Candidate forename		Candidate surname	
Centre number		Candidate number	

OXFORD CAMBRIDGE AND RSA EXAMINATIONS
A2 GCE
F335
CHEMISTRY B (SALTERS)
Chemistry by Design

WEDNESDAY 13 JUNE 2012: Morning
DURATION: 2 hours
plus your additional time allowance

MODIFIED ENLARGED

Candidates answer on the Question Paper.
A calculator may be used for this paper.

OCR SUPPLIED MATERIALS:

Data Sheet for Chemistry B (Salters) (inserted)

OTHER MATERIALS REQUIRED:

Scientific calculator

READ INSTRUCTIONS OVERLEAF

INSTRUCTIONS TO CANDIDATES

- **The Insert will be found in the centre of this document.**

- **Write your name, centre number and candidate number in the boxes on the first page. Please write clearly and in capital letters.**

- **Use black ink. HB pencil may be used for graphs and diagrams only.**

- **Answer <u>ALL</u> the questions.**

- **Read each question carefully. Make sure you know what you have to do before starting your answer.**

- **Write your answer to each question in the space provided. If additional space is required, you should use the lined page at the end of this booklet. The question number(s) must be clearly shown.**

INFORMATION FOR CANDIDATES

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

- Where you see this icon you will be awarded marks for the quality of written communication in your answer.

  This means for example you should:

  - ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear;

  - organise information clearly and coherently, using specialist vocabulary when appropriate.

- You may use a scientific calculator.

- A copy of the Data Sheet for Chemistry B (Salters) is provided as an insert with this question paper.

- You are advised to show all the steps in any calculations.

- The total number of marks for this paper is <u>120</u>.

Answer ALL the questions.

1   Nitrogen monoxide is formed when nitrogen and oxygen from the air combine.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$ **EQUATION 1.1**
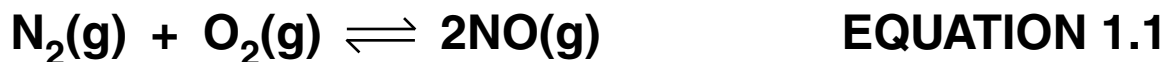
Under normal atmospheric conditions, a further reaction occurs in the air to form NO_2.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$ **EQUATION 1.2**
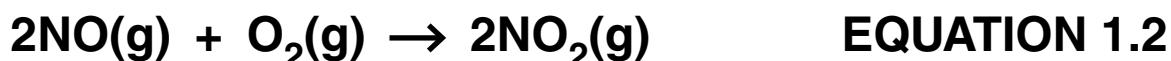
These reactions have both advantages and disadvantages for the environment.

(a) (i) Give the oxidation states of nitrogen in:

N_2 _____

NO _____   [2]

(ii) Give the systematic name of NO_2.

_____ [1]

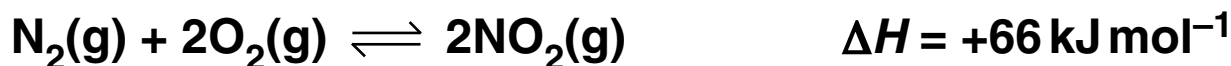(b) Describe what you would expect to SEE when the reaction in EQUATION 1.2 occurs.

_____ [1]

(c) Give ONE advantage and ONE disadvantage to the environment of the formation of NO_2 from N_2 in an industrial process.

advantage _____

_____

disadvantage _____

_____ **[2]**

5

(d) The overall equation for the formation of $NO_2(g)$ is given below.

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +66\,kJ\,mol^{-1}$$

EQUATION 1.3

(i) At room temperature and pressure:

- Show that the concentration of oxygen in air is $8.3 \times 10^{-3}\,mol\,dm^{-3}$.

- Calculate the concentration of nitrogen in air.

Assume that air consists of nitrogen and oxygen in the mole ratio 4.0 : 1.0 and that one mole of gas occupies $24\,dm^3$ at room temperature and pressure.

$[N_2]$ = _____ $mol\,dm^{-3}$ **[2]**

(ii) **Write the expression for the equilibrium constant, K_c, for the reaction shown in EQUATION 1.3.**
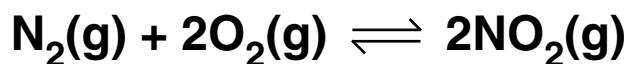
$$K_c =$$

[1]

(iii) **Use the concentrations of N_2 and O_2 from (i) to work out the equilibrium concentration of NO_2 in air at room temperature and pressure.**

$K_c = 4 \times 10^{-19}\,dm^3\,mol^{-1}$ at room temperature for **EQUATION 1.3.**

Give your answer to an APPROPRIATE number of significant figures.

$[NO_2] =$ _____ $mol\,dm^{-3}$ [3]

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +66\,kJ\,mol^{-1}$$

EQUATION 1.3

(iv) **How would the value of the EQUILIBRIUM CONSTANT for the equilibrium shown in EQUATION 1.3 change, if at all, if the temperature were raised to 1500 K?**

Give reasons for your answer.

_____

_____

_____

_____

_____ [3]

(v) **The pressure was increased to 100 atmospheres, keeping the temperature at room temperature.**

What effect would this have on the EQUILIBRIUM POSITION for EQUATION 1.3?

Give a reason for your answer.

_____

_____

_____ [2]

(e) NO_2 can be oxidised to form nitric(V) acid, HNO_3.

Nitric(V) acid is a strong acid in aqueous solution.

(i) Write an equation for the ionisation of nitric(V) acid in water.

[2]

(ii) Calculate the pH of a 0.015 mol dm^{-3} solution of nitric(V) acid.

pH = _____ [2]

(f) When concentrated nitric(V) acid reacts with concentrated sulfuric(VI) acid, each sulfuric(VI) acid molecule donates ONE proton to a nitric(V) acid molecule. The ion formed from nitric(V) acid breaks down to form water and another positive ion.

(i) Suggest an equation for the OVERALL reaction of sulfuric(VI) acid with nitric(V) acid.

$$\longrightarrow$$

[2]

(ii) Suggest the NAME of the conjugate base of sulfuric(VI) acid that is formed in the overall reaction in (i).
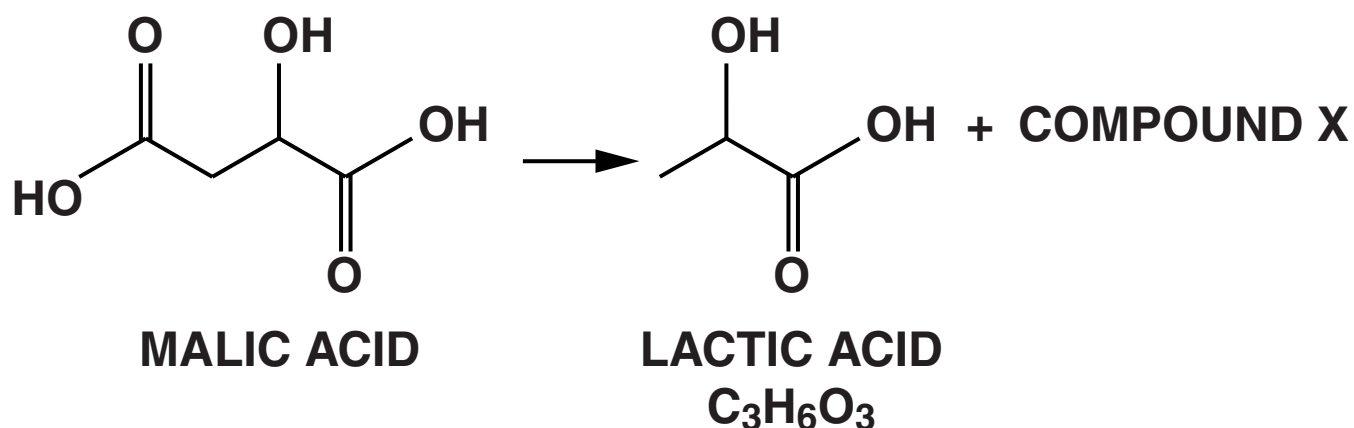
_____ [1]

(iii) Give a laboratory use for the solution formed in the reaction described in (i).

_____ [1]

[Total: 25]

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2 The 'malolactic fermentation' is a reaction that occurs when wine is matured before being bottled. The process results in the wine tasting smoother and less acidic.

MALIC ACID → LACTIC ACID $C_3H_6O_3$ + COMPOUND X

(a) (i) Name compound X.

_____ [1]

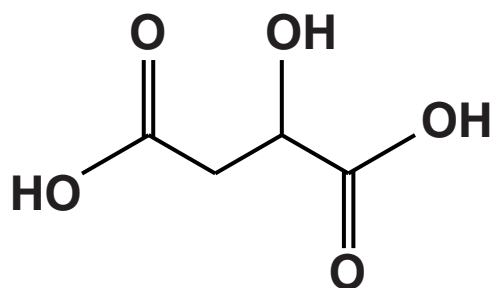(ii) Give the systematic name for lactic acid.

_____ [1]

(b) The lactic acid molecule has ONE chiral centre.

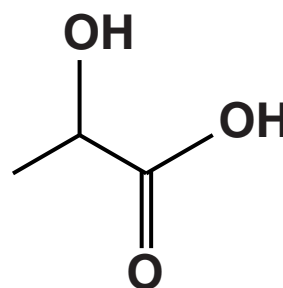   **(i)** Draw diagrams that show the two stereoisomers of lactic acid and how they are related.

    [2]

    (ii) Give the number of chiral centres in a MALIC ACID molecule.

    _____ **[1]**

O   OH

HO   ‖ | OH

O

MALIC ACID

OH

OH

O

LACTIC ACID

(c) The following data are available for the two acids.

	pK_a
malic acid	3.40 and 5.13
lactic acid	3.86

(i) Suggest why two pK_a values are given for malic acid.

_____

_____ [1]

(ii) Use the pK_a data to suggest why lactic acid produces a smoother, less acidic wine than malic acid.

_____

_____ [2]

(d) (i) Write an equation to represent the equilibrium that occurs when lactic acid dissolves in water.

Represent lactic acid as $C_3H_6O_3$.

[1]

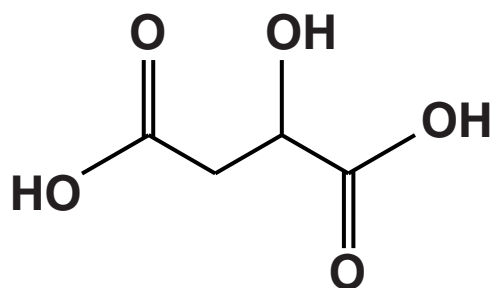(ii) The pK_a for lactic acid is 3.86. Show that the value of K_a is 1.4×10^{-4} mol dm^{-3}.

[1]

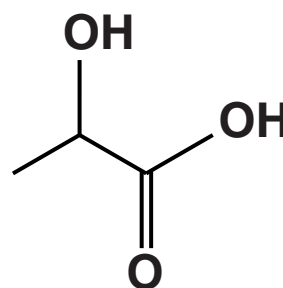(iii) Calculate the pH of a 0.10 mol dm^{-3} solution of lactic acid.

pH = _____ [2]

(iv) A wine has a pH of 3.0.

Calculate the ratio [salt]/[acid] for lactic acid at this pH. ($K_a = 1.4 \times 10^{-4}$ mol dm^{-3})

ratio [salt]/[acid] = _____ [2]

O OH

OH

HO

O

MALIC ACID

OH

OH

O

LACTIC ACID

(e) **When reacted with sulfuric acid, LACTIC ACID, $C_3H_6O_3$, loses water to form a compound with the molecular formula $C_6H_8O_4$. The infrared spectrum of this compound shows an absorption at 1735–1750 cm^{-1} and no absorptions above 3000 cm^{-1}.**

Suggest a structure for this compound, giving your reasoning.

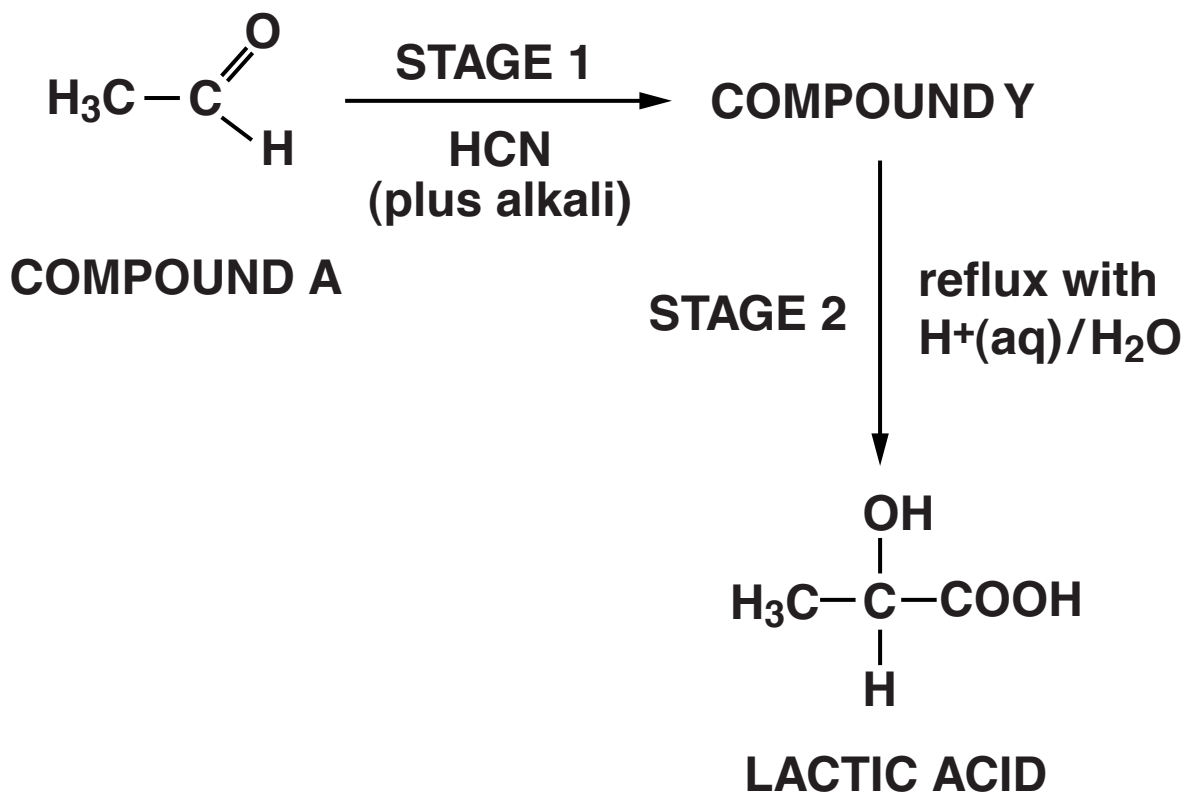_____

_____

_____

_____

_____ **[3]**

16

(f) **When MALIC ACID is heated, it loses water to form an acid anhydride with the molecular formula $C_4H_2O_3$.**

Suggest a structure for this compound.

[2]

(g) You may need to refer to the list of reactions in the Data Sheet in answering this part.

Lactic acid can be made in the laboratory using the following two-stage synthesis.

H_3C-C (with $=O$ and H attached)

STAGE 1

HCN (plus alkali)

COMPOUND A

→ **COMPOUND Y**

STAGE 2 — reflux with $H^+(aq)/H_2O$

$H_3C-C-COOH$ (with OH above and H below the central C)

LACTIC ACID

(i) Name compound A.

_____ [1]

(ii) Draw the structure of compound Y.

[1]

(iii) Underline TWO words in the following list that describe the mechanism of the reaction in STAGE 1.

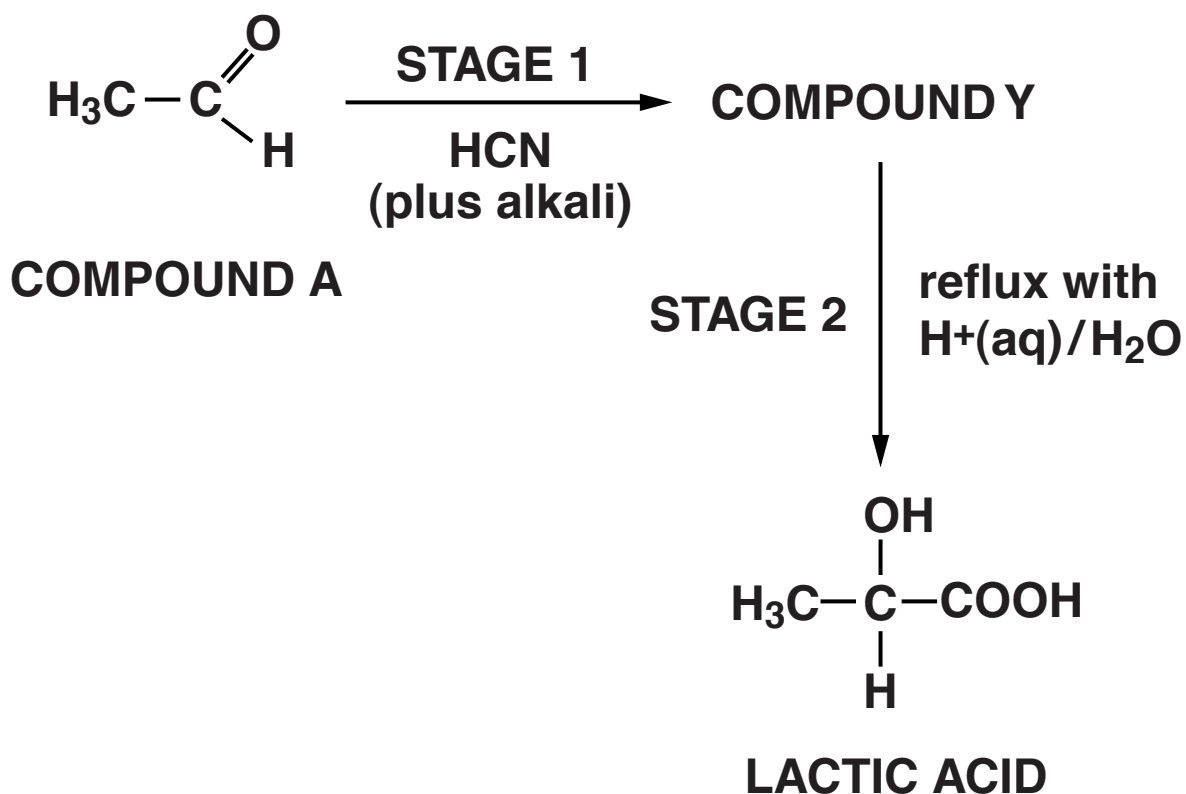ADDITION   ELECTROPHILIC   ELIMINATION

NUCLEOPHILIC   RADICAL   SUBSTITUTION

[2]

(iv) Suggest the other product of STAGE 2, apart from lactic acid.

_____ [2]

19

$$H_3C-C\overset{O}{\underset{H}{\big\langle}}$$

STAGE 1

HCN
(plus alkali)

→ **COMPOUND Y**

COMPOUND A

STAGE 2 | **reflux with**
H+(aq)/H₂O

$$H_3C-\overset{OH}{\underset{H}{\overset{|}{C}}}-COOH$$

LACTIC ACID

(h) **A student suggests that a test to distinguish between compound A and lactic acid would be to heat a sample of each with acidified potassium dichromate(VI).**

(i) Describe the colour change that compound A would give with this reagent and give the formula of the organic product.

colour change from _____

to _____

organic product

[2]

(ii) Explain why the test will NOT distinguish lactic acid from compound A.

_____

_____

_____

_____ [2]

[Total: 29]

3 In 2006, a 'green synthesis' method was developed for converting 'glycerin' into 'propylene glycol'. The new process involved the use of a transition metal catalyst.

Propylene glycol has many uses, including as an antifreeze.

The overall reaction is shown opposite.

(a) Give the systematic name for propylene glycol.

_____ [1]

(b) Glycerin is a co-product in the manufacture of biodiesel from vegetable oil.

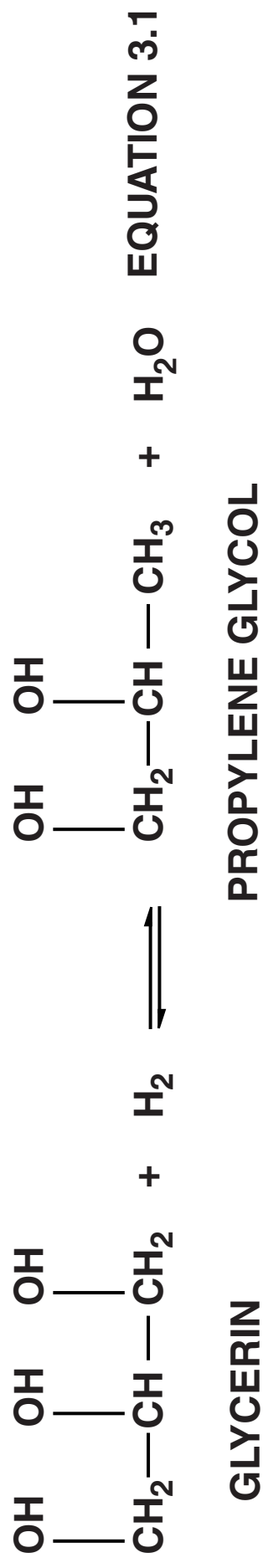(i) Explain what is meant by the term co-product, distinguishing it from by-product.

_____

_____

_____ [2]

(ii) Name the TYPE of reaction by which glycerin can be obtained directly from vegetable oil.

_____ [1]

(c) Suggest ONE reason why the synthesis in EQUATION 3.1 is described as 'green'.

_____

_____ [1]

$$\underset{\text{GLYCERIN}}{\underset{|}{\overset{|}{CH_2}}\text{—}\underset{|}{\overset{|}{CH}}\text{—}\underset{|}{\overset{|}{CH_2}}} \quad + \quad H_2 \quad \rightleftharpoons \quad \underset{\text{PROPYLENE GLYCOL}}{\underset{|}{\overset{|}{CH_2}}\text{—}\underset{|}{\overset{|}{CH}}\text{—}CH_3} \quad + \quad H_2O \qquad \text{EQUATION 3.1}$$

CH₂ has OH, CH has OH, CH₂ has OH (GLYCERIN); CH₂ has OH, CH has OH (PROPYLENE GLYCOL)

(d) The reaction in EQUATION 3.1 was carried out with the reactants and products in the gas phase under high pressure.

Suggest and explain a reason for the use of a high pressure in this reaction.

_____

_____

_____

_____ [2]

**(e)** A possible mechanism for the reaction in EQUATION 3.1 is shown opposite. The mechanism is incomplete.

   (i) Draw another 'curly arrow' on the glycerin molecule to complete the electron movements involved in STEP 1. [1]

   (ii) STEP 1 involves the dehydration of glycerin. Give another name for this TYPE of reaction.
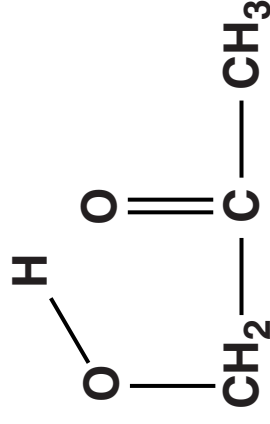
   _____ [1]

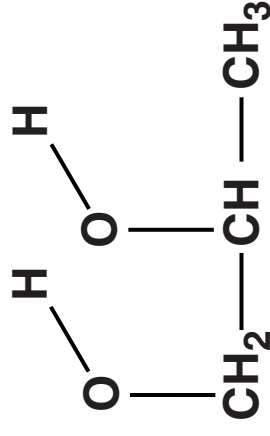   **(iii)** Name the functional groups in acetol.

   _____ [2]

GLYCERIN

$$CH_2OH - CHOH - CH_2OH$$

STEP 1
−H₂O

'ACETOL'

$$HO - CH_2 - C(=O) - CH_3$$
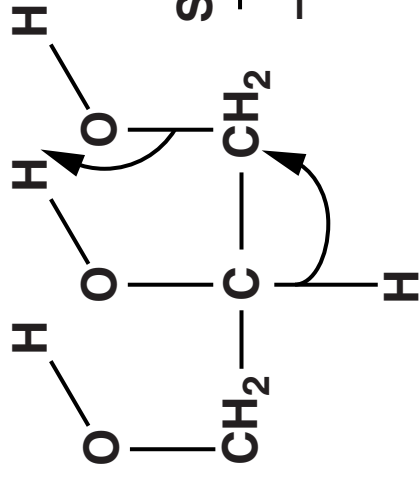
STEP 2
+H₂

PROPYLENE GLYCOL

$$HO - CH_2 - CH(OH) - CH_3$$

25

(iv) When the reaction is carried out under the same conditions but in the absence of hydrogen, acetol is formed as the end product.

- **Describe AND EXPLAIN how acetol can be distinguished from glycerin using BOTH infrared and NMR spectroscopy.**

- **Describe AND EXPLAIN the splitting (if any) of each of the peaks in the NMR spectrum of ACETOL.**

In your answer you should indicate how the spectroscopic peaks you predict are linked to the structure of the compound.

_____

_____

_____

_____

_____

_____

_____

_____ **[6]**

(f) **The catalyst for the reaction in EQUATION 3.1 is copper(II) chromite, $Cu_2Cr_2O_5$.**

 (i) **Give the oxidation state of chromium in this compound.**

 _____ [1]

 (ii) **Give with a reason, the effect, if any, of the presence of the catalyst on the equilibrium constant of the reaction in EQUATION 3.1.**

 _____

 _____

 _____ [2]

(g) **In a small-scale experiment, 15 g of glycerin, $C_3H_8O_3$, were treated with excess hydrogen.**

 9.0 g of propylene glycol, $C_3H_8O_2$, were formed.

 Calculate the percentage yield of the reaction.

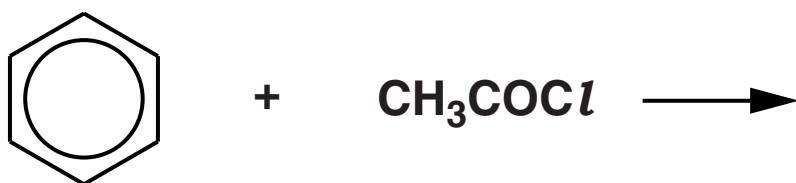 **% yield = _____ % [2]**

[Total: 22]

4   Ionic liquids are now often used as solvents for Friedel–Crafts acylation reactions.

These reactions now generate much less toxic waste than the old process.

(a) (i) Complete the equation for a Friedel–Crafts acylation of benzene.

Give the FULL structural formula of the group attached to the benzene ring.

 +   CH$_3$COCl $\longrightarrow$

[2]

(ii) Give the systematic name of CH$_3$COCl.

_____ [1]

(iii) Give TWO words that describe the TYPE of mechanism of the reaction described in (i).

_____ [2]

(b) In the 'old' process for Friedel–Crafts reactions, aluminium chloride is used as the catalyst. The products of these reactions cannot be recycled because they could easily cause contamination of the environment.

Suggest ONE way in which the products of the old process might contaminate the environment.

_____

_____ [1]

(c) Ionic liquids have large cations and anions, such as those shown in the table below.

(i) Complete the table below for the two ions.

ION	NUMBER OF ELECTRON PAIRS AROUND CENTRAL ATOM	SHAPE OF ION	BOND ANGLE AROUND CENTRAL ATOM/°
$(C_2H_5)_4N^+$			
PF_6^-			

[4]

(ii) Suggest why salts consisting of large cations and large anions have low melting points.

_____

_____

_____ **[2]**

(d) Friedel–Crafts reactions can be used to identify the presence of an aromatic ring in an organic compound. Benzene, for example, reacts with **COMPOUND Z** and aluminium chloride to form triphenylmethane. Many triphenylmethane derivatives are coloured.
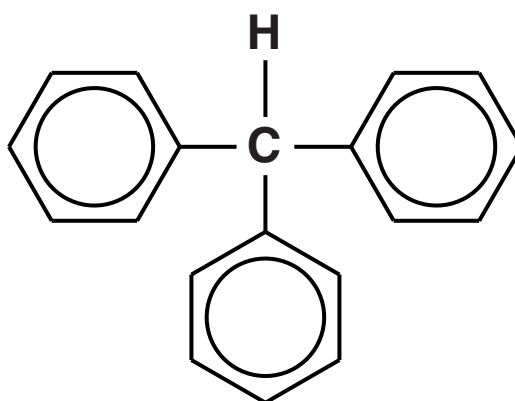
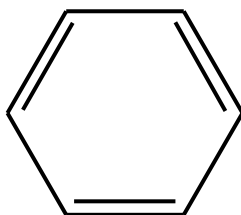**TRIPHENYLMETHANE**

(i) Suggest the formula of compound Z.

[1]

(ii) Explain why dyes absorb visible light (and thus appear coloured) whereas benzene absorbs ultraviolet light and appears colourless.

In your answer you should show how the points you make link together.

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____ **[6]**

(e) The Kekulé model of benzene shown below does not explain the bromination reaction of benzene.

- **Predict a product of the bromination of the Kekulé structure.**

- **Compare this product with the actual product formed when bromine reacts with benzene (in the presence of an iron catalyst).**

- **Explain why benzene reacts as it does.**

In your answer you should use appropriate technical terms spelled correctly.

_____

_____

_____

_____

_____

_____

_____ **[5]**

[Total: 24]

5   Zinc chloride, $ZnCl_2$, is used as a 'flux' for soldering as it removes the oxide coating of the metal being soldered, exposing the bare metal surface.

(a) Complete the electron configuration for a zinc atom.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

[1]

(b) Zinc forms exclusively 2+ ions. Its third ionisation enthalpy is much higher than the first and second ionisation enthalpies.

(i) Write the equation corresponding to the third ionisation enthalpy of zinc.

Show state symbols.

[1]

(ii) Suggest, in terms of electron configurations, why zinc forms only 2+ ions.

_____

_____ [1]

(iii) Give the formula of zinc sulfate(VI).

_____ [1]

(c) When hydrated zinc chloride is heated, HC*l* is formed and this helps the zinc chloride to function as a flux.

Hydrated zinc chloride has the formula $ZnCl_2 \cdot 2H_2O$ where two moles of water are included in the lattice with one mole of $ZnCl_2$.

Suggest an equation for the decomposition of one mole of $ZnCl_2 \cdot 2H_2O$ to give one mole of HC*l*.

[1]

(d) Anhydrous zinc chloride is very soluble in water. An energy level diagram for the dissolving process is shown.

enthalpy

$Zn^{2+}(g) + 2Cl^-(g)$

−2734 kJ mol^{-1}

$ZnCl_2(s)$

$ZnCl_2(aq)$
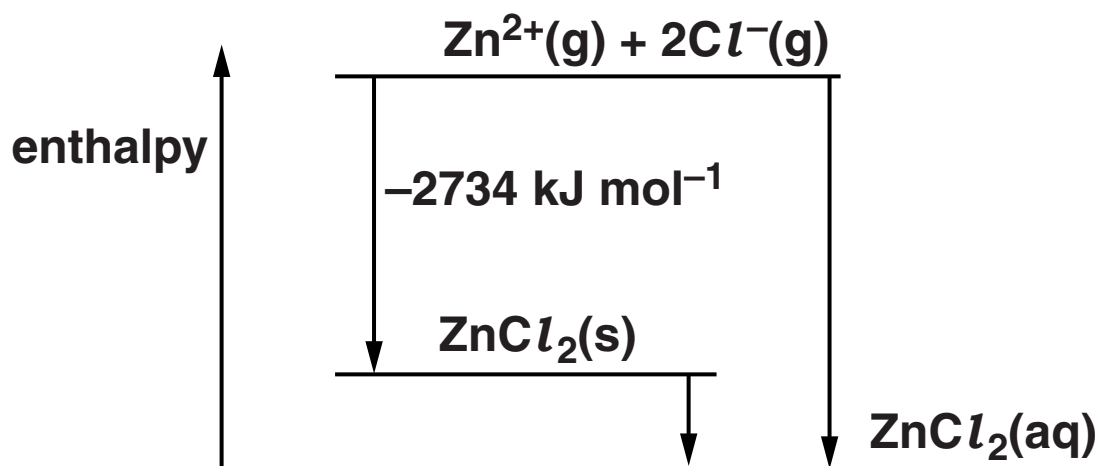
(i) What name is given to the enthalpy change which has the value −2734 kJ mol^{-1}?

_____ [1]

(ii) **The enthalpy changes of hydration of the ions are:**

Zn^{2+} **−2046 kJ mol^{-1}**
Cl^- **−363 kJ mol^{-1}**
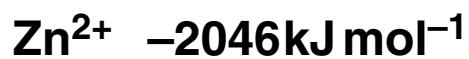
Calculate a value for the enthalpy change of solution, ΔH_{soln}, of $ZnCl_2$.

ΔH_{soln} $ZnCl_2$ = _____ kJ mol^{-1} [3]

(iii) **List the bonds that are broken and made when an ionic substance dissolves in water.**

broken _____

_____

made _____

_____ [3]

(e) Many ionic substances dissolve in water with a positive value for ΔS_{sys}.

However, when the salt consists of small highly charged ions (for example, Ca^{2+}), ΔS_{sys} has a negative value.

- Give the meaning of the term *entropy*.
- Suggest why ΔS_{sys} is often positive for dissolving processes but negative for the dissolving of some calcium salts.

_____

_____

_____

_____

_____

_____

_____ [4]

(f) A particular salt has an ENDOTHERMIC enthalpy change of solution.

State how the solubility of this salt would change, if at all, as temperature is increased.

Explain your answer in terms of entropy changes.

_____

_____

_____

_____

_____

_____

_____

_____ **[4]**

[Total: 20]

END OF QUESTION PAPER

ADDITIONAL PAGE

IF ADDITIONAL SPACE IS REQUIRED, YOU SHOULD USE THE LINED PAGE BELOW. THE QUESTION NUMBER(S) MUST BE CLEARLY SHOWN.

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