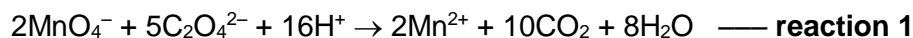


1 Planning (P)

When potassium manganate(VII) reacts with sodium ethanedioate, a redox reaction occurs as shown below:

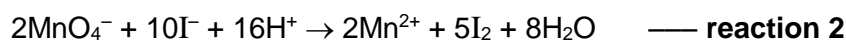
F



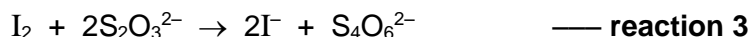
A product that is generated during the course of the reaction and helps to speed up the reaction rate is known as an autocatalyst. The autocatalyst for the above reaction is Mn^{2+} .

The kinetics of this reaction can be investigated by determining the concentration of MnO_4^- over the course of the reaction. Fixed aliquots (portions) of the reaction mixture are withdrawn at regular time intervals and added to an excess of potassium iodide.

The MnO_4^- in the aliquots reacts with excess iodide as shown below.



The amount of iodine formed can then be determined by titration with the sodium thiosulfate solution as shown below.



The volume of sodium thiosulfate used is proportional to the concentration of MnO_4^- .

- (a) In this experiment, both sodium ethanedioate and sulfuric acid are used in large excess. Explain the purpose of using a large excess of sodium ethanedioate and sulfuric acid.

This is to ensure that the concentration of sodium ethanedioate and sulfuric acid remains almost constant throughout the reaction / concentration do not affect rate. Hence, the order of reaction with respect to MnO_4^- can be determined.

- (b) Using the information given above, you are required to write a plan for the determination of the concentration of MnO_4^- at regular timing intervals.

You may assume that you are provided with the following:

- 0.0500 mol dm⁻³ potassium manganate(VII), KMnO_4
- 0.500 mol dm⁻³ sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$
- 1.00 mol dm⁻³ sulfuric acid, H_2SO_4
- 0.200 mol dm⁻³ potassium iodide, KI
- solid $\text{Na}_2\text{S}_2\text{O}_3$
- starch indicator
- stopwatch
- apparatus and chemicals normally found in a school or college laboratory.

Your plan should include:

- justification for
 - the volume of each reactants to be used in **reaction 1** so as to allow a minimum of **6 aliquots** of the reaction mixture to be withdrawn and the concentration of MnO_4^- in each aliquot to be determined;
 - the intended concentration of the sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, to be used;
- brief, but specific, details of the apparatus you would use, bearing in mind the levels of precision they offer;
- an outline of how the results would be obtained;
- a sketch of the graph you would expect to obtain.

[10]

Justification

Assuming 10 cm³ aliquot is withdrawn for each titration, minimum volume required for reaction 1 is 60 cm³.

Volume of MnO₄⁻ used = 25.0 cm³

Volume of Na₂C₂O₄ used = 50.0 cm³

Volume of H₂SO₄ used = 25.0 cm³

Total volume used for reaction 1 = 100 cm³
for all the volumes used.

Calculation for concentration of Na₂S₂O₃ to be used

$$\begin{aligned}\text{Amount of MnO}_4^- \text{ present in reaction 1} &= 0.0500 \times \frac{25.0}{1000} \\ &= 1.25 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of MnO}_4^- \text{ present in 10 cm}^3 \text{ aliquot} &= 1.25 \times 10^{-3} \times \frac{10.0}{100} \\ &= 1.25 \times 10^{-4} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of I}_2 \text{ produced in reaction 2} &= 1.25 \times 10^{-4} \times \frac{5}{2} \\ &= 3.13 \times 10^{-4} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of S}_2\text{O}_3^{2-} \text{ required in reaction 3} &= 3.125 \times 10^{-4} \times 2 \\ &= 6.25 \times 10^{-4} \text{ mol}\end{aligned}$$

Assuming a titre volume of 25.00 cm³ (acceptable range 10–30 cm³)

$$\begin{aligned}[\text{S}_2\text{O}_3^{2-}] \text{ used for titration} &= 6.25 \times 10^{-4} \div \frac{25.00}{1000} \\ &= 0.0250 \text{ mol dm}^{-3}\end{aligned}$$

To prepare a standard solution of 100 cm³ Na₂S₂O₃

$$\begin{aligned}\text{Mass of Na}_2\text{S}_2\text{O}_3 \text{ used} &= 0.0250 \times \frac{100}{1000} \times (158.2) \\ &= 0.396 \text{ g}\end{aligned}$$

Preparation of Na₂S₂O₃ standard solution

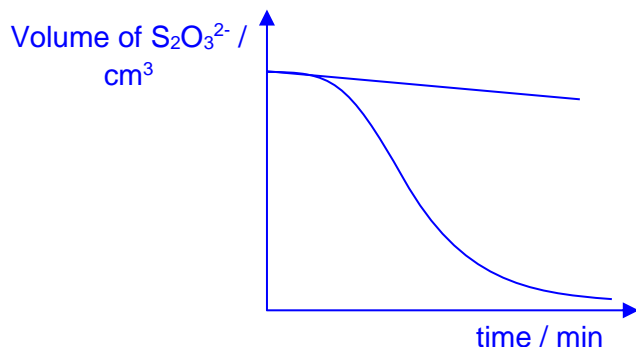
1. Weigh accurately about 0.315 g of Na₂S₂O₃ into a beaker.
2. Add distilled water to the beaker to dissolve Na₂S₂O₃ and transfer the solution quantitatively into a 100 ml standard flask.
3. Add distilled H₂O to the mark and shake the flask to give a homogenous solution.

Preparation of reaction mixture

1. Using a 100 cm³ measuring cylinder, add 50.0 cm³ of Na₂C₂O₄ and 25 cm³ H₂SO₄ into a conical flask.
2. Add 25 cm³ MnO₄⁻ to a 50 cm³ measuring cylinder.
3. Pour MnO₄⁻ to the reaction mixture in the conical flask and start the stopwatch immediately.
Ensure thorough mixing by swirling the flask.
(marking point for starting stopwatch is awarded only if MnO₄⁻ is added as the last reagent.)
4. At about 1 min, pipette 10.0 cm³ of the reaction mixture into a conical flask containing 10 cm³ of KI solution. Label conical flask 1.
5. Repeat step 4 five more times at about two minute intervals, transferring the aliquots into 5 separate conical flasks. Label conical flask 2 to 6.

Titration with sodium thiosulfate

1. Fill a 50 cm³ burette with Na₂S₂O₃.
2. Titrate the iodine in conical flask 1 against Na₂S₂O₃.
3. When the colour of the solution turns pale yellow, add about 1 cm³ of starch indicator. The solution will turn blue-black.
4. Continue the titration and the end-point is reached when the blue-black colour just disappears.
3. Repeat step 2 to 4 for conical flask 2 to 6.

Shape of graph expected

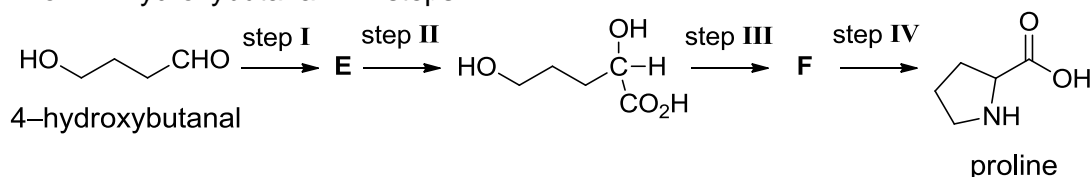
[12, max 10]

- (c) The order of reaction with respect to MnO₄⁻ can be determined by initial rate method. Use your graph, suggest how the initial rate can be determined.
As shown in the graph in (b), draw the tangent and then determine the gradient which gives the initial rate of reaction.

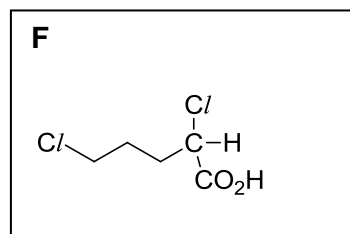
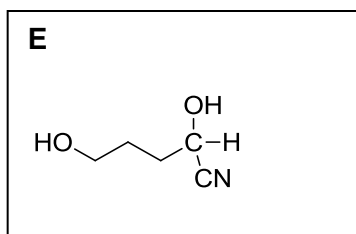
[1]

[Total: 12]

- 2 (a) Proline (pro) is one of the naturally occurring amino acids. It can be synthesised from 4-hydroxybutanal in 4 steps.



- (i) Suggest the structures of **E** and **F**.

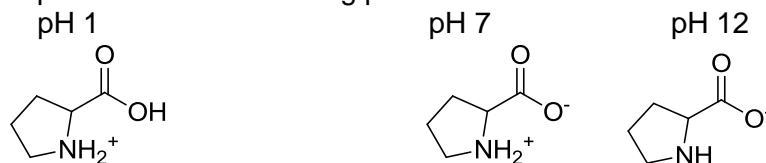


[2]

- (ii) Suggest the reagents and conditions required for the following steps.
 Step I: **HCN with KCN catalyst, room temperature**
 Step III: **conc HCl, ZnCl₂, heat,**
 Step IV: **NH₃(alc) heat in a sealed tube**

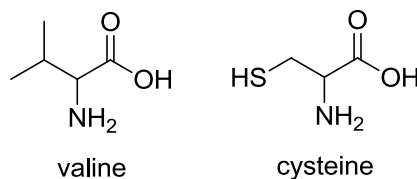
[3]

- (b) The two pK_a values associated with proline are 2.0 and 10.5. Make use of these pK_a values to suggest the major species present in the solution of proline with the following pH values.

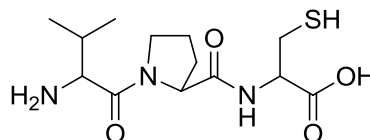


[3]

- (c) The structures of amino acids, valine (val) and cys are shown below.



- (i) Draw the structure of val-pro-cys peptide.



[2]

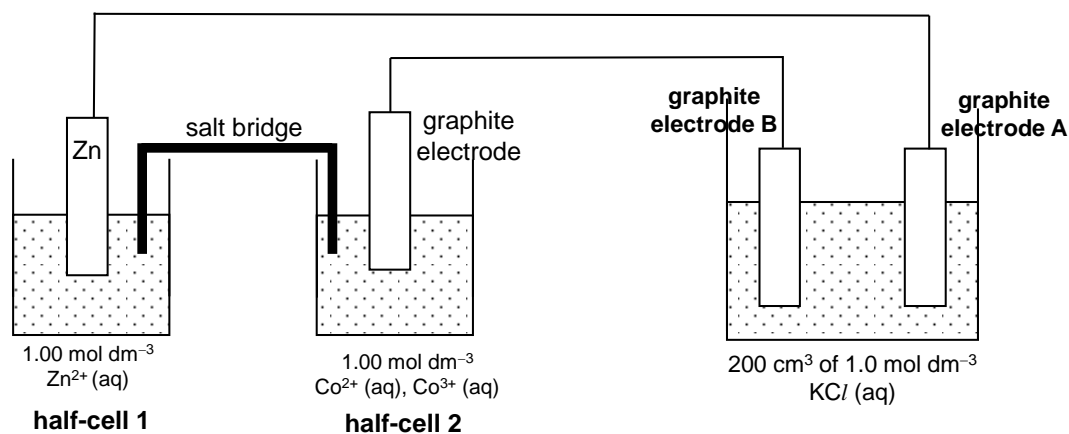
- (ii) State the possible R group interactions that val-pro-cys may have with another val-pro-cys peptide.

Disulfide bond formed between the CH_2SH in the cys groups.
van der waal's forces formed between the non-polar $\text{CH}(\text{CH}_3)_2$ groups in the valine or the non-polar $\text{CH}_2\text{CH}_2\text{CH}_2$ in the proline.

[2]

[Total: 12]

- 3 (a) A student used the following setup in an attempt to produce chlorine gas using potassium chloride solution.



- (i) Using relevant data from the *Data Booklet*, predict the type of redox reaction that occurs at each half-cell. State the polarity at the graphite electrodes **A** and **B**.

Half-cell 1: **oxidation**

Half-cell 2: **reduction**

Graphite electrode **A**: **negative (reduction occurs)**

Graphite electrode **B**: **positive (oxidation occurs)**

[2]

- (ii) 20 cm³ of hydrogen gas was collected on one of the electrodes after 10 minutes at room temperature and pressure. Assuming 20% of the hydrogen gas was lost during collection, calculate the current produced by the battery setup.

Graphite electrode A: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$

Amount of hydrogen gas collected = $20 / 24000 = 8.33 \times 10^{-4}$ mol

Actual amount of hydrogen produced = $(8.33 \times 10^{-4}) \times \frac{5}{4} = 1.04 \times 10^{-3}$ mol

**Number of moles of electrons transferred = $2 \times (1.04 \times 10^{-3})$
= 2.08×10^{-3} mol**

$Q = It$

$2.08 \times 10^{-3} \times (96500) = I \times (10 \times 60)$

Current, $I = 0.335$ A

[2]

- (iii) With reference to relevant data from the *Data Booklet*, explain the absence of chlorine being discharged on the other electrode.

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \quad E^\ominus = +1.23 \text{ V}$

$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^- \quad E^\ominus = +1.36 \text{ V}$

At the anode, $E^\ominus(\text{O}_2|\text{H}_2\text{O})$ is less positive than $E^\ominus(\text{Cl}_2|\text{Cl}^-)$, so H_2O will undergo oxidation preferentially to give O_2 .

[1]

- (b) 20 cm³ of a gas mixture containing gaseous ethanol, carbon monoxide and excess oxygen was burned completely. There was a contraction of 1 cm³. When the product mixture was passed through sodium hydroxide, there was a further contraction of 6 cm³. All gas volumes are measured at 400 K and 1 atm.

Determine the molar composition of the ethanol and carbon monoxide in this gas mixture.

Let the volume of $\text{C}_2\text{H}_5\text{OH}$ and CO measured at 1 atm be x cm³ and y cm³, respectively.



c/cm³ $-x$ $-3x$ $+2x$ $+3x$

Total change in volume = $2x + 3x - x - 3x = x$



c/cm³ $-y$ $-1/2y$ $+y$

Total change in volume = $y - y - 1/2y = -1/2y$

Hence $x - 1/2y = -1$

The further contraction is due to the removal of CO_2 by NaOH ,

Hence, $2x + y = 6$

$x = 1, y = 4$

Molar composition of ethanol = $1/20 \times 100\% = 5\%$

Molar composition of $\text{CO} = 4/20 \times 100\% = 20\%$

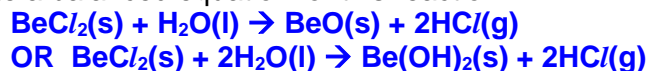
[3]

[Total: 8]

- 4 Magnesium and beryllium are Group II elements but beryllium behaves differently from that of magnesium. There is said to be a 'diagonal relationship' between beryllium and aluminium as they show similar chemical behaviour due to their similarities in electronegativity and charge density.

- (a) (i) When a few drops of water are added to solid beryllium chloride, steamy white fumes are evolved and a white solid remains, which is insoluble in water.

Write a balanced equation for this reaction.



[1]

- (ii) When a large amount of water is added to solid beryllium chloride, a clear, weakly acidic solution is obtained. Explain.

Due to the high charge density of Be^{2+} , BeCl_2 undergoes hydration and hydrolysis/ $\text{Be}^{2+}(\text{aq})$ pulls electrons away from one of the surrounding water molecules, hence weakening the O–H bond which results in the release of a proton and give rise to an acidic solution.

[1]

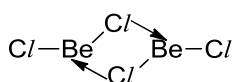
- (iii) At 750 °C, the relative molecular mass of gaseous beryllium chloride corresponds to the formula BeCl_2 . At 550 °C, gaseous beryllium chloride exists as a mixture of BeCl_2 and Y (relative molecular mass of Y is 160).

Determine the molar composition of gaseous beryllium chloride at 550 °C which has a relative molecular mass of 100. Draw a diagram to illustrate the nature of the bonding in Y and indicate the value of the bond angle about Be.

$$100 = 80x + 160(1-x)$$

$$x = 0.75 \text{ and } 1-x = 0.25$$

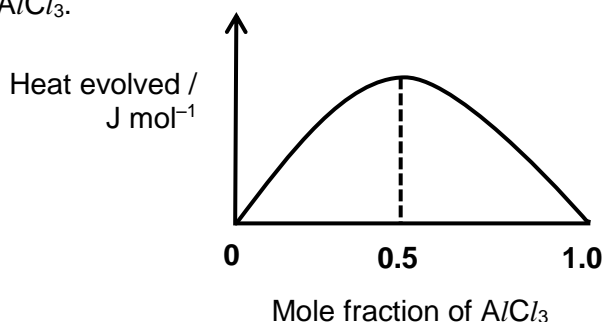
Composition is 75% BeCl_2 and 25% Y



Trigonal planar with respect to Be, hence bond angle is 120°

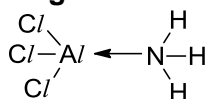
[2]

- (iv) When aluminium chloride, AlCl_3 , is mixed with ammonia, compound Z is formed and the reaction is exothermic. The diagram below shows the relationship between the heat evolved per mole of the mixture and the mole fraction of AlCl_3 .



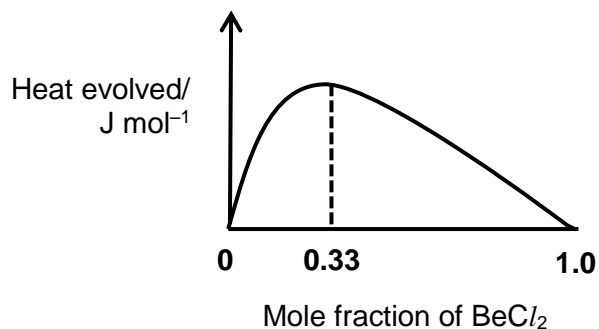
Draw a diagram to show the bonding in a molecule of compound Z.

Diagram of Compound Z :



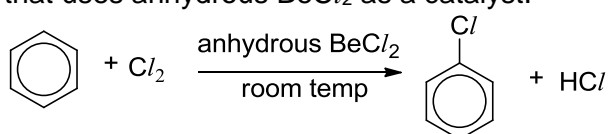
[1]

- (v) Sketch a labelled diagram similar to (a)(iv) that you would expect to obtain when AlCl_3 is replaced by BeCl_2 .



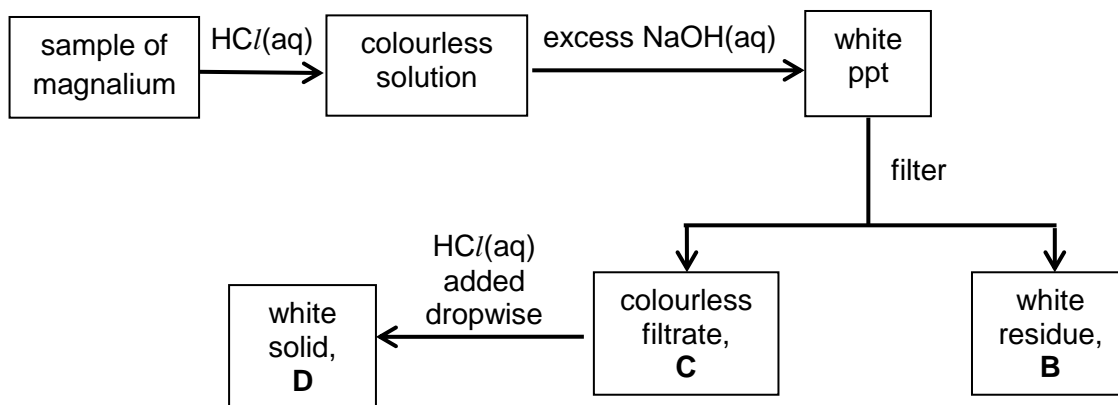
[1]

- (vi) Write a balanced equation of a chlorination reaction in Organic Chemistry that uses anhydrous BeCl_2 as a catalyst.



[1]

- (b) Magnalium is an alloy of aluminium and magnesium which is used in boat-building. The diagram below shows some reactions of magnalium.



Identify **B**, **C** and **D**.

B : Mg(OH)_2

C : Al(OH)_4^-

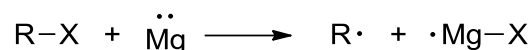
D : Al(OH)_3

[3]

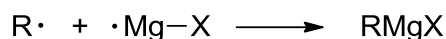
- (c) Grignard reagents, RMgX , can be prepared by the reaction of magnesium with halogenoalkane, RX , using dry ether as the solvent.

The mechanism of the reaction involves two steps.

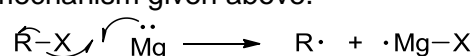
Step 1: It involves the transfer of one electron from Mg to the halogen X followed by the homolytic fission of the carbon–halogen bond. This forms MgX , which is a radical.



Step 2: MgX radical couples with the alkyl radical formed in step 1.



- (i) Draw curve arrows to show the movement of electrons in step 1 of the mechanism given above.



[1]

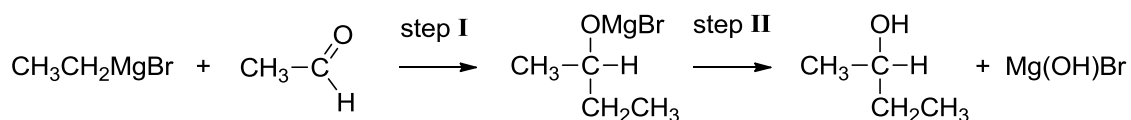
- (ii) Suggest which step in the mechanism is the rate-determining step. Explain your answer.

Step 1 is the rate-determining step

Step 1 has higher activation energy as it involves breaking of covalent bond.

[1]

Grignard reagents can be used to prepare alcohols from carbonyl compounds as shown by the reaction of $\text{CH}_3\text{CH}_2\text{MgBr}$ with ethanal below:



- (iii) What type of reaction takes place in steps I and II?

step I : Nucleophilic addition

step II : Hydrolysis or Acid–base reaction

[2]

- (iv) The variation of the rate constant k with temperature for the reaction of $\text{CH}_3\text{CH}_2\text{MgBr}$ with ethanal is given below:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where E_a denotes the activation energy in J mol^{-1} , R is the gas constant, and T is the temperature in Kelvin.

Given that at 25°C , the rate constant and activation energy of the reaction is $9.16 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and 102 kJ mol^{-1} respectively.

Explain, with calculations, the effect of temperature change on the rate of the reaction when the temperature is raised by 5°C .

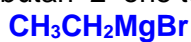
$$\ln \frac{k_2}{9.16 \times 10^{-3}} = -\frac{102000}{8.31} \left(\frac{1}{303} - \frac{1}{298} \right)$$

$$k_2 = 1.81 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

A rise in temperature results in a larger rate constant. Since the concentrations of the reactants are kept constant, a larger rate constant indicates a faster reaction. (or rate constant doubles, hence rate doubles)

[2]

- (v) Draw the structural formula of the Grignard reagent that will react with butan-2-one to form 3-methylpentan-3-ol in a similar two-step reaction.



[1]

- (vi) Suggest why $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_2\text{Br}$ and magnesium cannot be used to prepare the Grignard reagent $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_2\text{MgBr}$.

$\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_2\text{MgBr}$ cannot be prepared as it will react further with the ketone group in the same molecule.

[1]

- (vii) Ethanal is oxidised to ethanoic acid by acidified potassium dichromate. Using data from the Data Booklet and the data below, calculate E^\ominus_{cell} of the reaction.

$$E^\ominus(\text{CH}_3\text{CO}_2\text{H}|\text{CH}_3\text{CHO}) = +0.92 \text{ V}$$

Hence, explain why the reaction takes place only in the presence of heat.

$$\begin{aligned} E^\ominus_{\text{cell}} &= 1.33 - 0.92 \\ &= 0.41 \text{ V} \end{aligned}$$

$E^\ominus_{\text{cell}} > 0$, hence reaction is thermodynamically feasible.

Heat is needed to overcome the high activation energy needed to break strong covalent bonds.

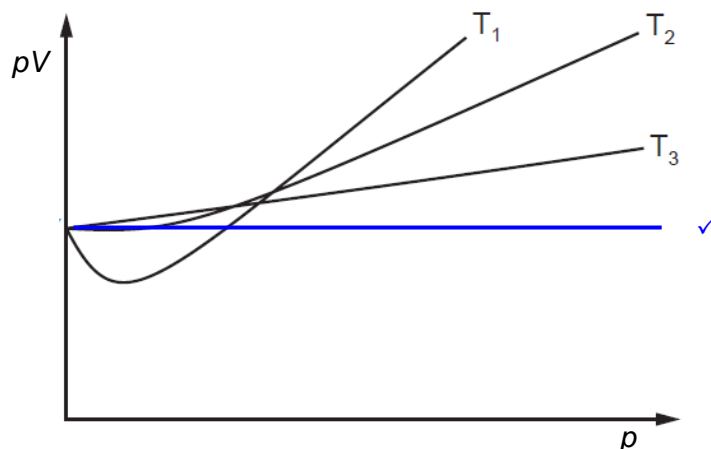
(or reaction is kinetically not feasible in the absence of heat as it involves breaking of strong covalent bonds)

[2]

[Total: 20]

- 5 (a) The relationship $pV = nRT$ can be derived from the laws of mechanics by assuming ideal behaviour for gases.

The graph represents the relationship between pV and p for a real gas at three different temperatures, T_1 , T_2 and T_3 .



- (i) Draw **one** line on the graph to show what the relationship should be for the same amount of an ideal gas and state which of T_1 , T_2 or T_3 is the lowest temperature.
 T_1 is the lowest temperature.

[1]

- (ii) State and explain the effect of pressure on the extent to which a gas deviates from ideal behaviour.
A gas deviates from ideal behaviour at high pressure as the molecular volume is significant / no longer negligible OR the intermolecular forces of attraction are significant.

[1]

- (b) A flask with a volume of 100 cm^3 was first weighed with air filling the flask. The same flask was then weighed with only gas, **Y**, filling the flask. The results, measured at 26°C and $1.00 \times 10^5 \text{ Pa}$, are shown.

Mass of flask containing air = 47.930 g
 Mass of flask containing **Y** = 47.989 g
 Density of air = $0.00118 \text{ g cm}^{-3}$

Calculate the relative molecular mass, M_r , of **Y**.

$$\begin{aligned} \text{Mass of air} &= 0.00118 \times 100 = 0.118 \text{ g} \\ \text{Mass of flask} &= 47.930 - 0.118 = 47.812 \text{ g} \\ \text{Mass of Y} &= 47.989 - 47.812 = 0.177 \text{ g} \\ 1.00 \times 10^5 \times 100 \times 10^{-6} &= \frac{0.177}{M_r} \times 8.31 \times (26 + 273) \end{aligned}$$

$$M_r \text{ of Y} = 44.0$$

[2]

- (c) In recent years there has been worldwide interest in the possible extraction of 'shale gas' (a form of natural gas) as an important energy source.

One of the problems associated with using shale gas is its variable composition. **Table 1** shows the percentage composition of shale gas from four different sources **J**, **K**, **L** and **M**.

Table 1

source	CH ₄	C ₂ H _x	C ₃ H _y	CO ₂	N ₂
J	80.3	8.1	2.3	1.4	7.9
K	82.1	14.0	3.5	0.1	0.3
L	88.0	0.8	0.7	10.4	0.1
M	77.5	4.0	0.9	3.3	14.3

In the formula above, **x** and **y** are variables.

- (i) Draw the structures of **three** possible compounds with the formula C₃H_y.

CH₃CH₂CH₃, CH₃CH=CH₂, CH₃C≡CH and CH₂CCH₂ [Any 3 of 4.]

[1]

- (ii) Which source of shale gas, **J**, **K**, **L** or **M**, will provide the most energy when burned? Explain your answer.

Source K

Source K has the highest percentage composition of hydrocarbons which will provide the most energy when burned.

[1]

- (iii) Suggest one method by which carbon dioxide can be removed from shale gas.

Carbon dioxide can be removed from shale gas by passing it through aqueous sodium hydroxide.

[1]

Table 2 shows a comparison of the relative amounts of pollutants produced when shale gas, fuel oil and coal are burned to produce **the same amount of energy**.

Table 2

air pollutant	shale gas	fuel oil	coal
CO ₂	117	164	208
CO	0.040	0.033	0.208
NO ₂	0.092	0.548	0.457
SO ₂	0.001	1.12	2.59
particulates	0.007	0.84	2.74

- (iv) Suggest why shale gas produces the smallest amount of CO₂.
Shale gas contains small hydrocarbon molecules with low C:H ratio unlike fuel oil and coal which contain more carbon atoms, and thus produces the smallest amount of CO₂.

[1]

- (v) Explain which of the three fuels, shale gas, fuel oil or coal, is the largest contributor to 'acid rain'.

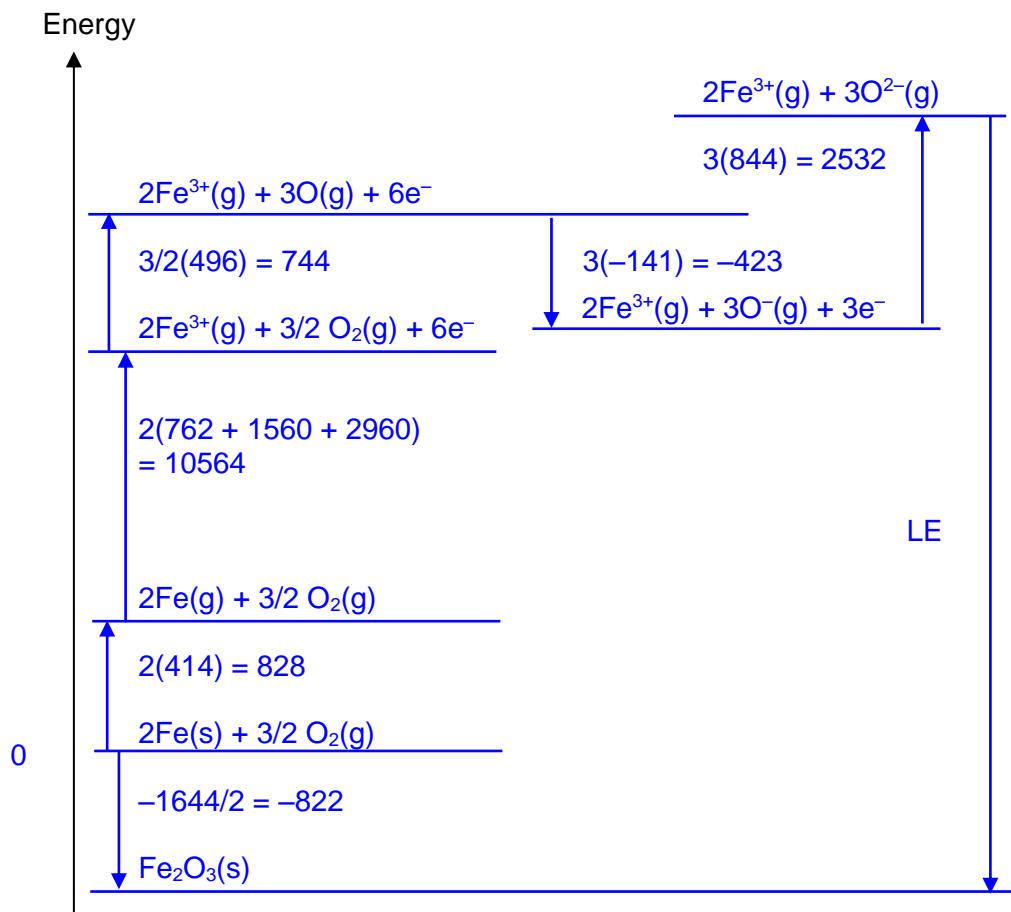
coal

Coal produced the largest relative amounts of CO₂, NO₂ and SO₂ when burned to produce the same amount of energy.

[1]

- (d) Use the following data and data from the *Data Booklet* to construct a labelled energy level diagram to determine the lattice energy of Fe_2O_3 .

enthalpy change of $4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$	$-1644 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of Fe(s)	$+414 \text{ kJ mol}^{-1}$
electron affinity of the oxygen atom	-141 kJ mol^{-1}
electron affinity of the O^- ion	$+844 \text{ kJ mol}^{-1}$



By Hess' law,

$$-822 = 828 + 10564 + 744 - 423 + 2532 + \text{LE (ecf)}$$

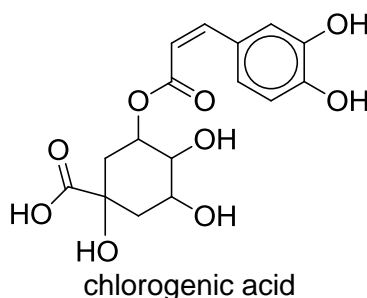
$$\text{LE} = -15067 \approx -1.51 \times 10^4 \text{ kJ mol}^{-1}$$

[5, max 4]

[4]

[Total: 13]

- 6 (a) Coffee beans contain chlorogenic acid.

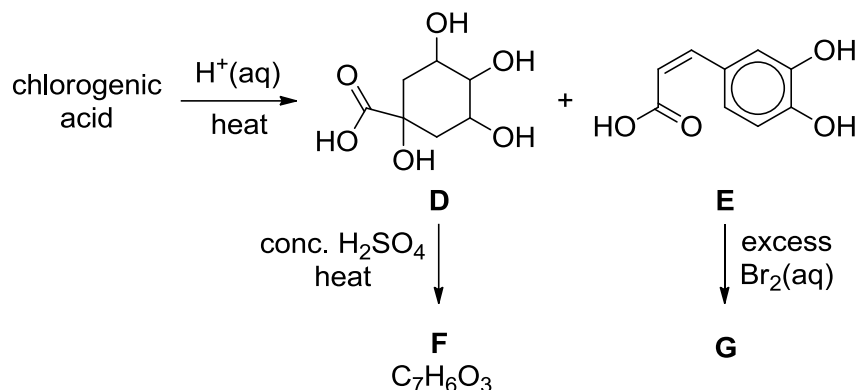


- (i) How many moles of $\text{H}_2\text{(g)}$ will be evolved when 1 mol of chlorogenic acid reacts with an excess of sodium metal?

3 mol

[1]

On heating with dilute aqueous acid, chlorogenic acid produces two compounds **D** and **E**.



When compound **D** is heated with concentrated H_2SO_4 , compound **F**, $\text{C}_7\text{H}_6\text{O}_3$, is formed.

Compound **F** does not decolourise cold dilute acidified KMnO_4 but reacts with $\text{Br}_2(\text{aq})$.

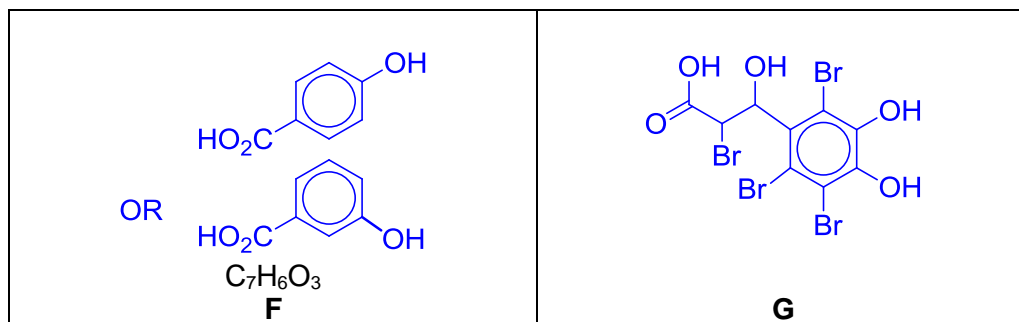
When compound **E** is treated with an excess of $\text{Br}_2(\text{aq})$, compound **G** is produced.

- (ii) If the test with cold dilute acidified KMnO_4 had been positive, which functional group would this have shown to be present in **F**?

C=C bond OR alkene functional group

[1]

- (iii) Suggest the structures for compounds **F** and **G**, and draw them in the relevant boxes below.



[2]

- (b) Allyl alcohol, $\text{CH}_2=\text{CHCH}_2\text{OH}$, is a colourless liquid which is soluble in water.

Crotyl alcohol, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$, is a colourless liquid which is used as a solvent.

- (i) Describe how you would distinguish between allyl alcohol and crotyl alcohol. The compounds may be distinguished by a preliminary chemical reaction followed by a subsequent testing of the reaction products. Include clearly the reagents, conditions and observations for each compound.

Step I: KMnO_4 , $\text{NaOH}(\text{aq})$, cold

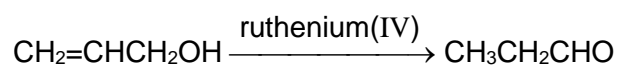
Step II: I_2 , $\text{NaOH}(\text{aq})$, warm

Crotyl alcohol gives yellow ppt.

Allyl alcohol does not give yellow ppt.

[2]

- (ii) Allyl alcohol may be converted into propanal by using a ruthenium(IV) catalyst in water.



State the type of reaction and explain your answer.

It is a disproportionation reaction where the C=C bond is reduced and the primary alcohol is oxidised.

[1]

[Total: 7]