PRELIMINARY EXAMINATIONS
HIGHER 2

TEMASEK
JUNIOR COLLEGE

CANDIDATE NAME								
CIVICS GROUP			/					
CENTER NUMBER	S					INDEX NUMBER		

CHEMISTRY **9729/02**

Paper 2 Structured Questions **24 August 2021**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name in the spaces at the top of this page.
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 in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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

For Examiner's Use	
1	
2	
3	
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5	
Total	

This document consists of XX printed pages and XX blank page.

[Turn over

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

1 **(a)** Excited states can be studied to gain information about the energies of orbitals that are unoccupied in an atom's ground state. The excited state of an element, **Q**, is represented by the electronic configuration $1s^22s^22p^63s^23p^63d^44s^24p^1$.

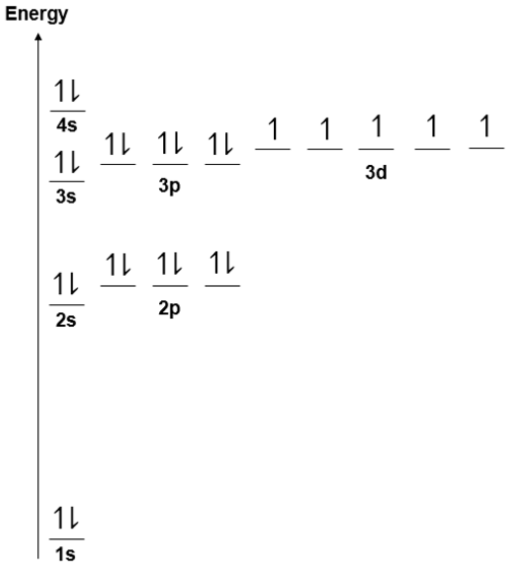
(i) Identify the element **Q**. [1]

Since the total number of electrons is 25, • Q is manganese.

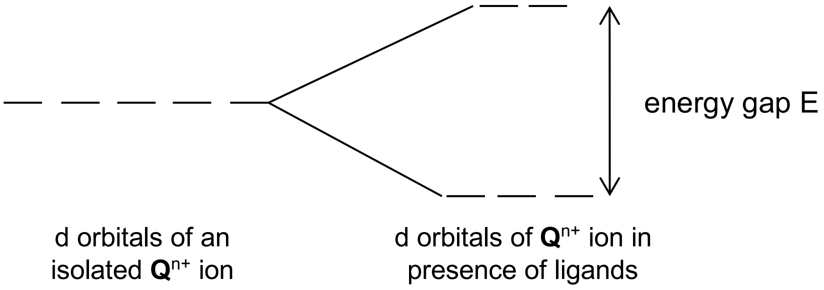
(ii) Draw the energy level diagram showing the electronic configuration of element **Q** in its ground state. [2]

- **Electronic configuration of Q in ground state - $1s^22s^22p^63s^23p^63d^54s^2$**

  (Either written out or shown correctly in energy level diagram)
- **Energy level diagram with axis and orbitals labelled, energy levels converge as distance from nucleus increase, energy diff between subshells < between shells.**



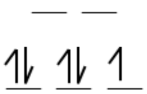
CLT **(iii)** The arrangement of electrons in the d orbitals depends on the spin states of complexes. The following diagram shows how the d orbitals are split in an octahedral environment for the ion $\mathbf{Q}^{n+}$.



In a ‘high spin’ state, the electrons occupy all the d orbitals singly, before starting to pair up in the lower energy d orbitals.

In a ‘low spin’ state, the lower energy d orbitals are filled first, by pairing up if necessary, before the higher energy d orbitals are used.

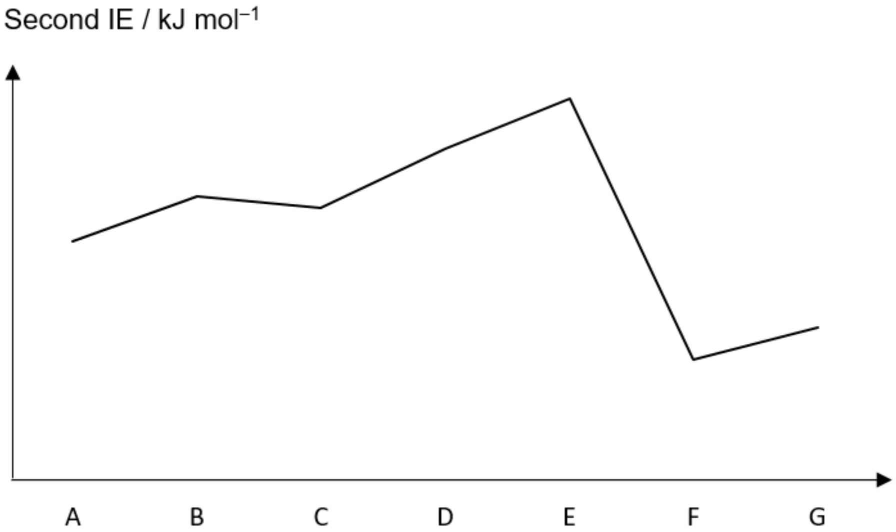
Use diagrams like the one given to show the electronic configuration of a ground state **Q**$^{2+}$ ion in low spin state. [1]



Q^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

- **1 mark for correct diagram**

(b) The second ionisation energies of seven consecutive elements **A** to **G** in the Periodic Table are shown below.



(i) Write an equation for the second ionisation energy of oxygen. [1]

- **$O^+ (g) \rightarrow O^{2+} (g) + e^-$**

Note: State symbols must be included for IE equation.

(ii) Explain the discontinuity in second ionisation energies between **E** and **F**, and between **B** and **C**. Hence deduce which element **A** to **G** is oxygen. [3]

- **There is a big drop in second IE from element E to F. <u>Second electron in element F is removed from outer electronic shell</u>. Element F is a Group 2 element (as it has two valence electrons).**

OR

There is a big drop in second IE from element E to F. Second electron in element E is removed from inner electronic shell. Element E is a Group 1 element (as it has one valence electron).

- Hence element B is oxygen (Group 16).
- Second IE of C (Group 17) involves the removal of paired 2p electron which experiences inter-electronic repulsion. Hence, less energy is required to remove the paired electron from C^+ ion.

(c) **(i)** State and explain the variation in bonding in Period 3 oxides in terms of electronegativity. [2]

- Across the Period, electronegativity of elements increases, electronegativity differences between the elements and oxygen decreases resulted in sharing of electrons.
- The oxides become changes from ionic to covalent/increasingly covalent in character across Period 3.

W, **X**, **Y**, and **Z** are four consecutive elements in the fourth period of the Periodic Table. The letters are not the actual symbols of the elements.

W forms an oxide that reacts with both acids and bases.

Z is a solid that can exist as several different allotropes. **Z** burns in air to form $\mathbf{Z}O_2$ which dissolves in water to form an acidic solution. This solution reacts with sodium hydroxide to form the salt $Na_2\mathbf{Z}O_3$.

(ii) Suggest the identities of **W** and **Z**. [1]

- W is gallium, Z is selenium.

(iii) Write equations for the reactions of oxide of **W** with sodium hydroxide and hydrochloric acid respectively. [2]

- $W_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaW(OH)_4$
- $W_2O_3 + 6HCl \rightarrow 2WCl_3 + 3H_2O$

(iv) Write an equation for the formation of an acidic solution when $\mathbf{Z}O_2$ dissolves in water. [1]

- $ZO_2 + H_2O \rightarrow H_2ZO_3$

[Total: 14]

2 **(a)** Chlorine reacts with iodine to form a compound **T**, ICl_7. When dissolved in an excess of aqueous potassium iodide, **T** liberates iodine, I_2, which is the only iodine-containing product in the reaction.

(i) State the oxidation number of iodine in ICl_7. [1]

- **+7**

(ii) Write the equation for the reaction between **T** and potassium iodide. [1]

- $\mathbf{ICl_7 + 7KI \rightarrow 4I_2 + 7KCl}$

+7 7(-1) 0

(iii) Calculate the amount of iodine liberated when 1.00 g of **T** reacts with an excess of aqueous potassium iodide. [1]

Amount of ICl_7

= 1/(126.9 + 7 x 35.5)

= 2.66×10^{-3} mol

Amount of iodine

= 4 x 2.66×10^{-3}

- **= 1.07×10^{-2} mol** (allow ecf from (a)(ii))

(iv) Sodium thiosulfate is a common reagent used for the reaction with iodine.

Write a balanced equation for the reaction between sodium thiosulfate and iodine and calculate the volume of 1.00 mol dm^{-3} sodium thiosulfate, in cm^3, required to react with all the iodine liberated in **(a)(iii)**. [2]

- $\mathbf{I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}}$

Volume of sodium thiosulfate required

= (1.07×10^{-2} x 2)/1 x 1000

= • 21.3 cm^3 (allow ecf from a(iii))

(b) Chlorine is produced together with carbon monoxide when phosgene, $COCl_2$, undergoes dissociation according to the equation below:

$$COCl_2(g) \rightleftharpoons Cl_2(g) + CO(g)$$

The above reaction takes place in a 2 dm^3 reaction vessel. At the start of the reaction, there was 4.0 mol of phosgene in the vessel. When dynamic equilibrium was established, only 1.6 mol of phosgene was left.

(i) Write the K_c expression for the above reaction, stating its units. [2]

- $$K_c = \frac{[Cl_2][CO]}{[COCl_2]}$$
- **Units: mol dm^{-3}**

(ii) Calculate the equilibrium amounts of CO and Cl_2, and hence, determine the value of K_c for the above reaction, showing your working clearly. [2]

	$COCl_2(g)$	$\rightleftharpoons$	$Cl_2(g)$	+	$CO(g)$
Initial amount / mol	4.0		0		0
Change / mol	- 2.4		+ 2.4		+ 2.4
Eqm amount / mol	1.6		2.4		2.4

- **Equilibrium amounts of CO and Cl_2 = <u>2.4 mol</u> respectively**
- $$K_c = \frac{(\frac{2.4}{2})(\frac{2.4}{2})}{(\frac{1.6}{2})} = \underline{1.80}$$ **mol dm^{-3} (ignore units in marking)**

(iii) In the same reaction vessel, calculate the amount of phosgene to be removed from the equilibrium mixture in **(b)(ii)** in order to reduce the equilibrium amount of Cl_2 to 2.0 mol. [2]

Let x be the amount of phosgene that needs to be removed.

	$COCl_2(g)$	$\rightleftharpoons$	$Cl_2(g)$	+	$CO(g)$
Initial amount / mol	1.6 - x		2.4		2.4
Change / mol	+ 0.4		- 0.4		- 0.4
Eqm amount / mol	2.0 - x		2.0		2.0

$$K_c = \frac{(\frac{2.0}{2})(\frac{2.0}{2})}{(\frac{2.0-x}{2})} = 1.8$$

- **Working**
- **x = 0.889 mol**

(iv) State *Le Chatelier's Principle*. [1]

• *Le Chatelier's Principle* states that when a system at dynamic equilibrium is subjected to a change which disturbs the equilibrium, the system will react in a way so as to counteract the effect of the change to re-establish equilibrium.

(v) State and explain how the equilibrium composition might change if the above reaction is subjected to a decrease in pressure. [2]

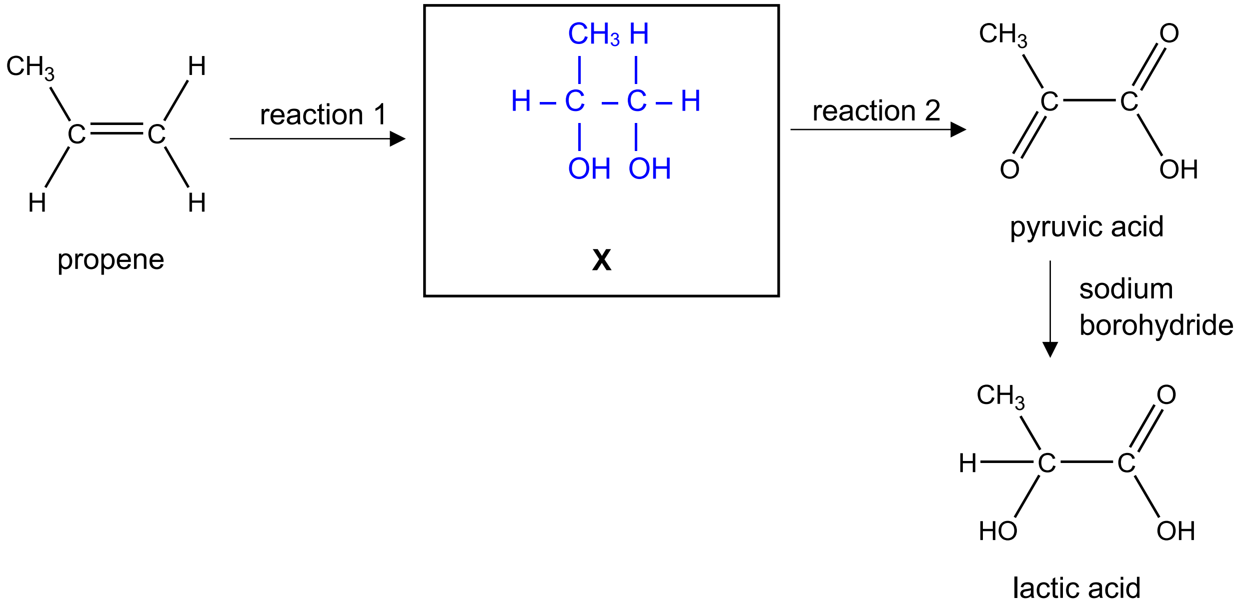
By *Le Chatelier's Principle*, a decrease in pressure will cause the

• equilibrium position to shift right to increase the number of moles of gases to increase pressure.

• The new equilibrium mixture contains more products, Cl_2 and CO, and less reactant, $COCl_2$.

[Total: 14]

3 Propene and lactic acid are commonly used as feedstock for polymers.



(a) **(i)** Suggest reagents and conditions for reaction 1 and 2. [2]

- **cold acidic dilute $KMnO_4$ or cold alkaline dilute $KMnO_4$**

  [Note: Do not accept hot or concentrated]
- **$K_2Cr_2O_7/H^+$, heat or $KMnO_4/H^+$, heat**

(ii) Suggest the structure of compound **X** in the box above. [1]

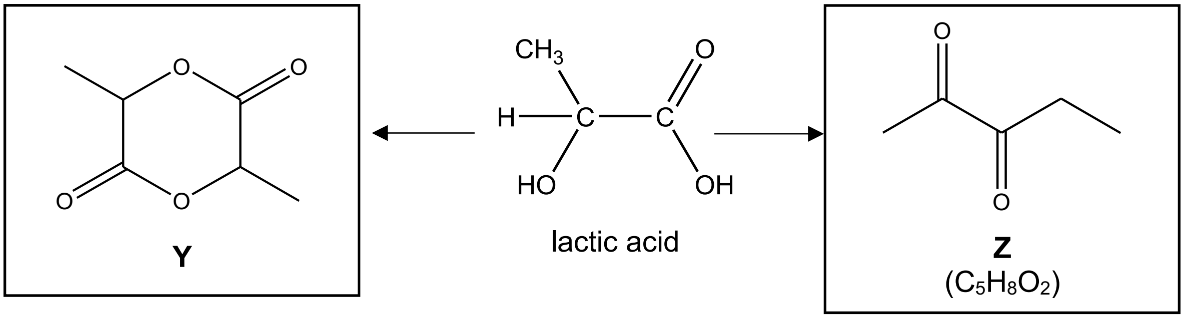
(b) Explain why sodium borohydride can reduce the carbonyl C=O bond in pyruvic acid but not C=C bond in propene. [2]

C in C=O is ✓electron deficient due to presence of electronegative O hence it is susceptible to nucleophilic attack by ✓ nucleophiles like BH_4^-.

C=C is ✓electron rich hence does not react with nucleophiles like BH_4^-.

3✓ = 2 marks ; 2✓ = 1 mark

(c) The condensation of two molecules of lactic acid produces compound **Y** and **Z**.



(i) Compound **Y** is a cyclic ester derived from the condensation of two molecules of lactic acid.

Show the skeletal structure of compound **Y** in the box above. [1]

(ii) Explain why compound **Y** have low solubility in methanol. [1]

- **The energy released from the interactions (pd-pd / H-bonds) formed with methanol are insufficient to overcome the hydrogen bonds between methanol molecules hence it is less soluble in methanol.**

(iii) The condensation of two lactic acid molecules also produces compound **Z** with the elimination of carbon dioxide and water.

Compound **Z** reacts with 2 moles of 2,4-dinitrophenylhydrazaine. It forms 1 mole of CHI_3 upon reaction with aqueous alkaline iodine and does not give silver mirror with Tollen's reagent.

Suggest the structure of compound **Z** in the box above. [1]

(iv) Explain why compound **Z** has a lower boiling point than lactic acid. [2]

✓ Both have simple molecular structure.

✓ More energy is required to break the ✓ hydrogen bonds between lactic acid molecules, compared to the ✓ the permanent dipole – permanent dipole interaction between molecules of compound Z. Hence, lactic has a higher boiling point than compound Z.

2✓ 1mark

[Total: 10]

4 **(a)** Nitrogen monoxide, NO(g), is a colourless, toxic gas that is formed by the oxidation of nitrogen. It can be reduced by hydrogen, H_2(g), under certain conditions to form harmless products.

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(l)$$

(i) Define the term 'rate of reaction'. [1]

Decrease (or change) in reactant concentration per unit time or increase (or change) in product concentration per unit time.

(ii) Identify a change in the reaction mixture that would allow the rate of reaction to be measured. [1]

Decrease (change) in gas volume or pressure.

A series of experiments was conducted to determine the rate equation for the above reaction. The following data was obtained.

Experiment	Initial [NO] / mol dm^{-3}	Initial [H_2] / mol dm^{-3}	Initial Rate / mol dm^{-3} s^{-1}
1	2.50×10^{-3}	2.50×10^{-3}	1.27×10^{-3}
2	2.50×10^{-3}	4.60×10^{-3}	2.34×10^{-3}
3	5.00×10^{-4}	7.50×10^{-3}	1.52×10^{-4}

(iii) Determine the order of reaction with respect to NO and H_2. Hence state the rate equation. [3]

Using Expt 1 & 2

[NO] kept constant, [H_2] increases by $4.60 \times 10^{-3}/2.50 \times 10^{-3} = 1.84$ times, rate increases by $2.34 \times 10^{-3}/1.27 \times 10^{-3} = 1.84$ times.

- **First order wrt [H_2]**

Using Expt 1 & 3

Rate = $k[NO]^y[H_2]$

$1.27 \times 10^{-3}/1.52 \times 10^{-4} = k(2.50 \times 10^{-3})^y(2.50 \times 10^{-3}) / k(5.00 \times 10^{-4})^y(7.50 \times 10^{-3})$

- **y = 2, Second order wrt [NO]**
- **Rate = $k[NO]^2[H_2]$**

(iv) Using the data from Experiment 2, calculate the rate constant, k. [1]

Rate = $k[NO]^2[H_2]$

$2.34 \times 10^{-3} = k(2.50 \times 10^{-3})^2(4.60 \times 10^{-3})$

k = 8.14×10^4 mol^{-2} dm^6 s^{-1}

The reaction was believed to proceed in three steps.

Step 1 : $2NO \rightarrow N_2O_2$
Step 2 : $N_2O_2 + H_2 \rightarrow N_2O + H_2O$
Step 3 : $N_2O + H_2 \rightarrow N_2 + H_2O$

(v) Deduce which of the 3 steps is the rate-determining step. [1]

From the rate equation, the rate-determining step (slow step) must have two NO molecules reacting with one H_2 molecule.

Step 2 is the rate-determining step as N_2O_2 is the intermediate from two NO molecules. Combining steps 1 and 2 gives two NO and one H_2 which is consistent with the rate equation.

Alternative

Step 2 is rate-determining step,

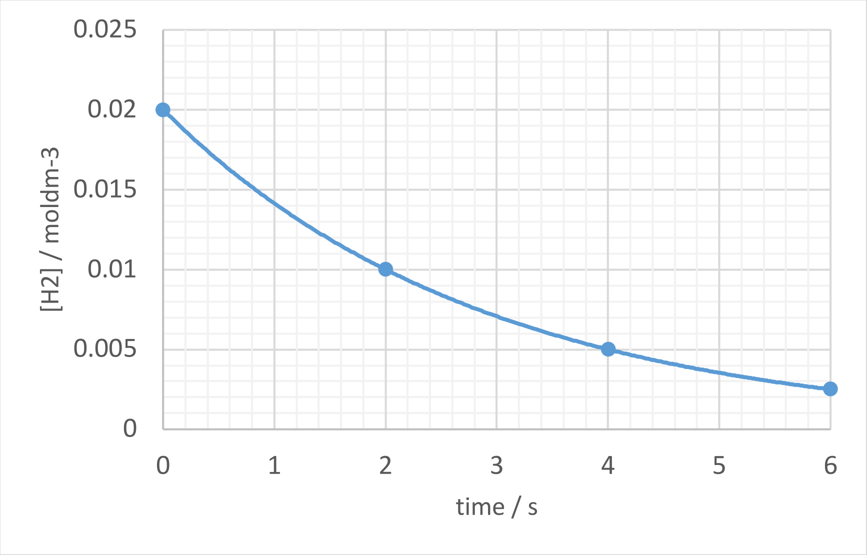
rate = $k[N_2O_2][H_2]$

Since 2NO forms $1N_2O_2$,

rate = $k[NO]^2[H_2]$

(b) Another experiment was conducted using 2.00 mol dm^{-3} of NO and 0.020 mol dm^{-3} H_2. The experiment was found to have a half-life of 2 s.

(i) Use the axes below to construct a graph of the variation in the concentration of 0.020 mol dm^{-3} $H_2(g)$ under the conditions specified. [1]



(ii) Determine the half-life if the experiment was repeated using

(I) 0.040 mol dm^{-3} H_2 and same concentration of NO

(II) 0.020 mol dm^{-3} H_2 and concentration of NO doubled.

Show clearly how you arrive at your answer. [2]

Rate = $k[NO]^2[H_2]$

Using large excess of NO, reaction becomes pseudo first order.

Rate = $k'[H_2]$ where $k' = k[NO]^2$

$t_{½}$ = ln 2/k'

(I) • $t_{½}$ = 2 s since <u>$t_{½}$ is a constant</u> for pseudo first order reaction and is independent of the $[H_2]$

(II) • $t_{½}$ = ln 2 / k'

= ln 2 / (k x $[NO]^2$)

= 2/4 = 0.5 s

(iii) NO can be easily oxidised to NO_2 which can act as a catalyst in the oxidation of atmospheric sulfur dioxide.

Write equations to show how NO_2 acts as a catalyst in this process. [2]

- **$SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$**
- **$NO(g) + ½\,O_2(g) \rightarrow NO_2(g)$**

(c) Recently much interest has been shown in the production of the fuel biodiesel from algae. 50% of the mass of the dried algae are triglycerides. To convert triglycerides into biodiesel, the following processes are carried out.

Triglyceride, M_r = 890

glycerol

$$C_{17}H_{35}CO_2H \xrightarrow{\text{II}} C_{17}H_{35}CO_2CH_3$$

Biodiesel, M_r = 298

(i) State the reactants and conditions for reactions I and II. [2]

I : • **dilute HC*l*, heat**

II : • **CH_3OH, conc.H_2SO_4, heat**

(ii) Calculate the mass of biodiesel that can be produced from 1000kg of dried algae.[2]

1000 kg algae contains 500 kg triglycerides

• 890 g of triglyceride produces 3 × 298 = 894 g of biodiesel

• 500 kg produces 500 × 894/890 = 502 kg biodiesel

Alternative

1000 kg algae contains 500 kg triglycerides

Amt of triglyceride = (500 x 1000)/890

= 562 mol

- **No. of moles of of $C_{17}H_{35}CO_2H$ produced = 562 x 3**

  = 1686 mol

  = amt of biodiesel

Mass of biodiesel = 1686 x 298

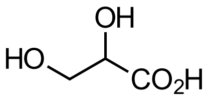
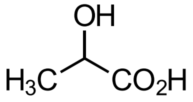
= 502 kg

(iii) The production of biodiesel is at present an expensive process. Suggest a reason why the development of biodiesel as an alternative to fossil fuels is important. [1]

Fossil fuels : causes serious environmental problems (global warming), imminent depletion

Biodiesel : renewable/sustainable, smaller C footprint (less global warming)

Glycerol, a by-product of biodiesel production, can be selectively oxidised to glyceric acid and lactic acid which have widespread applications. The table below shows the pK_a values of the acids.

Acid	pK_a
 Glyceric acid	3.42
 Lactic Acid	3.86

(iv) Explain the difference in the relative acidity of the two acids. [2]

•• **Glyceric acid is the √ stronger acid as it has √ 2 electron-withdrawing –OH groups compared to lactic acid with only 1 –OH group. The greater the number of –OH groups, the √ better the dispersal of the negative charge and hence the more √ stable carboxylate ion.**

(Lactic acid also has an electron donating methyl group that increases the charge density of the lactate ion resulting in a less stable lactate ion.)

2 √ : 1m

(v) 20 cm^3 of 0.20 mol dm^{-3} glyceric acid is added to 40 cm^3 of 0.10 mol dm^{-3} sodium hydroxide solution. Calculate the pH of the resultant solution. [3]

Amount of salt = 20/1000 x 0.20 mol

= 4.00 x 10^{-3} mol

• [Salt] = 1000/60 x 4.0 x 10^{-3} mol dm^{-3}

= 6.67 x 10^{-2} mol dm^{-3}

pK_a of acid = 3.42

pK_b of glycerate = 14 – 3.42

= 10.6

K_b = 2.51 x 10^{-11} mol dm^{-3}

• $[OH^-]$ = √(K_b x c

= √(2.51 x 10^{-11} x 6.67 x 10^{-2})

= 1.29 x 10^{-6} mol dm^{-3}

pOH = -lg$[OH^-]$

= -lg(1.29 x 10^{-6})

= 5.89

• pH = 14 - 5.89

= 8.11

[Total: 22]

5 **(a)** Hydrazine, N_2H_4, was first used as a component in rocket fuel in World War 2.

(i) Using the VSEPR theory, state and explain

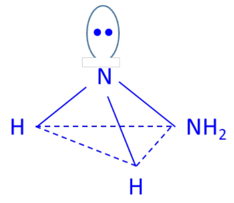
- the shape of hydrazine around each N atom;
- the H-N-H bond angle. [3]

There are ✓ 3 bond pairs and 1 lone pair of electrons in the outer/valence shell of each central N. By VSEPR theory, ✓ to maximise stability and minimise repulsion, the ✓ electron geometry is tetrahedral. Hence the shape is ✓ trigonal pyramidal.

Since ✓ lone pair – bond pair repulsion is greater than bond pair – bond pair repulsion, the H-N-H bond angle will be ✓ 107°.

Every 2 ✓ = 1 mark

(ii) Hence, draw the structure of hydrazine, showing clearly the shape around one nitrogen atom. [1]



•

When combined with hydrogen peroxide, the reaction produced nitrogen gas and water vapour, and released a large amount of energy that propelled the rocket to space.

$$N_2H_4 + 2H_2O_2 \rightarrow N_2 + 4H_2O \qquad \Delta H_r$$

(iii) What do you understand by the term *bond energy* of a covalent bond. [2]

Bond energy is the • average energy required to break one mole of covalent bond in the gas phase into constituent gaseous atoms under standard conditions of 298 K and 1 bar.

The • larger the bond energy, the stronger the covalent bond.

(iv) Calculate the enthalpy change, ΔH_r, of the gaseous reaction between hydrazine and hydrogen peroxide. [2]

Bonds broken: 1 N-N, 4 N-H, 2 O-O, 4 O-H

Bonds formed: 1 N≡N, 8 O-H

Energy absorbed during bond breaking

= 160 + 4(390) + 2(150) + 4(460) = 3860 kJ

Energy released during bond forming = 944 + 8(460) = 4624 kJ

• correct energy released and absorbed

ΔH_r = 3860 + (-4624) = • -764 kJ mol^{-1}

(b) When two pure liquids, A and B, which do not react, are mixed together, heat may be absorbed or released depending on the relative strength of intermolecular forces of attraction formed in the mixture.

$$A(l) + B(l) \rightarrow A\text{---}B\ (l) \qquad \Delta H_{mix}$$

--- refers to the intermolecular forces of attraction between liquids A and B.

Enthalpy change of mixing, ΔH_{mix}, is the enthalpy change when 1 mole each of pure A and pure B are added to form a binary A---B solution.

The enthalpy change of mixing of ethyl ethanoate and trichloromethane is determined experimentally in an insulated calorimeter and the following data is collected.

	ethyl ethanoate	trichloromethane
Molar mass / g mol^{-1}	88.0	119.5
Mass / g	8.80	–
Specific heat capacity / J g^{-1} K^{-1}	1.92	0.96
Initial temperature / °C	31.2	31.2
Final temperature / °C	40.7	40.7

(i) Calculate the heat change of ethyl ethanoate during the mixing process. [1]

Heat evolved = $mc\Delta T$ = 8.8(1.92)(40.7 – 31.2) = • 161 J

(ii) The heat change for an equimolar of trichloromethane at the same initial temperature is 109 J.

Calculate the heat change of the mixture and hence the enthalpy change of mixing, ΔH_{mix}, of ethyl ethanoate and trichloromethane. [2]

Total heat evolved = 161 + 109 = • 270 J

ΔH_{mix} = -270/(8.8/88) = • -2.70 kJ mol^{-1}

(iii) A student claimed that the heat change was due to the formation of intermolecular forces of attraction between ethyl ethanoate and trichloromethane molecules.

Comment on the student's claim and explain your answer. [1]

Student is • incorrect as heat energy absorbed to break the intermolecular forces of attraction between ethyl ethanoate molecules and between trichloromethane molecules needs to be considered as well.

(iv) With reference to structure and bonding, explain the significance of the sign of ΔH_{mix} in **(b)(ii)** and hence, predict the observation of mixing ethyl ethanoate and trichloromethane. [3]

Both ethyl ethanoate and trichloromethane have ✓ simple molecular structure. ✓ Formation of permanent dipole - permanent dipole between ethyl ethanoate and trichloromethane molecules ✓ release sufficient energy to break the ✓ permanent dipole - permanent dipole between individual molecules. There is a net release of energy, so $\Delta H_{mix} < 0$.

Hence, ethyl ethanoate and trichloromethane are • miscible and form a homogeneous solution.

Every 2 ✓ = 1 mark

[Total: 15]