Class	Adm No

Candidate Name: ____________________

H

millennia institute

2015 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY **9647/02**

Paper 2 Structured Questions

16th Sept 2015

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number 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.

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

Question	**1**	**2**	**3**	**4**	**5**	Total
Marks	**12**	**10**	**24**	**15**	**11**	**72**

This question paper consists of **11** printed pages and **1** blank page.

1 Planning (P)

Ascorbic acid is a naturally occurring organic compound commonly found in citrus fruits and Vitamin C supplements. It is sometimes called an ‘anti-oxidant’ or a reducing agent. Ascorbic acid is water soluble. Direct iodometric titration can be used to determine the amount of ascorbic acid in samples of juices and Vitamin C supplements.

Iodine rapidly oxidises ascorbic acid, $C_6H_8O_6$, to produce dehydroascorbic acid, $C_6H_6O_6$.

$$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2I^- + 2H^+$$

In the direct iodometric titration, the ascorbic acid is titrated against an iodine solution of known concentration using starch as an indicator. Once all the ascorbic acid has been oxidised, the excess iodine is free to react with the starch indicator.

A student was given a Vitamin C sample which the manufacturer claims to contain 0.25 g of ascorbic acid per tablet. She was tasked to plan an experiment to determine if the manufacturer’s claim was true.

The following reagents were provided:
FA 1 0.00500 mol dm^{-3} I_2 solution
FA 2 starch indicator

(a) State the colour at the end-point of the titration.

.... [1]

Dark blue/black

(b) The student was provided with a 250 cm^3 volumetric flask to prepare an ascorbic acid solution using one Vitamin C tablet. The solution was labelled **FA 3**.

Assuming that the manufacturer’s claim is true, calculate the concentration of ascorbic acid in **FA 3**.

[1]

Amount of ascorbic acid = $\frac{0.25}{176.0}$ = 0.001420 mol

[**FA3**] = $\frac{0.001420}{0.250}$ = 0.00568 mol dm^{-3}

(c) Given that the average titre volume should be in the range of 10.0 to 30.0 cm^3, determine the minimum volume of **FA 3** that should be used in the experiment.

Hence, suggest a suitable pipette volume for titration.

[3]

Using minimum titre volume,

amount of I_2 in 10.0 cm^3 **FA1** = 0.0100 x 0.00500 = 5.00 x 10^{-5} mol

amount of **FA3** required for reaction = 5.00 x 10^{-5} mol

Minimum volume of **FA3** required for reaction = $\frac{5.00\times10^{-5}}{0.005682}$ = 0.00880 dm^3 = 8.80 cm^3

Volume of pipette to be used = 10.0 cm^3

(d) Write a plan for the direct iodometric titration of ascorbic acid sample **FA 3**. You may use the reagents and apparatus normally found in a school or college laboratory. Your plan should include:

- details for the preparation of **FA 3** solution;
- the essential details of the titration procedure;
- how the results should be tabulated.

………………………………………………………………………………………………………

………………………………………………………………………………………………………

………………………………………………………………………………………………………

………………………………………………………………………………………………….....[7]

[Total: 12]

1. Dissolve one Vitamin C tablet in a 50.0 cm^3 beaker. Transfer the solution to the 250 cm^3 volumetric flask.
2. Rinse the beaker a few times and transfer the washings into the 250 cm^3 volumetric flask.
3. Add distilled water to the mark. Shake well.
4. Fill the burette with **FA1**. Using a pipette, transfer 10.0 cm^3 of **FA3** into the conical flask. Add about 1 cm^3 of starch solution into the conical flask.
5. Place conical flask on a white tile. Titrate the FA3 solution against FA1 until blue-black colour is observed at the end-point.
6. Repeat the titrations to obtain two readings with volumes consistent to ±0.10 cm^3.
7. Titration results

	1	2	3
Final burette reading/cm^3			
Initial burette reading/cm^3			
Volume of **FA1** used/cm^3			

2 Group II elements are known as alkaline earth metals. They have similar chemical properties and are soft silver metals.

(a) The ionisation energy of Group II elements varies down the group.

(i) Write an equation to represent the first ionisation energy of calcium.

………………………………………………………………………………………………… [1]

$Ca(g) \rightarrow Ca^{+}(g) + e$

(ii) State and explain how the first ionisation energy of group II elements varies down the group.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

………………………………………………………………………………………………… [2]

Down the group nuclear charge increases as no. of protons increases while shielding effect increases as number of inner shell electrons increases. The increase in shielding effect outweighs increase in nuclear charge, effective nuclear charge decreases. The distance between valence electrons and nucleus increases, energy required to remove outer electrons decreases, thus the 1st I.E. decreases down the group.

(iii) Write the full electronic configuration of a Ca atom and a Ca^{2+} ion.

Ca………………………………… Ca^{2+}…………………………………… [1]

Ca : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ Ca^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

(iv) Explain why the ionic radius of Ca^{2+} is smaller than the atomic radius of Ca.

………………………………………………………………………………………………… [2]

Loss of valence electrons results in shrinking of the electron cloud due to decrease in number of shells there is greater attractive force on the valence electrons, hence the ionic radius is smaller

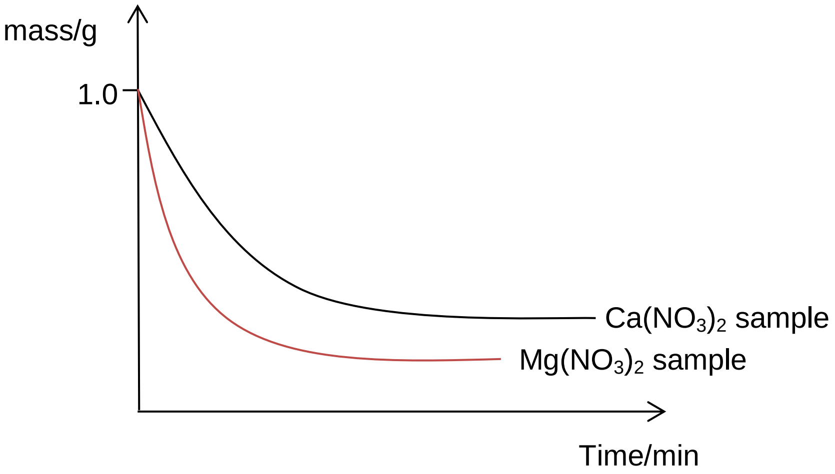
(b) Group II nitrates decompose on heating.

(i) Write a balanced equation to show the thermal decomposition of calcium nitrate.

.... [1]

$Ca(NO_3)_2 \xrightarrow{\text{heat}} CaO + 2NO_2 + \frac{1}{2}O_2$

(ii) A 1.0 g sample of powdered calcium nitrate is heated at a temperature, *T*. The graph below shows how the mass of the sample changes with time.



Sketch a curve in the graph above to show how you would expect the mass of a 1.0 g sample of magnesium nitrate would change with time when it is heated at the same temperature, *T*.

Explain your answer.

....

....

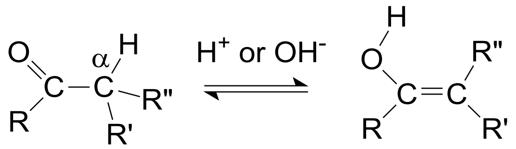
....

.... [3]

Mg^{2+} has a higher charge density than Ca^{2+}, hence it polarises the electron cloud of the nitrate ion more and weakens the N–O bonds to a greater extent in magnesium nitrate, thus lowering the decomposition temperature. Ease of decomposition increases, thus time taken for the magnesium nitrate to completely decompose is shorter.

[Total: 10]

3 **(a)** Carbonyl compounds can undergo acid or base catalysis to form enols.



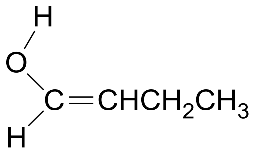
enol

Any carbon atom directly attached to the carbonyl carbon (C=O) is designated as an α-carbon. Any hydrogen atom directly attached to an α-carbon atom is termed as an α-hydrogen.

Enols are alkenes with a hydroxyl group attached to one of the carbon atoms of the double bond (C=C–OH). Enols are isomers of aldehydes or ketones in which one α-hydrogen has been removed and replaced on the oxygen atom of the carbonyl group.

(i) Draw the structural formula of the enol that could be formed from the acid catalysis of butanal.

[1]



(ii) Draw the structural formulae of the two other isomers of butanal, $CH_3CH_2CH_2CHO$, that gives a positive test with 2,4-dinitrophenylhydrazine.

A	**B**

[2]

A: $CH_3CH_2COCH_3$ **B**: $CH_3CH(CH_3)CHO$

(iii) Suggest a chemical test that could be used to distinguish the two isomers in **(a)(ii)**. You should state the reagents and conditions as well as observations for each compound.

Test: ……………………………………………………………………………………………

Observations:

A: ……………………………………………………………………………………………

B: ……………………………………………………………………………………………[2]

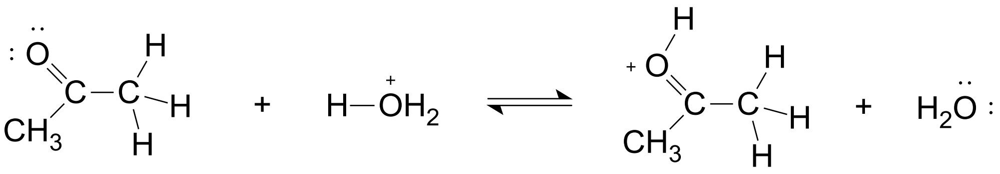
Test: Tollen's reagent, warm/Fehling's reagent, warm/aq iodine, NaOH(aq) warm/$K_2Cr_2O_7$, H_2SO_4(aq), warm/ $KMnO_4$, H_2SO_4(aq),warm

Observations:
A: no silver mirror/no brick red ppt/yellow ppt/remains orange/remains purple

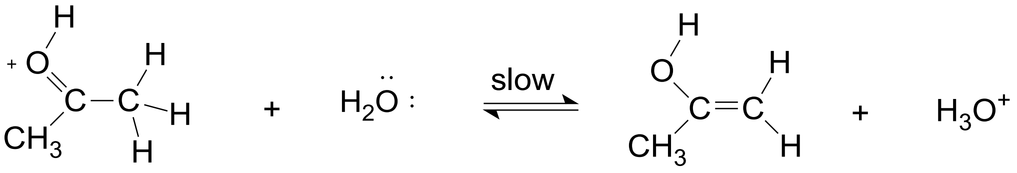
B: silver mirror/brick red ppt/no yellow ppt/turns from orange to green/turns from purple to colourless

(b) The incomplete mechanism for the acid catalysed reaction for propanone to form an enol is shown below.

Step 1:

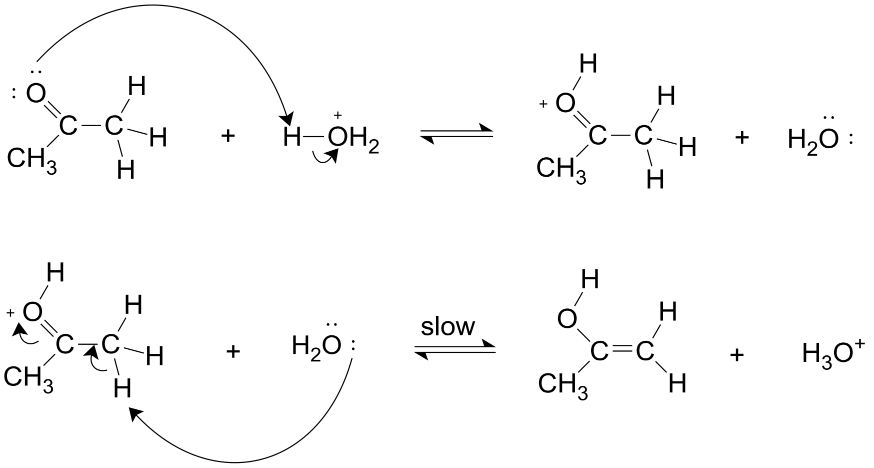


Step 2:



Compound **A**

(i) Complete the mechanism by drawing in the curly arrows in the mechanism above. [2]

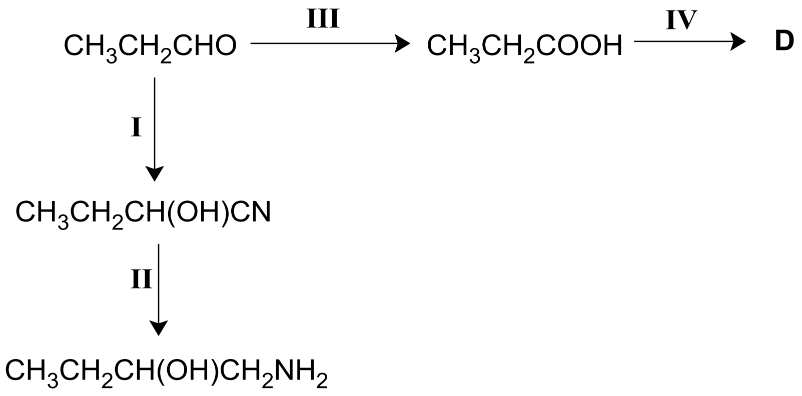


(ii) State the IUPAC name for Compound **A**.

.... [1]

propen-2-ol OR 2-hydroxypropene

(c) A reaction scheme involving propanal is shown below.



(i) State the reagents and conditions for steps **I** and **III** in the reaction scheme above.

Step	**Reagents and Conditions**
I	HCN with trace NaCN, 10 - 20°C
III	$K_2Cr_2O_7$, H_2SO_4(aq), heat under reflux/ $KMnO_4$, H_2SO_4(aq),heat under reflux

[2]

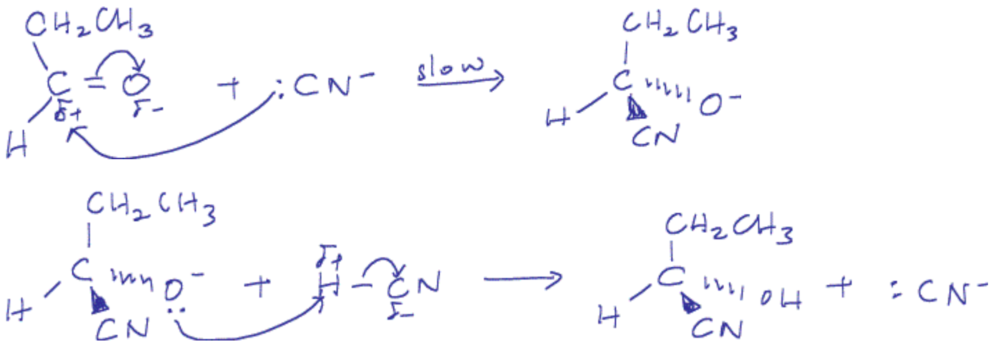
(ii) Describe the mechanism of the reaction for Step **I**, showing curly arrows, charges, dipoles and any relevant lone pairs.

[3]

Nucleophilic addition

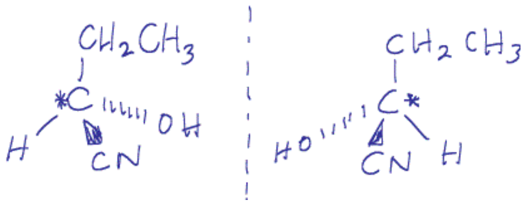
$$HCN \rightleftharpoons H^+ + CN^-$$

$NaCN \rightarrow Na^+ + CN^-$ OR $NaOH + HCN \rightarrow NaCN + OH^-$



(iii) $CH_3CH_2CH(OH)CN$ contains a *chiral centre* and it consists of a racemic mixture of two isomers.

Draw structures of the two isomers.



[1]

(iv) Draw the structural formulae of the product formed when $CH_3CH_2CH(OH)CH_2NH_2$ reacts with ethanoic acid at room temperature. State the type of reaction.

……………………………………………………………………………………………….[2]

$CH_3CH_2CH(OH)CH_2NH_3^+$ CH_3COO^-. Neutralisation.

Compound **D** has a relative molecular mass of 136.9 and the following percentage composition by mass, C, 26.30; H, 3.65; O, 11.69; **X**, 58.36 where **X** is a halogen. When aqueous silver nitrate is added to compound **D**, a cream precipitate is observed.

2 moles of compound **D** react with 1 mole of $CH_3CH_2CH(OH)CH_2NH_2$ at room temperature to form a neutral product **E** ($C_{10}H_{19}NO_3$).

(v) State the identity of the cream precipitate. Hence, deduce the molecular and structural formula of compound **D**.

Cream precipitate: …………………….

Molecular formula of **D**: ………………………………………..

Structural formula of **D**:

[4]

Cream precipitate: AgBr

	C	H	O	Br
Mass/g	26.30	3.65	11.69	58.36
A_r	12.0	1.0	16.0	79.9
Amount/mol	2.19	3.65	0.73	0.73
Mol ratio	3	5	1	1

Empirical formula of **D** is C_3H_5OBr

$n(3x12.0 + 5x1.0 + 16.0 + 79.9) = 136.9$

$n = 1$

Molecular formula of **D** is C_3H_5OBr

D: CH_3CH_2COBr

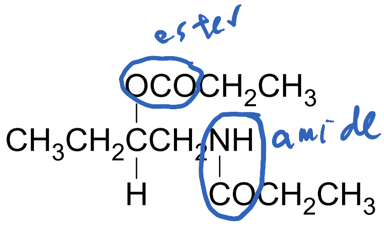
(vi) State the reagents and conditions for step **IV** in the reaction scheme above.

PBr_3, room temperature;……………………………………………………………………… [1]

vii) Draw the structure of the neutral product **E** formed. Hence, circle and name the functional groups present.

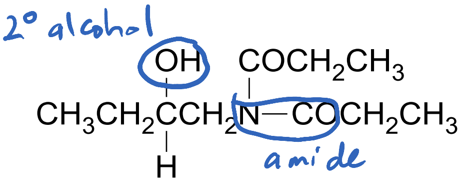
[3]

[Total: 24]



$$\mathrm{CH_3CH_2\overset{\displaystyle OCOCH_2CH_3}{\underset{\displaystyle H}{C}}CH_2\underset{\displaystyle COCH_2CH_3}{NH}}$$

OR



$$\mathrm{CH_3CH_2\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}CH_2\overset{\displaystyle COCH_2CH_3}{N}-COCH_2CH_3}$$

4 **(a)** Ethanol, CH_3CH_2OH, is one of the fuels that are being considered as an alternative to gasoline. Ethanol can be produced from fermentation of biomass such as corn and sugarcane. During fermentation, glucose, $C_6H_{12}O_6$, in the corn is converted into ethanol and carbon dioxide.

Gasoline is made up of a mixture of hydrocarbons of varying carbon chain lengths (C_4 to C_{12}). Pollutants from combustion of gasoline include carbon monoxide, sulfur oxides and nitrogen oxides. The increase in carbon dioxide in the atmosphere due to the combustion of fuels has been linked to global warming.

The table below shows the key properties of gasoline and ethanol.

Property	**Gasoline**	**Ethanol**
Chemical formula	C_xH_y	CH_3CH_2OH
Carbon weight % Hydrogen weight % Oxygen weight %	85 – 88 12 – 15 0	52.2 13.1 34.7
Boiling point/°C	26.7 – 225.0	77.8
Solubility in water	Negligible	complete
kg of CO_2 produced per kg of fuel	~ 3	x

(i) Write an equation for the production of ethanol from fermentation of glucose in biomass.

.... [1]

$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$

(ii) Calculate the mass of carbon dioxide, x (kg), produced from the combustion of 1 kg of ethanol.

[2]

$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

Amount of CH_3CH_2OH in 1 kg = $\frac{1000}{46.0}$ = 21.74 mol

Mass of CO_2 produced = 21.74 x 2 x 44.0 = 1913 g = 1.91 kg

x = 1.91 kg of CO_2 produced/kg ethanol

(iii) Explain the difference in the solubility of gasoline and ethanol in water.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

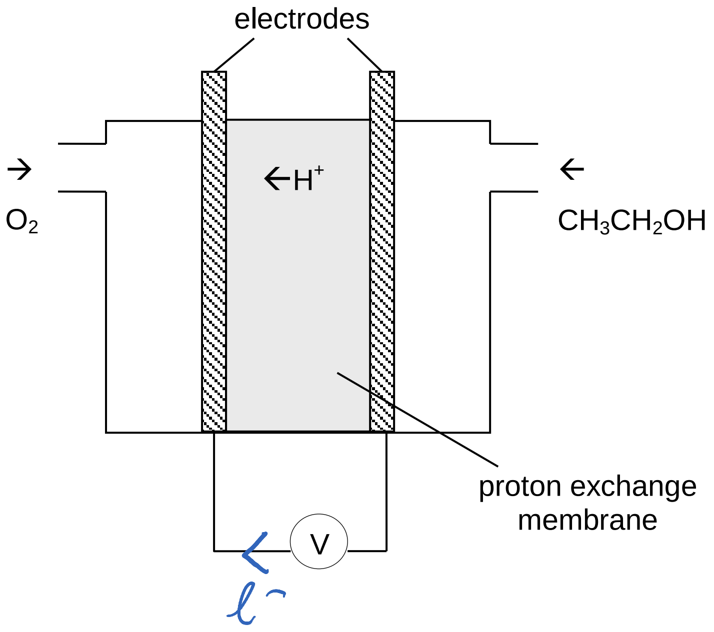
…………………………………………………………………………………………………… [2]

The energy evolved from the formation of hydrogen bonds between water and ethanol molecules is sufficient to overcome the hydrogen bonds between water molecules and ethanol molecules respectively, thus ethanol is completely soluble in water.

The energy evolved from the formation of td-id attractions between water and gasoline is insufficient to overcome the hydrogen between water molecules, thus gasoline is insoluble in water.

(b) Ethanol is also used in fuel cells to generate electrical energy from chemical energy to power electric vehicles. Direct-ethanol fuel cells or DEFCs are a category of fuel cells where ethanol is fed directly into the fuel cell. In the DEFC, ethanol is pumped into one of the electrodes in the presence of water on a catalyst layer to form carbon dioxide. Protons are transported across the proton exchange membrane to the other electrode where they react with oxygen to produce water. Electrons are transported through an external circuit to power the connected devices.

The following diagram shows a typical DEFC system with a proton exchange membrane between the electrodes.



A typical DEFC is capable of producing a voltage of 0.80 V and can be 60% efficient. It produces an average current of 2 A per day.

(i) Write the two ion-electron half equations for the reactions that take place at each electrode.

Anode: ……………………………………………………………………………………………

Cathode: ……………………………………………………………………………………………[2]

Anode: $CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

(ii) In the schematic diagram above show the direction of electron flow. [1]

From anode to cathode

(iii) By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the CO_2/CH_3CH_2OH electrode reaction.

[1]

$$E^\ominus_{cell} = E^\ominus_{cathode}(O_2/H_2O) - E^\ominus_{anode}(CO_2/CH_3OH)$$
$$0.80 = 1.23 - E^\ominus_{anode}(CO_2/CH_3CH_2OH)$$
$$E^\ominus_{anode}(CO_2/CH_3OH) = 1.23 – 0.80 = +0.43V$$

(iv) Calculate the mass of ethanol required to run one unit of DEFC for 30 days.

[3]

Total charge generated per day $= I \times t \times \frac{100}{60}$
$= 2 \times (24 \times 60 \times 60) \times \frac{100}{60}$
$= 288\,000$ C

Amount of electron transferred $= \frac{Q}{F} = \frac{288000}{96500} = 2.984$ mol

1 mol ethanol $\equiv$ 12 mol of e^-
Amount of ethanol required $= \frac{2.984}{12} = 0.2487$ mol
Mass of ethanol required per day $= 0.2487 \times 46.0 = 11.4$ g
Mass of ethanol required for 30 days $= 11.4 \times 30 = 343$ g

(v) Based on the physical properties of ethanol, suggest an advantage of the DEFC over a hydrogen-oxygen fuel cell.

…………………………………………………………………………………………………… [1]

Ethanol is a liquid at room temperature and can be handled and stored more easily than hydrogen gas;

(c) The lead–acid accumulator is a storage battery used in cars because it can be recharged. It consists of a series of cells containing lead plate anodes, lead dioxide plate cathodes and an electrolyte of 6 mol dm^{-3} sulfuric acid.

The two half equations for this cell are

$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$ $E^\ominus = -0.13$ V

$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$ $E^\ominus = +1.47$ V

(i) Write the overall equation for the reaction during charging.

.... [1]

$2Pb^{2+}(aq) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 4H^+(aq)$

(ii) State **one** disadvantage of the lead-acid accumulator battery.

.... [1]

[Total: 15]

It is large and heavy due to the lead, produces low power for its mass OR

Lead is toxic OR

$PbSO_4$ deposits on the electrodes in a finely divided form during discharge. The small grains of $PbSO_4$ may fall from the electrodes. If too much $PbSO_4$ is lost, the cell cannot be recharged and results in a loss of capacity.

5 **(a)** The water-gas shift reaction involves the reaction of carbon monoxide and steam to form carbon dioxide and hydrogen. The mixture of carbon monoxide and hydrogen is known as water gas. This reaction is a cost effective method to produce hydrogen gas.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H < 0$$

In an experiment a mixture of CO, H_2O, CO_2 and H_2 was allowed to reach equilibrium in a 0.5 dm^3 vessel at 1200 K. The equilibrium mixture was found to contain 0.527 mol of CO, 0.527 mol of H_2O, 0.500 mol of CO_2 and 0.500 mol of H_2.

(i) Write the expression for K_c.

.... [1]

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

(ii) Calculate the value for K_c at 1200 K.

[1]

$K_c = \frac{[0.500/0.5]^2}{[0.527/0.5]^2} = 0.900$

(iii) Sufficient CO and H_2O were added to the vessel containing the equilibrium mixture to momentarily raise the concentrations of both gases to 3.00 mol dm^{-3}. The vessel was maintained at a temperature of 1200 K and the system was allowed to reach equilibrium.

Determine the amount of each gas in the reaction mixture after equilibrium was achieved.

[3]

	CO(g)	H_2O(g)	CO_2	H_2
Initial/mol	3.00 x 0.5	3.00 x 0.5	0.500	0.500
Change/mol	$-x$	$-x$	$+x$	$+x$
Equilibrium/mol	$1.50-x$	$1.50-x$	$0.500+x$	$0.500+x$

$K_c = 0.900 = \frac{(0.500+x)^2}{(1.50-x)^2}$

$x = 0.4737$ mol

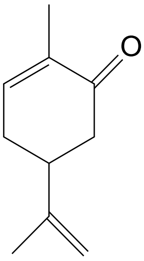
	CO(g)	H_2O(g)	CO_2	H_2
Equilibrium/mol	1.03	1.03	0.974	0.974

(iv) State the effect on the value of K_c if the temperature of the system was decreased to 600 K. Explain your answer.

………………………………………………………………………………………………… [2]

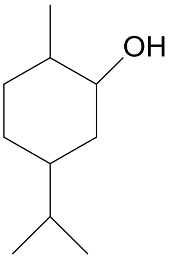
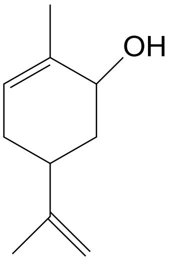
Value of K_c increases. As the forward reaction is exothermic, by LCP as the T is decreased the forward reaction is favoured to absorb heat, equilibrium position shifts to the right (k_f increases more than k_b).

(b) Carvone is an organic compound found in spearmint oil.



Carvone

(i) Draw the structures of the organic product formed when carvone reacts with each of the following reducing agents.

I. H_2 with Ni catalyst at 150 °C 
II. $LiAlH_4$ in dry ether 

[2]

[Turn over

(ii) Suggest a chemical test that could be used to distinguish the two organic products formed in **(b)(i)**. You should state the reagents and conditions as well as observations for each compound.

Test: ……………………………………………………………………………………………

Observations:

I: ……………………………………………………………………………………………

II: ……………………………………………………………………………………………[2]

Test: Br_2(aq) or Br_2 in CCl_4 in absence of UV

Observations:
I: brown aq bromine remains.

B: brown aq bromine turns colourless.

[Total: 11]