NATIONAL JUNIOR COLLEGE
PRELIMINARY EXAMINATIONS
Higher 1

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY
Paper 2 Structured Questions

8872/02
17 September 2009

2 hours

READ THE INSTRUCTION FIRST
Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions .

Section B
Answer any **two** questions.

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.

For Examiner's Use	
Section A	
1	
2	
3	
4	
5	
Section B	
B6	
B7	
B8	
Total	

This question paper consists of **13** printed pages (including this page).

Section A

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

1 5.00 g of impure iron solid was dissolved in an excess of sulfuric acid and the resulting solution containing Fe^{2+} was made up to 250 cm^3. 10.0 cm^3 of this solution was titrated against a solution of $KMnO_4$ of concentration 0.01 mol dm^{-3}. It was found that 24.00 cm^3 of $KMnO_4$ was required.

(a) Suggest a reason why an indicator was not required for this titration.

There is a distinct colour change from purple to pale pink /pale orange at end point.

[1]

(b) Write a balanced redox equation for the reaction between Fe^{2+} and MnO_4^-.

$5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

[2]

(c) A student claims that the percentage purity of iron in the sample is 33.5%. Justify if the statement made by the student is true.

No. of moles of MnO_4^- used = $24.00 \times 10^{-3} \times 0.01 = 2.4 \times 10^{-4}$ mol

No. of moles of Fe^{2+} in 10.0 cm^3 = $5 \times 2.4 \times 10^{-4} = 1.2 \times 10^{-3}$ mol

No. of moles in 250 cm^3 = $1.2 \times 10^{-3} \times \dfrac{250}{10} = 0.03$ mol

Mass of Fe in sample = $0.03 \times 55.8 = 1.674$ g

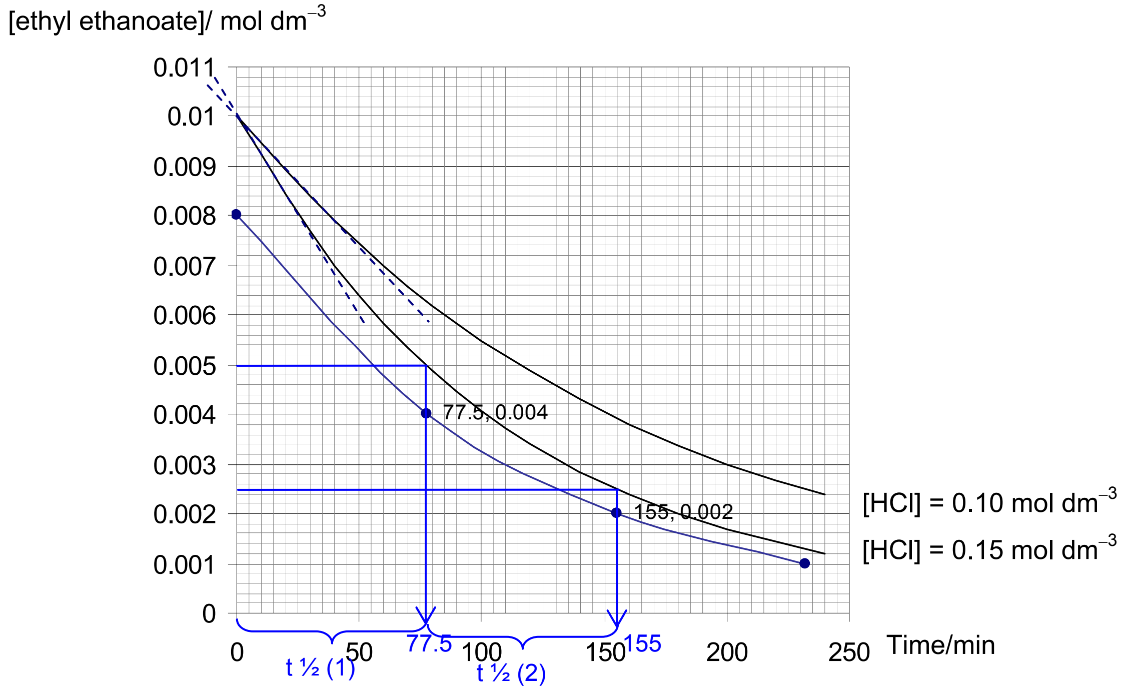
% of Fe in sample = $\dfrac{1.674}{5.00} \times 100 = 33.5\%$

Student's claim is true.

[3]

[Total: 6]

2 The graphs below shows the rate of hydrolysis of ethyl ethanoate, $CH_3COOC_2H_5$ in an acidic medium. The reaction was followed twice with different concentrations of HCl and the following results were obtained.



(a) Using the graphs, determine the order of reaction with respect to both ethylethanoate and HCl.

From the graph of [HCl] = 0.15 mol dm^{-3}, t ½ (1) = t ½ (2) = 77.5 min, thus the reaction is 1st order with respect to ethylethanoate.

To find order with respect to HCl, compare initial rates by drawing tangents at t = 0 when the graphs are the most linear.

For [HCl] = 0.15 mol dm^{-3}, rate = $\dfrac{0.01-0.006}{50-0}$ = 8.00 x 10^{-5} mol dm^{-3} min^{-1}

For [HCl] = 0.10 mol dm^{-3}, rate = $\dfrac{0.01-0.006}{75-0}$ = 5.33 x 10^{-5} mol dm^{-3} min^{-1}

Hence, when [HCl] increase 1.5 x (from 0.10 to 0.15 mol dm^{-3}), rate increases 1.5 times from 5.33 x 10^{-5} to 8.00 x 10^{-5} mol dm^{-3} min^{-1}.

(b) Deduce the rate equation and calculate the value of the rate constant, giving its units.

R = k [HCl][$CH_3COOC_2H_5$]

k = $\dfrac{8 \times 10^{-5}}{(0.01)(0.15)}$ = 0.0533 mol^{-1} min^{-1} dm^{3}

(c) On the same axis above, sketch the graph when the experiment is repeated using 0.008 mol dm^{-3} of ethylethanoate and 0.15 mol dm^{-3} HCl.

[Total: 7]

3 Methanol is a possible alternative to hydrocarbons as a liquid fuel.

(a) Given that the enthalpy of combustion of methanol is –715 kJ mol^{-1}, calculate the mass of methanol that should be burnt in order to boil 1000 cm^3 of water starting from an initial temperature of 20.0 °C. Assume that 50% of the heat obtained from the combustion of methanol is lost to the surroundings and that the specific heat capacity of water is 4.2 J K^{-1} g^{-1}.

$Q = 1000 \times 4.2\,(100 - 20) = 336$ kJ

Heat from combustion of methanol $= 336 \times \frac{100}{50} = 672$ kJ

No. of moles of methanol $= \frac{672}{715} = 0.94$ mol

Mass of methanol $= 0.94 \times (15.0 + 16.0 + 1.0) = 30.1$ g

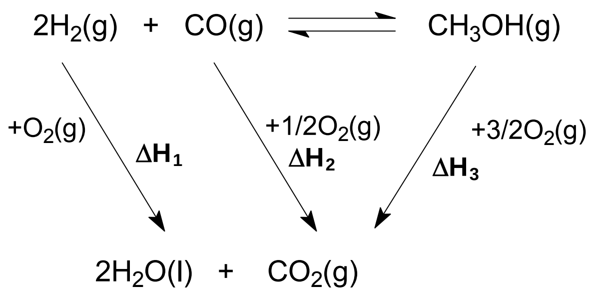
[3]

(b) Methanol can be produced by using a reversible reaction between carbon monoxide and hydrogen.

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

(i) Given the following standard enthalpy change of combustion and energy cycle, apply Hess's Law and calculate the enthalpy change for the production of methanol.

$\Delta H_c^\theta(H_2) = -286$ kJ mol^{-1}
$\Delta H_c^\theta(CO) = -283.3$ kJ mol^{-1}



$$\begin{aligned}\Delta H_{reaction} &= 2\Delta H_1 + \Delta H_2 - \Delta H_3 \\ &= 2(-286) - 283.3 - (-715) \\ &= -140 \text{ kJ mol}^{-1}\end{aligned}$$

[2]

(ii) When 2.00 mol of hydrogen and 1.00 mol of carbon monoxide were mixed and heated to a high temperature in a container of volume 1.50 dm^3, 0.80 mol of methanol was formed at equilibrium.

Calculate a value for the equilibrium constant, K_c, for this reaction at this temperature and give its units.

	$2H_2(g)$ +	$CO(g)$ $\rightleftharpoons$	$CH_3OH(g)$
Initial no. of moles	2.0	1.0	
Change	−2(0.8)	−0.8	+0.8
Final no. of moles	0.4	0.2	0.8
Conc/ mol dm^{-3}	$\frac{0.4}{1.5}$=0.267	$\frac{0.2}{1.5}$=0.133	$\frac{0.8}{1.5}$=0.533

$$K_c = \frac{[CH_3OH]}{[H_2]^2[CO]} = \frac{0.533}{(0.267)^2(0.133)} = 56.2 \text{ mol}^{-2} \text{ dm}^6$$

[3]

(iii) State and explain the effect on the position of equilibrium for the above reaction when:
(I) the pressure is increased.
(II) the temperature is increased.

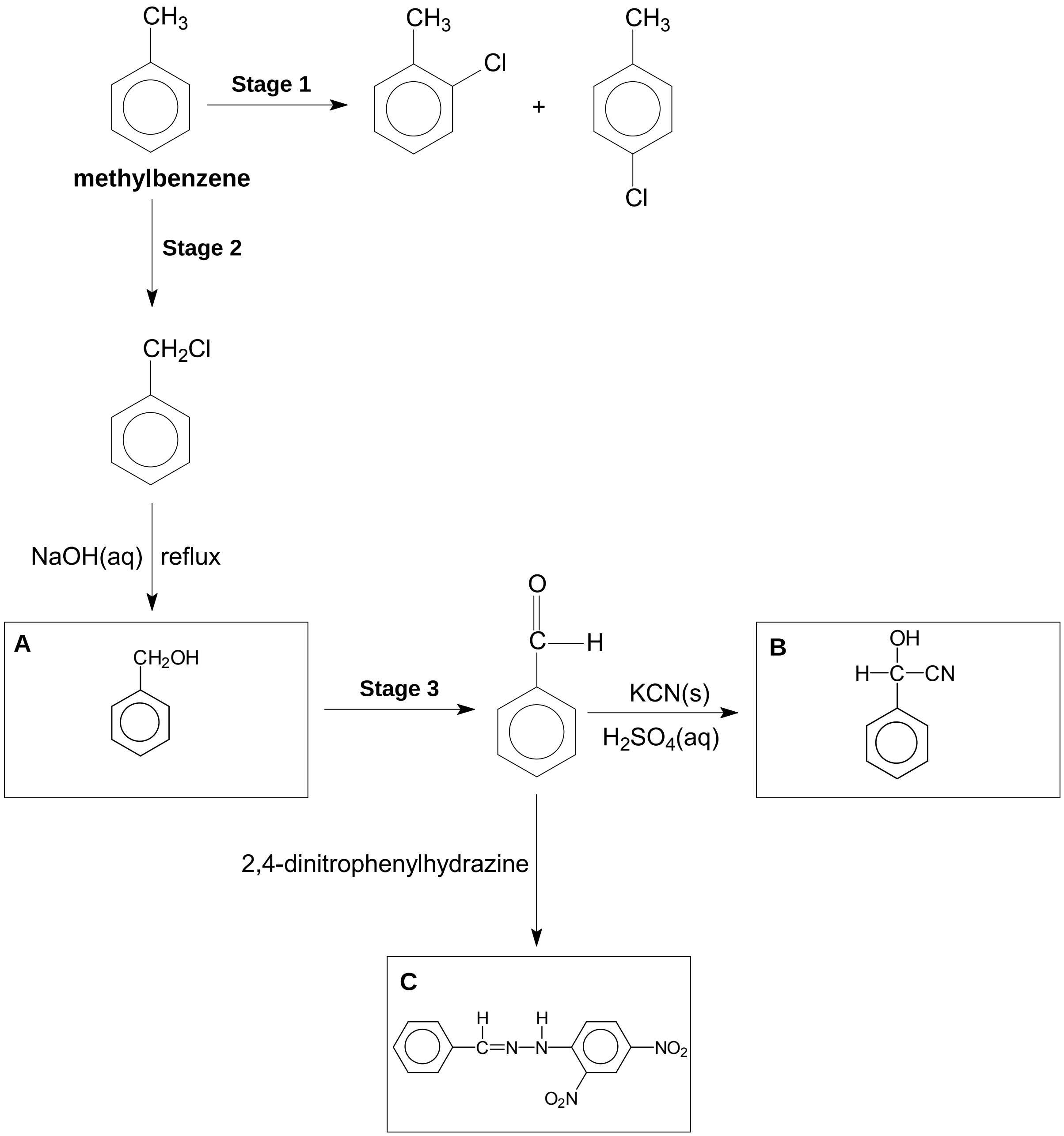
(I): By Le Chatelier's Principle, equilibrium shifts right towards less moles of gas to partially offset the increase in pressure.

(II) By Le Chatelier's Principle, equilibrium shifts left to favour the backward endothermic reaction to use up some of the heat so as to decrease the temperature.

[3]

[Total: 11]

4 The diagram below shows a reaction scheme starting from methylbenzene.



(a) Draw the structures for Compounds **A**–**C** in the boxes provided above.

[3]

(b) Suggest the reagents and conditions required for **Stages 1–3**.

Stage	**Reagents and Conditions**
1	Cl_2. $AlCl_3$
2	Cl_2, uv light (or heat to 300°C)
3	$K_2Cr_2O_7$, H_2SO_4, heat with immediate distillation

[3]

[Total: 6]

5 This question is about the extraction of iron from its ore, Fe_2O_3 (also known as haematite) using two different methods. The first method of extraction is by using the **Blast Furnace**. The second method is through a process known as the **Thermite Reaction**.

Extraction of iron using the Blast Furnace.

Ninety percent of all mining of metallic ores is for the extraction of iron. Industrially, iron is produced starting from iron ores, principally hematite, by reduction with carbon in a blast furnace at temperatures of about 2000 °C.

The following table shows the composition of haematite.

Compound	Percentage Composition
Fe_2O_3	92.0 %
SiO_2	6.0 %
Others	2.0 %

Haematite, carbon in the form of coke, and limestone are continuously fed into the top of the furnace, while a blast of heated air is forced into the furnace at the bottom.

In the blast furnace, the following reactions take place.

Stage 1: The coke reacts with oxygen in the air blast to produce carbon monoxide:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

Stage 2: The carbon monoxide formed then react with the iron ore to form molten iron, becoming carbon dioxide in the process:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

The main impurity in the ore is principally silicon dioxide, SiO_2. It is solid at the temperature of the furnace and the furnace would become blocked if it was not removed.

Limestone, which is principally calcium carbonate, $CaCO_3$ is decomposed in heat to form calcium oxide and carbon dioxide. Silicon dioxide then reacts with calcium oxide to form calcium silicate called slag which is a liquid. Slag flows to the bottom of the furnace where it floats on the liquid iron and is easily removed. The slag is allowed to cool until it becomes a solid and it is used for road construction.

Extraction of iron using the Thermite Reaction

The Thermite reaction is a batch process in which powdered aluminium reacts with iron(III) oxide. The aluminium is able to reduce the iron oxide to elemental iron because aluminium is highly combustible:

$$Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(s) + Al_2O_3(s)$$

The products are aluminium oxide and free elemental iron.

With reference to the extraction of iron using the Blast Furnace:

(a) State with a reason which compound is the reducing agent in **Stage 2.**

CO. It gains oxygen and gets oxidised to CO_2 and reduces Fe_2O_3 to Fe.

[2]

(b) If 100 kg of haematite is continuously fed into the blast furnace, calculate the mass of iron that can be obtained at the end of the reaction.

Mass of Fe_2O_3 in haematite = $\frac{92}{100}$ x 100 = 92 kg

No. of moles of Fe_2O_3 = $\frac{92 \times 10^3}{2(55.8)+3(16.0)}$ = 576.4 mol

No. of moles of Fe = 2 x 576.4 = 1153 mol

Mass of Fe obtained = 1153 x 55.8 = 64.3 kg

[2]

(c) Explain with the aid of an equation, how the impurity silicon dioxide is removed from the blast furnace.

$CaO\ (s) + SiO_2\ (s) \rightarrow CaSiO_3\ (l)$

SiO_2 is an acidic oxide which reacts with the basic oxide CaO in an acid base reaction to form liquid $CaSiO_3$ which can be drained off easily since it floats on liquid iron (as it is less dense).

[2]

(d) With reference to the extraction of iron using the Thermite Reaction:

The table below shows the values for the enthalpy of formation of Fe_2O_3 and Al_2O_3:

Compound	ΔH_f^θ / kJ mol^{-1}
Fe_2O_3	–824.2
Al_2O_3	(1676

Why are the values for the enthalpy of formation of Al and O2 not given in the table?

Al and O2 are elements at standard state thus enthalpy of formation is zero.

[1]

(e) Using the data above, show by means of calculation whether the Thermite Reaction is an endothermic or exothermic reaction.

$$
\begin{aligned}
\Delta H_r^\theta &= \Delta H_f^\theta (Al_2O_3) - \Delta H_f^\theta (Fe_2O_3) \\
&= -1676 - (-824.2) \\
&= -851.8 \text{ kJ mol}^{-1}
\end{aligned}
$$

The Thermite reaction is exothermic.

[2]

(f) Give one advantage of producing iron in the Blast Furnace rather than in the Thermite Reaction.

- Al is a costly raw material for the Thermite reaction.
- On the other hand, the Blast Furnance method produces the byproduct slag ($CaSiO_3$) which could be used for road re-surfacing and this can compensate the costs incurred in the extraction.

[1]

[Total: 10]

Section B

Answer **two** of the following three questions. Answer these questions on separate answer paper.

1 The table below shows some common reagents found in a chemistry laboratory.

HCl		$Ba(OH)_2$
	HNO_3	
NaCl		NH_3

(a) **(i)** Define the terms Bronsted Acid and Bronsted Base.

(ii) From the list of compounds given above, choose one Bronsted Acid and one Bronsted Base.

(iii) Write an equation to show how the Bronsted acid that you have chosen in **(aii)** function as an acid in presence of water. Indicate which species is the acid and base as well as their respective conjugate acid and base in the equation.

[6]

(b) **(i)** Calculate the pH of a 25.0 cm^3 $Ba(OH)_2$ solution of concentration 0.05 mol dm^{-3}.

(ii) What is the final pH when 5 cm^3 of HNO_3 of concentration 0.05 mol dm^{-3} is added to the solution in **(b)(i)**?

[4]

(c) When a weak base NH_3 is partially neutralized by HNO_3, solution **X** is obtained. Adding a small amount of either acid or base to solution **X** does not change the pH of the solution significantly.

(i) State the type of solution formed when NH_3 is partially neutralized by HNO_3.

(ii) Explain with the aid of equations why the pH of the solution **X** does not change significantly upon addition of a small amount of either acid or base.

[3]

(d) When gaseous HCl is added to 3-methylpent-2-ene, $CH_3CH{=}C(CH_3)CH_2CH_3$ a mixture of two products is formed.

(i) State the type of isomerism exhibited by 3-methylpent-2-ene.

(ii) Suggest the structural features present in 3-methylpent-2-ene that enables it to exhibit the type of isomerism suggested in **(d)(i)**.

(iii) Draw the structure of an isomer of 3-methylpent-2-ene which will not exhibit the type of isomerism suggested in **(d)(i)**.

(iv) Draw the structures of the two products formed when gaseous HCl is added to 3-methylpent-2-ene. Indicate which is the major and which is the minor product.

[7]

[Total: 20]

2 Boron trichloride, BCl_3 is produced industrially by direct chlorination of boron oxide and carbon at 500°C.

$$B_2O_3 + 3C + 3Cl_2 \rightarrow 2BCl_3 + 3CO$$

Nitrogen trichloride, NCl_3 on the other hand is formed when ammonia reacts with chlorine gas.

$$4NH_3 + 3Cl_2 \rightarrow NCl_3 + 3NH_4Cl$$

(a) **(i)** With the aid of dot-cross diagrams, explain why the shape of both BCl_3 and NCl_3 are different from each other.

[4]

(ii) Hydrogen sulphide, H_2S, reacts with boron trichloride, BCl_3 in a 1:1 ratio to form Compound **D**.

(I) Draw the structure of Compound **D**. Hence explain why BCl_3 would react with H_2S in a 1:1 ratio.
(II) Predict the value of the H-S-H bond angle in Compound **D**.

[4]

(iii) Both nitrogen and phosphorus come from Group V. NCl_3 does not react with more chlorine gas to form NCl_5 while PCl_3 is able to react with more chlorine gas to form PCl_5. Explain why this is so.

[2]

(iv) The table below shows the boiling point of three compounds. With reference to the structure and bonding present in the compounds, suggest explanation for the differences in their boiling point.

Compound	**Boiling Point / °C**
NH_3	– 33
NCl_3	71
NH_4Cl	520

[3]

(b) Describe, with the aid of equations, what happens when Universal Indicator is added to separate samples of NaCl and PCl_5 in water.

[4]

(c) An organic Compound **E** has the empirical formula CH_2O. Compound **E** undergoes the following reactions.

- It gives brisk effervescence with aqueous sodium carbonate.
- It forms a yellow precipitate when warmed with aqueous alkaline iodine.

(i) Draw a structure for Compound **E** which fits the above descriptions.

(ii) When Compound **E** is warmed with acidified potassium dichromate(VI), a Compound **F** is formed.
Suggest a structure for Compound **F** and hence state the expected observation.

[3]

[Total: 20]

3 Butene is a colourless gas present in crude oil as a minor constituent in quantities that are too small for viable extraction.
Butene can be formed from either butan-2-ol, $CH_3CH(OH)CH_2CH_3$ or 2-chlorobutane, $CH_3CH(Cl)CH_2CH_3$.

(a) **(i)** Illustrate the type of bonding present between butan-2-ol and water with the aid of a suitable diagram.

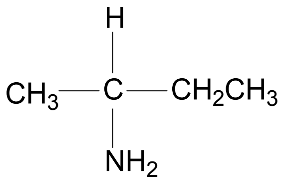
(ii) Suggest the reagents and conditions necessary to convert both butan-2-ol and 2-chlorobutane into butene.

(iii) Give the structures of the three alkenes formed.

(iv) Suggest the reagents and conditions necessary to distinguish one of the isomers from the other two. In each case, draw the structures of **ALL** the products formed and state the expected observations.

[12]

(b) Using butan-2-ol as a starting material, suggest a two-step synthesis in which the following compound can be made.



$$CH_3CH(NH_2)CH_2CH_3$$

[3]

(c) Butan-2-ol burns in excess oxygen to give a mixture of carbon dioxide gas and water as shown by the equation below.

$$CH_3CH(OH)CH_2CH_3(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

(i) Define the term standard bond energy using oxygen gas as an example.

(ii) Using the bond energy values from the *Data Booklet*, calculate the enthalpy change for the above reaction.

(iii) The bond energy values given in the *Data Booklet* are merely average values. Suggest another reason why the value that you have calculated from **(c)(ii)** differs from the actual value.

[5]

[Total: 20]

1 (a) (i) A Bronsted acid is a proton donor while a Bronsted base is a proton acceptor.

(ii) Bronsted Acid: HCl, HNO_3
Bronsted Base: NH_3

(iii)

HCl	+	H_2O	$\longrightarrow$	H_3O^+	+	Cl^-
Acid		Base		Conjugate acid		Conjugate base

HNO_3	+	H_2O	$\longrightarrow$	H_3O^+	+	NO_3^-
Acid		Base		Conjugate acid		Conjugate base

(b) (i) $[OH^-] = 2 \times 0.05 = 0.1 \text{ mol dm}^{-3}$
$pOH = -\lg(0.1) = 1.0$
$pH = 14.0 - 1.0 = 13.0$

(ii) No. of moles of $Ba(OH)_2 = 25 \times 10^{-3} \times 0.05 = 1.25 \times 10^{-3}$ mol
No. of moles of HNO_3 added $= 5 \times 10^{-3} \times 0.05 = 2.5 \times 10^{-4}$ mol

	$Ba(OH)_2$	+	$2\ HNO_3$	$\longrightarrow$	$Ba(NO_3)_2$	+	H_2O
initial	1.25×10^{-3}		2.5×10^{-4}		0		0
change	$-\frac{1}{2}(2.5 \times 10^{-4})$		-2.5×10^{-4}		$\frac{1}{2}(2.5 \times 10^{-4})$		
final	1.125×10^{-3}		0		1.25×10^{-4}		

No. of moles of $OH^- = 2 \times 1.125 \times 10^{-3} = 2.25 \times 10^{-3}$ mol

$$[OH^-] = \frac{2.25 \times 10^{-3}}{25+5} \times 1000 = 0.075 \text{ mol dm}^{-3}$$

$pOH = -\lg(0.075) = 1.12$
$pH = 14.0 - 1.12 = 12.9$

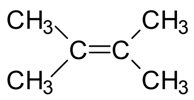
(c) (i) Alkaline buffer

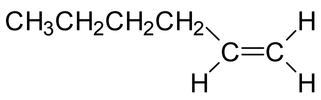
(ii) $NH_3 + H^+ \rightarrow NH_4^+$
$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

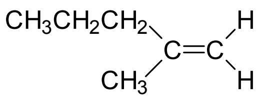
(d) (i) Geometric isomerism

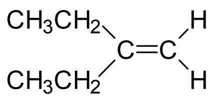
(ii) Double bond restrict free rotation; different groups attached to same carbon of double bond.

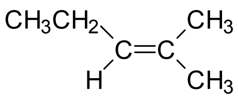
(iii)





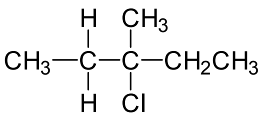






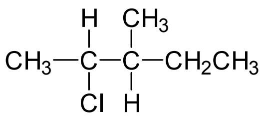
Any one of the above

(iv)



$CH_3-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{CH_3}{C}}-CH_2CH_3$

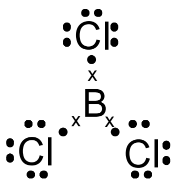
Major



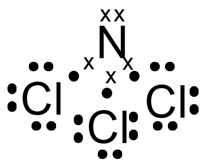
$CH_3-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-CH_2CH_3$

Minor

2 (a) (i)



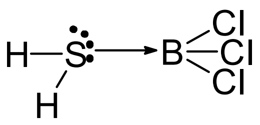
Trigonal planar



Trigonal pyramidal

By VSEPR, the three bond pairs of BCl_3 will space out to minimise repulsion between the three bond pairs resulting in a trigonal planar geometry.
NCl_3 has an extra lone pair of electrons on N which causes more repulsion with the three bond pairs. Thus, the bond pairs comes closer together resulting in a trigonal pyramidal geometry.

(ii)



B in BCl_3 has 6 valence electrons and it accepts a lone pair from H_2S into its empty p-orbital to achieve the octet configuration.

(iii) P has empty low energy 3d orbitals which it can utilize to accommodate more than 8 electrons in its valence shell.
The next available orbitals of N is the 3s orbital which is too high in energy compared to the 2p orbitals, this cannot be utilized for bonding. Thus, the 2nd principal quantum shell of N can only accommodate 8 electrons in NCl_3.

(iv) Both NH_3 and NCl_3 has a simple covalent structure. The bonding present is td-id. NCl_3 has a larger electron cloud than NH_3, thus the temporary dipole-induced dipole forces are stronger than the hydrogen bonds of NH_3, requiring more energy to break. NH4CL has a giant structure with ionic bonds. The ionic bonds between NH_4^+ and Cl^- are the strongest and requires the most energy to break.

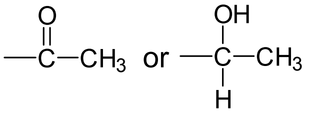
(b) $NaCl + aq \rightarrow Na^+ + Cl^-$

NaCl dissolves in water to formed a neutral solution of pH=7. Universal indicator remains green.

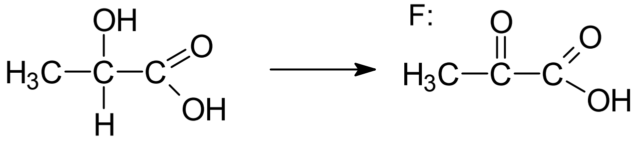
$PCl_5 + 4\ H_2O \rightarrow H_3PO_4 + 5\ HCl$

PCl_5 hydrolyses in water to from an acidic solution; hence the universal indicator turns red.

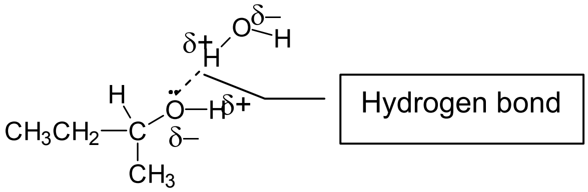
(c) Brisk effervescence with sodium carbonate: –COOH present.

Yellow ppt with aqueous alkaline iodine:  present.

$-\overset{\overset{O}{\|}}{C}-CH_3$ or $-\underset{H}{\overset{OH}{\overset{|}{C}}}-CH_3$

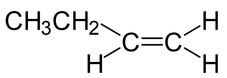
E: 

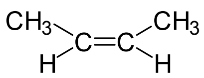
3 **(a)** **(i)**

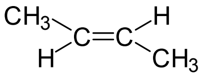


(c) **(i)** Butan-2-ol: excess conc H_2SO_4, 170 °C
2-chlorobutane: alcoholic KOH; heat.

(ii)





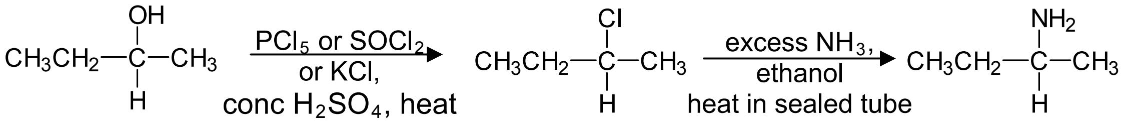


(iv) $KMnO_4$, H_2SO_4, heat

But-1-ene: Purple $KMnO_4$ turns colourless, effervescence of CO_2. CH_3CH_2COOH formed.

But-2-ene: Purple $KMnO_4$ turns colourless. CH_3COOH formed.

(b)



(c) **(i)** $O_2\ (g) \rightarrow 2\ O\ (g)$

(ii) $\Delta H_{reaction} = 3(350) + 9(410) + 360 + 460 + 6(496) - 8(740) - 10(460)$

= -1984 kJ mol^{-1}

(iii) Butan-2-ol and H_2O are liquids; energy has to be taken up for their vapourisation.

Paper 1 Multiple Choice Answers

1	C	11	B	21	A
2	C	12	C	22	B
3	A	13	D	23	B
4	C	14	B	24	A
5	A	15	B	25	B
6	C	16	C	26	A
7	C	17	B	27	D
8	C	18	C	28	D
9	B	19	D	29	A
10	B	20	C	30	B