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 SO_2, 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, $Mg(CH_3COO)_2$ and barium ethanoate, $Ba(CH_3COO)_2$, were heated to a temperature of 600^oC causing them to thermally decompose. White residues were formed in both cases and a common gaseous product, **X**, with the molecular formula of C_3H_6O 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**.

[1]

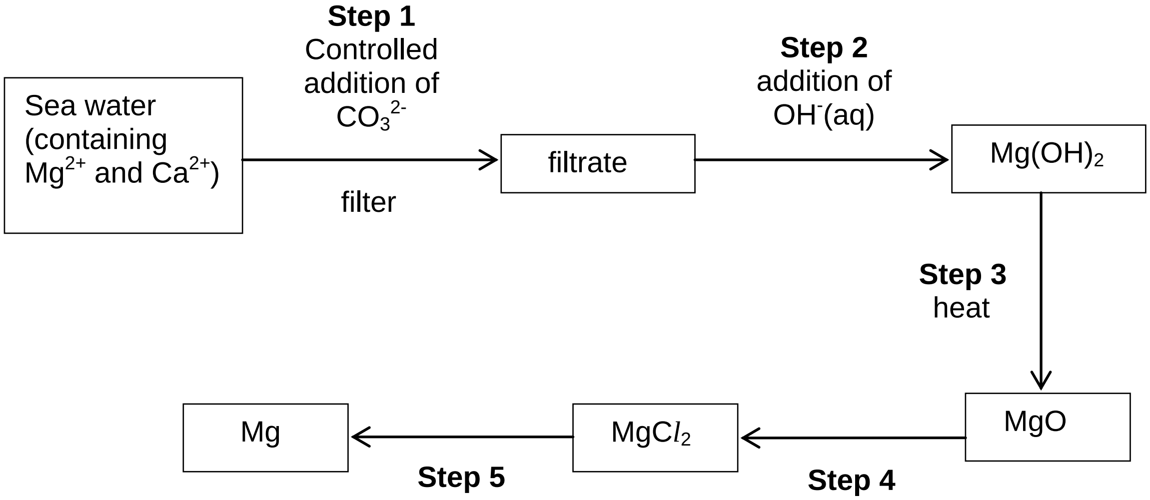
(ii) Write a balanced equation with state symbols, for each decomposition reaction.

[2]

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

[2]

(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 Mg^{2+} and Ca^{2+}. The steps involved are shown below:



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

Magnesium carbonate	1.0×10^{-5}
Calcium carbonate	8.7×10^{-9}
Magnesium hydroxide	1.1×10^{-11}
Calcium hydroxide	5.5×10^{-6}

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

[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.

[1]

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

[1]

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

[1]

(c) Some organic and inorganic compounds are classified under a category called 'non-existent 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:

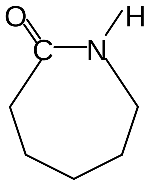
- unfavourable bond energy terms
- a redox incompatibility of the ions making up the compound
- reaction occurring between the ions

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, $Al_2(CO_3)_3$.

[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.



$H_2NCH_2CH_2CH_2CH_2CH_2CO_2H$

Caprolactum

6-aminohexanoic acid

[3]

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

[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.

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

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.

[3]

(b) In an experiment to determine the K_p of the above equilibrium, a mixture containing 0.200 mol of SO_2 and 0.100 mol of O_2 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:

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

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

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

[2]

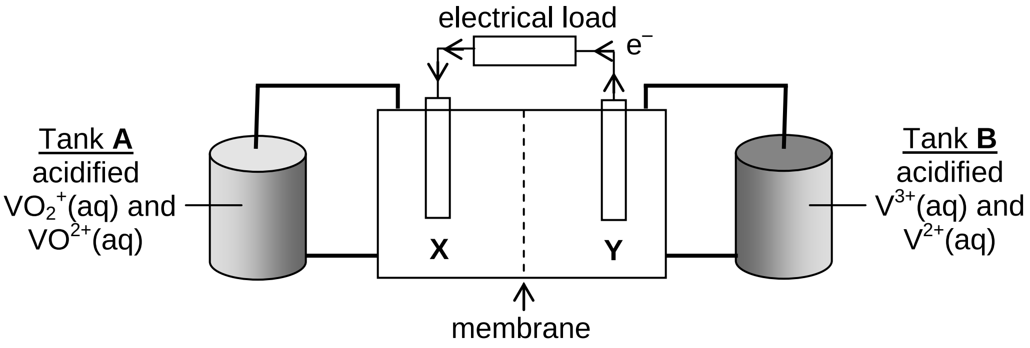
(ii) Hence, calculate a value for K_p, including its correct units.

[1]

(iii) In liquefying the SO_3, it was mentioned that the cooling was performed *rapidly*. Explain how the titration volume would be affected if the cooling had been performed slowly.

[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.

[1]

In a particular setup, compartment **X** contained 5 dm^3 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.

[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.

[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 $E^\ominus$ values from the *Data Booklet*, explain why the blue solution turns green.

[2]

(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.**

[2]

(iii) State the role of hydrogen peroxide in converting the dark green solution into **Y**.

[1]

(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**.

[1]

(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 sulfur are separately burned in air or oxygen. Write equations for the reactions that occur.

[3]

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

[1]

(iii) **X** and **Y** are Period 3 elements.

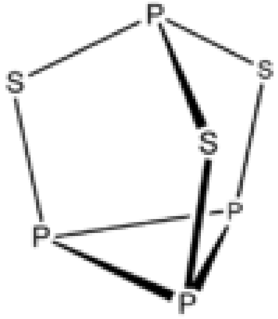
Element **X** forms a white oxide that is slightly soluble in cold water. Its chloride dissolves in water to form a weakly acidic solution.

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.

[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.

[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.

[2]

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

Given the enthalpy change for the following transformation

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

calculate the bond energy for the P–S bond.

[2]

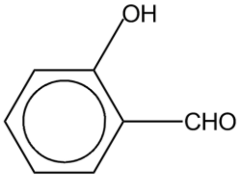
(iv) In the presence of excess sulfur, P_4S_3 can be converted to P_4S_{10}, which is structurally and chemically similar to P_4O_{10}. Give a balanced equation for the reaction between P_4S_{10} and H_2S which does **not** involve any change in oxidation state. Hence, state the role that P_4S_{10} plays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

[2]

(c) Aluminium is an important element in the reducing agent, $LiAlH_4$, for organic synthesis. When benzoic acid is reduced by $LiAlH_4$ in dry ether followed by addition of heavy water (D_2O), 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 $LiAlD_4$ in dry ether followed by H_2O.

[1]

(ii) $LiAlH_4$ reacts with H_2O to give two insoluble hydroxides and a gas. Give a balanced equation for the reaction.

[1]

(iii) When 2-hydroxybenzaldehyde reacts with aqueous BrC*l*, 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.

[1]

(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 N_2O. 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.

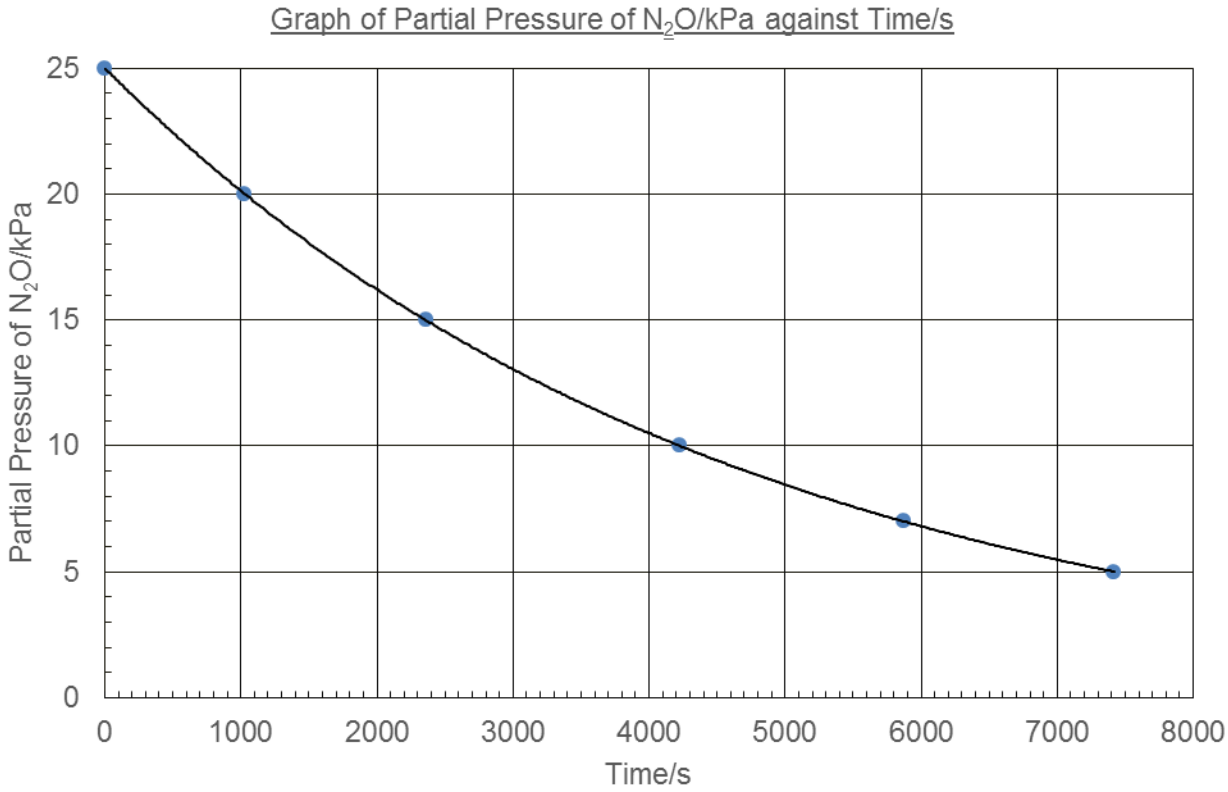
At a high temperature of 1200 K, in the presence of a gold surface, N_2O decomposes to its elements according to the following equation.

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

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, *p* /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_2O /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.

[1]

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

[1]

(iii) Calculate the rate constant for the reaction.

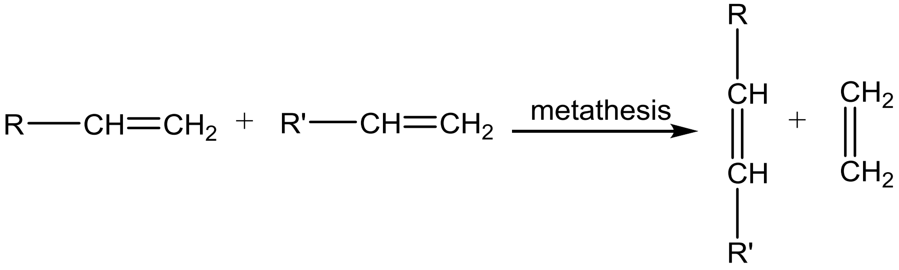
[1]

(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.

[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 sp^2 carbons that were not previously bonded. Metathesis is a Greek word that means “transposition.”

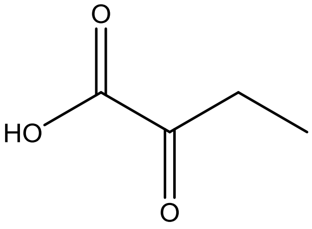


$$R{-}CH{=}CH_2 + R'{-}CH{=}CH_2 \xrightarrow{\text{metathesis}} RCH{=}CHR' + CH_2{=}CH_2$$

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 $KMnO_4$.

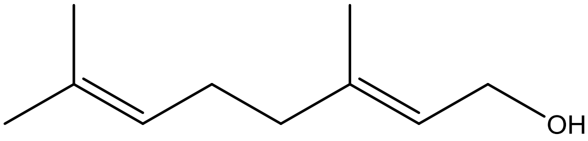


Compound **D**

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

[5]

(c) Geraniol ($C_{10}H_{18}O$) 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.

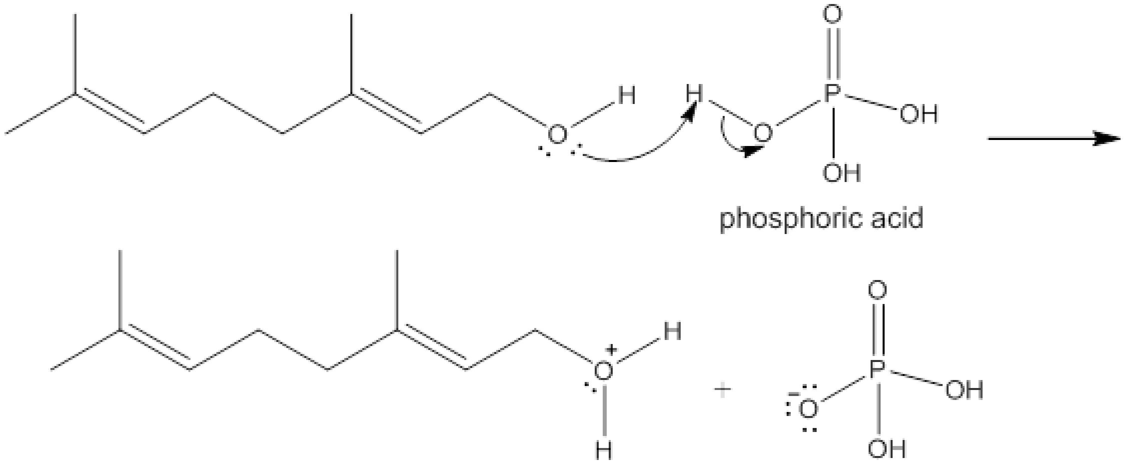


Geraniol

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:

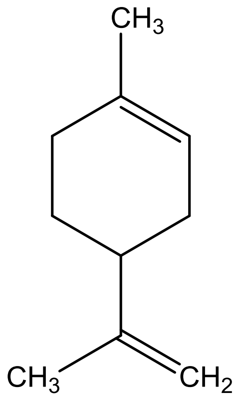
Step 1 The primary alcohol is protonated by phosphoric acid.



Intermediate **X**

Step 2 In a concerted manner, the C–O bond breaks resulting in the expulsion of a water molecule and the carbon atom is attacked by an electron-rich double bond leading to the formation of a carbocation with a six-membered ring.

Step 3 The octet electronic configuration is restored to the positively charged carbon in the carbocation by a transfer of electrons from a C–H bond. The transfer of electron is facilitated by $H_2PO_4^-$ acting as a base.
Dipentene, with the following structure, is formed as the product:



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.

[2]

(d) **(i)** Name the mechanism of the reaction between dipentene and bromine.

[1]

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

[1]

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

[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 point of around −10°C.

(i) Draw the structure of nerol and state the type of isomerism that exists between geraniol and nerol.

[2]

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

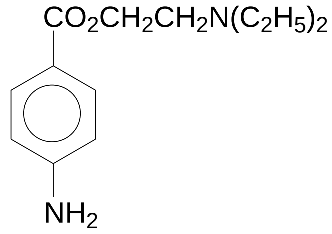
[2]

[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.



Procaine

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

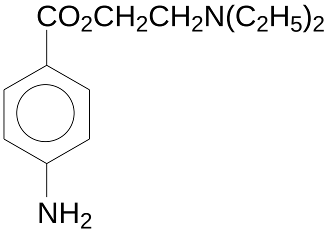
(i) Hot, dilute sulfuric acid

[2]

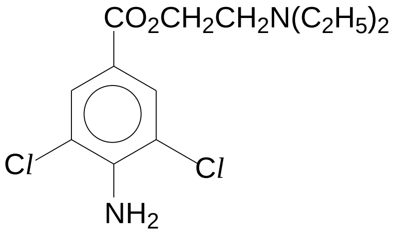
(ii) Aqueous bromine

[1]

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



Procaine



Compound **L**

[2]

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

[2]

(d) Dinitrogen tetroxide, commonly referred to as nitrogen tetroxide, N_2O_4, 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.

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

$NO(g) + NO_2(g) \rightarrow N_2O_3(g)$ $\Delta H^\theta_1 = -39.8$ kJ mol^{-1}

$NO(g) + NO_2(g) + O_2(g) \rightarrow N_2O_5(g)$ $\Delta H^\theta_2 = -113$ kJ mol^{-1}

$2NO_2(g) \rightarrow N_2O_4(g)$ $\Delta H^\theta_3 = -57.2$ kJ mol^{-1}

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H^\theta_4 = -114$ kJ mol^{-1}

$N_2O_5(g) \rightarrow N_2O_5(s)$ $\Delta H^\theta_5 = -54.1$ kJ mol^{-1}

[3]

(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^θ /J K^{-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:

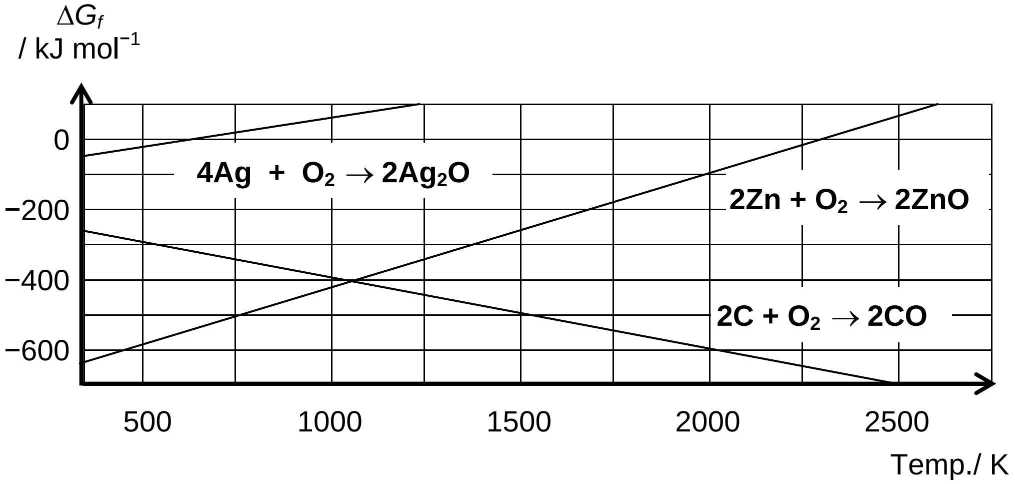
$$N_2O_3(g) + N_2O_5(s) \rightarrow 2N_2O_4(g)$$

[2]

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

[1]

(e) The graph below is an Ellingham diagram, which shows the variation in the Gibbs free energy change of formation, ΔG_f, 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.

[2]

(ii) What does the gradient of the graph in the Ellingham diagram represent? Hence, explain why the sign of the gradient for $2Zn + O_2 \rightarrow 2ZnO$ is as reflected on the graph.

[2]

(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.

[3]

[Total: 20]