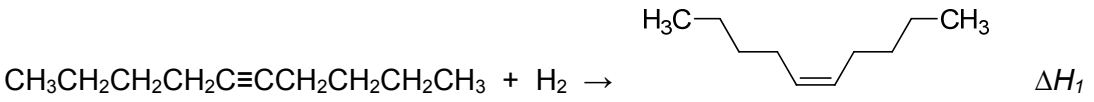
Answer **all** the questions.

For Examiner's Use

1 Planning (P)

The selective partial hydrogenation of alkynes, which contain C≡C triple bonds, to cis-alkenes represents an importance class of chemical transformations that have found extensive uses such as in bioactive molecules, in lubricants as well as in the syntheses of organic intermediates.

The partial hydrogenation of 5-decyne forms cis-dec-5-ene and the reaction is as shown :



The enthalpy change for hydrogenation of 5-decyne, ΔH_1 cannot be measured directly in the laboratory. You are required to plan an experiment to find the enthalpy change for hydrogenation of 5-decyne, ΔH_1 via Hess's Law.

The enthalpy change for the combustion of hydrogen is -286 kJ mol^{-1}. 5-decyne and cis-dec-5-ene are both liquids at standard conditions.

(a) Based on the given information and the equation above, state **two** enthalpy changes that are necessary to calculate ΔH_1.

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……[1]

(b) Using the information given above and your answer in **(a)**, you are required to write a plan to determine a value for the enthalpy change for hydrogenation of 5-decyne, ΔH_1.

You may assume that you are provided with

- liquid 5-decyne
- liquid cis-dec-5-ene
- copper calorimeter
- two spirit lamps with a 5 cm-wick each
- deionised water
- a lighter
- thermometer
- apparatus normally found in a school or college laboratory

Your plan should contain the following:

- a diagram of the experimental set-up
- appropriate quantities of chemicals and solutions
- all essential experimental details

Diagram of the experimental set-up

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Procedure:

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……[7]

(c) List the measurements that have to be tabulated and recorded to calculate the value of enthalpy change for hydrogenation of 5-decyne, ΔH_1. In your answer, you need to show how these measurements are used to obtain the value of ΔH_1.

You may assume the specific heat capacity of water is 4.18 J g^{-1} K^{-1} and density of water is 1 g cm^{-3}.

Tables used to tabulate and record experimental data:

Treatment of results:

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[4]

[Total: 12]

For Examiner's Use

2 Eighty-five percent of all pharmaceutical agents and vitamins involve chlorine chemistry; many drugs require chlorine, fluorine, or bromine to be effective.

Data about the halides are given below.

Halide (X)	pK_a (HX)	Percentage of HX decomposed at 2000°C	Boiling point of HX / °C	Dipole moment of C–X / D	K_a (HOX) at 298K
F	+3	6×10^{-5}	19.5	1.82	
C*l*	–7	4×10^{-1}	–84.2	1.08	2.9×10^{-8}
Br	–9	4	–67.1	0.82	2.4×10^{-9}
I	–10	30	–35.1	0.44	

(a) Hydrogen halides decompose at high temperature according to the equation:

$$2HX(g) \rightarrow H_2(g) + X_2(g)$$

Use relevant data from the *Data Booklet*, explain the trend indicated by percentage decomposition of HX.

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…… [3]

For Examiner's Use

(b) The boiling point of HF is higher than the rest of the hydrogen halides despite it being the smallest molecule. By means of a diagram, indicate the interaction between two molecules of HF that leads to this significant difference.

[2]

(c) When dissolved in water, the hydrogen halides show different pK_a values. Write balanced equations to represent the extent of ionisation of HF and HI in water.

HF : ……

HI : ……

[2]

(d) **(i)** Draw a diagram to illustrate the shape of oxoacid, HOC*l*, indicating clearly the bond angle.

[2]

(ii) Using the information from the table, state which of the two acids, HOC*l* or HOBr is stronger?

…… [1]

(iii) Hypoiodous acid has the formula HOI. Predict and explain whether HOI is a stronger or weaker acid than the acid you identified in **(d)(ii)**.

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……[2]

For Examiner's Use

(iv) Some solid NaOC*l* solution is dissolved in a solution of HOC*l* at 298 K. The pH of this mixture is determined to be 6.48. Calculate the ratio of OCl^- to HOC*l* in this mixture.

[2]

(e) The halides can react with concentrated sulfuric acid.

(i) When concentrated sulfuric acid was warmed with sodium chloride, white fumes of hydrogen chloride was evolved. Write a balanced equation for the reaction.

……[1]

(ii) The method described in **e(i)** cannot be used to prepare hydrogen iodide. Describe what you would observe when sodium iodide is heated with concentrated sulfuric acid. Explain the chemistry behind it, and give any relevant equations.

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…… [5]

[Total: 20]

For Examiner's Use

3 (a) A*l*C*l*$_3$ is a compound of interest to scientists due to its industrial applications. For example, A*l*C*l*$_3$ can react with molten aluminium to form A*l*C*l*(g). This is a useful procedure as the A*l*C*l* formed can be used to recover useful metalloids from their compounds.

Typically, the reaction has to be carried out in the presence of argon instead of air.

(i) The reaction has to be carried out in an atmosphere of argon. Suggest a reason for the need of argon.

……..[1]

Consider the reaction between A*l*C*l*$_3$(g) and molten aluminium that was carried out at 1573 K :

$$2Al(l) + AlCl_3(g) \rightleftharpoons 3\ AlCl(g) \qquad \text{reaction } \mathbf{1}$$

In the reaction vessel, 0.200 mol of A*l*C*l*$_3$(g) was reacted with 0.400 mol of molten A*l*. When the reaction system achieved equilibrium with a total pressure of 1.50 atm, it was determined that 0.200 mol of molten A*l* remained in the vessel.

(ii) Write an expression for the equilibrium constant, K_p for reaction **1** and hence calculate its value at 1573 K.

[3]

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The same reaction vessel was heated to 1700 K rapidly in a way such that no reaction took place during the short interval of heating. The reaction system was allowed to re-establish equilibrium. It was found that the partial pressure of $AlCl_3(g)$ was 0.390 atm when the equilibrium was re-established.

(iii) Using the information from **a(ii)**, determine the partial pressures of $AlCl_3(g)$ and $AlCl(g)$ at the instant when the reaction was heated to 1700 K, before the equilibrium was re-established. You can assume that the gases behave ideally and the volume of vessel is unchanged.

[2]

(iv) Using the calculated values from **a(iii)**, calculate K_p of the reaction at 1700 K. Hence, explain whether reaction **1** is endothermic or exothermic.

[4]

For Examiner's Use

(v) The rate equation for reaction between A*l* and A*lCl*$_3$ is shown below.

$$\text{rate} = k[AlCl_3][Al]$$

Suggest which of the two mechanisms shown is a possible mechanism for the reaction.

Mechanism **1**:

$Al + AlCl_3 \rightarrow AlCl_2 + AlCl$ (slow)

$Al + AlCl_2 \rightarrow 2\ AlCl$ (fast)

Mechanism **2**:

$AlCl_3 \rightarrow AlCl + Cl_2$ (slow)

$2\ Al + Cl_2 \rightarrow 2\ AlCl$ (fast)

……..

……..[1]

(b) Anhydrous A*lCl*$_3$ is often used as a catalyst in the Friedel-Crafts alkylation of benzene.

$$C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH_2CH_3 + HCl$$ reaction **2**

(i) Explain why A*lCl*$_3$ can act as a catalyst in Friedel-Crafts alkylation.

……..

……. [1]

(ii) With the aid of an equation, explain the need to have anhydrous condition when A*lCl*$_3$ is used for reaction **2**.

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……..[2]

(iii) Use information from the *Data Booklet,* calculate the enthalpy change of reaction for reaction **2**.

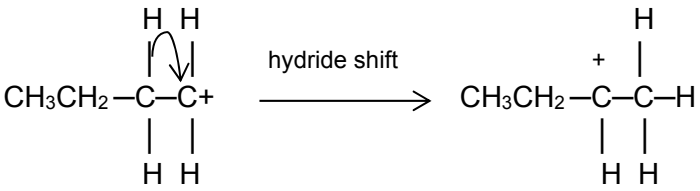
[2]

For Examiner's Use

(iv) Describe the mechanism for the formation of $C_6H_5CH_2CH_2CH_3$ in reaction **2**, showing clearly the movement of electrons and partial charges.

[3]

One key limitation of the alkylation reaction is that a mixture of products tends to form despite using only one type of halogenoalkane. For primary halogenoalkane, this is due to the occurrence of a process known as hydride shift which results in rearrangement of primary carbocation intermediates as shown :



(v) Explain why hydride shift occurs for primary halogenoalkane.

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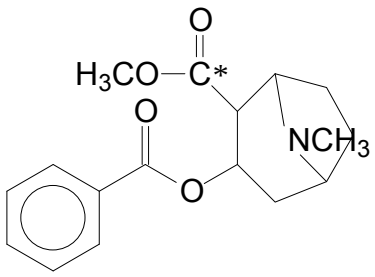
……[3]

[Total: 22]

For Examiner's Use

4 (a) Cocaine, $C_{17}H_{21}NO_4$, was first used as a local anaesthetic. It is also a powerful stimulant. Its structure is as shown:



cocaine

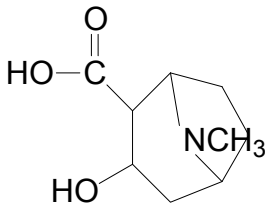
(i) State the functional groups, other than phenyl ring, present in cocaine.

……[1]

(ii) State the hybridisation of the carbon atom labelled with the asterisk (*).

……[1]

(b) Student **X** was asked to suggest a suitable synthetic route to prepare cocaine from methylbenzene and compound **A**.



compound **A**

Student **X** suggested the following steps:

Step **1**	Methylbenzene is oxidised with hot, acidified $KMnO_4$ to give benzoic acid.
Step **2**	Benzoic acid is converted into benzoyl chloride by reacting the resultant solution from step **1** with phosphorus pentachloride.
Step **3**	Benzoyl chloride is reacted with compound **A** at room temperature.
Step **4**	The resultant compound from step 3 is reacted with methanol in the presence of concentrated sulfuric acid at room conditions.

For Examiner's Use

Explain why steps **2** and **4** of the synthetic route will not work.

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……[2]

(c) Cocaine is sold in its protonated hydrochloride salt, known as cocaine hydrochloride. Suggest a possible reason for this.

……[1]

(d) Smoking cocaine is more stimulating than inhaling the salt as it is absorbed quickly by the capillaries in the lung tissues. The salt is converted back to cocaine before smoking.

(i) Suggest a suitable reagent to convert cocaine hydrochloride back into cocaine.

……[1]

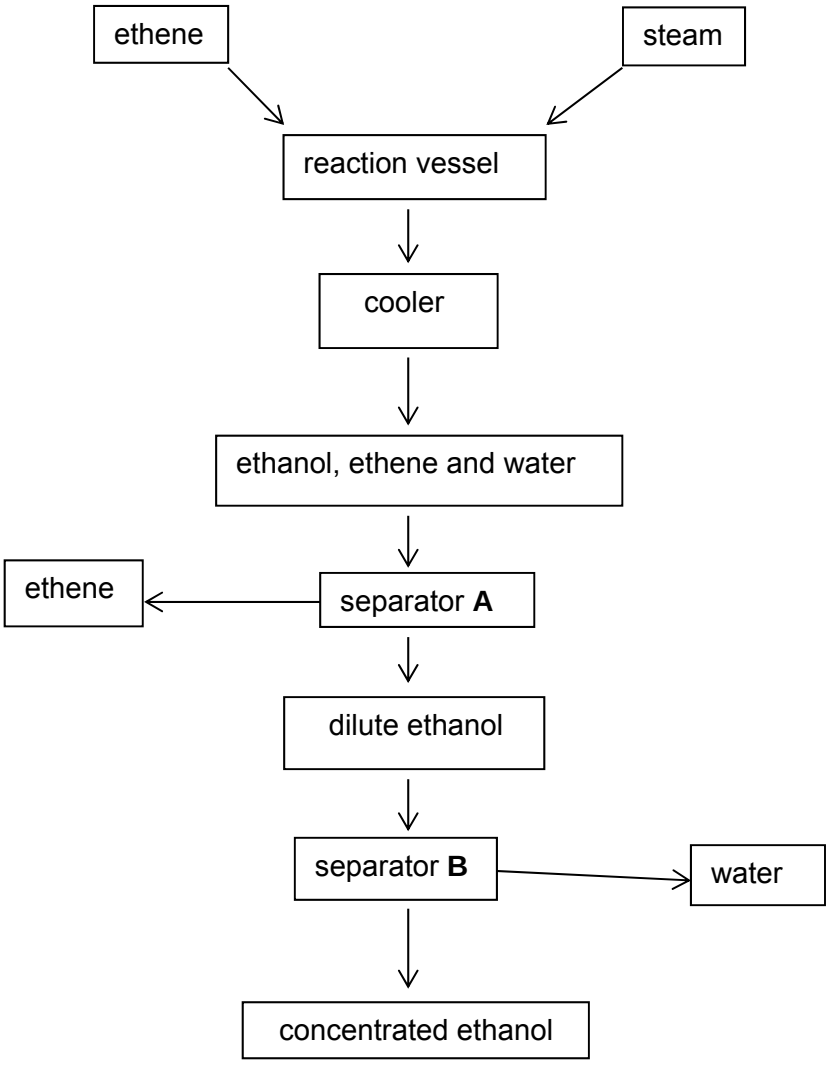
(ii) Suggest a suitable solvent to extract cocaine and separate it from its salt.

……[1]

[Total: 7]

For Examiner's Use

5 An industrial method for the production of ethanol, C_2H_5OH, is outlined in the following flow diagram.



(a) **(i)** Unreacted ethene is removed in separator **A**. Suggest how the separated ethene could be used to increase the efficiency of the overall process of the manufacture of ethanol.

……..……...

……[1]

(ii) Name the process that takes place in separator **B**.

……..……...[1]

(b) In the reaction vessel, ethanol is produced in an exothermic reaction.

(i) State the reagents and conditions for the industrial preparation of ethanol from ethene.

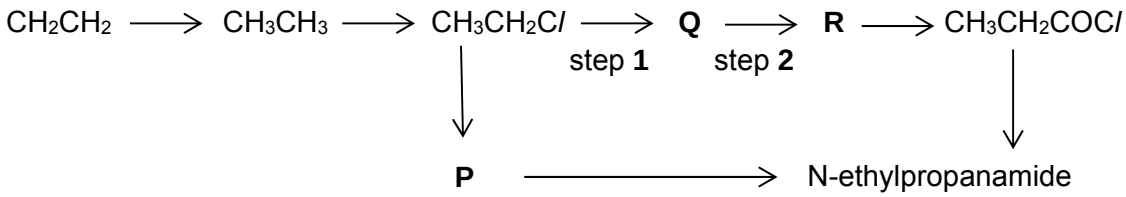
……..…… [2]

For Examiner's Use

(ii) If 1.64 kg of ethanol is produced from 10.0 kg of ethene, calculate the percentage yield of ethanol.

[2]

(c) Ethene is used to synthesise N-ethylpropanamide as shown in the following reaction scheme:



(i) Give the structural formulae of compounds **P**, **Q** and **R**.

Compound **P**: ……

Compound **Q**: ……

Compound **R**: ……

[3]

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

Step **1 :** ……..

Step **2 :** …….

[2]

[Total: 11]

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