1 (a) Phosphorus pentachloride, PCl_5, is a useful reagent in organic synthesis. It can undergo auto-ionisation in polar solvents according to the following equilibrium:

$$2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$$

Draw the dot-and-cross diagrams for PCl_4^+ and PCl_6^- ions and state the shapes around the central atom for each ion.

[3]

(b) PCl_5 exists in equilibrium with PCl_3 and chlorine gas as shown below:

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g) \qquad \Delta H = +124 \text{ kJ mol}^{-1}$$

At equilibrium, at 200 °C and a total pressure of 5 atm, 40% of PCl_5 is dissociated.

(i) Write an expression for K_p for the above equilibrium.

(ii) Calculate a value for K_p at 200 °C and state its units.

(iii) Predict and explain the effect of increasing the temperature on the value of K_p.

[5]

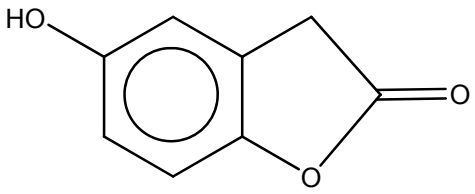
(c) Aluminium oxide is insoluble in water. However, it is able to dissolve in an aqueous solution of PCl_5.

(i) Explain why aluminium oxide is insoluble in water.

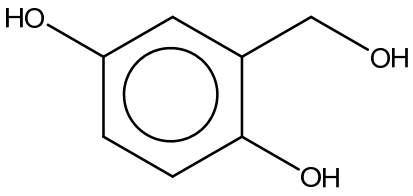
(ii) Explain why aluminium oxide can dissolve in an aqueous solution of PCl_5 and write balanced equations for any reactions that occur.

[4]

1 (d) 5-hydroxy-2-coumaranone can be synthesised using compound **F** as the starting material. The structural formulae of 5-hydroxy-2-coumaranone and compound **F** are shown below.



5-hydroxy-2-coumaranone

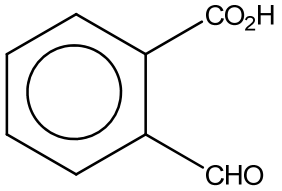


Compound **F**

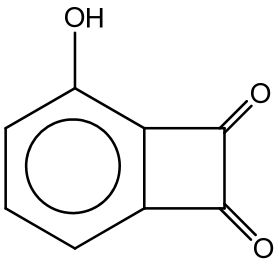
Suggest a synthesis to convert compound **F** into 5-hydroxy-2-coumaranone in not more than five steps. State all reagents and conditions used and all intermediates formed.

[4]

(e) **G** and **H** have the following structure:



Compound **G**



Compound **H**

Describe a chemical test which would distinguish between **F** and **G** and a **different** chemical test to distinguish between **F** and **H**.

[4]

[Total: 20]

2. (a) Hydroxyapatite, $Ca_5(PO_4)_3OH$, is a group of phosphate minerals which can be found in the teeth and bones of the human body. Thus, it is commonly used as a filler to replace amputated bone or as a coating to promote bone ingrowth into prosthetic implants.

(i) Write an equation to illustrate what is meant by the term enthalpy change of formation of hydroxyapatite.

(ii) Using the following information and with the aid of the *Data Booklet*, construct a Born Haber cycle to calculate the enthalpy change of lattice energy of hydroxyapatite.

	Value / kJ mol^{-1}
$\Delta H_{formation}$ $Ca_5(PO_4)_3OH$ (s)	-12 969
$\Delta H_{formation}$ OH^- (g)	-230
$\Delta H_{formation}$ PO_4^{3-} (g)	-1913
$\Delta H_{atomisation}$ Ca (s)	+178.2

(iii) Hydroxyapatite thermally decomposes to produce calcium phosphate, calcium oxide and steam. Write a balanced equation to show the thermal decomposition of hydroxyapatite. Hence, calculate the mass of calcium oxide that could be obtained by decomposing 9 g of hydroxyapatite.

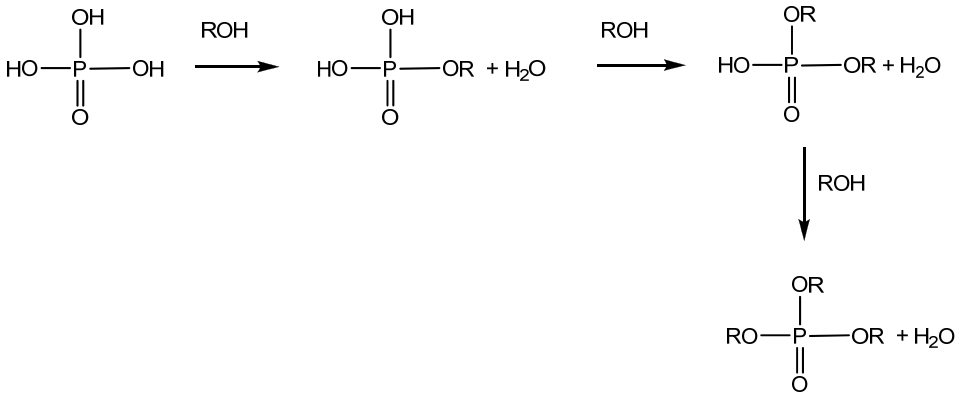
(iv) $Al_2PO_4(OH)_3$ is a recently discovered phosphate mineral found in high pressure metamorphic rocks. Suggest, using the *Data Booklet*, why it has been found that $Al_2PO_4(OH)_3$ decomposes at a lower temperature than hydroxyapatite.

[8]

2 **(b)** An organophosphate is the general name for esters of phosphoric acid. Acephate is an organophosphate which is used in many insecticides and herbicides. Acephates are acutely toxic where recent studies suggest a possible link to adverse effects in the neurobehavioral development of foetuses and children.

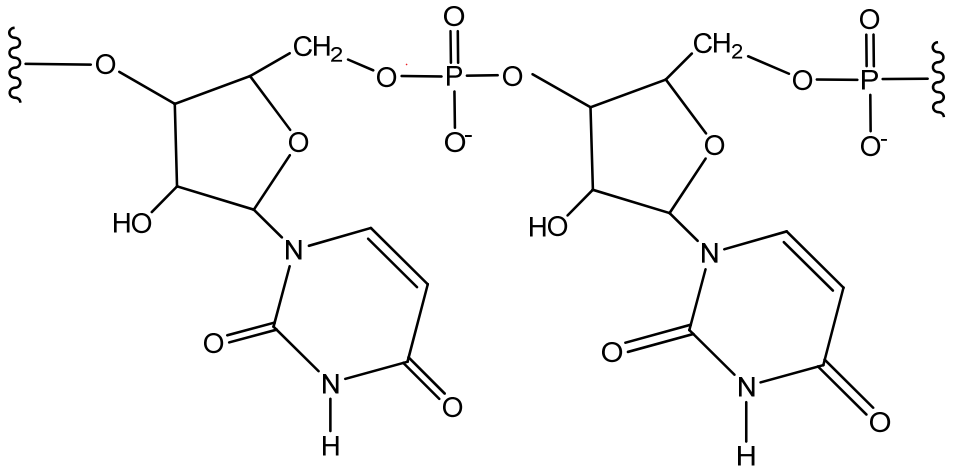
(i) Experts have recommended that the concentration of acephate in fruits should not exceed 7 ppm (1 ppm = 1 mg of acephate in 1 kg of fruits). Calculate the maximum mass in grams of acephate that a fruit weighing 50 g can contain before it is deemed hazardous.

(ii) Alkyl phosphates are phosphate esters that are formed when 1 mole of phosphoric acid combines stepwise with 3 moles of an alcohol as shown in the reaction below.



State the type of reaction in the formation of the phosphate esters.

2 (b) (iii) Alkyl phosphates play a central role in biochemistry. Phosphate ester linkages compose the backbone of the nucleic acid, RNA, which performs multiple vital roles such as genetic expression. Ribose, an alcohol, forms part of the RNA backbone.

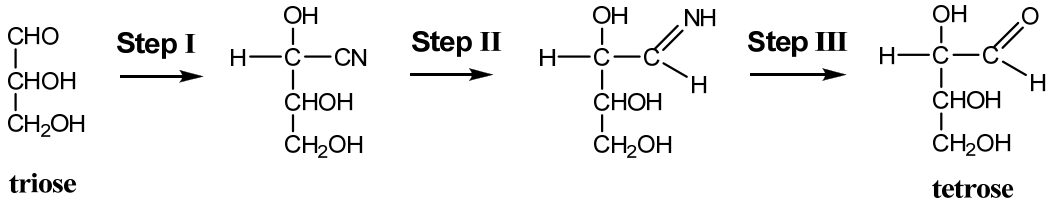


Using the segment of the RNA molecule above and **(b)(ii)**, suggest the structural formula of the alcohol which reacted with phosphoric acid.

(iv) Name three functional groups in the segment of the RNA molecule.

[6]

2 (c) An **aldose** is an alcohol that contains only one aldehyde group per molecule. The *Killiani-Fischer synthesis* lengthens an aldose carbon chain by adding one carbon to the aldehyde end of the aldose. An example of the synthesis of tetrose from triose is illustrated below.



triose **tetrose**

(i) Outline the mechanism of the reaction in **Step I**.

(ii) Tetrose is reacted with $NaBH_4$ to form compound **X**. Tetrose is reacted with acidified potassium dichromate to form compound **Y**.

Using the structural formulae of **X** and **Y**, write balanced equations to explain each of the above reactions.

[6]

[Total: 20 marks]

3 (a) Electrophoresis is a technique used to separate a mixture of amino acids. Often, this process is carried out using a gel which is soaked in a buffer solution to ensure pH is kept at a relatively constant value. A small well is etched on the gel and the solution containing the mixture of amino acids is dropped carefully in the well. An electric field is then applied across the gel.

The table below shows three amino acids to be separated by electrophoresis and their isoelectric points.

Amino acid	**Formula of side chain (R in $RCH(NH_2)CO_2H$)**	**Isoelectric point**
Cysteine (Cys)	$-CH_2SH$	5.07
Lysine (Lys)	$-(CH_2)_4NH_2$	9.74
Serine (Ser)	$-CH_2OH$	5.58

(i) Explain what is meant by a buffer solution.

(ii) Draw the predominant species of each amino acid when the pH of the buffer solution is 7.20.

(iii) Illustrate **two** ways in which vinegar might interact with a protein that contains the three amino acids in the table above to bring about denaturation. You may find that including sketches or diagrams will help you in your answer.

[8]

(b) Keratin is an important protein which is a major component in hair. Keratin contains large amounts of cysteine which gives strength to our hair. Perming hair involves creating permanent waves in hair. This process includes forming new disulfide bonds via oxidation. Hydrogen peroxide is often used as the oxidising agent.

(i) Briefly explain how the presence of cysteine in keratin strengthens hair.

(ii) Using the *Data Booklet*, write the half-equations involved in the formation of new disulfide bonds using hydrogen peroxide.

[3]

3 (c) Hydrogen peroxide can also act as a reducing agent. It is used to react with sodium hypochlorite, NaC*l*O, to produce oxygen gas. The resulting solution is then reacted with aqueous silver nitrate and a white precipitate is seen. The white precipitate disappears on addition of dilute aqueous ammonia.

(i) Using the *Data Booklet*, write the overall equation that produces oxygen gas.

(ii) Identify the white precipitate and explain its subsequent disappearance with the aid of relevant equations.

(iii) Sodium hypochlorite can be prepared using chlorine in the laboratory. Suggest a reason why this preparation should not involve heating.

(iv) A 250 cm^3 solution contains 0.05 mol dm^{-3} silver nitrate and 0.04 mol dm^{-3} copper(I) nitrate. By carefully adding solid NaC*l*, it is possible to precipitate Ag^+ while keeping Cu^+ in solution.

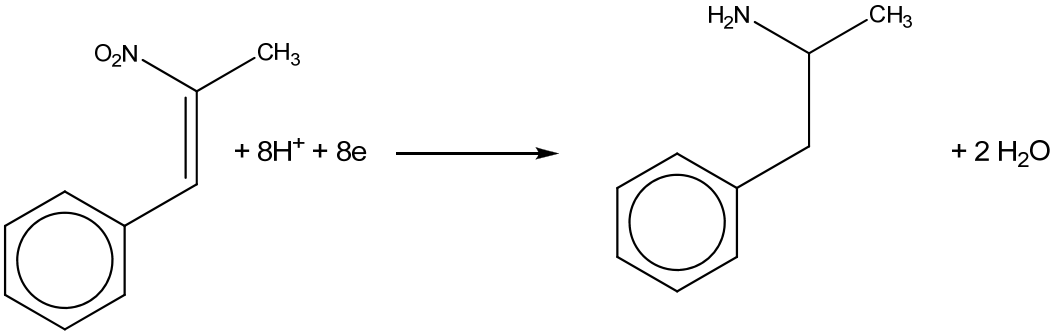
Compound	K_{sp} value
AgC*l*	1.8×10^{-10}
CuC*l*	1.2×10^{-6}

Using the data in the table above, determine the maximum mass of NaC*l* that can be added before Cu^+ starts to precipitate.

[9]

[Total: 20]

4 **(a)** Electrosynthesis in organic chemistry is the synthesis of chemical compounds in an electrochemical cell using inert electrodes. In 1932, Gordon Alles reported his investigations into the electrolysis of an aqueous solution of nitroalkene to an amine. 1-phenyl-2-aminopropane can be obtained from the cathode by the following reaction.



Phenyl nitropropylene **1-phenyl-2-aminopropane**

(i) Suggest the products of the reaction at the anode. Hence, construct an equation for the overall reaction.

(ii) Calculate the mass of 1-phenyl-2-aminopropane produced when a current of 0.25 A is passed through an aqueous solution of phenyl nitropropylene for a day.

[4]

(b) On completion of the electrosynthesis reaction, the purification of 1-phenyl-2-aminopropane is effected by exactly neutralising the impure product with aqueous hydrochloric acid.

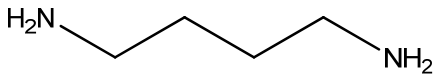
(i) Write a balanced chemical equation between 1-phenyl-2-aminopropane and hydrochloric acid.

(ii) 1-phenyl-2-aminopropane crystals are dissolved in ethanol and made up to 250 cm^3 in a volumetric flask. 25 cm^3 of this solution is then pipetted and required 27.4 cm^3 of 0.05 mol dm^{-3} aqueous hydrochloric acid for reaction. Calculate the concentration of the solution of 1-phenyl-2-aminopropane in g dm^{-3}.

(iii) Hence, determine the percentage purity of the 1-phenyl-2-aminopropane crystals produced during the electrosynthesis reaction in **(a)(ii)**.

[4]

4 (c) (i) 1,4-diaminobutane is a bidentate ligand which can be synthesised from a suitable nitroalkene.



1,4-diaminobutane

Using information from **(a)**, suggest the structural formula of this nitroalkene.

(ii) What do you understand by the term bidentate ligand?

(iii) Addition of 1,4-diaminobutane to an aqueous solution containing Cu^{2+} ion causes the formation of a violet complex. Account for this change in colour of the copper-containing compounds.

(iv) Suggest the formula of this violet complex ion.

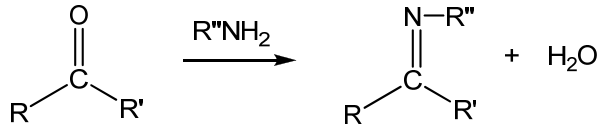
[5]

(d) (i) 2-aminopropane can be synthesised using NH_3 and a suitable chloroalkane. Draw the displayed formula of this chloroalkane.

(ii) A by-product in the formation of 2-aminopropane from **(d)(i)** gives an immediate precipitate with ethanolic silver nitrate and is able to conduct electricity in the molten and aqueous state. Suggest a structure for this by-product given that its molecular formula is $C_{12}H_{28}NCl$.

[2]

4 (e) Amines react with carbonyl compounds to yield imines as shown in the following reaction.



imine

One of the pathways by which organisms make alanine involves the addition of ammonia to alpha-keto acids such as pyruvic acid.

pyruvic acid **alanine**

(i) Using the above information, suggest the structural formula of imine **W**.

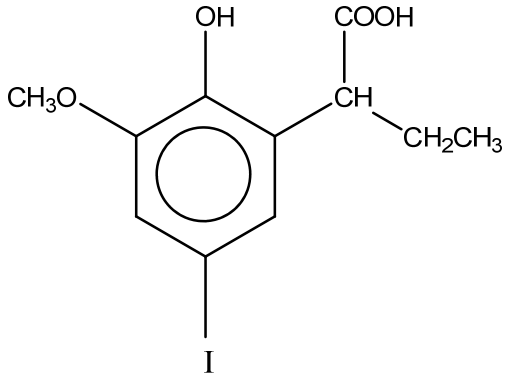
(ii) With reference to structure and bonding, explain why alanine has a higher melting point than pyruvic acid.

(iii) Propose a two-step synthetic pathway for the synthesis of pyruvic acid from propene.

[5]

[Total: 20 marks]

5 (a) **J** has the following structural formula:



The pK_{a1} and pK_{a2} values of **J** are 3.25 and 7.60 respectively.

(i) Calculate the pH of a 0.025 mol dm^{-3} solution of **J** (ignore the effect of pK_{a2} on the pH).

(ii) 30 cm^3 of 0.025 mol dm^{-3} NaOH is added to 10.0 cm^3 of 0.025 mol dm^{-3} of **J**. Draw the structural formulae of the predominant organic species when 15 cm^3 of NaOH is added.

(iii) Sketch the shape of the pH curve you would expect to obtain from **(ii)** and briefly describe how you have calculated the various key points on the curve.

[8]

(b) **A**, $C_{10}H_{14}O_2NI$, dissolves in aqueous HNO_3. **A** is formed, along with a brown precipitate, when **B** reacts with potassium manganate(VII) at 0°C. On addition of ethanolic silver nitrate to **A**, a yellow precipitate is formed. When aqueous bromine is added to **A**, the orange-red solution decolourises and a white precipitate, **C**, $C_{10}H_{11}O_2NIBr_3$, is formed. 0.125 mol of **A** produces 2800 cm^3 of gas at s.t.p. when sodium metal is added. **D**, $C_{10}H_{13}O_2NICl$, is produced when potassium dichromate and hot dilute hydrochloric acid is added to **A**. **D** reacts with 2,4-DNPH but not with Tollen's reagent. **E** and a yellow precipitate are formed when warm aqueous iodine and aqueous sodium hydroxide are added to both **A** and **D** separately.

Deduce the structures of **A** to **E**, and explain the reactions described.

[12]

[Total: 20]

~~~ END OF PAPER ~~~