. B is a ketone with $CH_3CO–$ structure since B has only one O atom.**
- **B undergoes electrophilic substitution with concentrated nitric acid and sulfuric aci, hence B is aromatic or has benzene ring.**
- **B forms two possible mono-nitro compounds. B is a symmetrical molecule which is 1,4-disubstituted. D is formed according to the orientating effect of groups already present on the benzene ring.**
- **C undergoes acid-base reaction with Na_2CO_3(aq). Thus, C is a carboxylic acid.**
- **C undergoes condensation reaction with itself when warmed with concentrated H_2SO_4 to form E, a diester.**
- **Thus, C has both alcohol and carboxylic acid functional groups.**

(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]

- **F: $[Cu(NH_3)_4]SO_4$ or $[Cu(NH_3)_6]SO_4$**
- **G: CuO**

(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]

- **The reaction occurring is ligand exchange.**
- **The chemical formula of the ammonium salt is $(NH_4)_2CuCl_4$**
- **$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$**
  $CuSO_4$ dissolves in water to form a blue $[Cu(H_2O)_6]^{2+}$. When concentrated NH_4Cl was added, ligand exchange takes place to form yellow $[CuCl_4]^{2-}$. Presence of a mixture of blue $[Cu(H_2O)_6]^{2+}$ and yellow $[CuCl_4]^{2-}$ causes the solution to appear yellow-green.

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

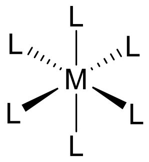


Figure 3.2

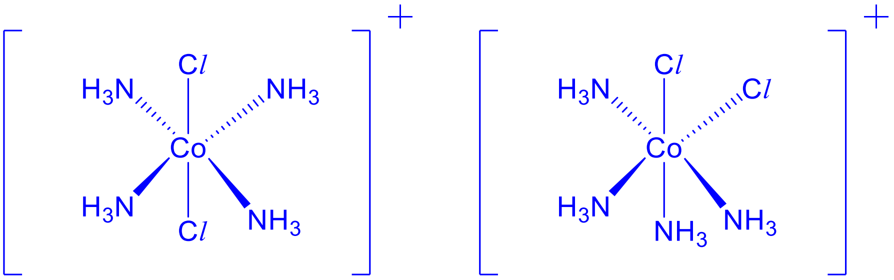
With reference to an octahedral complex, the *cis-trans* configuration is defined as follows:

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]



Trans **Cis**

(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]

- **$Ra(s) + 2H_2O(l) \rightarrow Ra(OH)_2(aq) + H_2(g)$**

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

- **The reaction will be <u>more vigorous</u> as radium is a stronger reducing agent.**
- **Down the group, electrons are being added to a higher energy principal quantum shell which is further away from the nucleus. Since there is an <u>increase in distance between the nucleus and the valence electrons</u>, there is <u>weaker attraction between the nucleus and the valence electrons</u>, making it easier for electrons to be removed from radium.**

[Total: 20]

Section B

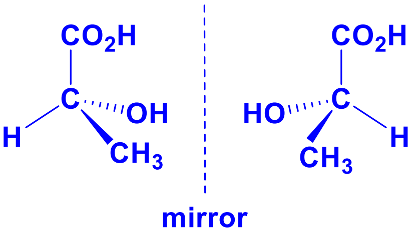
Answer **one** question from this section.

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]

- **The $E^\ominus(X_2|X^-)$ values become less positive (OR decrease) down the group.**
- **Thus, the halogens are less reactive as oxidising agents down the group.**

(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]

- **Enantiomerism**
- 

Lactic acid can be synthesised from ethanol as shown below.

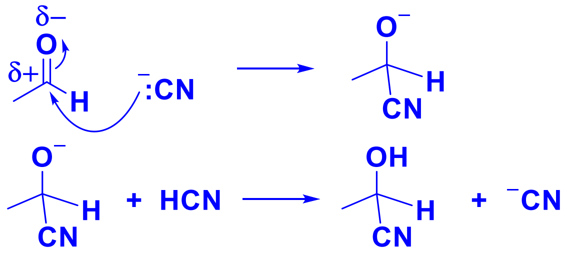
$$CH_3CH_2OH \xrightarrow{\text{step 1}} CH_3CHO \xrightarrow{\text{step 2}} CH_3CH(OH)CN \xrightarrow{\text{step 3}} CH_3CH(OH)CO_2H$$

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

- **step 1: $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat with immediate distillation**
- **step 2: HCN(aq) with NaCN(aq) catalyst**

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

Mechanism: nucleophilic addition
CN^- is the nucleophile.



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

- **K_a of lactic acid is larger than that of propanoic acid.**
- **When lactic acid dissociates, $CH_3CH(OH)CO_2^-$ ion is formed which is more stable than $CH_3CH_2CO_2^-$ ion from the dissociation of propanoic acid. The OH group exerts an electron-withdrawing inductive effect to help disperse the negative charge on oxygen. Hence, lactic acid is a stronger acid with a larger K_a.**

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

$$2CH_3CH(OH)CO_2H(g) \rightleftharpoons \underset{\text{dimer}}{(CH_3CH(OH)CO_2H)_2(g)}$$

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]

Let x bar be the partial pressure of dimer formed at equilibrium. At equilibrium,

partial pressure of lactic acid = $6.65 - 2x$ bar
partial pressure of dimer = x bar
total pressure of gas mixture = $6.65 - 2x + x = 6.65 - x = 3.52$
• **$x = 3.13$**

Hence, in the gas mixture,
partial pressure of dimer = 3.13 bar
• **partial pressure of lactic acid = 6.65 – 2(3.13) = 0.39 bar (ecf)**

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

• $$K_p = \frac{P_{dimer}}{P^2_{lactic\ acid}}$$

• $$K_p = \frac{3.13}{(0.39)^2} = 20.6\ bar^{-1}\ \text{(ecf)}$$

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]

$\Delta G = -RT\ln K_p$
• **$= -(8.31)(127 + 273)$ (ln 20.6)**
$= -10100$ J mol^{-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]

$\Delta G = \Delta H - T\Delta S$
• **$-10100 = \Delta H - (127 + 273)(-30.0)$**
$\Delta H = -22100$ J mol^{-1} = –22.1 kJ mol^{-1}

Strength of hydrogen bond
• **= 22.1 ÷ 2 = 11.05 = 11.1) kJ mol^{-1}**

(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]

Let lactic acid be HA.

$$HA + HCO_3^- \rightleftharpoons A^- + H_2CO_3$$

$$K_c = \frac{[A^-][H_2CO_3]}{[HA][HCO_3^-]} = \frac{[H^+][A^-]}{[HA]} \times \frac{[H_2CO_3]}{[H^+][HCO_3^-]}$$

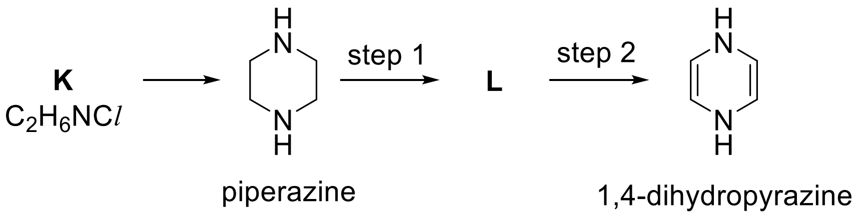
- $= \frac{1.4 \times 10^{-4}}{4.5 \times 10^{-7}}$
- $= 311$

(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]

- **I disagree with this claim. Since K_c is a large number, the equilibrium position lies to the right.**

[Total: 20]

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.

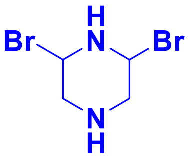


(i) Suggest and explain if 1,4-dihydropyrazine can exhibit *cis-trans* isomerism. [1]

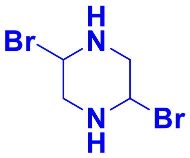
- **1,4-dihydropyrazine cannot exhibit *cis-trans* isomerism. Both C=C bonds are in the six-membered ring. Due to ring strain, the *trans* isomer cannot be formed.**

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

- **K: $NH_2CH_2CH_2Cl$**
- **L:**



OR



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

- **step 1: Br_2, UV light**
- **step 2: NaOH in ethanol, heat**

(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]

- **Step 1 results in a low yield as any one of the eight hydrogen atoms bonded to the four C atoms can be substituted by Br with equal probability. Thus, a mixture of different substituted products can be obtained with the given condition. Only two of them can give the desired product and hence, it results in a low yield.**

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

- **K_b of piperazine is smaller than that of diethylamine.**

- **There is an additional electronegative N on piperazine and it exerts an electron-withdrawing inductive effect which makes the lone pair on N less available for donation. Thus, piperazine is a weaker base with a smaller K_b value.**

(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]

Let piperazine be B. After protonation, BH^+ is formed initially.

Amount of HC*l* added = $1.00 \times 100 \times 10^{-3}$ = 0.100 mol
- **Amount of B added = $11.2 \div (12.0 \times 4 + 1.0 \times 10 + 14.0 \times 2)$ = 0.130 mol (excess)**

HC*l* will react with B to give BH^+.
Amount of BH^+ = 0.100 mol
- **Amount of B left = 0.130 – 0.100 = 0.030 mol**

$$K_{b1} = \frac{[BH^+][OH^-]}{[B]}$$

$$[OH^-] = \frac{(10^{-5.35})(0.030)}{0.100} = 1.34 \times 10^{-6}$$

pOH = –lg [OH^-] = 5.87
- **pH = 14 – 5.87 = 8.13**

(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]

- **As the blood becomes too acidic, HCO_3^- ions will react with the H^+ ions.**
  $$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$
  Large reservoir of HCO_3^- ions help to ensure that most of the added H^+ ions are removed. Hence, pH of blood remains almost constant.

- **As the blood becomes too alkaline, H_2CO_3 molecules will react with the OH^- ions.**
  $$H_2CO_3^-(aq) + OH^-(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$$
  Large reservoir of undissociated H_2CO_3 molecules help to ensure that most of the added OH^- ions are removed. Hence, pH of blood remains almost constant.

(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]

- **If this is an elementary step reaction, from the given equation of the reaction, there will be one molecule of NO_2 colliding with one molecule of SO_2 in the rate determining step. Hence, both NO_2 and SO_2 should have first order of reaction. However, this is not consistent with the experimentally determined rate equation. Thus, it is not an elementary step.**

(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 convertor. [1]

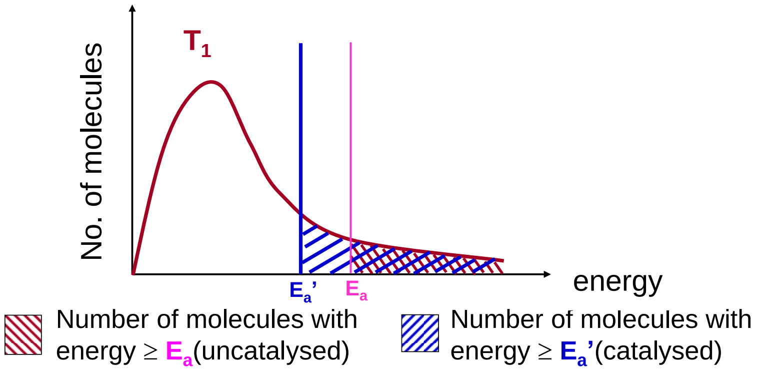
CO is another pollutant produced in the car engine. In the presence of the catalytic convertor,

- **$2NO_2 + 4CO \rightarrow N_2 + 4CO_2$**

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

- **Adsorption of reactant molecules on the catalyst's surface increases rate of reaction as adsorption weakens the covalent bonds within the reactant molecules, thereby reducing the activation energy for the reaction.**
- **Adsorption also increases the concentration of reactant molecules at the catalyst surface allowing reactant molecules to come into close contact with proper orientation for reaction. In the final stage, products formed desorb from the catalyst surface.**

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



- **Catalyst increases the value of rate constant.**
- **At the same temperature T_1, a catalyst provides an alternative reaction pathway with a lower activation energy, E_a'. Thus, there is a larger number of molecules with energy ≥ E_a' leading to a larger rate constant.**

[Total: 20]