ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/03

Paper 3 Free Response

24 August 2018

Candidates answer on separate paper.

2 hours

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your index number and name, form class and tutorial class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question**.**

Start each question on a new sheet of writing paper.

A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely behind a cover sheet.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **15** printed pages and **1** blank page.

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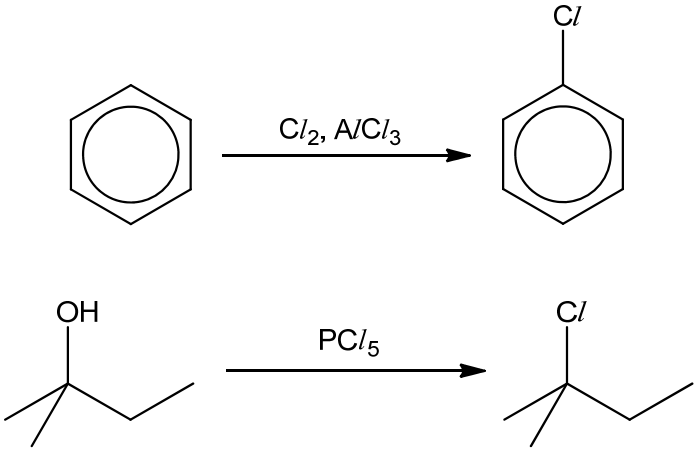
Section A

Answer **all** questions in this section.

1 (a) (i) Due to reactivity of $AlCl_3$ and PCl_5 in water, the following reactions are carried out under anhydrous conditions.



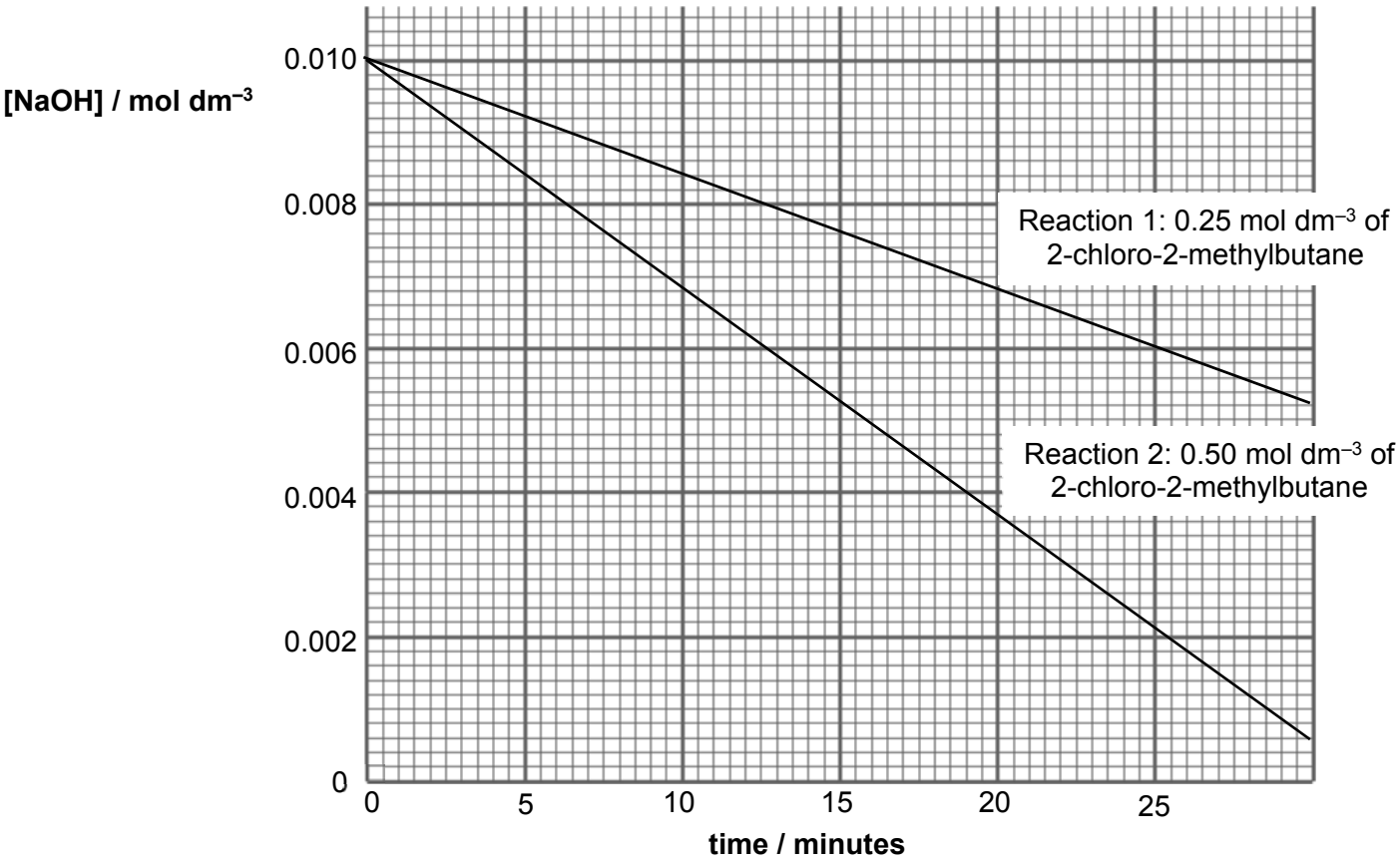
Write equations showing the reactions of aluminium chloride and phosphorus pentachloride in water. State the pH of resulting solutions. [3]

(ii) Chlorobenzene and 2-chloro-2-methylbutane are separately boiled with aqueous sodium hydroxide and acidified with nitric acid before aqueous silver nitrate is added.

State and explain the difference in observations. Write equations for the reactions that occur. [3]

(b) To study the kinetics of the reaction between 2-chloro-2-methylbutane and sodium hydroxide in alcoholic medium, two experiments with different initial concentrations of 2-chloro-2-methylbutane were carried out at constant temperature.

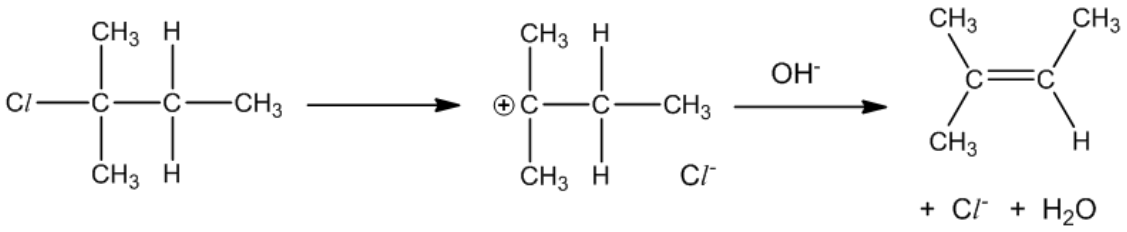
A [NaOH]–time graph was plotted using the results obtained from the experiments.



(i) Deduce the orders of reaction with respect to 2-chloro-2-methylbutane and NaOH. [2]

(ii) Hence state the rate equation of this reaction. [1]

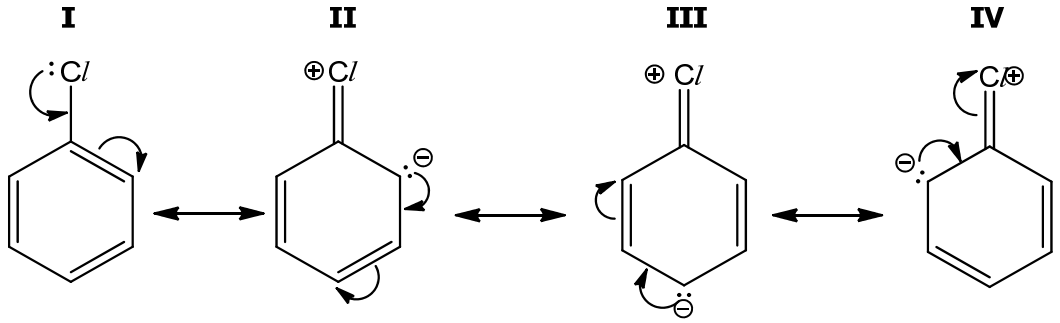
(iii) The proposed mechanism of 2-chloro-2-methylbutane with alcoholic sodium hydroxide is given below.



Using your answer in **(b)(ii)** and the above steps, suggest the complete mechanism by

- drawing curly arrows,
- showing lone pair(s) of electrons and
- identifying the slow step. [3]

(c) Chlorobenzene has the following resonance structures which represent the alternative distribution of electrons on the molecule. Using these structures, suggest why the electrophilic substitution of chlorobenzene is 2,4-directing. [2]



(d) When butane is reacted with chlorine gas under strong UV rays, a mixture of compounds is formed.

(i) Assuming that primary and secondary hydrogen atoms have similar reactivity, draw the structures of alkyl radicals formed during the reaction and state their likely ratio of formation. [2]

(ii) During the termination stage, the alkyl radicals in **(d)(i)** form three structures with the molecular formula C_8H_{18}. Suggest their structures and the ratio of these structures. [4]

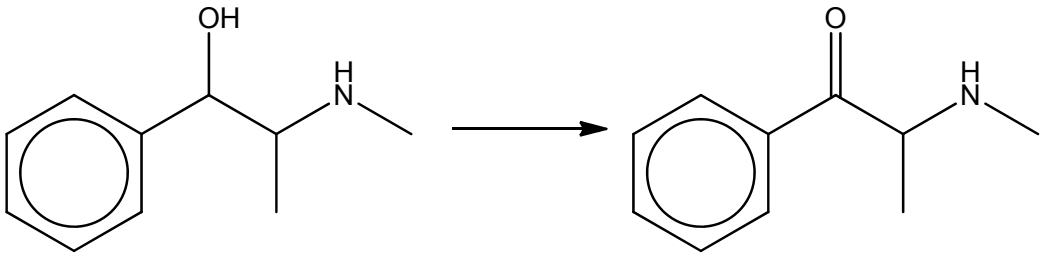
(e) Chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer.

(i) Suggest one reason why CFCs were originally used for this purpose. [1]

(ii) Suggest one potential hazard of using alkanes instead of CFCs. [1]

[Total: 22]

2 Recreational drugs like methamphetamine and methcathinone can be synthesised easily from pseudoephedrine, a common nasal decongestant found in cough medicine.

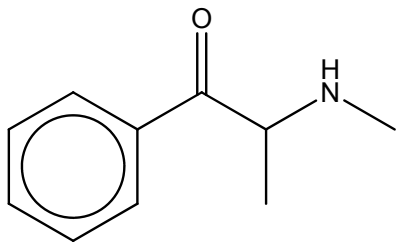
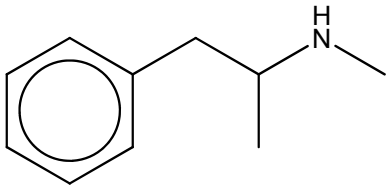


pseudophedrine methcathinone

HI, followed by neutralisation

X

(a) (i) The structures of methcathinone and methamphetamine, with pK_b values at 298 K, are shown in the table below.

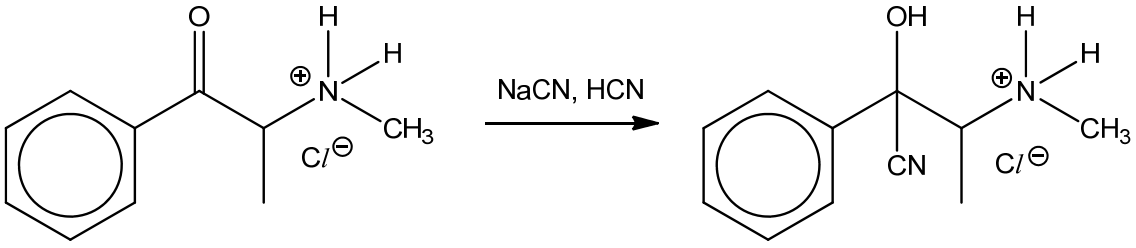
compound	pK_b
 methcathinone	5.98
 methamphetamine	3.79

Explain why methcathinone has a higher pK_b value than methamphetamine. [2]

(ii) Suggest the structure of intermediate **X**. [1]

(b) Commercially, methcathinone is sold in its salt form as solid methcathinone hydrochloride.

Methcathinone hydrochloride undergoes the following reaction to form a possible analogue, **Y**, with hallucinogenic properties.



methcathinone hydrochloride

Y

Name the type of reaction and describe its mechanism, showing curly arrows, charges and any relevant lone pairs. [3]

(c) Hydrogen iodide, HI, is listed as a controlled substance as it is often used illegally to produce popular recreational drugs like methamphetamine.

The commercial preparation of hydrogen iodide, HI, involves the reaction of iodine I_2, with hydrazine, N_2H_4, which has ammonia-like properties.

$$N_2H_4(l) + 2I_2(aq) \longrightarrow N_2(g) + 4HI(g)$$

(i) During the preparation, gaseous hydrogen iodide produced must be removed immediately. Suggest a reason why this is done. [1]

(ii) Hydrogen halides can be unstable to heat. Write an equation for the reaction undergone on heating hydrogen iodide, HI. [1]

(iii) Using your knowledge of the chemistry of Group 17, deduce with reason how the thermal stability of hydrogen astatide, HAt, differ from that of hydrogen iodide, HI. [2]

(d) A 40.0 g sample of solid ammonium carbonate is placed in a closed evacuated 3.0 dm^3 flask and heated to 400°C. It decomposes to produce ammonia, water and carbon dioxide according to the equation :

$$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$$

The value of the equilibrium constant, K_p, for the reaction is 0.295 at 400 °C.

In a gaseous reaction, the reactants and products can be expressed in partial pressures in atmospheres (atm). The relationship between K_c and K_p is given :

$$K_p = K_c(RT)^4$$

Assume that the gases are under ideal conditions.

(i) Write down the expression of K_p for the above equilibrium system. Hence show that $K_p = K_c(RT)^4$. [2]

(ii) Calculate the partial pressure of $NH_3(g)$ at equilibrium at 400°C. [2]

(iii) Calculate the total pressure inside the flask at equilibrium. [1]

(iv) Calculate the mass of solid ammonium carbonate in the flask at equilibrium. [3]

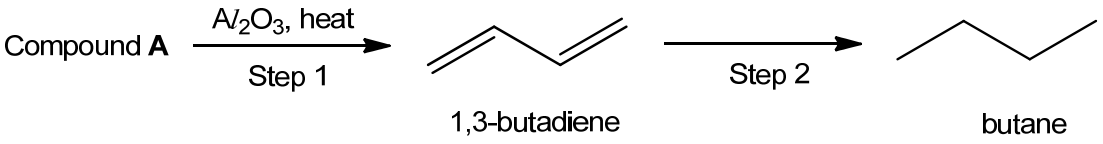
[Total: 18]

3 In chemistry, a conjugated system refers to a system of overlapping p orbitals which allows the delocalisation of π electrons in a molecule. It is represented by having alternating single and multiple bonds in the molecule.

1,3-butadiene is the simplest conjugated diene which has double bonds that is separated by a single bond. It is a colourless gas which is industrially important as a monomer in the production of synthetic rubber.

In general, conjugated dienes have similar chemical properties as the usual alkenes. However, they are associated with extra stability as the delocalisation of π electrons lowers the overall energy of the molecule.

(a) The 2-step synthesis of butane shown in the figure below makes use of 1,3-butadiene as the intermediate.



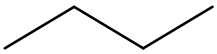
(i) Given that compound **A** does not rotate plane polarised light, suggest a structure for it and state the type of reaction that takes place in step 1. [2]

(ii) Write an equation to show the standard enthalpy change of hydrogenation, $\Delta H^{\ominus}_{\text{hydrogenation}}$ of 1,3-butadiene in step 2. [1]

(iii) A student calculated the expected $\Delta H^{\ominus}_{\text{hydrogenation}}$ of 1,3-butadiene in step 2 to be –252 kJ mol^{-1}. However, 1,3-butadiene is 16 kJ mol^{-1} more stable than expected.

Calculate the actual $\Delta H^{\ominus}_{\text{hydrogenation}}$ of 1,3-butadiene. [1]

(iv) Hence, using the value calculated in **(iii)** and the information given below, construct a fully labelled energy level diagram to determine the standard enthalpy change of combustion, $\Delta H^{\ominus}_{c}$ of 1,3-butadiene. [3]

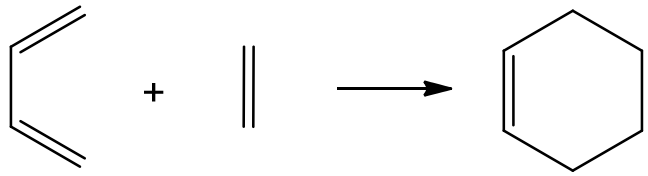
substance	$\Delta H^{\ominus}_{c}$ / kJ mol^{-1}
	**–**2877
H_2	**–**286

(v) According to valence bond theory, the stability of conjugated diene could also be explained by orbital hybridisation.

By making reference to the C–C single bond formed in 1,3-butadiene and butane, and the hybridisation of the orbitals in the two molecules, explain the extra stability of 1,3-butadiene. [2]

(b) Conjugate dienes can undergo addition with alkenes in a process called Diels-Alder reaction to form cyclic products. It is an important synthetic method which is widely used in organic chemistry to form unsaturated cyclic products.

An example of the Diels-Alder reaction is shown below where 1,3-butadiene reacts with ethene to form cyclohexene.:



In the process, the two reactants react in a single step through a cyclic redistribution of bonding electrons and two new carbon-carbon bonds are formed at the same time.

(i) By using full-headed curly arrows, suggest the mechanism that takes place in the above reaction to form cyclohexene. [1]

(ii) Compound **B** has the molecular formula of $C_8H_{12}O$ and it can be synthesised when 1,3-butadiene reacts with compound **C**, C_4H_6O, in the **Diels-Alder** reaction. It is known that compound **C** is able to react with 2 moles of hydrogen gas in the presence of Pt and produce a yellow precipitate with alkaline aqueous I_2. Compound **C** also gives a positive test with 2,4-dinitrophenylhydrazine and negative test with Tollens' reagent.

Suggest structures for compounds **B** and **C**, and explain the reactions described. [5]

(c) Compounds of aluminium such as aluminium oxide, Al_2O_3 and aluminium chloride, $AlCl_3$ are often used in organic reactions as catalysts.

(i) Aluminium oxide has unique chemical properties as it is able to react with both acid and base.

Write balanced chemical equations for the reactions between aluminium oxide and the following respectively.

- HBr
- KOH [2]

(ii) Account for the acid-base behaviour of aluminium oxide by making reference to its structure and bonding and state the nature of the oxide. [3]

[Total: 20]

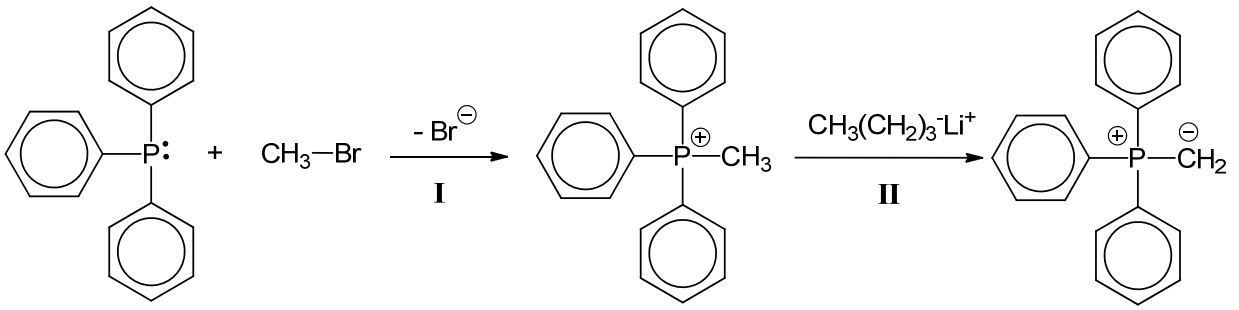
TURN OVER FOR SECTION B

Section B

Answer **one** question from this section.

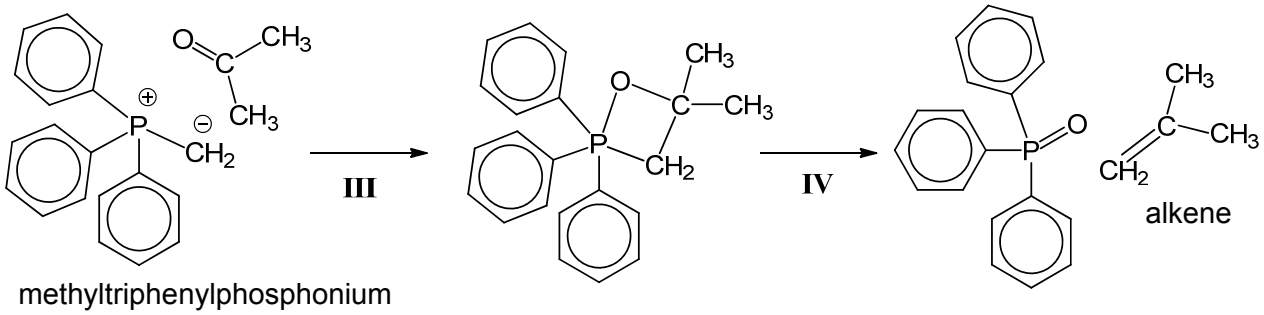
4 (a) The Wittig reaction converts carbonyl compounds into alkenes by reacting aldehydes or ketones with alkyltriphenylphosphonium, such as methyltriphenylphosphonium.

Stage 1 – Preparation of methyltriphenylphosphonium



triphenylphosphine methyltriphenylphosphonium

Stage 2 – Formation of alkene



methyltriphenylphosphonium

Different alkenes can be formed by using different carbonyl compounds and R-groups on the alkyltriphenylphosphonium.

(i) The melting points of four compounds, including triphenylphosphine and methyltriphenylphosphonium bromide are given below.

compound	formula	melting point / °C
triphenylphosphine	$P(C_6H_5)_3$	80
water	H_2O	0
methyltriphenylphosphonium bromide	$(C_6H_5)_3P{=}CH_2^+Br^-$	232
sodium chloride	NaC*l*	801

With reference to their structure and bonding, suggest why the melting point of

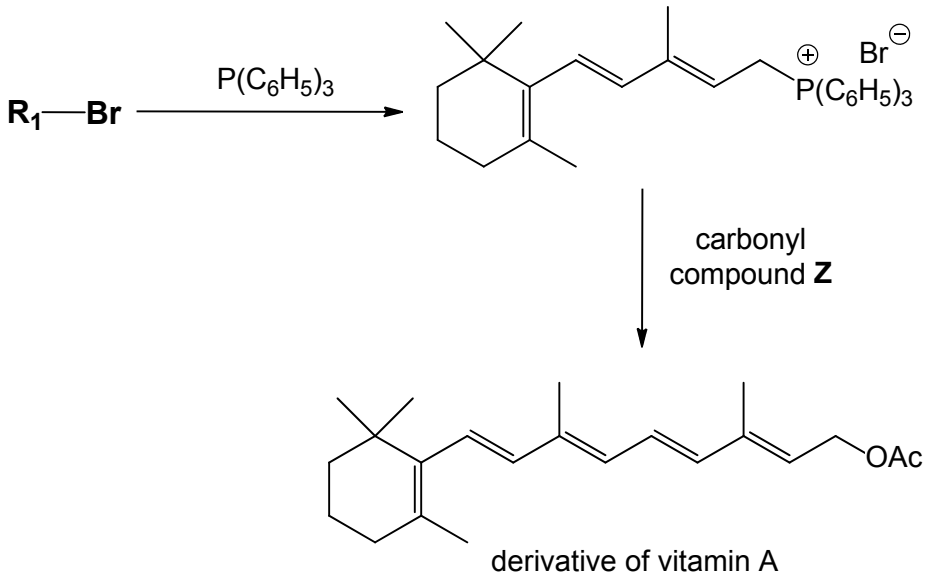
1. triphenylphosphine is higher than water; and
2. methyltriphenylphosphonium bromide is lower than sodium chloride

[4]

(ii) State the type of reaction in step **I**. [1]

(iii) State the role of $CH_3(CH_2)_3^-Li^+$ in step **II**. [1]

(iv) The advantage of Wittig reaction is the predictability of its alkene product. It is used in industrial processes such as the formation on vitamin A.



derivative of vitamin A

Suggest the structures of alkylbromide **R_1–Br** and carbonyl compound **Z** for forming the derivative of vitamin A. You may assume that the OAc group remains unchanged during the reaction. [2]

(b) Triphenylphosphine, $P(C_6H_5)_3$, is prepared by reacting phosphorus trichloride, chlorobenzene and sodium. Sodium chloride is precipitated during the reaction due to its insolubility in the organic mixture.

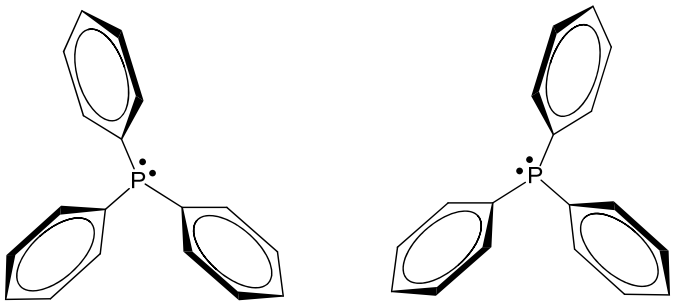
(i) Write the balanced equation for the preparation of triphenylphosphine. [1]

(ii) Triphenylphosphine does not form in the above reaction when water is present. Given that phosphorus trichloride reacts with water according to this equation

$$PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$$

describe, with the aid of equation(s), any other reactions that will take place when water is used as a solvent. Hence or otherwise, suggest the colour of universal indicator in the resulting mixture. [3]

(iii) It has been suggested that triphenylphosphine is a chiral compound. Two structures of triphenylphosphine are shown below.



State the relationship of the two structures and suggest why triphenylphosphine is a chiral compound. [2]

(c) (i) The aqueous solutions of two acids were prepared and their pH measured.

acid	concentration / mol dm^{-3}	pH
M	0.75	1.11
N	0.25	0.60

Given that **M** and **N** are monobasic acids, show calculations to explain whether each acid is a strong or weak acid. [3]

(ii) It is known that the electronegativity of the central atom in the acid affects its acidity.

With reference to the increasing trend of electronegativity across the period, suggest the correct identities of the acids **M** and **N**, given that they could be H_3PO_2 or $HClO_3$. [3]

[Total: 20]

5 *Use of the Data Booklet is relevant to this question*.

Osmium is a bluish-white metal found as a trace element in alloys, mostly in platinum ores. Not surprisingly, osmium was discovered in 1803 by Smithson Tennant when he noticed a residue remaining after dissolving crude platinum in aqua regia – a mixture of concentrated nitric acid and concentrated hydrochloric acid.

Platinum reacts with concentrated nitric acid to produce aqueous platinum(IV) cations, nitrogen dioxide and water. The platinum(IV) cations are then complexed with chloride *ligands* to produce hexachloroplatinate(IV) anions which are recovered through the reaction with ammonium chloride to produce yellow crystals.

(a) **(i)** Define the term *ligand*. [1]

(ii) Write a balanced ionic equation to represent the reaction of platinum with concentrated nitric acid. [1]

(iii) Suggest the identity of the yellow crystals obtained. [1]

(iv) The solubility of the yellow crystals in water at room temperature is 5.0 g dm^{-3} but decreases to 0.028 g dm^{-3} in 1 mol dm^{-3} ammonium chloride at the same temperature.

Write an equation to represent the dissolution of the yellow crystals in **(a)(iii)** and use the equation to account for the decreased solubility in 1 mol dm^{-3} ammonium chloride. [2]

(v) Explain why hexachloroplatinate(IV) is coloured. [3]

When powdered osmium is exposed to air, it forms the toxic compound osmium tetroxide, OsO_4 with a strong odour like that of chlorine.

$$Os + 2O_2 \longrightarrow OsO_4$$

(b) **(i)** Use the standard electrode potential given and choose another appropriate equation from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for the reaction between osmium and air. [1]

$$OsO_4 + 8H^+ + 8e^- \rightleftharpoons Os + 4H_2O \qquad E^{\ominus} = +0.84\ V$$

(ii) Hence calculate $\Delta G^{\ominus}_{cell}$ for the reaction in **(b)(i)**, leaving your answer in kJ mol^{-1}. [1]

(iii) Suggest, with reasoning, the sign for the standard enthalpy change of reaction for the reaction between osmium and air, making reference to the terms in the Gibbs free energy equation and your answer in **(b)(ii)**. [2]

The figure below shows part of a label on a bottle of osmium tetroxide.

Osmium Tetroxide, OsO_4

Molar mass: 254.2 g mol^{-1}
Density: 4.9 g cm^{-3}
Vapour pressure: 933 Pa
Max. permissible exposure limit: 200 µg m^{-3}

Net weight: 1000 g
Volume of container: 250 cm^3

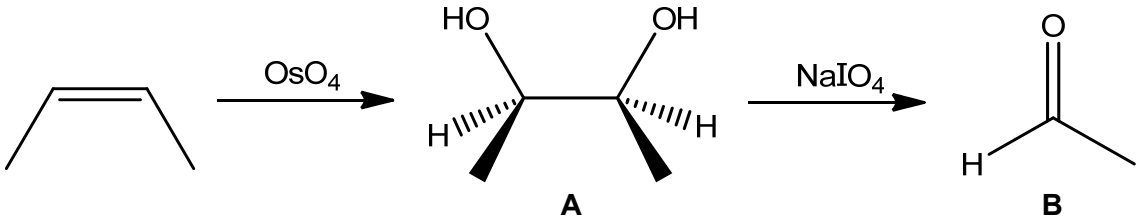
Note:
Vapour pressure – the pressure of vapour in equilibrium with its solid/liquid form.
1 µg = 1 x 10^{-6} g

(c) **(i)** Use the information above to calculate the amount of OsO_4 in the vapour phase within an unopened container of OsO_4 at room temperature. Assume ideal gas behaviour. [2]

(ii) Hence determine the concentration of OsO_4, in µg m^{-3}, in the air of a 100 m^3 laboratory where a new container is opened. Assume that the air has evenly mixed. [2]

(iii) Discuss whether it is safe for researchers to open the container in this laboratory without a proper fume cupboard, considering your answer in **(c)(ii)** and the approach used to calculate it. [1]

Osmium tetroxide, OsO_4 can oxidise alkenes to give diols. $NaIO_4$ will react further with the diol to produce carbonyl compounds.



A **B**

(d) Suggest a simple chemical test to distinguish between compounds **A** and **B** and write a balanced equation for the positive test. [3]

[Total: 20]