Answer **all** the questions.

Planning (P)

1 Fermentation is a natural process. Man applied fermentation to make products such as wine, mead, cheese and beer long before the biochemical process was understood. In the 1850s and 1860s, Louis Pasteur became the first scientist to be known to have studied fermentation when he demonstrated fermentation was caused by living cells.

The fermentation of carbohydrates into alcohol can be represented as:

Sugar → alcohol + carbon dioxide

This reaction is catalyzed by yeast enzymes called zymases. A balanced chemical equation for this process using table sugar or sucrose is:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4CH_3CH_2OH + 4CO_2$$

This type of yeast fermentation can be studied through its CO_2 production. Using the information above, you are required to write a plan to determine the rate of CO_2 production in a 30–minute fermentation process.

You are provided with the following materials:

- 0.100 mol dm^{-3} sucrose solution
- yeast suspension
- apparatus normally found in a school laboratory

(a) Write a step-by-step plan on how you would carry out this experiment.

Your plan should include the following:

- show how the quantity of sucrose used is calculated
- all essential experimental details
- a diagram of your experimental set up
- a table with appropriate headings to show the data you would record when carrying out your experiment

Quantity of sucrose

$C_{12}H_{22}O_{11} \equiv 4CO_2$

Note volume of syringe = V_1 cm^3 then V_{CO2} collected should be less than V_1 cm^3

$$\frac{V_1}{24000} = \eta_{CO2} = a \text{ mol}$$

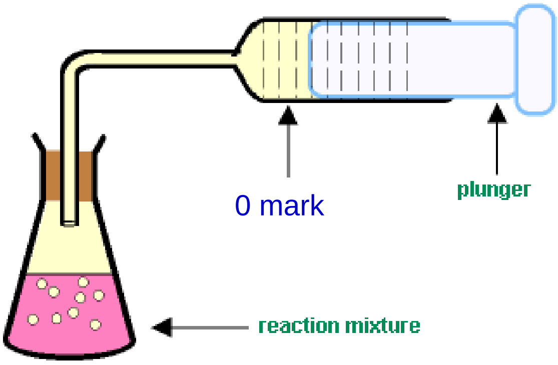
$$\Rightarrow \eta_{sucrose} = \tfrac{1}{4} a \text{ mol}$$

∴ volume of sucrose (aq) used must be less than $\dfrac{\frac{1}{4} a \times 1000}{0.1}$ cm^3

Let the volume of aq. sucrose used be V_2 cm^3.

Experimental details:

1. Place V_2 cm^3 of sucrose (aq) and equal volume of yeast suspension into a 250 cm^3 conical flask and stopper the flask.
2. Allow the mixture to incubate for 5 minutes. Note temperature of the surroundings.
3. Attach a calibrated syringe (Volume = V_1 cm^3) to the flask according to the diagram:



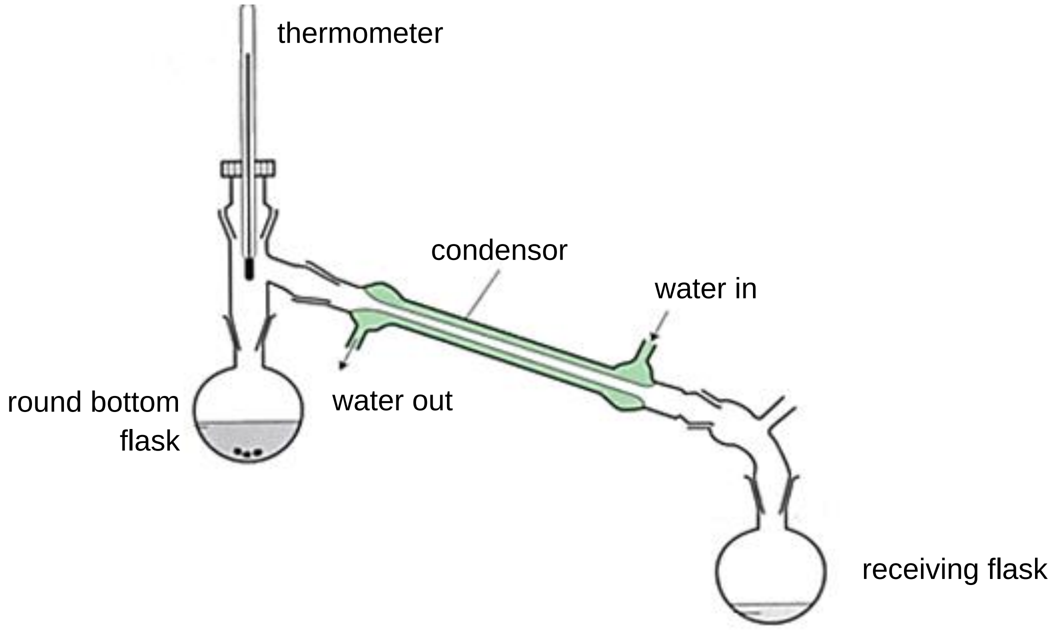
4. As soon as the piston reaches the 0 mark on the syringe, start the stop watch.
5. Take volume readings at 2 minute intervals for 30 minutes and record the data collected in the table below.

Time, t (min)	**Reading on syringe = Vol of CO_2 (cm^3)**

[6]

Alcohol produced by this fermentation, from the aqueous solution in which the fermentation takes place is concentrated or enriched by distillation.

A quantity of reaction mixture, after the fermentation process, is placed in the following set-up.



(b) What is meant by distillation?

A separation process for a mixture of liquid/oil. It relies on the difference in boiling point of components to be separated.

[1]

(c) Why is this simple distillation suitable for the fermentation mixture? Give **two** reasons.

1. The two boiling points are sufficiently far apart.
2. There are only two components in mash (water and CH_3CH_2OH)

[2]

(d) What is a disadvantage of this type of distiilation?

Purity of distillate is rarely 100%.

[1]

(e) Alcohol content in a distillate is often determined by measuring its density, which depends heavily on the percentage of alcohol. A measure density is compared with tabulated values of the density of known mixture of alcohol and water to determine its alcohol content; typically given as a volume percentage.

Most manufacturers of liquor report the alcohol content by its Proof. The Proof is double the volume percentage alcohol:

Proof = 2 x volume %

You are provided with the data on a distillate obtained from the mash/distillation process:

1. Mass of sample = 97.0 g
2. Volume of sample = 100.0 cm^3
3. Data of alcohol % volume versus density (g/cm^3).

Use these data below to determine the Proof of this sample.

% by Volume	**Density [g/cm^3]**
10.0	0.98569
15.0	0.98024
20.0	0.97518
25.0	0.97008
30.0	0.96452
35.0	0.95821
40.0	0.95097
45.0	0.94277
50.0	0.93350

- Use mass and volume of sample to determine its density

  $\rho = \frac{97}{100} = 0.97 \text{ g cm}^{-3}$

- From the table, alcohol % volume = 25.00 %

- Proof of distillate sample = 2 x 25.00
  = 50.0 %

[2]

[Total : 12]

2 "Hard water" is water that has high mineral content such as calcium ions. In domestic settings, hard water is often indicated by a lack of suds formation when soap is agitated in water.

A typical sample of 'hard water' has a concentration of calcium ions of 2.50×10^{-4} mol dm^{-3}.

(a) In order for a detergent to be used in 'hard water', sodium tripolyphosphate, $Na_5P_3O_{10}$, is added as a water softening agent.

The sodium tripolyphosphate 'softens' water by complexing with calcium ions. The complexation reaction is a follows:

$$Ca^{2+}(aq) + P_3O_{10}^{5-}(aq) \rightleftharpoons CaP_3O_{10}^{3-}(aq)$$

For this reaction with calcium ions, the equilibrium constant is 7.7×10^{8} mol^{-1} dm^{3}

(i) Write the K_c expression for the reaction.

$$K_c = \frac{[CaP_3O_{10}^{3-}(aq)]}{[Ca^{2+}(aq)][P_3O_{10}^{5-}(aq)]}$$

(ii) Hence, calculate the concentration of tripolyphosphate ion required to reduce the calcium ion concentration in a typical sample of 'hard water' to 1.0×10^{-6} mol dm^{-3}.

	$Ca^{2+}(aq)$	+ $P_3O_{10}^{5-}(aq)$	$\rightleftharpoons CaP_3O_{10}^{3-}(aq)$
Initial [ ]	2.50×10^{-4}	X	0
Change [ ]	-2.49×10^{-4}	-2.49×10^{-4}	$+2.49 \times 10^{-4}$
Eqm [ ]	1.00×10^{-6}	$X - 2.49 \times 10^{-4}$	2.49×10^{-4}

$$K_c = 7.7 \times 10^{8} = \frac{2.49 \times 10^{-4}}{(1.00 \times 10^{-6})(X - 2.49 \times 10^{-4})}$$

$$X = \underline{2.49 \times 10^{-4} \text{ mol dm}^{-3}}$$

Alternatively, $7.7 \times 108 = \dfrac{2.49 \times 10^{-4}}{(1.00 \times 10^{-6})[P_3O_{10}^{5-}]}$

$[P_3O_{10}^{5-}]_{eqm} = 3.23 \times 10^{-7}$ moldm^{-3}

$[P_3O_{10}^{5-}]_{initial} = 3.23 \times 10^{-7} + 2.49 \times 10^{-4} = \underline{2.49 \times 10^{-4} \text{ moldm}^{-3}}$

[3]

(b) 'Hard water' also contains magnesium ions which can form a precipitate with the detergent. For example, magnesium ions form magnesium iodide, MgI_2, in the presence of potassium iodide.

(i) The lattice energy of MgI_2 is –2327 kJ mol^{-1} while the values of the enthalpy change of hydration are listed below:

Ions	**ΔH_{hyd} / kJ mol^{-1}**
Mg^{2+}	–1920
I^-	–295

Calculate the enthalpy change of solution of magnesium iodide.

$$\begin{tikzcd}
MgI_2\,(s) + H_2O\,(l) \arrow[rr, "\Delta H_{sol}"] & & Mg^{2+}\,(aq) + 2\,I^-\,(aq) \\
& Mg^{2+}\,(g) + 2\,I^-\,(g) \arrow[ul, "-2327"] \arrow[ur, "-1920"'] \arrow[ur, bend right, "2(-295)"'] &
\end{tikzcd}$$

By Hess' Law,

$$\Delta H_{sol} = -2327 + (-1920) + 2(-295)$$

$$\mathbf{= -183\ kJ\ mol^{-1}}$$

(ii) Using your answer from **(b)(i)** and the fact that entropy change of solution of magnesium iodide is positive, predict whether magnesium iodide is soluble in water at room temperature. Give your reasoning.

$$\Delta G = \Delta H - T\,\Delta S$$

$$\Delta G = (-ve) - T\,(+ve)$$

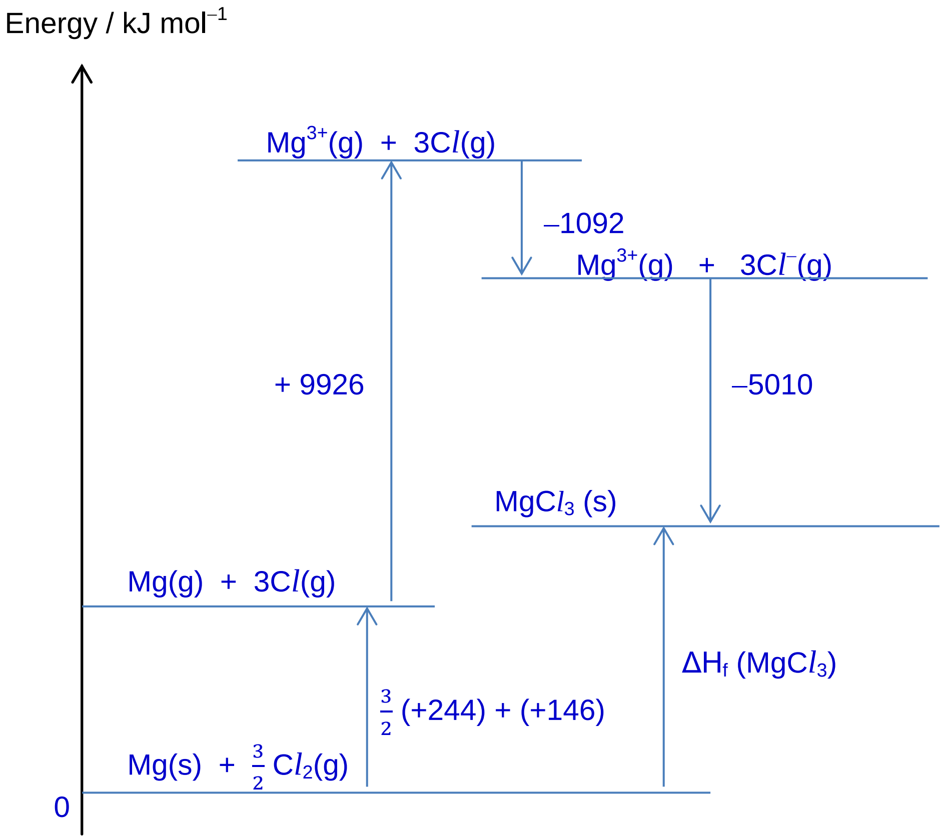
ΔG is always negative since ΔH is negative and ΔS is positive, dissolving process is always spontaneous.

Therefore, at room temperature, MgI_2 is soluble.

[4]

(c) Construct a Born-Haber cycle in the grid below to calculate the enthalpy change of formation of $MgCl_3$. Use the relevant data given below as well as from the *Data Booklet*.

Enthalpy change of atomisation of Mg	+146 kJ mol^{-1}
1st electron affinity of C*l*	–364 kJ mol^{-1}
ΔH_f ($MgCl_2$)	–652 kJ mol^{-1}
Lattice energy of $MgCl_3$(s)	–5010 kJ mol^{-1}



By Hess' Law,

$$\Delta H_f (MgCl_3) = \frac{3}{2}(+244) + (+146) + 9926 + (-1092) + (-5010)$$

$$= +4336 \text{ kJ mol}^{-1}$$

Comment on enthalpy change of formation of $MgCl_3$.

$\Delta H_f(MgCl_2)$ is more exothermic than that of $MgCl_3$, and so $MgCl_2$ is energetically more stable than $MgCl_3$.

[4]

(d) Calcium is a fairly soft, silvery-grey metal which quickly tarnishes in air. Vanadium is a hard grey metal which is resistant to corrosion at ordinary temperatures. Metallic calcium has no commercial uses; vanadium is widely used as an alloying element in steels.

Data about calcium and vanadium are given below:

	Calcium	**Vanadium**
Electronic configuration	[Ar] $4s^2$	[Ar] $3d^3$ $4s^2$
Atomic radius / nm	0.197	0.122
Melting point / °C	843	1710
Density / g cm^{-3}	1.54	6.07
Oxidation states in aqueous solution	+2	+2, +3, +4, +5

(i) Although the vanadium atom has more electrons than the calcium atom, the atomic radius of vanadium is smaller than that of calcium. Suggest an explanation for this.

This is due to an increase of nuclear charge as 3d electrons do not effectively shield the valence electrons, which brings about a greater attraction on the electrons.

(ii) The melting point of vanadium is significantly higher than that of calcium. Explain this in terms of the type and strength of bonding in each metal.

Although both Ca and V are metals, consisting of metallic bonding, the number of valence electrons involved in the metallic bonding for V is greater than that for calcium because for V, both the 4s and 3d electrons contributes to the sea of delocalized electrons. As a result, there is greater attraction between the metal cations and sea of delocalized electrons. More energy is required to break this metallic bond. Hence, melting point of V is higher than that of Ca.

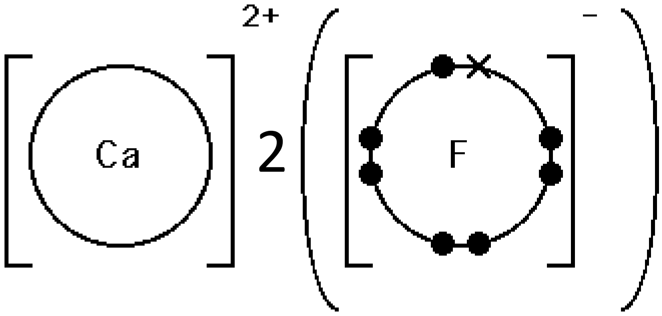
(iii) Compounds of calcium contain Ca^{2+} while the corresponding compounds of vanadium contain V^{3+}. Use the *Data Booklet* to explain in thermodynamic terms why Ca^{3+} compounds do not exist and V^{3+} compounds do.

From the Data Booklet,
3rd Ionisation energy of V = +2870 kJ mol^{-1}
Energy required to form Ca^{3+} = 590 + 1150 + 4940 = 6680 kJ mol^{-1}
The extremely high 3rd ionization energy for Ca is due to the 3rd electron being removed from a fully filled inner quantum shell which is nearer to the nucleus.

[8]

(e) Fluorspar is an important mineral composed of calcium and fluorine. It is used in a wide variety of chemical; metallurgical and ceramic processes.

Fluorspar, CaF_2, is an ionic compound. Draw a 'dot-cross' diagram to show the chemical bonding in fluorspar.



[1]

(f) Fluorspar reacts with concentrated sulfuric acid to form hydrogen fluoride gas.

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

Data about HF, HC*l*, HBr and HI are given below.

	HF	**HC*l***	**HBr**	**HI**
Boiling point / °C	+20	–85	–67	–35
Bond energy / kJ mol^{-1}	562	431	366	299
$\Delta H^{\ominus}_{f}$ / kJ mol^{-1}	–269	–92	–36	+26

(i) Explain why the boiling points of HC*l*, HBr and HI increases down the group.

Total number of electrons in HX molecule increases as X goes down the group. This brings about an increase in van der Waal's forces between molecules. Hence, more energy is required to overcome the van der Waal's forces.

(ii) Suggest why the boiling point of HF is much higher than those of the other three.

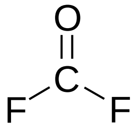
Higher boiling point of HF is due to stronger intermolecular hydrogen bonding between HF molecules.

[3]

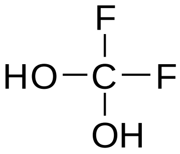
[Total: 23]

3 Being the most reactive of all elements, fluorine is commonly found in organic compounds.

Carbonyl fluoride, COF_2 (structure as shown below) exists as a toxic gas which reacts rapidly with water to evolve two different acidic gases.



(a)(i) The reaction of carbonyl fluoride with water is found to proceed via the formation of an intermediate as shown:



$$HO-\overset{\overset{F}{|}}{\underset{\underset{OH}{|}}{C}}-F$$

State the reaction that has occurred to produce the above intermediate.

Nucleophilic addition

(ii) The above intermediate is found to dissociate rapidly to give two different acidic gases. One of these gases is carbon dioxide. State the identity of the other gas.

Hydrogen fluoride gas or HF

(iii) Write a balanced equation of the reaction between carbonyl fluoride and water.

$$COF_2\,(g) + H_2O\,(l) \rightarrow 2HF\,(g) + CO_2\,(g)$$

[3]

(b) An unknown amount of carbonyl fluoride was reacted with water (in excess). The two acidic gases released are then reacted with NaOH (aq). $25.00 cm^3$ of $0.100 mol dm^{-3}$ of NaOH (aq) was required for complete neutralisation.

(i) Calculate the number of moles of NaOH used.

$$\eta_{NaOH} = 0.100 \times \frac{25.00}{1000} = 2.50 \times 10^{-3} \text{ mol}$$

(ii) Calculate the number of moles of CO_2 produced.

2 moles of HF requires 2 moles of OH^- and 1 mole of CO_2 requires 2 moles of OH^-. Therefore, a total of 4 moles of OH^- is required.

$\therefore$ η_{CO2} produced = $\frac{1}{4} \times 2.50 \times 10^{-3}$

$= 6.25 \times 10^{-4}$ mol

(iii) Using your answer in **(b)(ii)**, calculate the volume of carbon dioxide in m^3 produced under the conditions of 30 °C and 1 atm (assuming ideal gas behavior).

$pV = \eta RT$

$V = \dfrac{\eta RT}{P}$

$= \dfrac{6.25 \times 10^{-4} \times 8.31 \times (273 + 30)}{1.01 \times 10^5}$

$= 1.56 \times 10^{-5}\ m^3$

(iv) Calculate the mass of carbonyl fluoride used.

$COF_2 \equiv CO_2$

Mass of COF_2 used = $6.25 \times 10^{-4} \times 66$

$= 0.0413$ g

[6]

[Total: 9]

4 The acidity of hydrogen-containing compounds varies remarkably from one compound to another.

The South African plant *Dichapetalum cymosum* contains fluoroethanoic acid, FCH_2COOH. Data about ethanoic acid, fluoroethanoic acid and chloroethanoic acid are given below:

	CH_3CO_2H	**FCH_2CO_2H**	**$ClCH_2CO_2H$**
pK_a	4.76	2.57	2.87

(a)(i) Define the term pK_a.

$pK_a = -\log K_a$

(ii) Calculate K_a for fluoroethanoic acid.

$K_a = 10^{-2.57}$

$= 2.69 \times 10^{-3}$ mol dm^{-3}

[2]

(b)(i) Comparing the three acids given above, state the strongest acid and the weakest acid.

Strongest acid: FCH_2COOH

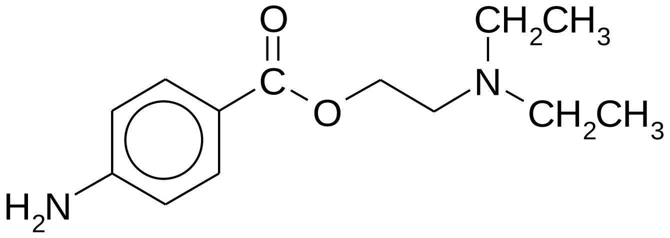
Weakest acid: CH_3COOH

(ii) Suggest an explanation for the differences in acid strengths of the three acids in terms of their structure and bonding.

Effect of “F” on the O – H bond : F is very electronegative and so dispersing the negative charge to the largest extent and the FCH_2COO^- is the most stable of the three. Cl is less electronegative than F and so the e withdrawing effect on the negative charge of the $ClCH_2COO^-$ is to a lesser extent compared to that of F. CH_3COO^- does not have an electronegative atom attached. Hence, negative charge is least dispersed and anion is least stable.

[4]

(c) Procaine is a local anaesthetic drug used primarily to reduce the pain of intramuscular injection of penicillin.



Procaine

There are two monoprotic basic functional groups in the procaine molecule, with pK_b values of 4.19 and 9.37.

(i) Name the two basic functional groups present in the procaine molecule.

Tertiary amine; phenylamine

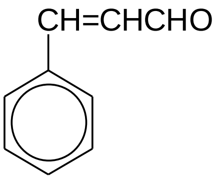
(ii) Match the given pK_b values to the corresponding functional groups.

pK_b	Functional Group
4.19	Tertiary amine
9.37	phenylamine

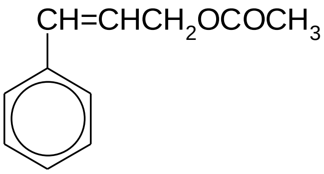
[4]

[Total: 10]

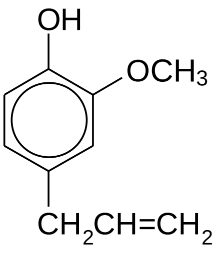
5 Dengue fever and dengue haemorrhagic fever are the most common mosquito-borne viral disease in the world. There was no drug to treat dengue until 2014. According to The Straits Times' report dated 12 July 2014, the first safe and effective dengue vaccine in the world could be out commercially by July 2015. Before the announcement on the vaccine, cinnamon oil makes the most effective natural mosquito repellent known to man. Each of the following compounds, which are present in cinnamon, appears to be effective as pesticide.



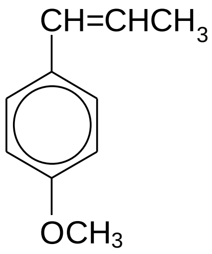
A



B



C

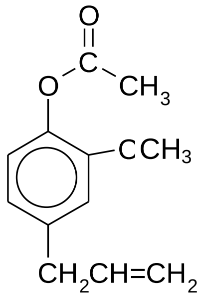
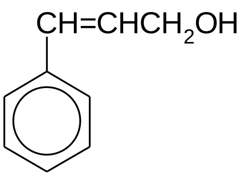


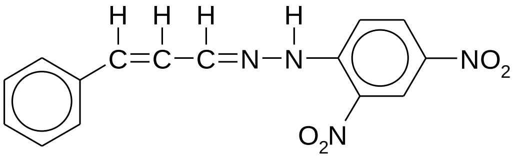
D

The group $-OCH_3$ which is present in compounds **C** and **D** can be regarded as inert.

(a) Only **one** of the compounds **A**, **B**, **C** or **D** will react with **each** of the following reagents. In each case, identify the compound concerned and draw the structural formula of the organic product formed.

Each compound may be used once, more than once, or not at all.

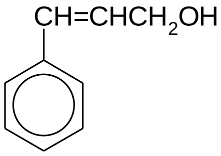
reagent	compound **A**, **B**, **C** or **D**	structural formula of the organic product(s)
CH_3COCl	C	
Hot dilute H_2SO_4	B	 + CH_3COOH

reagent	compound **A**, **B**, **C** or **D**	structural formula of the organic product(s)
2,4-dinitrophenylhydrazine	**A**	

[7]

(b) Compound **A** may be converted into compound **B** in a two-stage process.

(i) What is the structural formula of the intermediate in this conversion?



(ii) For each stage, in the reaction sequence, give reagents and conditions.

Stage I: Reagents $LiAlH_4$ in dry ether OR $NaBH_4$ in dry ether

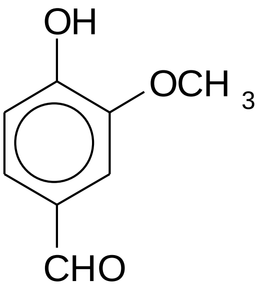
Conditions room temperature

Stage II: Reagents CH_3COCl OR CH_3COOH, conc H_2SO_4

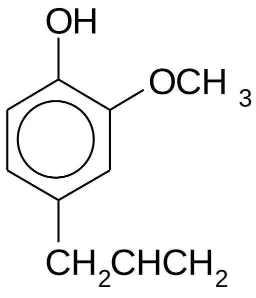
Conditions room temperature OR heat

[4]

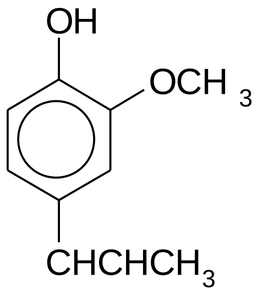
Another similar aromatic flavouring agent is vanillin. Vanillin is a phenolic aldehyde with the molecular formula $C_8H_8O_3$:



vanillin



eugenol



isoeugenol

Eugenol was used in the production of isoeugenol for the manufacture of vanillin.

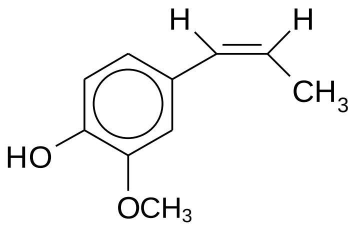
(c) What type of isomerism do eugenol and isoeugenol exhibit?

Structural / positional isomerism

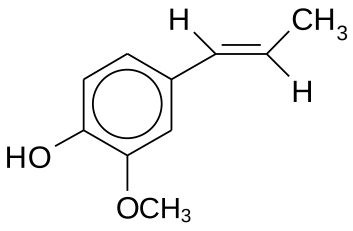
[1]

(d) Isoeugenol exists as a pair of stereoisomers. Draw the structures of the isomers and state the type of isomerism shown.

Type of isomerism: geometrical isomerism



Cis isomer



trans isomer

[2]

(e) 16.4 g of eugenol yield 13.0 g of vanillin. Calculate the percentage yield of vanillin.

Mr, eugenol = 164; Mr, vanillin = 152

Amount of eugenol = 16.4/164 = 0.10 mol

Theoretical yield = 0.10 mol = 15.2 g

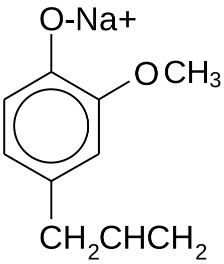
$\therefore$ % yield = $\frac{13.0}{15.2} \times 100\% = 88.5\ \%$

[2]

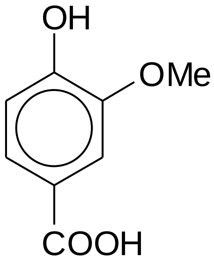
(f) Name a reaction in which these three compounds (vanillin, eugenol and isoeugenol) react similarly, and give the structure of the major organic product formed from eugenol.

Reaction: acid-base reaction (with hydroxide)
OR redox (with Na solid)
OR oxidation (with $KMnO_4$/dil H_2SO_4)
OR electrophilic substitution (with aq. Br_2)
OR reduction (with H_2/Ni)
OR condensation (with $CH_3COC\mathit{l}$, rtp)

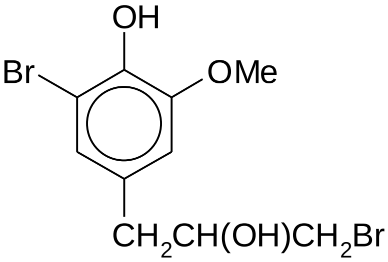
Structure of major organic product:

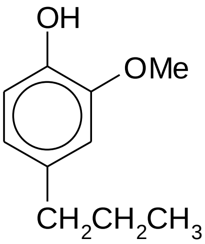


OR

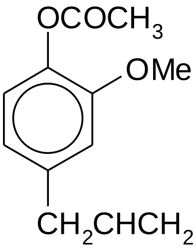


OR





OR



[2]

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