Victoria Junior College 2015 H2 Chemistry Prelim Exam 9647/3 Suggested Answers

- 1 Magnesium ethanoate is commonly used as a source of magnesium or ethanoate ions in chemistry experiments. One of the more prevalent uses of magnesium ethanoate is in the mixture called calcium magnesium ethanoate (CMA). It is a mixture of calcium ethanoate and magnesium ethanoate. CMA acts as a powerful SO₂, NO_x, and toxic particulate emission control agent in coal combustion processes to reduce acid rain, and as an effective catalyst for the facilitation of coal combustion.
- (a) Samples of anhydrous magnesium ethanoate, Mg(CH₃COO)₂ and barium ethanoate, Ba(CH₃COO)₂, were heated to a temperature of 600°C causing them to thermally decompose. White residues were formed in both cases and a common gaseous product, X, with molecular formula of C₃H₆O was also given off. X gives a yellow precipitate upon warming with aqueous alkaline iodine.

In addition, the decomposition of magnesium ethanoate also produced a second gaseous product which formed a white precipitate with calcium hydroxide solution.

(i) Identify the gaseous product, **X**.

Propanone, CH₃COCH₃

[1]

(ii) Write a balanced equation with state symbols, for each decomposition reaction.

 $\begin{array}{rcl} Mg(CH_{3}COO)_{2}\,(s) &\longrightarrow & MgO(s) \,+\, CO_{2}(g) \,+\, CH_{3}COCH_{3}(g) \\ Ba(CH_{3}COO)_{2}\,(s) &\longrightarrow & BaCO_{3}(s) \,+\, CH_{3}COCH_{3}(g) \end{array}$

[2]

(iii) Account for the difference in the decomposition products.

The Mg^{2+} ion is <u>much smaller</u> than Ba^{2+} ion, hence its <u>higher charge density</u> enables it to <u>polarise the CH_3COO^- ion</u> and <u>distort the C-O bond</u> to a greater extent resulting in complete decomposition.

(b) Magnesium, is an extremely important light weight structural metal which can be produced by the electrolysis of magnesium chloride. Magnesium chloride can be prepared from magnesium oxide which is obtained from sea-water containing a significant amount of Mg²⁺ and Ca²⁺. The steps involved are shown below:



The numerical values of the relevant solubility products are given below.

Magnesium carbonate	1.0 x 10⁻⁵
Calcium carbonate	8.7 x 10⁻ ⁹
Magnesium hydroxide	1.1 x 10 ⁻¹¹
Calcium hydroxide	5.5 x 10⁻ ⁶

(i) Calculate and compare the solubility between magnesium carbonate and magnesium hydroxide.

$$\begin{split} &\mathsf{K}_{sp} \mbox{ (Magnesium carbonate) = [Mg^{2+}][CO_3^{2-}]} \\ & 1.0 \ x \ 10^{-5} \ = \ (x)(x) \\ & x \ = \ 3.16 \ x \ 10^{-3} \ mol \ dm^{-3} \\ & \mathsf{K}_{sp} \mbox{ (Magnesium hydroxide) = [Mg^{2+}][OH_1^{-2}]} \\ & 1.1 \ x \ 10^{-11} \ = \ (y) \ (2y)^2 \\ & y \ = \ 1.40 \ x \ 10^{-4} \ mol \ dm^{-3} \\ & \mathsf{Solubility of MgCO_3 is higher than that of Mg(OH)_2} \end{split}$$

[3]

(ii) Assuming the concentration of magnesium ions in the filtrate in **step 2** is 3.0×10^{-5} mol dm⁻³, calculate the concentration of hydroxide ions present in the filtrate when trace of solid magnesium hydroxide first appears.

First trace of ppt appears when lonic product = K_{sp} $[Mg^{2+}][OH^{-}]^2 = 1.1 \times 10^{-11}$ $(3.0 \times 10^{-5})(z)^2 = 1.1 \times 10^{-11}$ $z = 6.06 \times 10^{-4}$ mol dm⁻³

(iii) Explain why the addition of carbonate ions in **step 1** has to be controlled.

To ensure maximum precipitation of Ca^{2+} in the form of $CaCO_3$ which is then removed while preventing the precipitation of Mq^{2+} in Step 1.

[1]

(iv) Give a reason why the electrolysis of magnesium chloride is preferred to that of magnesium oxide.

The <u>melting point of $MgCl_2$ is lower than MgO and hence less energy</u> will be required to melt $MgCl_2$.

[1]

- (c) Some organic and inorganic compounds are classified under a category called 'nonexistent compounds'. They are called non-existent because so far chemists had been unable to synthesise them. Some of the reasons why these compounds are unstable are:
 - unfavourable bond energy terms
 - a redox incompatibility of the ions making up the compound
 - reaction occurring between the ions

For the following cases, suggest an explanation for each observation. You may use data from the *Data Booklet* to assist you in your answers. Give relevant equations to support your answers.

(i) When aqueous sodium carbonate is added to aqueous aluminium chloride, a colourless gas is liberated and the precipitate formed is not aluminium carbonate, $Al_2(CO_3)_3$.

Aluminium carbonate is not precipitated because $Al^{\beta^+}(aq)$ is acidic and will react with the carbonate, liberating carbon dioxide gas.

When aluminum chloride dissolves in water, it undergoes hydrolysis to produce an acidic solution as follows: $Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$

This acidic solution will react with sodium carbonate to produce carbon dioxide: $2H_3O^+ + CO_3^{2^-} \rightarrow CO_2 + 3H_2O$ [OR 2H⁺ + CO₃^{2^-} $\rightarrow CO_2 + H_2O$]

The precipitate is aluminium hydroxide formed due to hydrolysis of sodium carbonate. $CO_3^{2^-} + H_2O \rightleftharpoons HCO_3^- + OH^ A^{\beta^+}(aq) + 3OH^-(aq) \rightarrow A/(OH)_3(s)$

[4]

(ii) Caprolactum, a monomer of the polymer nylon 6, exists as an alicyclic ring structure and not as 6-aminohexanoic acid, a straight chain aliphatic structure as most monomers do.



Caprolactum

6-aminohexanoic acid

•6-aminohexanoic acid can undergo internal nucleophilic substitution [OR cyclisation] to form caprolactum.



Energy requirements: To break N–H and C–O bonds = $+390 + 360 = +750 \text{ kJ mol}^{-1}$ To form O–H and C–N bonds = $-460 - 305 = -765 \text{ kJ mol}^{-1}$

Overall $\Delta H = -15 \text{ kJ mol}^{-1}$. Reaction is exothermic and feasible. [Note: Overall there is also an increase in entropy of the system.]

(iii) It is possible to find $MnCl_2$ in the laboratory but not $MnCl_3$.

C <i>l</i> ₂ + 2e [−] ==== 2C <i>l</i> [−]	<i>E</i> ° = +1.36 V
Mn ³⁺ + e ⁻ ==== Mn ²⁺	<i>E</i> ° = +1.49 V

 $2Mn^{3+} + 2Cl \rightarrow 2Mn^{2+} + Cl_2$ $E_{cell}^{\bullet} = 1.49 - (1.36)$ = +0.13 V

Since $E_{cell}^{\Theta} \ge 0$, a redox reaction will occur in which Mn^{3+} is reduced to Mn^{2+} and $C\Gamma$ is oxidized to chlorine gas when Mn^{3+} is combined with $C\Gamma$.

[2]

[Total: 20]

2 (a) The Contact Process is an industrial process for manufacturing sulfuric acid. The key stage in this process is the reaction between sulfur dioxide and oxygen.

 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -197 \text{ kJ mol}^{-1}$

Vanadium(V) oxide, V_2O_5 , is used as a *heterogeneous catalyst* for this process. Describe the mode of action by which V_2O_5 fulfils this role.

<u>Availability of partially filled 3d orbitals</u> in vanadium allow <u>reactant molecules</u> to be adsorbed onto metal surface.

Reactant molecules are <u>brought closer together</u> and <u>bonds within them are</u> <u>weakened</u>. <u>Activation energy is lowered</u>.

Subsequently, products formed desorb from the catalyst surface.

[3]

(b) In an experiment to determine the K_p of the above equilibrium, a mixture containing 0.200 mol of SO₂ and 0.100 mol of O₂ was heated in a closed flask and allowed to reach equilibrium at 550°C and 3.5 atm.

The flask was then *rapidly* cooled to liquefy the SO_3 so that it can be separated from the gaseous SO_2 and O_2 . Excess water was carefully added to the liquid SO_3 , causing the following reaction to occur:

 $SO_3(I) + H_2O(I) \rightarrow H_2SO_4(aq)$

The resulting solution was made up to 250 cm³ in a standard volumetric flask. 25.0 cm³ of this solution was titrated with 1.00 mol dm⁻³ NaOH and required 36.0 cm³ for complete neutralisation.

(i) Calculate the equilibrium amount of SO_2 , O_2 and SO_3 at 550°C.

 $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

No. of moles of H_2SO_4 in 25.0 cm³ = $\frac{1}{2} \times 36.0 / 1000 \times 1.00$ = 0.0180 mol

No. of moles of H₂SO₄ in 250 cm³

= (250 / 25.0) × 0.0180 = 0.180 mol = no. of moles of SO₃

	2SO ₂ (g) +	O ₂ (g)	=	2SO ₃ (g)
Initial mol	0.200	0.100		0
Change in mol	-0.180	- ½ (0.180)		+0.180
Eqm mol	0.020	0.01		0.180

(ii) Hence, calculate a value for K_p , including its correct units.

Total	number of moles	= 0.020 + 0.010 + 0.180 = 0.210 mol
	P_{SO3}^2	- 0.210 mor
K _p	$= \overline{\mathbf{P}_{\mathrm{SO2}^2 \times \mathbf{P}_{\mathrm{O2}}}}$	
	$= \frac{\left[\frac{0.180}{0.210} \times 3\right]^2}{\left[\frac{0.020}{0.210} \times 3.5\right]^2} \left[\frac{1}{100}\right]^2}$	3.5] ² 0.010 0.210 × 3.5]
	= 486 atm ⁻¹	

[1]

(iii) In liquefying the SO₃, it was mentioned that the cooling was performed *rapidly*. Explain how the titration volume would be affected if the cooling had been performed slowly.

If the cooling had been performed slowly, equilibrium position will be affected. By Le Chatelier's Principle, equilibrium position will shift to the right since the forward reaction is <u>exothermic</u>, <u>releasing heat to</u> <u>counteract the decrease in temperature</u>. Hence, <u>more SO₃</u> will be formed, causing <u>titration volume to be larger</u>.

[2]

(c) One important use of vanadium compounds is the vanadium redox battery, a rechargeable battery which utilizes graphite electrodes. The electrolytes are pumped from separate storage tanks A and B into compartments X and Y of the cell respectively, where they are separated by a semi-permeable proton exchange membrane which allows only passage of protons.



The direction of the electron flow during the **discharging** process is indicated in the diagram of the battery above.

(i) By means of the letters **X** and **Y**, state and briefly justify the direction of proton flow across the membrane during the discharging process.

Protons flow from <u>Y to X</u> to <u>maintain electrical neutrality</u> of the electrolytes.

In a particular setup, compartment **X** contained 5 dm³ of the electrolyte, with VO_2^+ and VO^{2+} each having an original concentration of 1.5 mol dm⁻³. The cell discharged until 90% of the reactants was consumed, after which the cell was recharged by connecting an electricity source across the electrodes.

(ii) With the aid of the *Data Booklet*, write half–equations for the reactions that occur at the electrodes in **X** and **Y** during the **charging** process.

X: $VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e$ Y: $V^{3+} + e \rightarrow V^{2+}$

[1]

(iii) If the current used for the charging process is 14 A, calculate the time taken, in hours, needed to restore the concentration of the vanadium-containing ions in compartment X to their original value.

Moles of reactant (VO_2^+) consumed during discharging = 0.90 × 1.5 × 5 = 6.75 mol Since $n_{reactant}$: $n_{electrons}$ = 1:1, Moles of electrons = 6.75 mol Moles of electrons = I × t / 96500 6.75 = 14 × t / 96500 t = 46500 s = 12.9 h

- [2]
- (d) Chromium is another transition metal adjacent to vanadium in the Periodic Table. Some of its reactions are described below:

When chromium metal is dissolved in dilute sulfuric acid, it produces a blue solution containing $Cr^{2+}(aq)$. The blue solution slowly turns green even in the absence of air.

This mixture is then filtered to remove the unreacted metal. To the green filtrate V, sodium hydroxide solution was added, forming a grey-green precipitate, W. In excess sodium hydroxide, the precipitate dissolves to form a dark green solution containing an anion, X. The dark green solution turns into a yellow solution, Y, upon warming with hydrogen peroxide solution.

(i) By quoting and using relevant E° values from the *Data Booklet*, explain why the blue solution turns green.

 $Cr^{3+} + e^{-} = Cr^{2+} \qquad E^{\circ} = -0.41 V$ $2H^{+} + 2e^{-} = H_{2} \qquad E^{\circ} = 0.00 V$ $E_{cell}^{\circ} = 0 - (-0.41)$ = +0.41 V

Since $E_{cell}^{\Theta} \ge 0$, reaction is feasible and the blue Cr^{2+} is oxidised to green Cr^{3+} .

(ii) Identify the precipitate **W** and the anion **X** and suggest ionic equations, with state symbols, for the formation of **W**, and for the formation of **X**.

```
W is Cr(OH)<sub>3</sub>
X is [Cr(OH)_6]^{3-}
Cr<sup>3+</sup>(aq) + 3OH<sup>-</sup>(aq) \rightleftharpoons Cr(OH)<sub>3</sub>(s)
Cr(OH)<sub>3</sub>(s) + 3OH<sup>-</sup>(aq) \rightleftharpoons [Cr(OH)<sub>6</sub>]<sup>3-</sup>(aq)
[OR Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>(aq) + 6OH<sup>-</sup>(aq) \rightleftharpoons [Cr(OH)<sub>6</sub>]<sup>3-</sup>(aq) + 6H<sub>2</sub>O(I)]
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(iii) State the role of hydrogen peroxide in converting the dark green solution into Y.

Oxidising agent

[1]

[2]

(e) A particular chromium compound has the formula $Cr(H_2O)_6Cl_3$. It contains a complex **Z** in which the coordination number of chromium is 6.

When a solution containing 0.02 mol of the compound, $Cr(H_2O)_6Cl_3$, is treated with excess aqueous $Pb(NO_3)_2$, a white precipitate is formed. After filtration and drying, the mass of the precipitate is found to be 2.78 g.

(i) Use the given information to determine the formula of the complex, Z.

The precipitate formed is PbCl₂. Hence,

Amount of free C/ anions = 2.78 / (207 + 71.0) × 2 = 0.02 mol

 $\frac{\text{Moles of free C} l \text{ anions}}{\text{Moles of compound}} = \frac{0.02}{0.02}$

= 1

Hence, 2 Cl ligands are present in the complex.

Formula of the complex is $[Cr(H_2O)_4Cl_2]^+$.

(ii) Z is known to exist as two stereoisomers. Draw the structures of these two stereoisomers, showing clearly the spatial arrangement of the ligands around the central metal ion.



[2]

[Total: 20]

- **3** Phosphorus belongs to Period 3, an element that is essential for life. The elemental form of phosphorus consists of tetrahedral P_4 molecules, in which each Phosphorus atom forms three single bonds with three other Phosphorus atoms. Phosphates, compounds containing the PO_4^{3-} ion, are a component of DNA, RNA, ATP and also the phospholipids, which form all cell membranes.
 - (a) Each of the Period 3 elements, Na to S, reacts at a different rate with oxygen to form oxides of different oxidation states.
 - (i) Describe what you see when magnesium and sulphur are separately burned in air or oxygen. Write equations for the reactions that occur.

 $2Mg(s) + O_2(g) \rightarrow 2 MgO(s)$ Mg burns with a brilliant white flame to give a white solid. The reaction is vigorous.

 $S(s) + O_2(g) \rightarrow SO_2(g)$ S burns with a pale blue flame to give a pungent gas (with burning S smell). The reaction is slow.

[3]

(ii) Explain briefly why the bonding of the oxides of Period 3 elements vary from ionic to covalent.

The **difference between the electronegativity values** of the Period 3 elements and oxygen **decreases across the period**.

(iii) X and Y are Period 3 elements.

Element **X** forms a white oxide that is slightly soluble in cold water. Its chloride dissolves in water to form a weakly acidic solution.

Element **Y** forms two oxides. 0.03 mol of one of the two oxides produces 6.99 g of white precipitate when shaken with excess barium chloride solution. Another solution containing 0.05 mol of this oxide of element **Y** forms a neutral solution when the same amount of the oxide of the element **X** is added to it.

Identify the elements **X**, **Y**, the oxide of **Y** and the white precipitate that is formed in the above reaction. Explain why the chloride of element **X** is acidic.

Element X : Magnesium Element Y: Sulfur Formula of the oxide of Element Y: SO₃ 6.99g of white ppt correspond to the mass of 0.03 mol of BaSO₄. Upon addition of BaC*l*₂, white ppt formed is BaSO₄. Due to the <u>high charge density</u> of the Mg²⁺ ion, MgC*l*₂ <u>hydrolyses slightly</u> to form a weakly acidic solution.

[3]

(b) Sulfur, another Period 3 element, forms a wide range of sulfides with phosphorus. One of the most well-known examples is the three-fold symmetric P_4S_3 used in strike-anywhere matches.



(i) State the two oxidation states of phosphorus that exist in P_4S_3 .

The oxidation states are **+1** and **+3**.

[1]

(ii) P_4O_3 has a structure that is similar to P_4S_3 . Explain why the O–P–O bond angle is smaller than the S–P–S bond angle.

As <u>O atom is more electronegative than S atom</u>, the <u>shared electrons are</u> <u>attracted more towards the O atom</u> in the P–O bond than for the P–S bond. Hence, the <u>smaller bond pair–bond pair repulsion</u> causes the O–P–O bond angle to be smaller than the S–P–S bond angle.

(iii) The bond energy for the P–P single bond is 197 kJ mol^{-1} .

Given the enthalpy change for the following transformation

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 $P_4S_3(g) \to P_4(g) + 3S(g)$ $\Delta H = +1029 \text{ kJ mol}^{-1}$,

calculate the bond energy for the P-S bond.

6 P–S bonds are broken and 3 P–P bonds are formed.



(iv) In the presence of excess sulfur, P_4S_3 can be converted to P_4S_{10} , which is structurally and chemically similar to P_4O_{10} . Give a balanced equation for the reaction between P_4S_{10} and H_2S which does **not** involve any change in oxidation state. Hence, state the role that P_4S_{10} plays in the reaction.

 $\begin{array}{l} P_4S_{10} + 6H_2S \rightarrow 4H_3PS_4 \\ P_4S_{10} \text{ is acting as a base.} \end{array}$

[2]

(c) Aluminium is an important element in the reducing agent, LiA/H₄, for organic synthesis. When benzoic acid is reduced by LiA/H₄ in dry ether followed by addition of heavy water (D₂O), the product, benzyl alcohol-OD, is formed:

$C_6H_5CH_2OD$

(i) Give the structure of the product formed when 2-hydroxybenzaldehyde

, is reduced by LiA/D_4 in dry ether followed by H_2O .



[1]

(ii) LiA/H₄ reacts with H₂O to give two insoluble hydroxides and a gas. Give a balanced equation for the reaction.

$$LiAlH_4(s) + 4H_2O(l) \rightarrow LiOH(s) + Al(OH)_3(s) + 4H_2(g)$$
[1]

(iii) When 2-hydroxybenzaldehyde reacts with aqueous BrCl, an insoluble white precipitate is formed. The M_r of the precipitate is 157.8 units more than that of 2-hydroxybenzaldehyde.

Write a balanced equation to show the reaction.



(iv) Give a 2-step synthesis to convert methylbenzene to $C_6H_5CH_2OD$.



[3]

[Total: 20]

4(a) Nitrous oxide is a chemical compound with formula N₂O. It is commonly known as laughing gas due to the euphoric effects of inhaling it, a property that had led to its recreational use as a hallucinogenic anaesthetic.

At a high temperature of 1200 K, in the presence of a gold surface, N_2O decomposes to its elements according to the following equation.

 $2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$

The rate of decomposition of pure N_2O may be followed by measuring the total pressure of the system. In such an experiment, the total pressure, p, increased as follows:

Total pressure, <i>p</i> /kPa	25.0	27.5	30.0	32.5	34.0	35.0
Time /s	0	1030	2360	4230	5870	7420
Partial pressure of N ₂ O /kPa	25.0	x	15	10	7	5

The data were plotted on the following graph.



(i) Explain mathematically, or otherwise, that the partial pressure of N_2O at 1030 s is 20 kPa.

The reaction results in an overall increase in number of moles of gas. From two moles of gaseous reactant to a total of three moles of gaseous products. The increase in total pressure from 25 kPa to 27.5 kPa is due to the difference between the number of moles of gaseous reactant and products. Since two moles of gaseous reactants are consumed for every one mole increase in gaseous products therefore, partial pressure of N₂O at 1030 s = 25 - 2(2.5) = 20 kPa

[1]

(ii) By using a graphical method, determine the order of the reaction with respect to N_2O .

Since half-life is constant at 3200 s, reaction is first order wrt N₂O.

[1]

(iii) Calculate the rate constant for the reaction.

$$k = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{\ln 2}{3200} = 2.17 \times 10^{-4} s^{-1}$$
[1]

(iv) Suggest a reaction mechanism consisting of two elementary steps for the decomposition of nitrous oxide that is consistent with the rate equation.

Label the slow step of the reaction clearly.

•
$$N_2O \xrightarrow{\text{slow}} N_2+O$$

•
$$N_2O+O \xrightarrow{fast} N_2+O_2$$

[2]

(b) Alkene metathesis is a reaction that breaks the double bond in an alkene and then rejoins the fragments. When the fragments are joined, each new double bond is formed between two sp² carbons that were not previously bonded. Metathesis is a Greek word that means "transposition."

Compound **A** ($C_8H_{12}O_2$), is a sweet-smelling compound that undergoes metathesis reaction to give ethene and compound **B** ($C_6H_8O_2$), which possesses a five-membered ring.

When reacted with hot $H_2SO_4(aq)$, **B** gave compound **C** ($C_6H_{10}O_3$).

One mole of compound C gave two moles of carbon dioxide gas and one mole of

compound **D** ($C_4H_6O_3$) when treated with hot acidified concentrated KMnO₄.



Suggest structures for **A**, **B** and **C** and explain the reactions.

If a single molecule of A can undergo metathesis, this means A contains two C=C double bonds.

A is sweet-smelling, therefore, A is an ester.

The number of C=C double is conserved during a metathesis reaction, B must contain a C=C double bond since the other metathesis product is ethene. B still contains the original ester group since metathesis does not affect ester. B undergoes ester hydrolysis to give C.

C contains one carboxylic acid FG, one alcohol FG and one alkene FG. C undergoes oxidative cleavage to give D and two moles of CO₂ gas.



The ketone carbon in D must have come from a cleavage of a C=C.

[5]

(c) Geraniol (C₁₀H₁₈O) appears as a clear to pale-yellow oil that is insoluble in water but soluble in most common organic solvents. It has a rose-like scent and is commonly used in perfumes.



On treatment with phosphoric acid, H_3PO_4 at 200°C, geraniol dehydrates to give dipentene, $C_{10}H_{16}$, which reacts with an excess of bromine to give a tetrabromide, $C_{10}H_{16}Br_4$.

The dehydration reaction can be broken into the following steps:





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Dipentene

Copy the structure of the organic intermediate **X** formed in **step 1** onto your answer script and complete the remaining **steps 2** and **3** of the mechanism.

In the description of the mechanism, you should clearly show curly arrows, charges, dipoles and any relevant lone pair.



two arrows indicating flow of electrons in first step two arrows indicating flow of electron in second step

electrophilic addition

(d) (i)

(ii) Draw the structure of the tetrabromide that is produced from the reaction between dipentene and bromine.



[1]

[1]

(iii) State the type of stereoisomerism exhibited by the tetrabromide compound and the number of isomers present.

optical isomerism number of isomers = $2^4 = 16$

[2]

- (e) Nerol, which is present in the essential oil, bergamot, has the same formula as geraniol and undergoes the same dehydration reaction to give the same dipentene. The main difference between geraniol and nerol is the melting point: geraniol has a melting point of 15°C while nerol has a melting pointing of around −10°C.
 - (i) Draw the structure of nerol and state the type of isomerism that exists between geraniol and nerol.



structure of nerol (with 120° bond angle about double bond) cis-trans isomerism

(ii) Hence, explain why there is a difference in melting point between the two isomers.

The trans isomers pack <u>more compactly / efficiently</u> resulting in <u>stronger</u> <u>dispersion forces of attraction</u> between molecules. More energy is required to break the dispersion forces between the trans isomers than cis isomers resulting in nerol (cis isomer) having lower melting point than geraniol.

[2]

[Total: 20]

5 This question is about the chemistry of some nitrogen and oxygen containing compounds.

Nitrogen and oxygen are two very electronegative elements which make up about 78% and 20% of the atmosphere by volume respectively. Nitrogen containing compounds are vital components of foods, fertilizers, and explosives while oxygen is the third most abundant element found in the sun.

(a) Procaine is a nitrogen containing compound which is used primarily to reduce the pain of intramuscular injection of penicillin.



Draw the structure of the compound(s) formed when procaine reacts with:

(i) Hot, dilute sulfuric acid



$$\begin{pmatrix} H \\ HOCH_2CH_2N^+(C_2H_5)_2 \end{pmatrix}_2 SO_4^{2^2}$$

[2]

(ii) Aqueous bromine



(b) Compare and explain the relative basicity between the two nitrogen-containing compounds below in terms of their structures.



Procaine is more basic.

C/ in compound L is <u>electronegative</u>. It exerts <u>electron-withdrawing inductive</u> <u>effect</u> which <u>reduces the availability of the lone pair electrons on N</u> for donation to acid.

[OR C/ in compound L is <u>electronegative</u>. It exerts <u>electron-withdrawing</u> <u>inductive effect</u> which <u>intensifies the positive charge</u> on the conjugate acid ion and hence <u>destabilises it</u>.]

[2]

(c) Suggest a chemical test that allows you to distinguish procaine from compound L.

Add <u>Br₂(aq)</u> to each compound. There will be <u>decolourisation of reddishbrown Br₂ for procaine but no colour change for L.</u>

- (d) Dinitrogen tetroxide, commonly referred to as nitrogen tetroxide, N₂O₄, is a useful reagent in chemical synthesis. It is also a powerful oxidizer that spontaneously reacts upon contact with various forms of hydrazine, which makes the pair a popular bipropellant for rockets.
 - (i) Given the following reactions and their standard enthalpy changes, construct an energy cycle to calculate the enthalpy change for the reaction below involving the formation of gaseous N_2O_4 .

$$N_2O_3(g) + N_2O_5(s) \rightarrow 2N_2O_4(g)$$

$NO(g) + NO_2(g) \rightarrow N_2O_3(g)$	$\Delta H^{\theta}_{1} = -39.8 \text{ kJ mol}^{-1}$
$NO(g) + NO_2(g) + O_2(g) \rightarrow N_2O_5(g)$	$\Delta H_2^{\theta} = -113 \text{ kJ mol}^{-1}$
$2NO_2(g) \rightarrow N_2O_4(g)$	ΔH_{3}^{θ} = -57.2 kJ mol ⁻¹
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	$\Delta H^{\theta}_{4} = -114 \text{ kJ mol}^{-1}$
$N_2O_5(g) \rightarrow N_2O_5(s)$	$\Delta H_5^{\theta} = -54.1 \text{ kJ mol}^{-1}$



[2 m for energy cycle, -1/2m for every mistake]

By Hess's Law:

$$\Delta H^{\theta}_{\text{reaction}} = 39.8 + 54.1 + 113 + (-114) + 2(-57.2) = -21.5 \text{ kJ mol}^{-1}$$

(ii) The standard molar entropy, S^{θ} is the entropy content of one mole of substance under standard conditions of 298 K and 1 atm. The S^{θ} values of some nitrogen oxides are given in the table below:

Nitrogen oxides	$S^{\theta}/JK^{-1}mol^{-1}$
$N_2O_4(g)$	304.29
$N_2O_3(g)$	314.63
$N_2O_5(s)$	178.20

Given that $\Delta S^{\theta}_{\text{reaction}} = \sum S^{\theta}(\text{products}) - \sum S^{\theta}(\text{reactants})$ and using the data above, calculate the ΔG^{θ} value for the reaction below at 298 K:

$$N_2O_3(g) + N_2O_5(s) \rightarrow 2N_2O_4(g)$$

 $\Delta S^{\theta}_{\text{reaction}} = 2(304.29) - 178.20 - 314.63$ = 116 J K⁻¹ mol⁻¹

$$\Delta G^{\theta}_{\text{reaction}} = \Delta H^{\theta}_{\text{reaction}} - T\Delta S^{\theta}_{\text{reaction}}$$

= -21.5 x 10³ - 298(116)
= -56.1 kJ mol⁻¹

[2]

[3]

(iii) Hence, calculate the minimum temperature at which the reaction will take place.

Using $\Delta G = \Delta H - T \Delta S$ and noting that reaction will take place when $\Delta G = 0$, T = -21.5 x 10³ / 116 = -185 K

(e) The graph below is an Ellingham diagram, which shows the variation in the Gibbs free energy change of formation, $\Delta G_{f_{r}}$ with temperature, T, for some oxides. This graph is used to evaluate the ease of reduction of metal oxides.



(i) Which oxide is the least stable to heat at 1250 K? Explain your choice. AgO

 $\Delta G < 0$ for the <u>decomposition of AgO</u>, $2Ag_2O \rightarrow 4Ag + O_2$ It means that the decomposition of AgO is <u>spontaneous</u> at 1250 K.

[2]

- (ii) What does the gradient of the graph in the Ellingham diagram represent? Hence, explain why the sign of the gradient for 2Zn + O₂ → 2ZnO is as reflected on the graph.
 Gradient represents <u>-ΔS^θ</u> (equation of line is ΔG^θ = -TΔS^θ + ΔH^θ).
 A positive gradient implies that ΔS^θ is negative. A decrease in disorderliness of the system (Or ΔS^θ < 0) is due to a decrease in amount of gases (from 1 to 0 mol) as the reaction proceeds.
- (iii) Calculate the ΔG value for the reduction of zinc oxide by carbon at 2000K. Hence, comment on the feasibility of the reaction at 2000 K.

At 2000 K, $2C + O_2 \rightarrow 2CO \qquad \qquad \Delta G^{\theta} = -\underline{600 \text{ kJ mol}^{-1}} \dots \dots (1)$ $2Zn + O_2 \rightarrow 2ZnO \qquad \qquad \Delta G^{\theta} = -\underline{100 \text{ kJ mol}^{-1}} \dots \dots (2)$ Hence, $2ZnO \rightarrow 2Zn + O_2 \qquad \qquad \Delta G^{\theta} = +\underline{100 \text{ kJ mol}^{-1}} \dots \dots (3)$ Reduction of ZnO by C: (1) + (3) gives $2ZnO + 2C \rightarrow 2Zn + 2CO$ Hence, $\Delta G^{\theta} = -\underline{600} + \underline{100} = -\underline{500 \text{ kJ mol}^{-1}}$ Since $\underline{\Delta G^{\theta}} < \underline{0}$, the reaction is therefore <u>thermodynamically feasible at</u>} 2000 K.

[3]

[Total: 20]