1

For Examiner's Use

Answer **all** questions in the spaces provided.

1 Planning (P)

Acids can be classified in terms of their basicity depending on the number of protons that can be donated to a base. A student is investigating the basicity of a solution of 0.80 mol dm^{-3} acid, **A**, using just the acid and sodium hydroxide of the same concentration. He conducted two experiments by mixing different volumes of **A** and sodium hydroxide, and taking the temperature rise for each experiment.

(a) Based on the definition of the enthalpy change of neutralisation (ΔH_n) and his results, deduce the basicity of acid **A**.

Experiment	Volume of acid	Volume of NaOH	ΔT /°C
1	40	20	3.6
2	20	40	7.2

If it is a dibasic acid, n(H_2O) formed in experiment 2 is twice that of experiment 1. Since total volume is constant, ΔT for experiment 2 is doubled. Hence it is dibasic.

If it is a monobasic acid, n(H_2O) formed in expt 1 = n(H_2O) formed in expt 2
Since total volume is constant, ΔT must be the same for both experiments.

(b) (i) The temperature rise of the reaction can be determined graphically by measuring how the *temperature changes with time*.

You are to plan an experiment to determine the ΔH_n between a solid sample of **A** and sodium hydroxide.

You are provided with a solid sample of **A** (M_r = 174) and sodium hydroxide solution of 0.80 mol dm^{-3}.

In your plan, you should give:

- details including calculations to determine the quantities of the reactants to use;
- choice of apparatus (You may use apparatus normally found in the school laboratory.);
- the essential details for obtaining the graph of temperature against time in order to determine the temperature rise;
- table(s) of readings to taken.

Calculations:

Volume of NaOH to use = 40 cm^3

Amount of acid used in experiment 2 = 0.016 mol
Mass of acid used in experiment 2 = 0.016 x 174 = 2.784 g
To ensure acid is limiting here, we use 2.5 g.

Procedure:

1. Using a weighing balance, weigh accurately about 2.5 g of **A**.
2. Using a 50 cm^3 measuring cylinder, measure 50 cm^3 of NaOH and add into a Styrofoam cup and cover with a lid.
3. Using a 0.2 ^oC division thermometer, note the temperature of the solution at 1 min interval for the first 3 minutes.
4. At 3.5 min, *rapidly* add sample **A** into the cup, close the lid.
5. Stir the mixture.
6. Measure the temperature of the mixture at the 4^{th} minute, and at every 1 minute interval until the 10^{th} minute.

Apparatus: weighing balance, 50 cm^3 measuring cylinder, Styrofoam cup, 0.2 ^oC division thermometer. (2 items missing, 0)

Timing: take initial temp for at least 3 min, time intervals (at most 1 min), read minimum of 5 readings after mixing. (2 items missing, 0)

General procedure: rapidly pour, stir, close lid. (2 missing, 0)

Quantities: vol. of NaOH, mass of **X** (no penalty since calculation was done)

Table of readings:

Mass of X and weighing bottle /g	
Mass of weighing bottle and residue /g	
Mass of empty weighing bottle /g	
Mass of X used /g	

Time /min	**Temperature /^oC**

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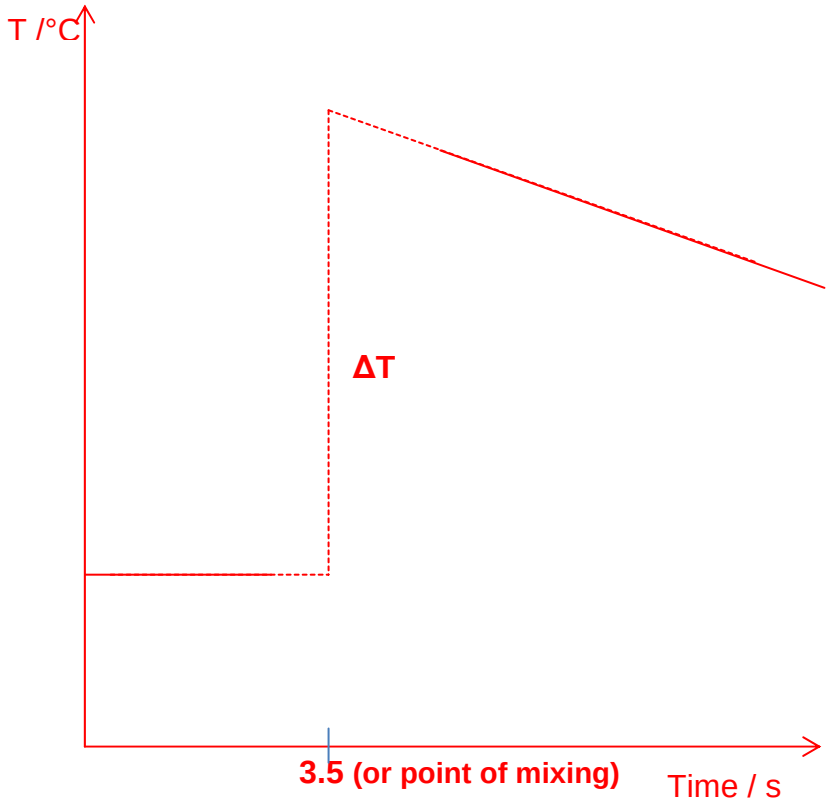
(ii) Sketch the graph that you would expect, showing clearly how you can determine the temperature rise.



[8]

(c) Explain why temperature rise in the experiment should not be too low.

Too low, result in high percentage error.

[1]

(d) An alternative method to determine the temperature rise is to measure the highest temperature reached. Explain if this is a better method.

Poorer method as it does not take into account heat loss to the surroundings.

[1]
[Total: 12]

2 One of the most important features of the transition elements is that they exhibit variable oxidation states. This question illustrates the various oxidation states shown by iron in its compounds.

(a) The reaction between iodide ions, I^-, and peroxidisulfate ions, $S_2O_8^{2-}$, is slow. The reaction can be catalysed by adding a small amount of Fe^{2+} ions.

The initial rate of the slow reaction between iodide ions and peroxidisulfate ions can be studied by using thiosulfate ions. The equations for the reactions are as follows.

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-} \quad \text{(slow)} \quad \text{reaction } \mathbf{I}$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-} \quad \text{(fast)} \quad \text{reaction } \mathbf{II}$$

In the presence of a constant amount of thiosulfate ions, the iodine being slowly produced by reaction **I** will immediately react in reaction **II** until all the thiosulfate ions has been used up. At that point, free iodine will be present in the solution, which will cause a sudden appearance of a deep blue colour if starch is present.

A series of experiments was carried out using different volumes of the five reagents. The following results were obtained.

Expt	Volume of $S_2O_8^{2-}$ /cm^3	Volume of I^- /cm^3	Volume of $S_2O_3^{2-}$ /cm^3	Volume of distilled water /cm^3	Volume of Starch /cm^3	Time for the appearance of deep blue colour/s
1	20	20	10	5	5	30
2	20	15	10	10	5	40
3	5	25	10	15	5	t_3
4	10	15	10	20	5	80

(i) If the orders of reaction with respect to peroxidisulfate ions and iodide ions are both one respectively, deduce an expression relating the volume of these two reactants and time taken for the appearance of deep blue colour.
Explain your reasoning.

Rate = k $[S_2O_8^{2-}][I^-]$

* Since total volume of solution is constant,
  concentration of a reactant $\propto$ volume of reactant
* rate $\propto$ 1/time

1/time = k (volume of $S_2O_8^{2-}$)(volume of I^-)

(volume of $S_2O_8^{2-}$)(volume of I^-) x time = constant

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(ii) Hence, predict the time, t_3, required for the appearance of deep blue colour in experiment 3.

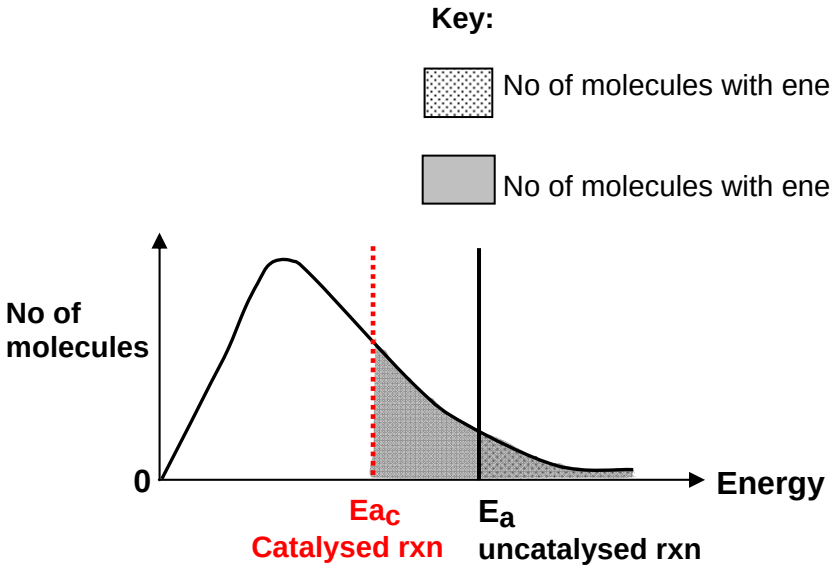
time for expt 3, t_3 = 96 s

[3]

(b) **(i)** In the Haber process, the rate of formation of ammonia is increased by using an iron catalyst. State the type of catalysis occurring here and describe using the Maxwell-Boltzmann Distribution curve, how the iron catalyst increases the rate of reaction.

Heterogeneous catalysis

Boltzmann Distribution Diagram:



In the presence of a catalyst,

- a reaction has a different mechanism with a lower activation energy compared to the uncatalysed reaction.
- More molecules will possess energy greater than this lowered activation energy,
- hence frequency of effective collisions will increase.

Hence, rate of reaction increases.

(ii) Ammonia shows significant deviations from the ideal behaviour that is predicted by the kinetic theory of gases. State two assumptions of the kinetic theory of gases.

2 assumptions for ideal gas behaviour are:

- Particles in gaseous state do not exert any force or negligible forces of attraction;
- volume of particles is negligibly small compared with that of the container.

(iii) A sample of ammonia can be liquefied at room temperature just by increasing the pressure of the sample. Why does the application of pressure cause the gas to liquefy?

At high pressure, volume of gas decreases, and the particles are much closer to one another. They are able to form more significant intermolecular forces (hydrogen bond between ammonia molecules) and hence, gases condense into liquid.

[7]

(c) Iron(III) chloride is a dark brown solid which dissolves in water to give an acidic solution. This solution is often used, in the electronics industry, to etch (dissolve) the copper used in printed circuit boards.

(i) Explain, with the aid of a chemical equation, why aqueous iron(III) chloride is acidic.

$Fe^{3+}(aq)$ can undergo hydrolysis with water due to its high charge density and hence it's able to polarize one of the water ligands to produce H_3O^+

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+} + H_3O^+$$

(ii) By selecting appropriate E^θ values from the *Data Booklet*, explain why aqueous iron(III) chloride etches (dissolves) copper. Construct a balanced equation for this reaction.

$Cu^{2+} + 2e \rightleftharpoons Cu \qquad E^\theta = +0.34V$
$2Fe^{3+} + 2e \rightleftharpoons 2Fe^{2+} \qquad E^\theta = +0.77V$

Since $E^\theta_{cell} = +0.43V > 0$, reaction is feasible

$$2Fe^{3+} + Cu \longrightarrow Cu^{2+} + 2Fe^{2+}$$

[4]

(d) Iron(III) iodide has been successfully made under non-aqueous conditions by following method.

Iron pentacarbonyl, $Fe(CO)_5$, reacted with iodine in hexane solution to form a solution of compound **E**, whose molecular formula is $FeC_4O_4I_2$.

A further calculated amount of iodine is added, and the solution exposed to uv light. A black precipitate of iron(III) iodide results, and a colourless gas is evolved.

(i) State the co-ordination number of iron in the complex, $Fe(CO)_5$ and hence predict the shape of the complex, $Fe(CO)_5$.

Co-ordination number: 5

Shape: trigonal bipyramidal

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(ii) Describe the bonding between iodine and iron in compound **E** and write a balanced equation for the reaction between compound **E** and iodine.

Co-ordinate bond / Dative bond / Dative covalent bond [1]

$2FeC_4O_4I_2 + I_2 \longrightarrow 2FeI_3 + 8CO$

[4]

(e) When a solution of NaClO is added to a strongly alkaline suspension of Fe_2O_3, a purple solution results. When $BaCl_2(aq)$ is added to the solution, a red solid is precipitated with the composition by mass: Ba, 53.4%; Fe, 21.7%; O,24.9%.

(i) Calculate the empirical formula of the red solid, and hence determine the oxidation number of iron in the red solid.

	Ba	Fe	O
Mass/g	53.4	21.7	24.9
No of mole/mol	53.4/137 = 0.390	21.7/55.8 = 0.390	24.9/16 = 1.56
simplest ratio	1	1	4

Empirical formula is $BaFeO_4$
Oxidation number = +6

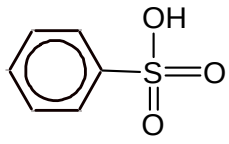
(ii) Construct a balanced ionic equation for the reaction between Fe_2O_3, ClO^- and OH^-.

[O] $Fe_2O_3 + 10OH^- \longrightarrow 2FeO_4^{2-} + 5H_2O + 6e$
[R] $ClO^- + H_2O + 2e \longrightarrow Cl^- + 2OH^-$

Overall:
$Fe_2O_3 + 3ClO^- + 4OH^- \longrightarrow 2FeO_4^{2-} + 3Cl^- + 2H_2O$

[4]
[Total: 22]

3 Aromatic sulfonic acid is an important precursor to industrial materials and has the following structure:



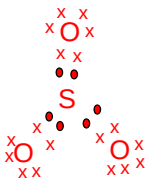
Aromatic sulfonic acid

(a) Sulfonation of benzene is the reaction mechanism between benzene and sulfuric acid. The first step of the reaction mechanism is given by the following equation.

$$H_2SO_4 \rightleftharpoons H_2O + SO_3$$

Sulfur trioxide is an important intermediate in the reaction mechanism.

(i) Draw a dot-and-cross diagram of sulfur trioxide.

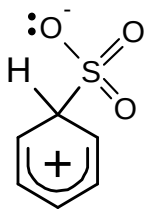


(ii) With reference to the structure of the molecule, state and explain the function of sulphur trioxide in the mechanism.

Electrophile
The three oxygen atoms are more electronegative than the sulphur [1] and so draw electrons towards themselves. The sulphur atom is electron deficient and is attacked by the benzene ring.

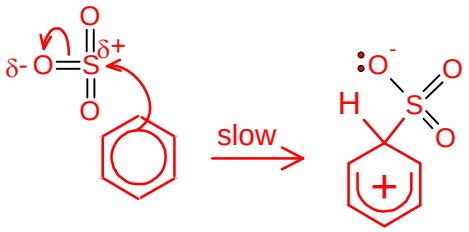
(iii) The final step of the mechanism is different from other benzene reactions because the hydrogen atom is not removed from the ring by a separate negative ion. Instead it is removed by a lone pair of electrons on a negative oxygen atom in the sigma complex.

The sigma complex formed has the following structure:

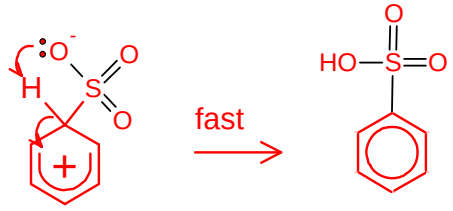


Sigma complex

With the above information, complete the mechanism for the reaction between benzene and sulfuric acid.
Electrophilic Substitution
Step 2: Formation of the sigma complex (Slow step)



Step 3: Loss of proton to form the substitution product



(iv) Sulfonation of aniline produces sulfanic acid compounds with an unusually

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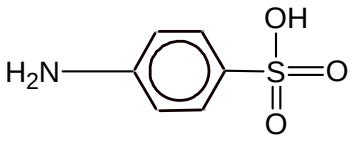
high melting point. With reference to the structure of sulfanic acid, suggest why this is so.



Sulfanic acid

Sulfanic acid forms zwitterions, hence the electrostatic forces of attraction between oppositely charge ions on neighboring give rise to the high melting point.

[7]

(b) The key reaction during the Contact process is as follows:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g); \qquad \Delta H = -98\ kJ\ mol^{-1}$$

Industrially, the gases are compressed to a pressure of 3 atm before it is passed over a bed of vanadium(V) oxide at 430 °C. Explain the conditions used.

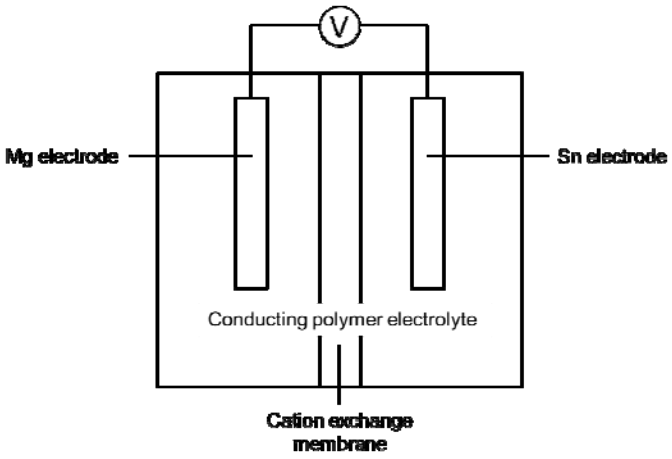
By Le Chatelier's principle, high pressure and low temperature are conditions favorable for the production of the product, SO_3.
At high pressure, the foward reaction is favoured and POE shifts to the right as there are less gas molecules produced, hence helping to remove the stress of high pressure. However it is costly to operate the reaction at too high a pressure as stronger pipes and vessels are needed. Hence an optimal pressure of 3 atm is used.
At low temperature, the forward reaction is favoured and POE shifts to the right as the forward reaction is exothermic, hence helping to remove the stress of low temperature. However rate of reaction would be affected by the low temperature. Hence an optimal temperature of 450°C and catalyst is used.

[3]
[Total: 10]

4 Magnesium is the fourth most abundant element in the earth. Scientists are

working on developing rechargeable magnesium-ion batteries for use in electric cars, as they offer a cheaper and more energy efficient alternative to lithium-ion batteries.

A simplified representation of a magnesium-ion battery is shown below. When the battery discharges, magnesium ions are formed, which move across the cation exchange membrane to the Sn electrode, forming solid Mg_2Sn.



(a) **(i)** Write half equations for the reactions occurring at the cathode and the anode when the battery discharges.

Cathode: $2Mg^{2+} + Sn + 4e \rightarrow Mg_2Sn$
Anode: $Mg \rightarrow Mg^{2+} + 2e$

(ii) The magnesium-ion battery provides a voltage of 3.01 V. With reference to the *Data Booklet*, calculate $E^{\theta}(Sn/Mg_2Sn)$, assuming standard conditions.

$E^{\theta}_{cell} = E_{[R]} - E_{[O]}$
$3.01 = E_{[R]} - (-2.38)$
$E_{[R]} = +0.63$ V

(iii) The car battery has to be recharged after use. After clocking a mileage of 500 km, 83.8 g of Mg_2Sn was deposited on the electrode of the battery. How many hours will it take for the car battery to be recharged, using a current of 10.0 A? What is the polarity of each electrode during the charging process?

$n(Mg_2Sn) = 0.500$ mol
1 mol of Mg_2Sn requires 4 mol of electrons

$It = nzF$
$10.0t = (0.500)(4)(96500)$
$t = 5.36$ hours (3sf)

Sn electrode: +ve, Mg electrode: -ve

(iv) Besides cost, explain another advantage the magnesium-ion battery has over

the lithium-ion battery.

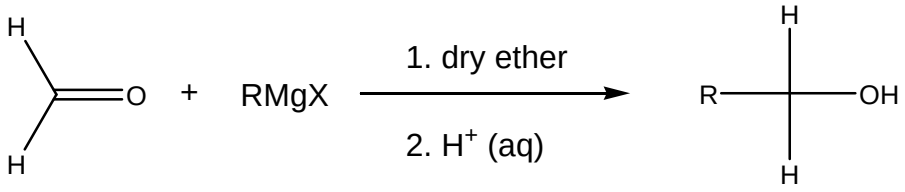
1 mol of Mg can transfer 2 mol of electrons as compared to 1 mol for Li, so the process is more efficient. OR
Mg reacts less vigorously with water than Li, so it poses less of a safety hazard if the battery is accidentally exposed to moisture.

[8]

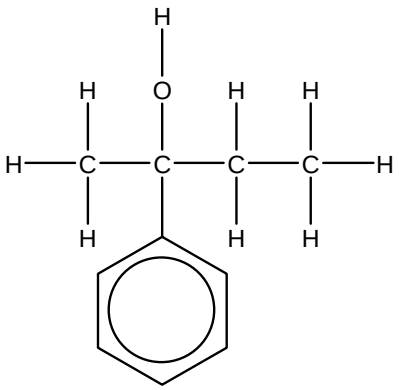
(b) Magnesium is also used in the synthesis of Grignard reagents, RMgX (R = alkyl or aryl groups, X = Cl or Br), from organic halides. The organic halide is added to a suspension of magnesium in dry ether, forming the Grignard reagent

$$RX + Mg \rightarrow RMgX$$

Grignard reagents are examples of organometallic compounds as they contain a carbon-metal bond. They are useful for organic synthesis as they can form new carbon-carbon bonds with unsaturated compounds such as carbonyls. The reaction of methanal and a general Grignard reagent is illustrated below:



(i) Draw the displayed formula of the product of the reaction between butanone and C_6H_5MgCl.

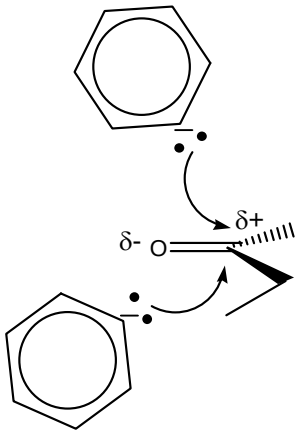


[1]

(ii) How would you determine if the reaction in **b(i)** has gone to completion?

To a small portion of reaction mixture, add 2,4 dinitrophenylhydrazine, warm. If there is no orange ppt, the reaction is complete.

(iii) The Grignard reagent can be considered as a good source of a carbanion, "R^-". Using this information, explain whether the product mixture formed will be optically active. Explain your answer with the aid of a diagram.

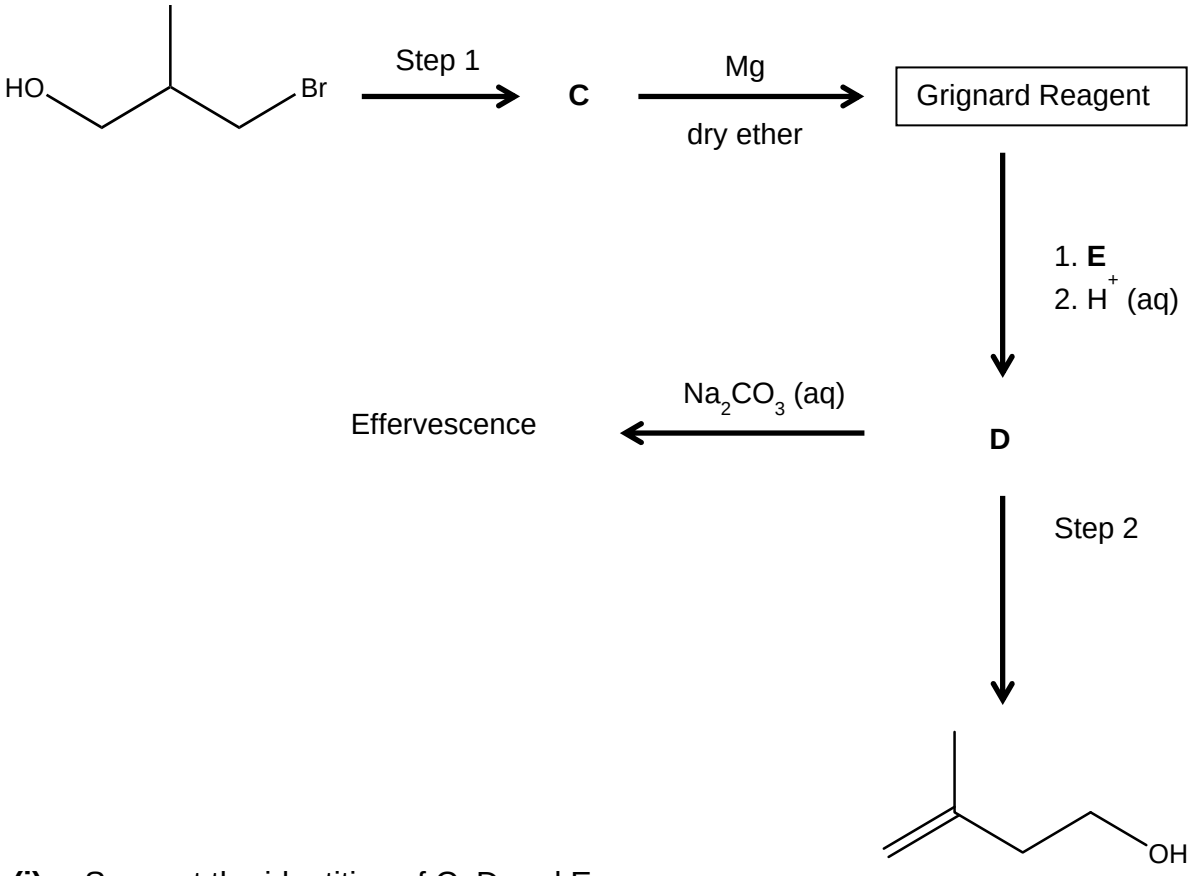


Product is not optically active as the nucleophile has equal probability of attack from above or below the planar carbonyl centre.

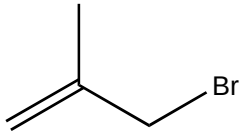
[5]

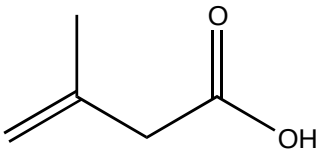
(c) Refer to the reaction scheme involving a Grignard reagent below.

13



(i) Suggest the identities of C, D and E.

C: 

D: 

E: CO_2

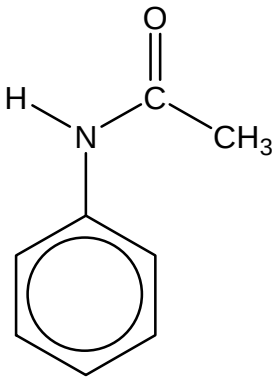
(ii) Suggest reagents and conditions for Step 1 and 2.

Step 1: concentrated H_2SO_4, 170 °C or Al_2O_3, 350 °C
Step 2: $LiAlH_4$ / dry ether

[5]
[Total: 18]

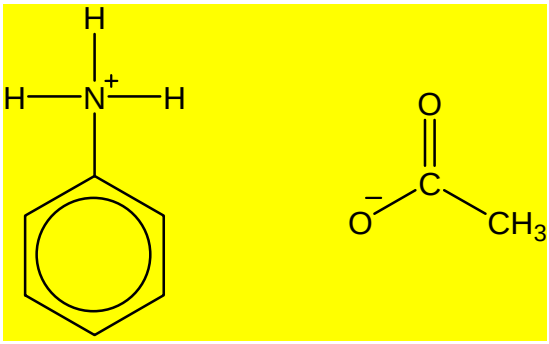
5 Some chemistry students were doing an organic chemistry practical.

(a) Student X heated Compound **F** with hydrochloric acid to form two organic products. In order to isolate both products, the reaction mixture was placed in a separating funnel and shaken with water.



Compound **F**

(i) Draw the products of the above reaction.



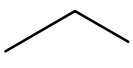
(ii) Explain why the separation will not be successful.

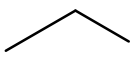
The amine will form ion-dipole interactions with water molecules.
The acid will form hydrogen bonds with water molecules.

(iii) Describe the correct procedure to separate the hydrolysis products.

Add NaOH to hydrolysis products until moist litmus paper turns blue.
Shake the reaction mixture with water in the separating funnel to isolate the () in the aqueous medium, leaving behind the amine.

(b) Under acidic conditions, Student Y treated ethylamine with excess iodomethane in an attempt to form a quarternary amine salt. Explain why this synthesis will not be successful.

Under acidic conditions, 

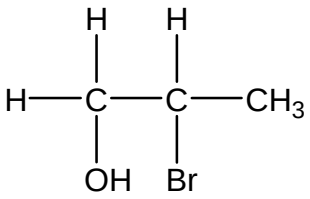
is protonated to 

.
The lone pair on the nitrogen is not available for the nucleophilic substitution to form the quarternary amine salt.

[2]

(c)

15

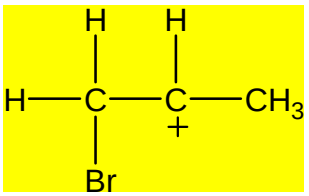


Compound **G**

Student Z predicted that Compound **G** was formed from the reaction of propene and aqueous bromine in the presence of concentrated sodium chloride.

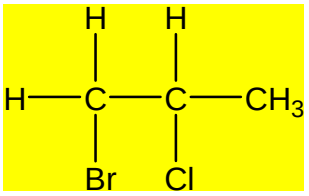
(i) Explain why his prediction is wrong.

Propene undergoes an electrophilic addition reaction with $Br_2(aq)$ in conc. NaCl. The secondary carbocation is more stable than the primary carbocation as it has one more electron donating alkyl groups help to stabilise the carbocation intermediate by increasing the electron density



There is a high concentration of Cl^-, thus it will form a bond with the carbocation.

(ii) Hence, suggest the structure of the major product formed.



[3]
[Total: 10]