1 **(a)** The table below shows the first, second and third ionisation energies of some elements in the Periodic Table.

Element	**First Ionisation energy (kJ mol^{-1})**	**Second Ionisation energy (kJ mol^{-1})**	**Third Ionisation energy (kJ mol^{-1})**
Ca	590	1150	4940
Mn	716	1510	3250
Fe	762	1560	2960
Co	757	1640	3230
Ni	736	1750	3390

(i) Explain why the first and second ionisation energies of the transition metals are relatively invariant.

[2]

The first and second I.E of the transition elements involves the removal of 4s electrons. Across the period, • nuclear charge increases due to increasing number of protons. Screening effect increases as electrons are added to the penultimate 3d subshell, providing a shield between nucleus and outer 4s electrons. • Increase in nuclear charge is only *slightly* more significant than the increase in screening effect. Hence, small increase in both the first and second I.E.

(ii) Write the electronic configurations of Ca and Fe atoms at ground state. Explain the differences in the values of the third ionisation energies between iron and calcium.

[2]

- **Electronic Configuration of Fe: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^6$ $4s^2$**

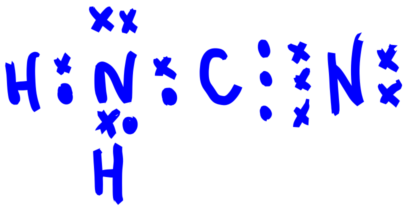
Electronic Configuration of Ca: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$

- **The third ionisation energy of calcium is more than that of iron because an electron is removed from a 3p orbital of Ca^{2+} whereas an electron is removed from a 3d orbital of the Fe^{2+}. The 3p electron is nearer to the nucleus compared to the 3d electron and hence required more energy to remove.**

(b) Calcium cyanamide, $CaCN_2$, is used as a fertiliser in agriculture. Through hydrolysis in the presence of carbon dioxide, calcium cyanamide produces cyanamide, NH_2CN. Cyanamide can be extracted by organic solvents.

(i) Draw the dot–and–cross diagram for the cyanamide molecule, NH_2CN.

[1]



(ii) With reference to structure and bonding, deduce whether $CaCN_2$ has a higher or lower melting point as compared to NH_2CN.

[2]

• NH_2CN has simple molecular structure with hydrogen bonds between its molecules.

$CaCN_2$ has a giant ionic lattice structure held by strong electrostatic forces of attraction/ionic bonds between the oppositely charged ions.

• Melting involves the breaking of the stronger electrostatic forces of attraction between the oppositely charges ions (Ca^{2+} and CN_2^{2-}) as compared to the (or) weaker hydrogen bonds between NH_2CN molecules. Hence more energy is required to melt $CaCN_2$, hence higher melting point.

[Total: 7]

2 A saturated solution of magnesium methanoate, $Mg(HCO_2)_2$, has a solubility of approximately 143 g dm^{-3} at room temperature. The exact solubility can be determined by titrating magnesium methanoate solution against a standard potassium manganate(VII) solution.

During the titration, the methanoate ion, HCO_2^-, is oxidised to carbon dioxide while the manganate(VII) ion, MnO_4^-, is reduced to Mn^{2+}.

(a) **(i)** Write the overall equation for the reaction between HCO_2^- and MnO_4^- under acidic conditions.

[1]

Oxidation :$HCO_2^- \rightarrow CO_2 + H^+ + 2e^-$ (x5)

Reduction : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (x2)

• $2MnO_4^- + 11H^+ + 5HCO_2^- \rightarrow 2Mn^{2+} + 8H_2O + 5CO_2$

(ii) Calculate the approximate concentration of HCO_2^- ions present in the saturated solution.

[1]

• $[HCO_2^-]$ in saturated solution = $\frac{143}{24.3+2(1+12+2\times16)} \times 2$

= 2.50 mol dm^{-3}

[Turn over

(iii) The titre value from titrating 25.0 cm^3 of saturated magnesium methanoate solution against 0.0500 mol dm^{-3} potassium manganate(VII) solution is found to be too high.

Describe the steps to prepare a suitable solution of magnesium methanoate from the saturated solution. Your plan should include details of quantities measured and apparatus used.

[3]

Assuming the titre volume of potassium manganate(VII) solution to be 25.00 cm^3 (accept 20.00 to 25.00 cm^3),

No. of moles of HCO_2^- in 25.0 cm^3 of diluted solution
$= \frac{25}{1000} \times 0.05 \times \frac{5}{2}$ = 3.125 x 10^{-3} mol
No. of moles of HCO_2^- in 250 cm^3 of diluted solution = 3.125 x 10^{-2} mol

- **Volume of saturated HCO_2^- solution needed for dilution**
  $= \frac{3.125 \times 10^{-2}}{2.5} \times 1000$ = 12.50 cm^3

●●
Using a burette, transfer 12.50 cm^3 of saturated magnesium methanoate solution into a 250 cm^3 standard flask. Make up to the mark with water and shake well.

(b) An industrial chemist introduced 2 atm of carbon dioxide and 2 atm of hydrogen gas into a 1 dm^3 container at 300 K. The temperature is then raised to 900 K, at which the K_p is 0.641.

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

(i) Calculate the partial pressure of H_2 present at equilibrium at 900 K.

[3]

Since P ∝ T,

- **$P_{CO_2} = P_{H_2}$ = 6 atm at 900K**

	$CO_2(g)$ +	**$H_2(g)$ ⇌**	**$H_2O(g)$ +**	**$CO(g)$**
Initial partial pressure /atm	**6**	**6**	**0**	**0**
Change in partial pressure /atm	**-x**	**-x**	**+x**	**+x**
Equilibrium partial pressure /atm	**6-x**	**6-x**	**x**	**x**

$K_p = \frac{P_{H_2O} \times P_{CO}}{P_{CO_2} \times P_{H_2}}$

- **$0.641 = \frac{x^2}{(6-x)^2}$**
  x = 2.67 atm
- **P_{H_2} = 6 – 2.67 = 3.33 atm**

(ii) Explain if the K_p value at 300 K is higher or lower than 0.641.

[2]

- **The value of K_p at 300 K is higher than 0.641.**
- **By Le Chatelier's Principle, at the lower temperature of 300 K, the system will favour the exothermic forward reaction to produce more heat. Thus position of equilibrium shifts to the right and K_p increases.**

[Total: 10]

3 **(a)** Sulfur tetrachloride decomposes to sulfur dichloride and a gas that bleaches litmus.

[3]

(i) Using the VSEPR theory, deduce and draw the shape of SCl_2. Give a value for the bond angle.

There are 2 bond pairs and 2 lone pairs of electrons around S. To minimize repulsion and maximize stability, the 4 electron pairs are directed to the corners of a tetrahedron. The shape is bent.

√ 2 bond pairs and 2 lone pairs around S.

√ 4 electrons pairs arranged tetrahedrally to

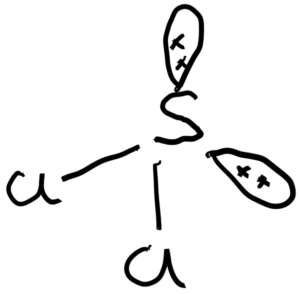
√ minimize repulsion and maximize stability.

√ bent

√ diagram

√ bond angle : any angle between 90^0 & 109.5^0.

2 √ : 1m



(ii) State whether the bond angle of SCl_2 is expected to be larger or smaller than SF_2. Explain your answer.

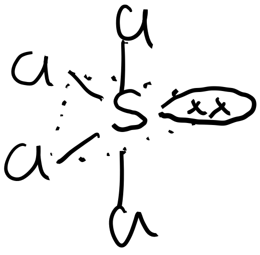
[1]

Cl is less electronegative than F. The bond pair of electrons is closer to S for SCl_2 resulting in a greater bond pair-bond pair repulsion. Hence the bond angle of SCl_2 is larger.

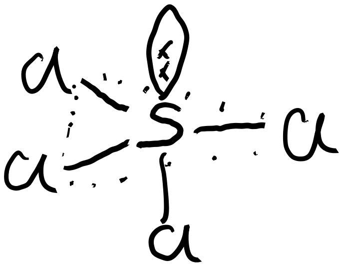
(b) **(i)** There are two possible molecular arrangements for SCl_4 with different relative stabilities. Draw these two molecular arrangements in the boxes below, showing clearly the shape around the central atom.

[2]

(I)



(II)



(ii) Apply the principles of the VSEPR theory to discuss the relative stabilities of molecular arrangements (I) and (II).

[1]

- **Since electron pairs exert repulsion on one another in the following order:**

lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion

Arrangement I gives the more stable molecule when the lone pair is placed in the equatorial positions (120^0 apart).

(c) SCl_4 combines with BCl_3 to give **X** with the composition by mass: S, 11.0% ; B, 3.7%.

(i) Derive the empirical formula of **X**.

[1]

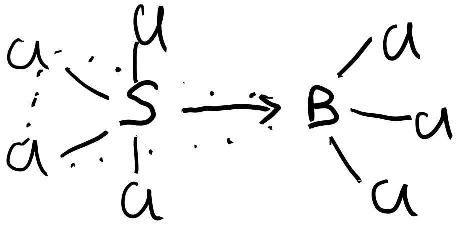
	S	**B**	**C*l***
Mole ratio	**11/32.1**	**3.7/10.8**	**85.3/35.5**
	0.343	**0.343**	**2.40**
Simplest ratio	**1**	**1**	**7**

Empirical formula : $SBCl_7$

(ii) Draw a likely structure of **X**, showing clearly the shape around the central atom(s). State the type of bond formed when SCl_4 and BCl_3 combine to form **X**.

[2]

●



●Type of bond : Dative/co-ordinate

[Total: 10]

4 **(a)** Hydrogen halides are acids resulting from the chemical reaction of hydrogen with one of the halogens.

(i) Briefly explain the trend in the boiling point for hydrogen chloride, hydrogen bromide and hydrogen iodide.

[2]

● Order of boiling point : HI > HBr > HC*l*

● Down the group, <u>size of electron cloud of HX increases</u>, leading to <u>greater distortion of electron cloud</u>. Extent of <u>instantaneous dipole-induced dipole interactions becomes stronger</u> and more extensive. Larger amount of energy required to break these intermolecular forces of attraction between the molecules.

(ii) By quoting appropriate data from the *Data Booklet*, explain the trend in the thermal stability of the hydrogen halides.

[2]

● Bond energy of H-C*l*, H-Br and H-I are <u>431, 366 and 299 kJ mol^{-1}</u> respectively.
● As seen from the data, the <u>H-X bond energy decreases down the group</u> resulting in <u>a decrease in the strength of the H-X bond</u>. Hence, <u>thermal stability of the hydrogen halides decreases</u> down the group. *OR*
● Radius of Cl, Br, I are <u>0.099, 0.114, 0.133 nm</u> respectively.
● <u>H-X bond length increases down the group</u>, <u>extent of effective orbital overlap decreases</u> and the <u>H-X bond strength decreases</u>. Hence, <u>thermal stability of the hydrogen halides decreases</u> down the group.

(b) The chlorides of aluminium and silicon react differently with water to produce acidic solutions.

(i) A sample of aluminum chloride is dissolved in water.

State and explain the pH and the colour observed when universal indicator is added to the resulting solution. Write equations where appropriate.

[3]

• Orange & pH = 3 to 4

• $AlCl_3$ undergoes both hydration and hydrolysis as Al^{3+} has a high charge density, hence a high polarising power. It draws electrons away from its surrounding water molecules and weakens the O-H bond.

Hydration: $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

Hydrolysis: $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$

1m for both equation

(ii) Explain why $SiCl_4$ can be hydrolysed by water.

[1]

• $SiCl_4$ is a covalent chloride that undergoes hydrolysis in water. Hydrolysis occurs due to energetically accessible & vacant 3d-orbitals available for dative bonding with water/accept lone pair electron from water.

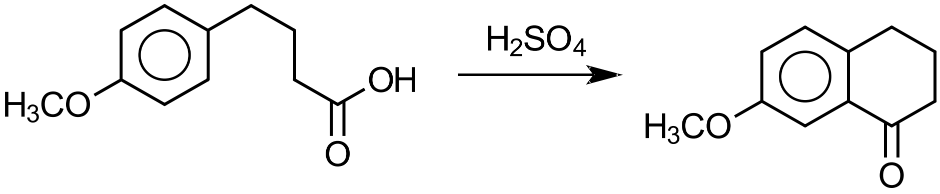
(c) In electrophilic substitution reactions, $AlCl_3$ can function as a Lewis acid catalyst to generate the electrophile.
Deduce whether Al_2Cl_6 can also function in the same manner.

[1]

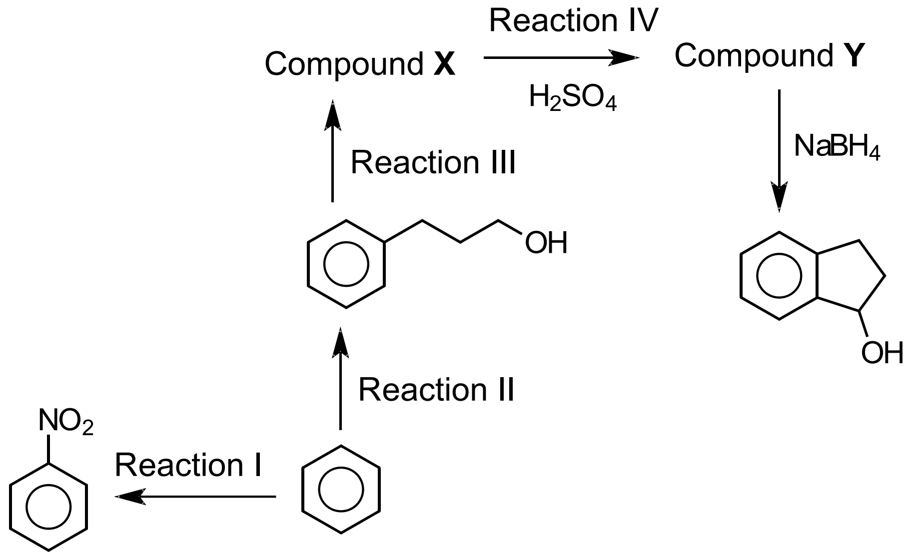
• No, because Al_2Cl_6 is not electron-deficient/has achieved octet structure and is less likely to accept a lone pair of electrons to form a dative bond.

(d) French scientist Charles Friedel and American scientist James Crafts, first discovered Friedel-Crafts Acylation in 1877.

Intramolecular Friedel-Crafts reaction could also work for some carboxylic acids, as seen from the example below.

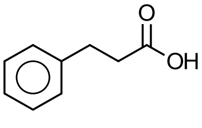


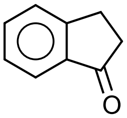
The synthesis of compound **Y** involves the intramolecular Friedel-Crafts reaction in Reaction **IV**.



Suggest reagents and conditions for Reaction **I** to Reaction **III** and give the structural formula for compounds **X** and **Y**.

[5]

- **Reaction I: concentrated nitric acid, concentrated sulfuric acid, heat < 60°C**
- **Reaction II: $ClCH_2CH_2CH_2OH$, anhydrous $AlCl_3$ as catalyst, rtp**
- **Reaction III: acidified $K_2Cr_2O_7$, heat under reflux (cannot use $KMnO_4$)**
- **X:** 

- **Y:** 

[Total: 14]

5 This question is about the use of catalytic reagents in green chemistry.

Green chemistry is the study and design of chemical processes and products to reduce the use and generation of hazardous chemicals. One principle of green chemistry proposes the use of catalytic reagents over stoichiometric reagents to reduce the amount of by-products and to increase efficiency.

In 1997, Roger Sheldon proposed E factor and Atom Utilisation as indicators of the amount of waste generated in a chemical reaction.

The E factor is defined as the mass of by-products produced per kg of product in chemical industry. The table below shows the typical product mass and E factor for the different industries.

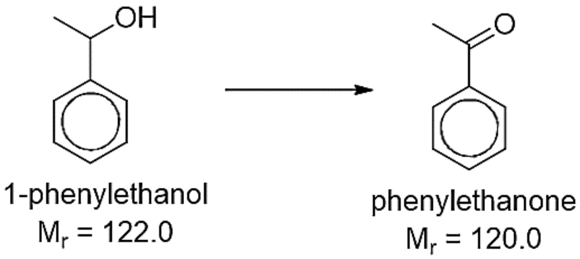
Industry	Typical product mass / 10^3 kg	Typical E factor
Bulk chemicals	10,000	2
Pharmaceuticals	100	50

The Atom Utilisation is defined as

$$\frac{\text{molar mass of the desired product}}{\sum \text{molar mass of all materials produced}} \times 100\%$$

In general, a reaction with a low E factor and a high Atom Utilisation value indicates that less waste is generated.

(a) 1-phenylethanol can be oxidised to phenylethanone via a stoichiometric reaction using chromium(VI) oxide in acidic medium or via a catalytic reaction using oxygen in the presence of ruthenium metal catalyst.



Details of each reaction are given in the table below.

Type of reaction	Reagents used	By-product(s)	Atom Utilisation
Stoichiometric reaction	CrO_3 and H_2SO_4	$Cr_2(SO_4)_3$ and H_2O	44%
Catalytic reaction	O_2 and Ruthenium	H_2O	x

(i) Calculate the Atom Utilisation, x, for the oxidation of 1-phenylethanol via catalytic reaction. Hence explain which type of reaction is more efficient for producing phenylethanone. [2]

- **Atom Utilisation for the catalytic reaction**
  = M_r of phenylethanone / (M_r of phenylethanone + M_r of water)
  = 120/(120+18) = 87.0%

- **Catalytic reaction is more efficient as the Atom Utilisation value is higher implying less waste is produced from the reaction.**

The environmental friendliness of a process can be represented by the overall environmental quotient, EQ, of the by-products which is given by

$$\sum_{\text{by-products}} E \times Q$$

where E is the E factor and Q is the unfriendliness quotient.

The higher the EQ value, the more toxic the by-product is to the environment. Q values for several substances are given below.

Substance	Q value
$Cr_2(SO_4)_3$	1000
CrO_3	1000
Ru	100
H_2SO_4	100
H_2O	1
O_2	1

(ii) 1-phenylethanol is oxidised to phenylethanone in both bulk chemical and pharmaceutical industry using the stoichiometric reaction.

Determine which industry is more environment-friendly in producing phenylethanone, showing clearly all workings.

[2]

- **Bulk chemical industry: 1000x2 + 1x2 = 2002**
  Pharmaceutical industry: 1000x50 + 1x50 = 50,050
- **Hence, the bulk chemical industry is more environmental friendly as the EQ value is lower, implying less amount of toxic waste is generated.**

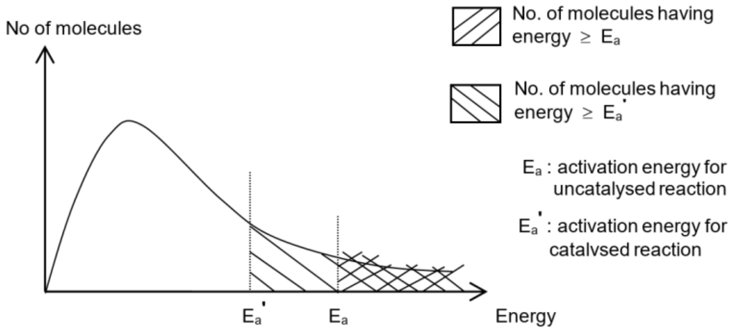
(b) Catalysts such as ruthenium are known as *heterogeneous* catalysts.

(i) Outline briefly how this type of catalyst speeds up the reaction between oxygen and 1-phenylethanol. [2]

- **Ruthenium provides the surface in which adsorption of reactant molecules and desorption of product molecules take place.**
- **The activation energy is lower than that of the uncatalysed reaction because the effective surface concentration of oxygen and 1-phenylethanol on the catalyst is higher and the intramolecular bonds of reactants are weakened by the adsorption effect.**

(ii) With a sketch of a suitable Boltzmann distribution curve below, explain the effect of ruthenium on the rate constant of the reaction.

[3]



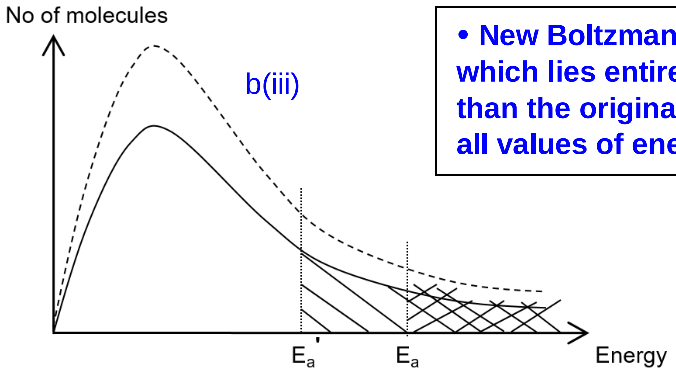
- **Correct Boltzmann curve with legends and correct Ea and Ea' shown**

- **The ruthenium catalyst provides an alternative pathway which involves a lower activation energy, E_a'. The number of reactant molecules having energy greater than or equal to Ea' increases significantly.**
- **Frequency of effective collisions increases and rate constant increases, hence rate increases.**

(iii) The reaction rate between oxygen and 1-phenylethanol can be increased by pumping more oxygen gas into a constant-volume reaction vessel.

On the same graph in **(b)(ii)**, sketch a new curve to represent energy distribution of reactants when more oxygen gas is added. Label the graph clearly as **(b)(iii)**.

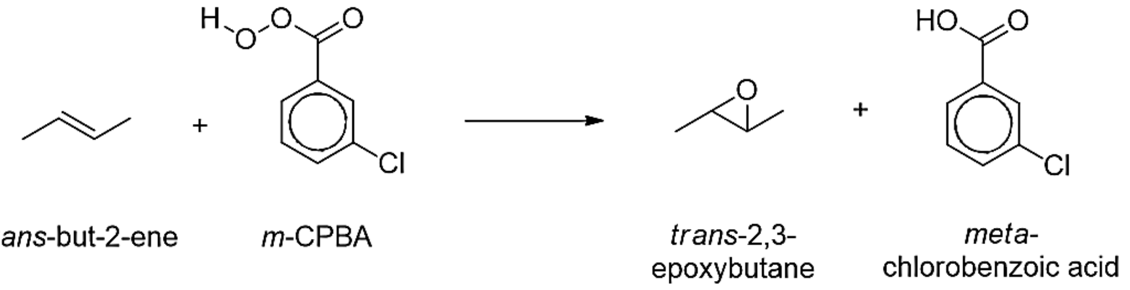
[1]



- **New Boltzmann curve which lies entirely higher than the original curve at all values of energy**

(c) Epoxidation is a reaction to synthesise epoxides from alkenes.

Trans-2,3-epoxybutane, an epoxide, is synthesised by reacting trans-but-2-ene with m-CPBA.



To study the kinetics between trans-but-2-ene and m-CPBA, several experiments were conducted using different volumes of m-CPBA and trans-but-2-ene, topped up with suitable volumes of hexane solvent. The set-up is placed on a piece of paper with an "X" mark.

The product, meta-chlorobenzoic acid, has low solubility in hexane and is precipitated out as soon as it is formed and the reaction is monitored by measuring the time taken for the "X" to disappear.

Experiment	Volume of trans-but-2-ene / cm^3	Volume of m-CPBA / cm^3	Volume of hexane / cm^3	Time taken for "X" to disappear / s
1	20	10	15	10.0
2	20	15	10	6.7
3	10	5	30	40.0
4	40	20	30	y

(i) Briefly explain the low solubility of the product meta-chlorobenzoic acid in hexane. [2]

Formation of • id-id interaction between meta-chlorobenzoic acid and hexane release insufficient energy to overcome the • hydrogen-bonding interactions between molecules of meta-chlorobenzoic acid and id-id interactions between hexane molecules.

(ii) Determine the order of reaction with respect to trans-but-2-ene and m-CPBA. Showing your workings clearly. [2]

Total volume is constant at 45 cm^3, so the volume ∝ concentration. Rate of reaction ∝ 1/t.

Relative rate for expt 1 = 1/10 = 0.100

Relative rate for expt 2 = 1/6.7 = 0.149

Relative rate for expt 3 = 1/40 = 0.025

• Comparing expt 1 and 2, keeping conc of trans-but-2-ene constant, when conc of m-CPBA increases by 1.5 times, rate increases by 1.5 times → 1st order reaction wrt m-CPBA.

• Comparing expt 1 and 3, when conc of m-CPBA and trans-but-2-ene each halves, rate decreases by 4 times → 1st order reaction wrt trans-but-2-ene.

(iii) Hence, construct a rate equation for the reaction between trans-but-2-ene and m-CPBA.

[1]

• Rate = k[trans-but-2-ene][m-CPBA]

(iv) State the value of y in experiment 4.

[1]

• 10s

(d) A thermal experiment was conducted to determine the enthalpy change of combustion of trans-2,3-epoxybutane.

8.26 g of trans-2,3-epoxybutane was burnt in excess oxygen and the temperature of water in the bomb calorimeter was measured. The following data are collected.

Heat capacity of calorimeter: 154 J K^{-1}

Volume of water: 400 cm^3

Temperature rise: 32 ^oC

The experiment was only 20% efficient.

(i) Calculate the enthalpy change of combustion of trans-2,3-epoxybutane.

[3]

• Total heat gained by water & calorimeter = 400x4.18x32 + 154x32 = 58432 J

• Total heat given out by burning 10cm^3 of trans-2,3-epoxybutane = 58432 x 100/20 = 292160 J

Amount of trans-2,3-epoxybutane burnt = 8.26/(4x12+8+16) = 0.1147 mol

• Enthalpy change of combustion = -292 160 / 0.1147 = -2550 kJ mol^{-1}

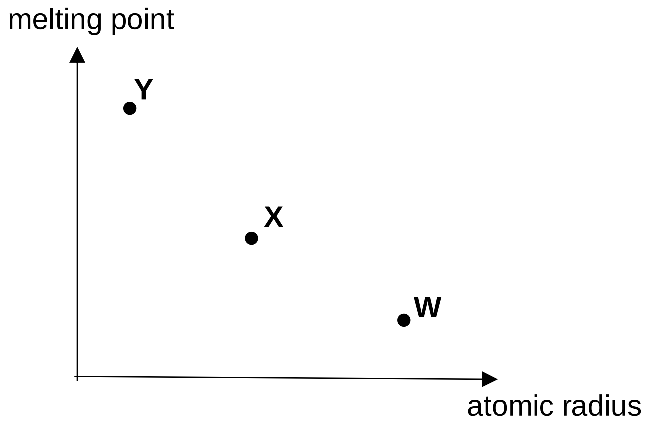
(ii) Suggest one modification to the set-up so that the experiment can be made more efficient.

[1]

Install windshield / conduct the experiment in a draught-free room / insulate the copper calorimeter

[Total: 20]

6 **(a)** **W**, **X** and **Y** represent consecutive elements in Period 3. The following shows a graph of their melting points plotted against the atomic radius (not drawn to scale).



The oxide of **Y** is insoluble in water but dissolves when the oxide of **W** is subsequently added.

(i) Suggest the identities of **Y** and **W**.

- **Y is <u>aluminum</u> and W is <u>Sodium</u> (X: Magnesium)**

(ii) Explain the above observations and write equations for all the reactions that has occurred.

[3]

- **Al_2O_3 is insoluble in water due to its <u>high lattice energy</u>.**

  When Na_2O dissolves in water, it forms NaOH(aq).

- **$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$**

  Since Al_2O_3 is an amphoteric oxide, it can react with NaOH(aq) and hence dissolves.

- **$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$**

Note: Y is not Si because SiO_2 does not dissolve in weakly alkaline solution.

(b) An experiment was conducted to investigate the thermal decomposition of Group 2 carbonates.

Equal amounts of carbonates of magnesium, strontium and barium were heated for two minutes. The gas produced was bubbled through calcium hydroxide and the time taken for the white ppt to be formed was recorded as follows:

Group 2 carbonate	$MgCO_3$	$SrCO_3$	$BaCO_3$
Time taken for white ppt to be formed / s	40	240	never

(i) Using relevant data from the *Data Booklet*, explain the results obtained.

[3]

- **The ionic radius of Mg^{2+}, Sr^{2+} and Ba^{2+} are 0.065 nm, 0.113 nm and 0.135 nm respectively.**

[Turn over

Down Group 2, the ionic charge of the cation remains the same while the ionic radius increases, hence √ <u>charge density decreases</u> down the group.

Hence, Mg^{2+} has the greatest polarising power and can √ <u>distort the electron cloud of CO_3^{2-}/polarise the C-O bond to the greatest extent</u>, √ <u>weakening the C–O bond</u> the <u>most</u>.

As a result, $MgCO_3$ √ <u>decomposes most readily/is least stable to heat</u> than $SrCO_3$ and $BaCO_3$ and requires the least amount of time to for the white ppt to be formed with calcium hydroxide.

•• Every 2√ 1 mark

(ii) If the experiment was repeated with calcium carbonate under the same conditions, suggest a value for the time needed for the white ppt to be observed.

[1]

The time needed for the white ppt to be observed is <u>70 s</u> (accept any value between 40 – 240).

(c) Inorganic reducing agents such as lithium aluminium hydride and sodium borohydrides are commonly used in organic chemistry.

A student attempted to synthesise propanal by reducing propanoic acid. He found that there was no reaction when sodium borohydride was used and the product formed with lithium aluminium hydride was not propanal.

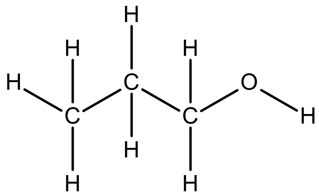
(i) Explain why lithium aluminium hydride can be used to reduce propanoic acid but not sodium borohydride.

[1]

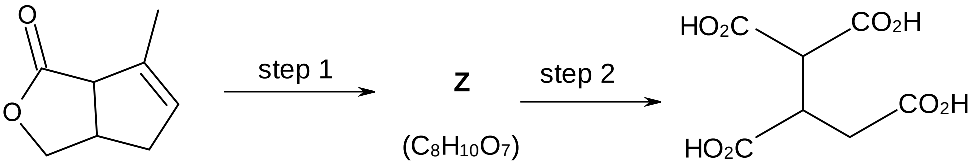
$LiAlH_4$ is a <u>stronger reducing agent</u> than $NaBH_4$ as the <u>H in the *Al*-H bond is more electron rich.</u> This is due to the <u>greater electronegativity difference between *Al* and H</u> in the *Al*-H bond (electronegativity difference is 2.1-1.5).

(ii) Draw the displayed formula of the organic product formed instead of propanal.

[1]



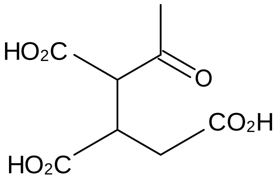
(d) Carboxylic acids can be made from a variety of other compounds. In the following reaction scheme, identify the intermediate compound **Z** and suggest reagents and conditions for the two steps.



[3]

- **Step 1: $KMnO_4$, H_2SO_4, heat**

- **Z:**



- **Step 2: alkaline I_2(aq), heat, followed by acidification using H_2SO_4(aq) or HC*l*(aq)**

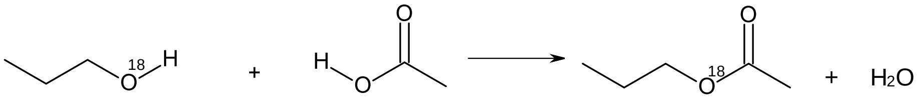
(e) Carboxylic acids are also useful compounds to synthesise esters such as propyl ethanoate which is responsible for the smell of pears and is used as a flavor additive.

In the synthesis of propyl ethanoate, the oxygen atom in a suitable alcohol is labelled with the oxygen isotope, ^{18}O.

Write an equation for this reaction, indicating clearly where the ^{18}O atom(s) are.

[1]

-



[Total: 14]