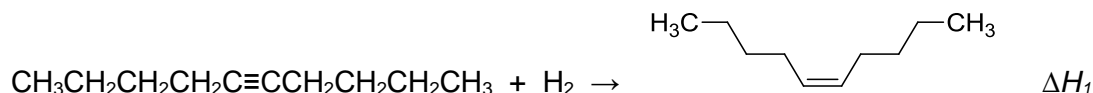


1 Planning (P)

The selective partial hydrogenation of alkynes, which contain $\text{C}\equiv\text{C}$ 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 .

Enthalpy change for combustion of 5-decyne and enthalpy change for combustion of cis-dec-5-ene.

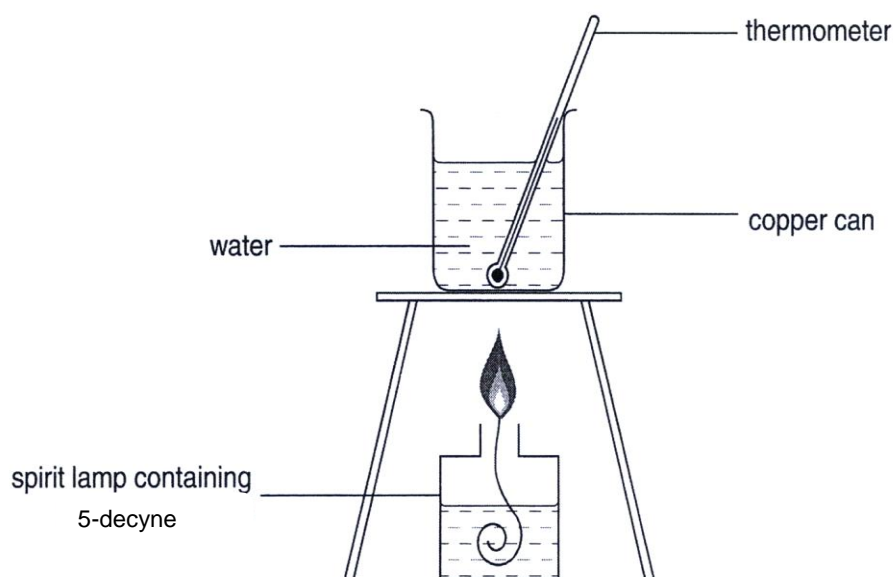
- (b) Using the information given above and your answer in (a), you are required to write a plan to determine a value for the enthalpy change for hydrogenation of 5-decyne, ΔH_1 .

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-upFor
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Use**Procedure:**

1. Using a 100 cm³ measuring cylinder, measure 100 cm³ of water into the copper calorimeter provided. Place the thermometer and record the initial temperature of water in the calorimeter.
2. Add 5-decyne to the spirit lamp until it is about half filled. Weigh using a weighing balance and record the total mass.
3. Place the spirit lamp under the calorimeter and light the wick of the lamp.
4. Stir the water with the thermometer until there is a rise of about 5°C. Extinguish the flame and record the final temperature of the water.
5. Reweigh the spirit lamp and content and record the final mass.
6. Repeat the whole procedure with cis-dec-5-ene.

- (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 $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ and density of water is 1 g cm^{-3} .

Tables used to tabulate and record experimental data:

Mass of spirit lamp and 5-decyne before combustion / g	A
Mass of spirit lamp and 5-decyne after combustion / g	B

Mass of spirit lamp and cis-dec-5-ene before combustion / g	C
Mass of spirit lamp and cis-dec-5-ene after combustion / g	D

Temperature of water in calorimeter (for experiment involving 5-decyne) before combustion / °C	E
Temperature of water in calorimeter (for experiment involving 5-decyne) after combustion / °C	F

Temperature of water in calorimeter (for experiment involving cis-dec-5-ene) before combustion / °C	G
Temperature of water in calorimeter (for experiment involving cis-dec-5-ene) after combustion / °C	H

Treatment of results:

Mass of 5-decyne combusted = (A–B) g

Amount of 5-decyne combusted, $n = (A-B)/\text{molar mass of 5-decyne} = X \text{ mol}$

Rise in temperature, $\Delta T = (F-E) \text{ K}$

Volume of water used = 100 cm^3

Density of water = 1 g cm^{-3}

Mass of water = 100 g

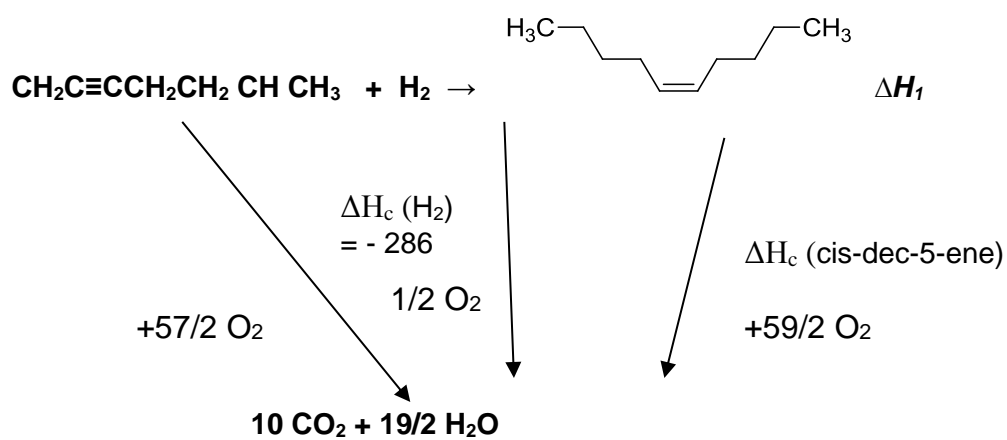
Assume no heat loss to surroundings and negligible heat capacity of copper calorimeter

Heat evolved from combustion, $q = \text{heat absorbed by water} = mc\Delta T$
 $= (100)(4.18)(\Delta T) \text{ J}$

Enthalpy change for combustion of 5-decyne = $-(q/n) \text{ kJ mol}^{-1}$

Repeat same steps for cis-dec-5-ene

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By ΔH_c (5-decyne)

Hess's law,

$$\Delta H_1 = \Delta H_c (\text{5-decyne}) + \Delta H_c (\text{H}_2) - \Delta H_c (\text{cis-dec-5-ene})$$

$$\Delta H_1 = \Delta H_c (\text{5-decyne}) - 286 - \Delta H_c (\text{cis-dec-5-ene})$$

[Total: 12]

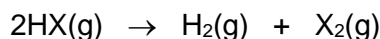
- 2 Eighty-five percent of all pharmaceutical agents and vitamins involve chlorine chemistry; many drugs require chlorine, fluorine, or bromine to be effective.

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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	
Cl	–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:



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

Bond energies of HX in kJ mol^{–1} in decreasing order:

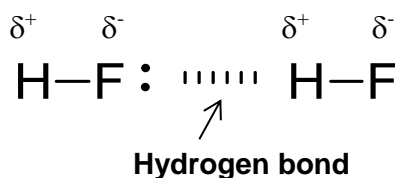
HF – 562 ; HCl – 431; HBr – 366; HI – 299

shows decreasing bond strength from HF to HI.

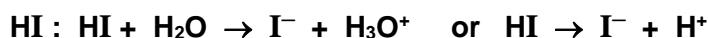
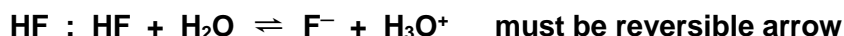
Covalent bond strength decreases from HF to HI is due to increasing atomic radius of F to I, leading to less effective overlap of orbitals from F to I with H.

Hence thermal stability decreases in the order HF, HCl, HBr, HI and percentage decomposition increases from HF to HI as indicated in the table.

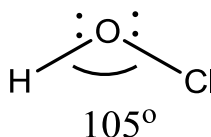
- (b) The boiling point of HF is higher than the rest of the hydrogen halides despite it being the smallest molecule. By means of a diagram, indicate the interaction between two molecules of HF that leads to this significant difference.



- (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.



- (d) (i) Draw a diagram to illustrate the shape of oxoacid, $HOCl$, indicating clearly the bond angle.



shape : bent

bond angle: 105°

- (ii) Using the information from the table, state which of the two acids, $HOCl$ or $HOBr$ is stronger?

$HOCl$ is a stronger acid as its K_a value is larger than that of $HOBr$.

- (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).

HOI is a weaker acid. The conjugate base OCI^- is more stable than OI^- . This is due to Cl being more electronegative hence more electron withdrawing and disperses the negative charge on oxygen to a larger extent, stabilising OCI^- . Hence $HOCl$ ionises more than HOI .

OR

HOI is a weaker acid. The conjugate base OI^- is less stable than OCI^- . This is due to I being less electronegative hence less electron withdrawing disperses the negative charge on oxygen to a smaller extent. Hence HOI ionises less than $HOCl$.

- (iv) Some solid $NaOCI$ solution is dissolved in a solution of $HOCl$ at 298 K. The pH of this mixture is determined to be 6.48. Calculate the ratio of OCI^- to $HOCl$ in this mixture.

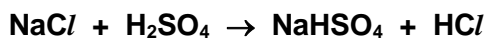
Using $pH = pK_a + \lg ([OCI^-] / [HOCl])$

$6.48 = -\lg (2.9 \times 10^{-8}) + \lg ([OCI^-] / [HOCl])$

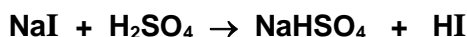
$[OCI^-] / [HOCl] = 0.0876$

(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.



- (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.



Black solid and violet fumes of I₂ seen and pungent (or rotten egg smell) H₂S evolved.

HI is a stronger reducing agent than HCl.

HI is oxidized to iodine, hence pure HI cannot be obtained.

[Total: 20]

- 3 (a) AlCl_3 is a compound of interest to scientists due to its industrial applications. For example, AlCl_3 can react with molten aluminium to form AlCl(g) . This is a useful procedure as the AlCl 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.

To prevent oxygen in air from reacting with molten aluminium.

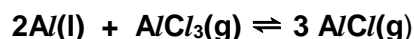
Consider the reaction between $\text{AlCl}_3(\text{g})$ and molten aluminium that was carried out at 1573 K :



In the reaction vessel, 0.200 mol of $\text{AlCl}_3(\text{g})$ was reacted with 0.400 mol of molten Al. When the reaction system achieved equilibrium with a total pressure of 1.50 atm, it was determined that 0.200 mol of molten Al 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.

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Use



$$n_i/\text{mol} \quad 0.400 \quad 0.200 \quad 0$$

$$n_e/\text{mol} \quad -0.200 \quad -0.100 \quad + 3/2 \times 0.200$$

$$n_e/\text{mol} \quad 0.200 \quad 0.100 \quad 0.300$$

Total number of moles of gases at equilibrium = $0.100 + 0.300 = 0.400 \text{ mol}$

$$K_p = (P_{\text{AlCl}})^3 / (P_{\text{AlCl}_3}) = (0.3/0.4 \times 1.5)^3 / (0.1/0.4 \times 1.5) = 3.80 \text{ atm}^2$$

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 $\text{AlCl}_3(\text{g})$ was 0.390 atm when the equilibrium was re-established.

- (iii) Using the information from a(ii), determine the partial pressures of $\text{AlCl}_3(\text{g})$ and $\text{AlCl}(\text{g})$ 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.

PV = nRT, since V, R and n are constant, $P \propto 1/T$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Thus,

$$\frac{P_{\text{AlCl}}}{1700} = \frac{\frac{0.300}{0.400} \times 1.5}{1573}$$

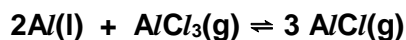
$$P_{\text{AlCl}} = 1.22 \text{ atm}$$

$$\frac{P_{\text{AlCl}_3}}{1700} = \frac{\frac{0.100}{0.400} \times 1.5}{1573}$$

$$P_{\text{AlCl}_3} = 0.405 \text{ atm}$$

- (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.

For
Examiner's
Use



$$P_i/\text{atm} \quad - \quad 0.405 \quad 1.22$$

$$P_f/\text{atm} \quad - \quad -0.015 \quad +0.045$$

$$P_e/\text{atm} \quad - \quad 0.390 \quad 1.265$$

$$K_p = (1.265)^3/0.390 = 5.19 \text{ atm}^2$$

K_p value is larger at 1700K compared to 1573K showing forward reaction is favoured. By Le Chatelier's Principle, reaction 1 equilibrium position has shifted to the right to remove excess heat.

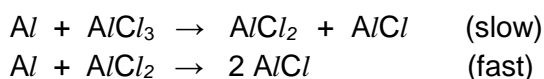
Hence reaction 1 is endothermic.

- (v) The rate equation for reaction between Al and AlCl_3 is shown below.

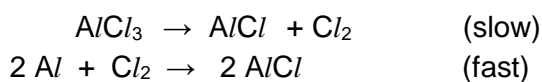
$$\text{rate} = k[\text{AlCl}_3][\text{Al}]$$

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

Mechanism 1:

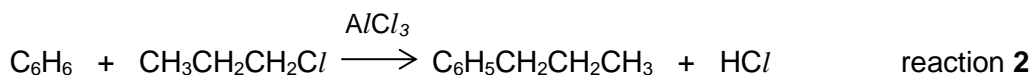


Mechanism 2:



Mechanism 1 is the possible mechanism. It tallies with the rate equation where one mole of Al reacts with 1 mole of AlCl_3 in the slow step.

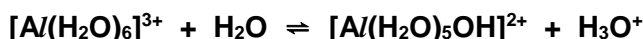
- (b) Anhydrous AlCl_3 is often used as a catalyst in the Friedel-Crafts alkylation of benzene.



- (i) Explain why AlCl_3 can act as a catalyst in Friedel-Crafts alkylation.

Al has empty 3p orbital (or empty p orbital) to accept a lone pair of electrons when generating electrophile.

- (ii) With the aid of an equation, explain the need to have anhydrous condition when AlCl_3 is used for reaction 2.



AlCl_3 will dissolve (or undergoes hydration) in water to form $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ which then undergoes hydrolysis in water.

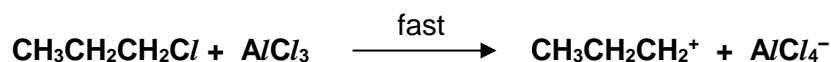
- (iii) Use information from the *Data Booklet*, calculate the enthalpy change of reaction for reaction 2.

$$\begin{aligned}\Delta H &= [\text{BE}(\text{C}-\text{H}) + \text{BE}(\text{C}-\text{Cl})] - [\text{BE}(\text{H}-\text{Cl}) + \text{BE}(\text{C}-\text{C})] \\ &= (410 + 340) - (431 + 350) = -31 \text{ kJ mol}^{-1}\end{aligned}$$

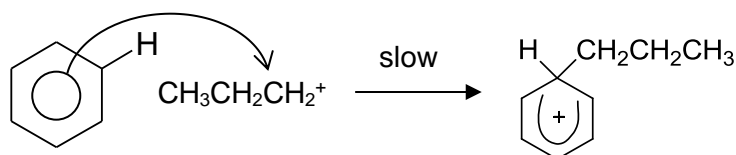
- (iv) Describe the mechanism for the formation of $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$ in reaction 2, showing clearly the movement of electrons and partial charges.

Electrophilic substitution

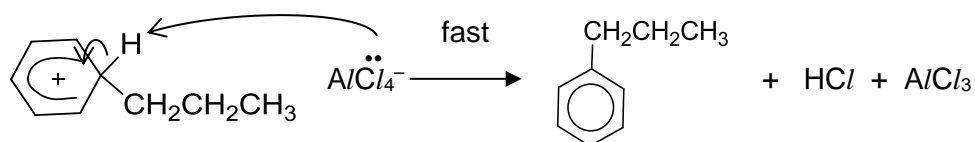
Step 1: Generation of strong electrophile



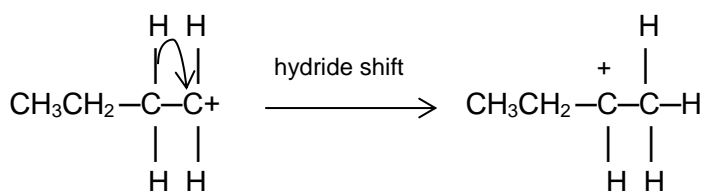
Step 2: Electrophilic attack on ring to form a carbocation intermediate



Step 3: Restoring the benzene ring and regeneration of catalyst



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 :

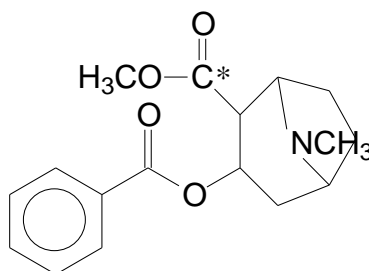


- (v) Explain why hydride shift occurs for primary halogenoalkane.

Hydride shift leads to a more stable secondary carbocation as there are more electron donating alkyl groups directly bonded to positively charged carbon. Hence the positive charge in the carbocation is dispersed.

[Total: 22]

- 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

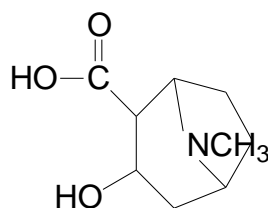
- (i) State the functional groups, other than phenyl ring, present in cocaine.

Ester and tertiary amine

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

sp^2

- (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.

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

In step 2, phosphorus pentachloride will be hydrolysed in the presence of aqueous solution. (or phosphorus pentachloride will react with water)

Heat is required for step 4.

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

It has a higher melting point and is more stable.

- (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.

NaOH(aq)

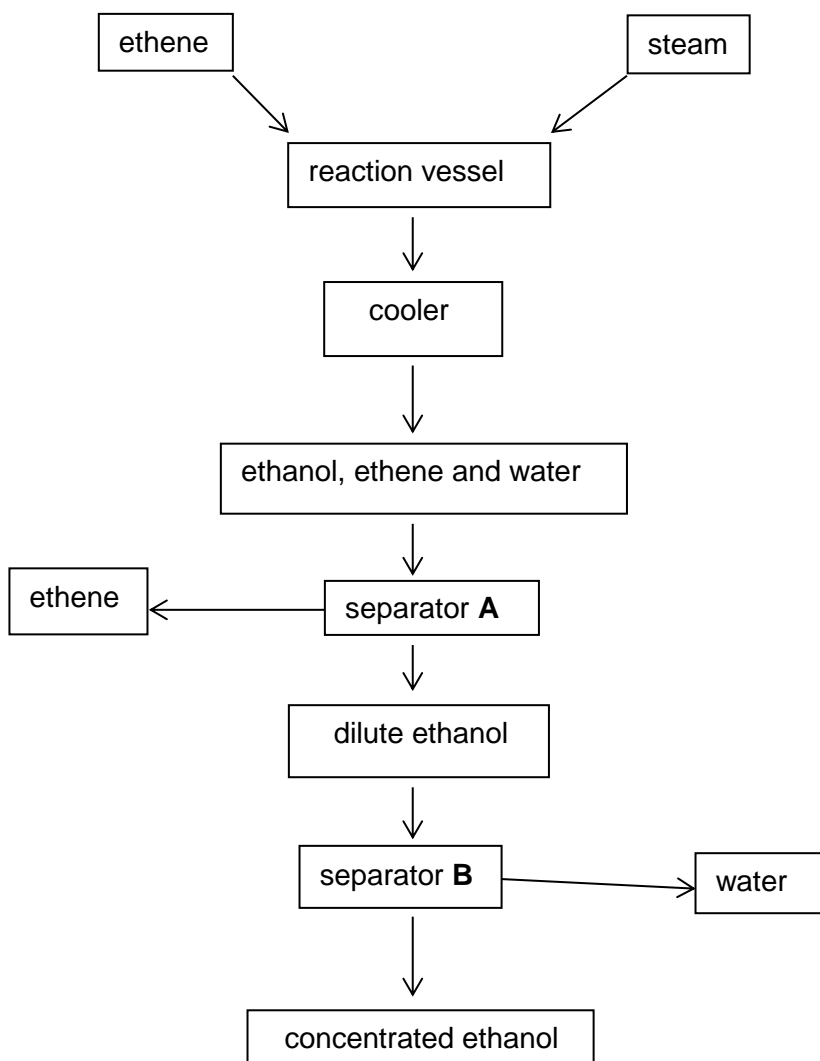
- (ii) Suggest a suitable solvent to extract cocaine and separate it from its salt.

Ether (or any other organic solvent less polar than water)

[Total: 7]

- 5 An industrial method for the production of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is outlined in the following flow diagram.

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- (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.

The separated ethene can be returned back to the reaction vessel to produce more ethanol.

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

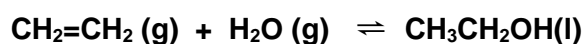
Fractional distillation (or distillation)

(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.

H₂O and concentrated H₃PO₄
300°C, 60 atm

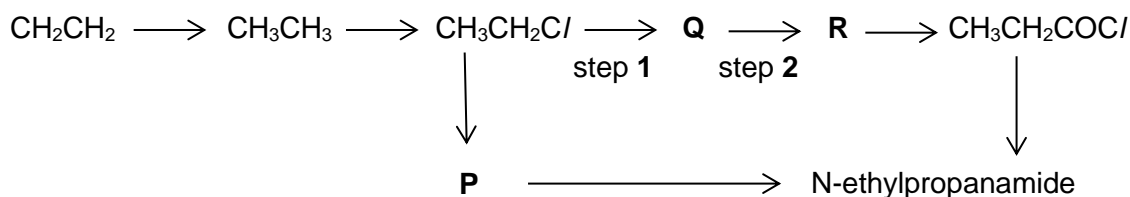
- (ii) If 1.64 kg of ethanol is produced from 10.0 kg of ethene, calculate the percentage yield of ethanol.



$$\begin{aligned} \text{Theoretical yield of} &= \frac{10 \times 1000}{12 \times 2 + 4} \times (12 \times 2 + 6 + 16) = 1.6429 \times 10^4 \text{ g} \\ &= 16.429 \text{ kg} \\ &= 16.4 \text{ kg} \end{aligned}$$

$$\text{Percentage yield} = \frac{1.64}{16.4} \times 100 = 10.0 \%$$

- (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**.

P : CH₃CH₂NH₂
Q : CH₃CH₂CN
R : CH₃CH₂COOH

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

step 1 : ethanolic KCN, heat
step 2 : dilute sulfuric acid, heat

[Total: 11]

End of Paper