

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE
NAME

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INDEX
NUMBER

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CHEMISTRY

9647/02

Paper 2 Structured

13 September 2016

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your class, index number and name on all 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 workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

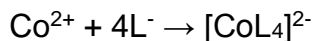
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

FOR EXAMINER'S USE			
Paper 2			
1	/ 12	5	/ 9
2	/ 12	6	/ 17
3	/ 14	Penalty	sf units
4	/ 8	Total	/ 72

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

1 Planning (P)

The formation of a cobalt(II) complex ion, from Co^{2+} and an unknown ligand (L^-), is accompanied by the appearance of a blue colouration.



A machine, known as a spectrometer, is able to measure the amount of light that is absorbed when a specific wavelength of visible light is shone through a few cm^3 of the solution. The amount of light absorbed is then expressed as an absorbance value, and the absorbance value is proportional to the concentration of the cobalt(II) complex ion.

This technique can be used to confirm the formula of the cobalt(II) complex ion. A series of solutions containing varying volume ratios of L^- to Co^{2+} , both of the same concentration, while keeping the total volume of the Co^{2+} and L^- constant, is prepared. A spectrometer is used to measure the absorbances of the solutions. A graph of absorbance against volume of L^- is then plotted.

Using the graph of absorbance against volume of L^- , the ratio of L^- to Co^{2+} equal to that in the cobalt(II) complex ion can be then determined from the maximum point. This is known as the “Job’s Method”.

- (a) The spectrometer is set to use the wavelength of the light that is absorbed most strongly by the complex ion.

Colour	Wavelengths (nm)
Red	620-750
Orange	590-620
Yellow	570-590
Green	495-590
Cyan	475-495
Blue	450-475
Violet	380-450

Suggest a wavelength in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

[2]

Any value from 591 to 619 nm.

The observed colour of the cobalt complex ion is blue thus the colour complementary to blue, orange, will be absorbed.

- (b) Using the information given above, you are required to write a plan to confirm the formula of the cobalt(II) complex ion as $[\text{CoL}_4]^{2-}$.

You may assume that you are provided with:

- solid cobalt(II) nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$;
- solution of L^- , of concentration $0.100 \text{ mol dm}^{-3}$;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of 250 cm^3 of $0.100 \text{ mol dm}^{-3}$ aqueous cobalt(II) nitrate;
- the preparation of five 50 cm^3 complex ion solutions containing varying volume ratios of L^- to Co^{2+} ;
- how the absorbance values would be obtained;
- a sketch of the graph of absorbance against volume of L^- that you would expect to obtain;
- how the calculation can be performed to determine the formula of $[\text{CoL}_4]^{2-}$.

[10]

Preparation of aqueous Co^{2+}

M_r of cobalt nitrate = 290.9

Amount of cobalt nitrate in $250 \text{ cm}^3 = (0.1 / 1000) \times 250 = 0.0250 \text{ mol}$

Mass of cobalt nitrate required = $0.0250 \times 290.9 = 7.27 \text{ g}$

Using a clean and dry weighing boat / bottle, weigh accurately 7.27 g of solid cobalt nitrate with an electronic balance.

Transfer the solid into a 100 cm^3 beaker.

Rinse the weighing boat with deionised water and transfer the washings into the beaker.

Dissolve the solid with deionised water.

Transfer the solution into a 250 cm^3 graduated flask with the aid of a filter funnel and a glass rod.

Rinse the beaker with deionised water and transfer the washings into the graduated flask.

Top the graduated flask to the mark with deionised water.

Cap the graduated flask and shake well to ensure the solution is well mixed.

Preparation of 4 solutions

Flask	Vol of L^- / cm^3	Vol of Co^{2+} / cm^3
1	25.00	25.00
2	35.00	15.00
3	40.00	10.00
4	42.00	8.00
5 (max 6:1 ratio)	45.00	5.00

- 5 solutions
- Total volume = 50 cm^3
- At least 2 volume smaller or greater than 40 cm^3 of L^-
- No volume of L^- or Co^{2+} should be 0 cm^3 .

Procedure

- Fill a burette with the prepared Co^{2+} solution and another with the L^- solution.
- Transfer 25 cm^3 of Co^{2+} solution into a 100 cm^3 conical flask, followed by 25 cm^3 of L^- solution.
- Swirl the solution to ensure it is homogeneous
- Repeat steps 1 to 3 for with the stated volumes of solutions for Flask 2 to 4.
- Set up the spectrometer to absorb yellow light.
- Measure and record the absorbance of each of the 4 solutions.
- Plot a graph of absorbance against volume of L^- solution.

Calculations

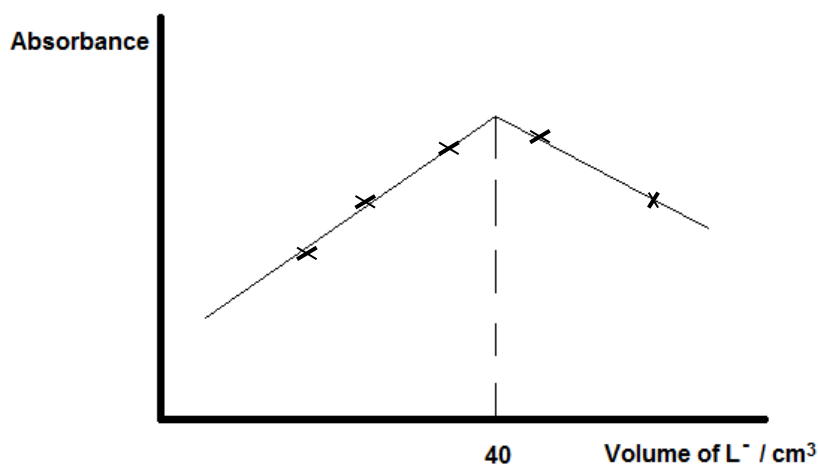
Maximum of point = 40 cm^3 of L^-

Amount of $\text{L}^- = (40 / 1000) \times 0.1 = 0.00400 \text{ mol}$

Amount of $\text{Co}^{2+} = (10 / 1000) \times 0.1 = 0.00100 \text{ mol}$

Ratio of L^- to $\text{Co}^{2+} = 4:1$

Graph

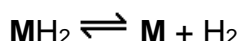


[10]
[Total: 12]

- 2 The mission of the Hydrogen and Fuel Cells Programme by the U.S. Department of Energy (DoE) is to reduce petroleum use, greenhouse gas emissions, and air pollution and to contribute to a more diverse and efficient energy infrastructure by enabling the widespread commercialisation of hydrogen and fuel cell technologies.

One such technology involves creating an energy system concept that stores hydrogen in the form of metal hydrides. Magnesium hydride (MgH_2) is one of the compounds currently being researched on its viability on hydrogen storage. One way to release hydrogen from metal hydrides is to react them with water, where a hydroxide is formed as a side product.

The other way to obtain hydrogen is through the thermal decomposition of the metal hydride MH_2 . When hydrogen is needed, these metal hydrides can be heated to release molecular hydrogen.



This adsorption and desorption of hydrogen in metals serves like a 'hydrogen bank'. The rate of desorption of hydrogen is proportional on the strength of ionic bonds formed between the metal and hydride ions.

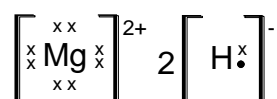
Apart from MgH_2 , other Group II hydrides are also being studied and researched on the same purpose. The table below shows some properties of the Group II hydrides.

	MgH_2	CaH_2	SrH_2	BaH_2
Percentage of H / % by mass of H	7.7	4.8	2.2	1.4
Density / g cm^{-3}	1.74	1.54	2.64	3.62
Melting point / $^{\circ}\text{C}$	650	842	777	727
$\Delta H_f / \text{kJ mol}^{-1}$	-114	-144	-119	-118

- (a) (i) Write an equation for the reaction between solid MgH_2 and water.
 $\text{MgH}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Mg}(\text{OH})_2(\text{s}) + 2\text{H}_2(\text{g})$

[1]

- (ii) Draw the dot-and-cross diagram for MgH_2 .



[1]

- (b) (i) Explain, with reasoning, the trend on the rate of desorption of hydrogen for the Group II metal hydrides from CaH_2 to BaH_2 .

$$\text{Strength of ionic bond} \propto \frac{q_+ q_-}{r_+ + r_-}$$

Radius of cation, r_+ : $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$

Strength of ionic bond : $\text{BaH}_2 < \text{SrH}_2 < \text{CaH}_2$

Rate of desorption of hydrogen from $\text{CaH}_2 < \text{SrH}_2 < \text{BaH}_2$ (fastest)

[2]

- (ii) Which metal hydride, CaH_2 or BaH_2 , would you expect to decompose more readily? Explain your answer by using relevant data from the above table.

ΔH_f becomes less exothermic from CaH_2 to BaH_2

$-\Delta H_f$ becomes less endothermic from CaH_2 to BaH_2

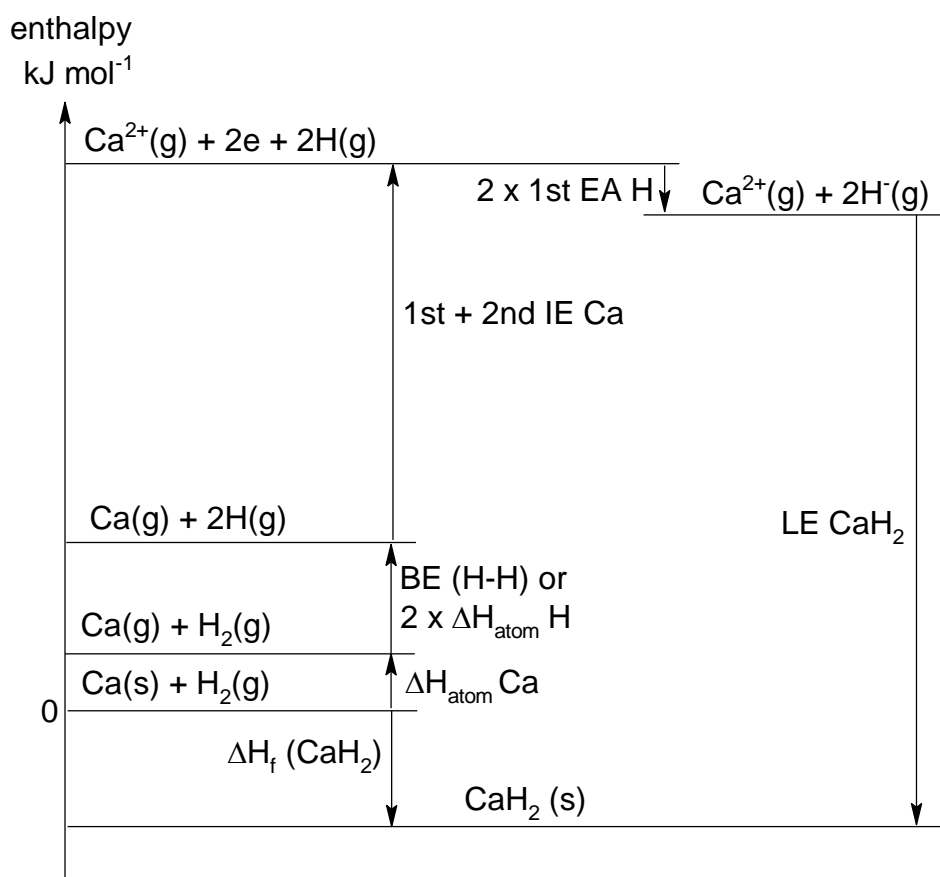
Hence,

Ease of decomposition: $\text{CaH}_2 < \text{BaH}_2$

[2]

- (iii) Using relevant information from the *Data Booklet* and the information given below, construct a Born-Haber cycle to calculate the lattice energy for CaH_2 .

(The first electron affinity for hydrogen is $-72.8 \text{ kJ mol}^{-1}$ and the enthalpy change of atomisation of calcium is $+178 \text{ kJ mol}^{-1}$)



$$\Delta H_f^\ominus (\text{CaH}_2) = \Delta H_{\text{at}}^\ominus (\text{Ca}) + 2\Delta H_{\text{at}}^\ominus (\text{H}) + 1^{\text{st}} \text{IE}(\text{Ca}) + 2^{\text{nd}} \text{IE}(\text{Ca}) + 2 \times 1^{\text{st}} \text{EA}(\text{H}) + \Delta H_{\text{latt}}^\ominus (\text{CaH}_2)$$

$$-144 = 178 + 436 + 590 + 1150 + 2(-72.8) + \Delta H_{\text{latt}}^\ominus (\text{CaH}_2)$$

$$\text{LE} = \underline{-2.35 \times 10^3 \text{ kJ mol}^{-1}}$$

[3]

- (c) A car company is planning to develop cars that run on hydrogen fuel produced by MgH_2 .

The following information is for a typical petrol-fuelled car.

Weight of vehicle / kg	1088
Fuel tank / L	42
Fuel consumption / km L⁻¹	17
Energy consumption of petrol / kJ kg⁻¹	46.4
Density of petrol / g cm⁻³	0.8 g

- (i) Calculate the energy produced by a petrol-fuelled car which is running at full tank.

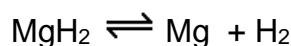
$$\text{Mass of fuel at full tank} = 42 \times 1000 \times 0.8 = 33600 \text{ g}$$

$$\begin{aligned} \text{Energy produced by the petrol at full tank} &= 33600/1000 \times 46.4 \\ &= 1559.04 \text{ kJ} \end{aligned}$$

[1]

- (ii) It was found that 1 kg of hydrogen produce 3 times more energy than petrol with the same mass.

Assuming 100% efficiency, calculate the amount of magnesium metal needed to store the hydrogen as the hydride to provide the same amount of energy in the hydrogen-fuelled car. (1 L = 1000 cm³)



1 kg petrol produces 46.4 kJ of energy

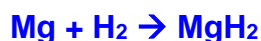
1 kg H₂ produces (46.4 x 3) = 138.9 kJ of energy

Hence to produce 1559.04 kJ of energy,

$$\text{mass of hydrogen required} = 1559.04/138.9 = 11.15 \text{ kg}$$

or

$$\text{Mass of H}_2 = 33600 / 3 = 11.2 \text{ kg}$$



$$\text{Number of mole of H}_2 \text{ needed} = 11.15 \times 1000/2 = 5575 \text{ or } 5600$$



$$\text{Number of mole of Mg needed} = 5575$$

$$\text{Mass of Mg metal needed} = 5575 \times 0.0243$$

$$= 135 \text{ kg or } 136 \text{ kg}$$

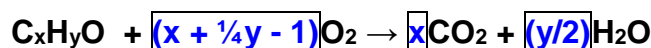
[2]

[Total: 12]

- 3 (a) In the presence of excess oxygen, a liquid alcohol, compound **A**, C_xH_yO , undergoes complete combustion to produce 3.19 dm^3 of hot gases at a temperature of 250°C at a pressure of 1 atm ,

Upon cooling to room temperature, the volume contracted to 836 cm^3 . The gases were then passed through aqueous sodium hydroxide and the final volume remaining was 100 cm^3 .

- (i) Fill in the following blanks for the equation for the complete combustion of **A**.



[1]

- (ii) Using the *ideal gas equation*, find the amount of CO_2 and amount of H_2O that was produced respectively from the complete combustion of compound **A**.

$$\text{Amount of gases in hot gases} = (101000 \times 3.19 \times 10^{-3}) / (8.31 \times 523) = 0.0741 \text{ mol}$$

$$\text{Volume of } CO_2 = 836 - 100 = 736 \text{ cm}^3$$

$$\text{Amount of } CO_2 = (101000 \times 736 \times 10^{-6}) / (8.31 \times 298) = 0.0300 \text{ mol}$$

$$\text{Volume of } O_2 = 100 \text{ cm}^3$$

$$\text{Amount of } O_2 = (101000 \times 100 \times 10^{-6}) / (8.31 \times 298) = 0.00408 \text{ mol}$$

$$\text{Amount of } H_2O = 0.0741 - 0.0300 - 0.00408 = 0.0401 \text{ mol}$$

[3]

- (iii) Using your answer to (a)(i) and (a)(ii), solve for x and y in C_xH_yO and hence determine the empirical formula of **A**.

$$\text{Amount of C} = 0.0300 \text{ mol}$$

$$\text{Amount of H} = 0.0401 \times 2 = 0.0802 \text{ mol}$$

$$\text{Empirical ratio (C:H)} = 0.0300 : 0.0802$$

$$x = 3; y = 8$$

$$\text{Empirical formula} = C_3H_8O$$

[1]

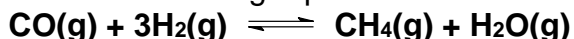
- (ii) The actual number of moles of gases obtained from the combustion is found to be **higher** than that calculated when using the *ideal gas equation*.

Account for the difference between the two results.

Significant intermolecular forces exists between the gas molecules, hence the gases deviates from ideality.

[1]

- (b) Methane can be obtained when carbon monoxide is heated to 900 °C with hydrogen gas as shown in the following equation.



- (ii) Write an expression for the K_c of the reaction, stating its units.

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} \text{ mol}^{-2} \text{ dm}^6$$

[1]

- (iii) 1 mol of carbon monoxide was heated with 4 mol of hydrogen gas in a 10 dm³ vessel. At equilibrium, the vessel contained 0.387 mol of methane.

Calculate the K_c for the reaction of carbon monoxide.

	CO	3H ₂	⇌	CH ₄	H ₂ O
Initial mol	1	4		0	0
Δ mol	-0.387	-1.161		+0.387	+0.387
Eq mol	0.613	2.839		0.387	0.387
[] mol dm ⁻³	0.0613	0.284		0.0387	0.0387

$$K_c = \frac{(0.0387)(0.0387)}{(0.0613)(0.284)^3} = 1.07 \text{ mol}^{-2} \text{ dm}^6$$

[2]

- (iv) Suggest, with an explanation, how the position of equilibrium might alter when 1 mol of helium was added into the vessel.

When an inert gas is added, the total pressure increase but the partial pressure of the reactants and products do not change. There would not be any change to the position of equilibrium.

OR

When an inert gas is added, since the volume of the vessel remains the same, the concentration of the reactants and products do not change. There would not be any change to the position of equilibrium.

[1]

- (c) Anhydrous aluminium sulfate is commonly used in organic reactions to remove water. It decomposes at 600 °C to produce only an insoluble white solid and misty fumes. The white solid dissolves in both aqueous sodium hydroxide and aqueous hydrochloric acid while the misty fumes turn moist blue litmus red.

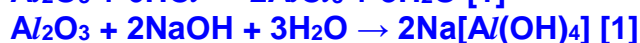
- (i) Suggest the identities of the white solid and the misty fumes. Hence, write a balanced equation for the decomposition of aluminium sulfate.

White solid: Al₂O₃ Misty fumes: SO₃



[2]

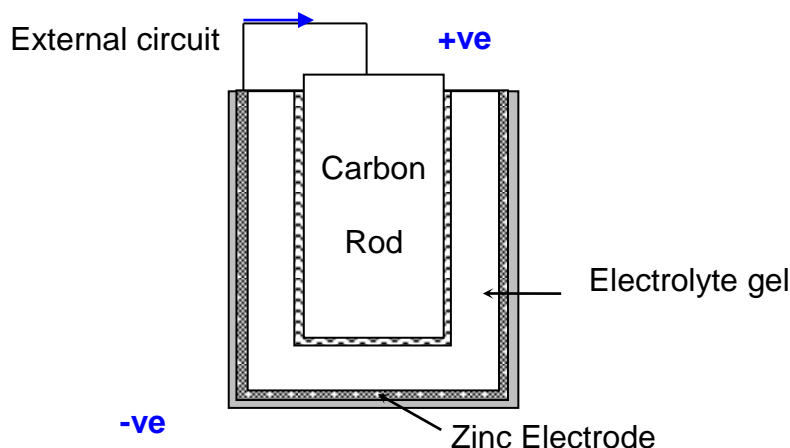
- (ii) Write equations for the reactions of the white solid with aqueous sodium hydroxide and hydrochloric acid.



[2]

[Total: 14]

- 4 Batteries for hearing aids comprise of zinc and carbon electrodes. These electrodes in an electrolyte, maintained at a pH of 11, forms a galvanic cell in which zinc is oxidised and oxygen from the air is reduced.



- (a) Write a balanced equation for the overall chemical reaction and calculate the E°_{cell} of this cell.



$$E^\circ_{\text{cell}} = +0.40 + (+0.76) = +1.16 \text{ V}$$

[2]

- (b) Indicate, on the diagram above, the polarity of both electrodes and the direction of electron flow in the external circuit.

[2]

- (c) Explain how the e.m.f. of the cell would change if the pH of the electrolyte decreases.

When pH decreases, $[\text{OH}^-]$ falls and so, position of equilibrium of the reduction half-cell shifts to the right. Hence, $E_{\text{reduction}}$ becomes more positive, making e.m.f. more positive.

[2]

- (d) If a current of $4 \times 10^{-5} \text{ A}$ was drawn from the cell, calculate how long a zinc electrode weighing 2 g will last before it needs to be replaced. Give your answer correct to the nearest day.

$$\text{Amount of Zn} = \frac{2}{65.4} = 0.03058 \text{ mol}$$



$$\text{Amount of electrons} = 2 \times 0.03058 = 0.06116 \text{ mol}$$

$$\therefore Q = 0.06116 \times 96500 = 5902 \text{ C}$$

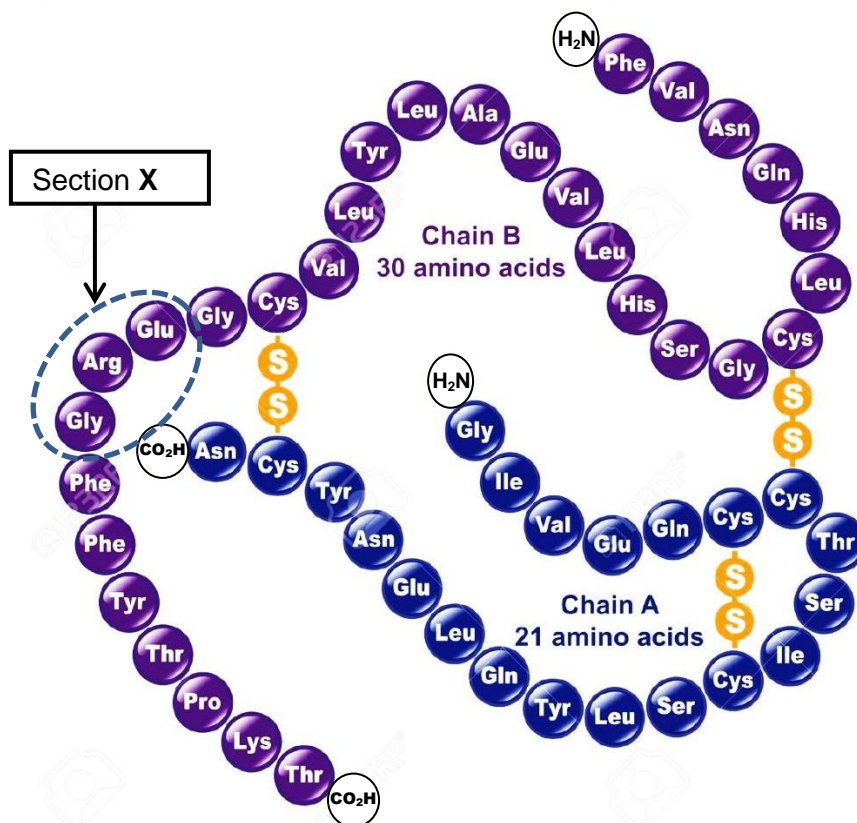
$$t = \frac{Q}{I} = \frac{5902}{4 \times 10^{-5}} = 1.476 \times 10^8 \text{ s} = \underline{1708 \text{ days}}$$

[2]

[Total: 8]

- 5 Insulin is a hormone made by the pancreas that allows your body to use glucose from carbohydrates in the food that you eat for energy. Insulin helps keeps your blood sugar level from getting too high or too low.

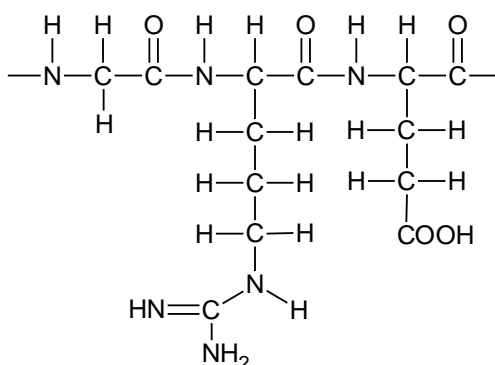
The insulin molecule consists of 51 amino acid residues, in two polypeptide chains.



Some information on the amino acids of insulin is given below.

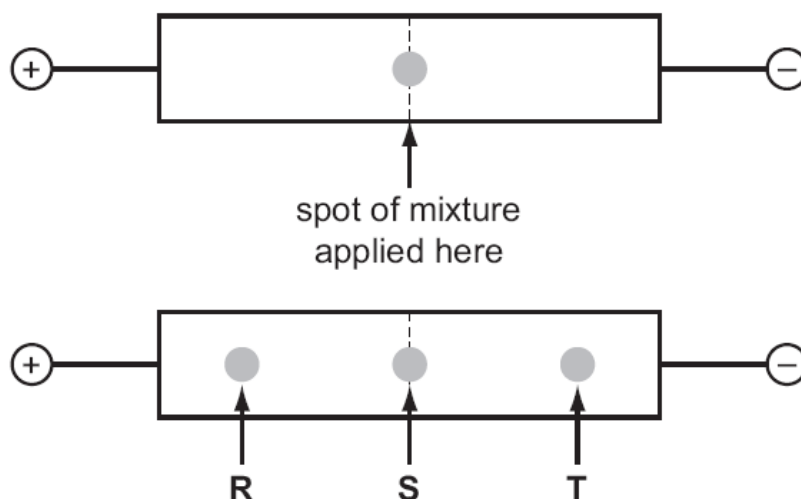
amino acid	Abbreviated name	Formula of side chain (R in $\text{RCH}(\text{NH}_2)\text{CO}_2\text{H}$)	pI
arginine	arg	$-(\text{CH}_2)_3\text{NHC}(\text{NH}_2)=\text{NH}$	10.76
cysteine	cys	$-\text{CH}_2\text{SH}$	5.07
glutamic acid	glu	$-\text{CH}_2\text{CH}_2\text{COOH}$	3.22
glycine	gly	$-\text{H}$	5.97

- (a) Draw the structural formula of section X in insulin.
Formula must start with N terminus, showing R groups, ending with C terminus:



[1]

- (b) The diagram shows the results of electrophoresis on a mixture of the amino acids obtained from hydrolysis of section X at pH 6.0.



Draw the structure of the species responsible for the spots labelled **R**, **S** and **T**.

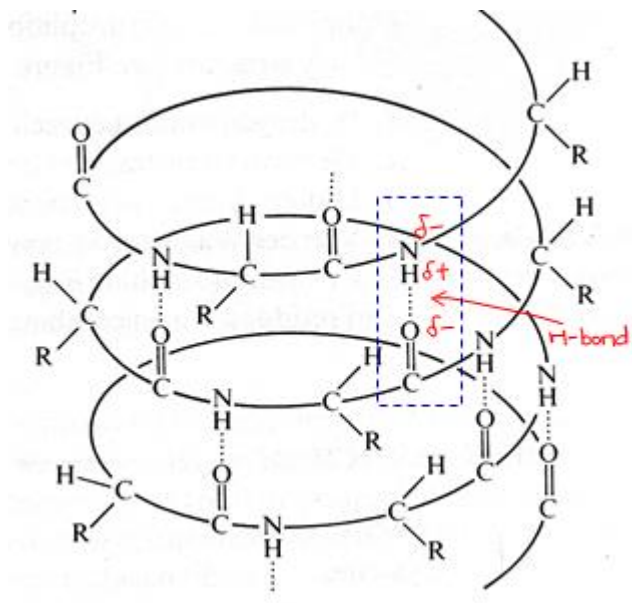
R	S	T
$\begin{array}{c} \text{H}_3\text{N}^+-\text{CH}-\text{CO}_2^- \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CO}_2^- \end{array}$	$\begin{array}{c} \text{H}_3\text{N}^+-\text{CH}-\text{CO}_2^- \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H}_3\text{N}^+-\text{CH}-\text{CO}_2^- \\ \\ (\text{CH}_2)_3\text{NHC}(\text{NH}_3)^+=\text{NH} \end{array}$ <p>Accept protonation on any basic amine group of side chain. (more than 1 protonation also allowed)</p>

k

[3]

- (c) The polypeptide chains of insulin coil to form short sections of α -helix which stabilises the secondary structure.

Describe with the aid of a sketch, how a polypeptide chain is held in the shape of an α -helix.



[3]

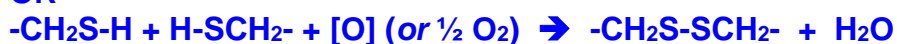
- (d) The three-dimensional structure of insulin is further stabilised by disulfide linkages.

Write an equation for the formation of such linkage and state the type of reaction involved.

Type of reaction: oxidation



OR

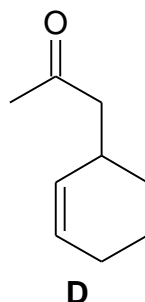


[2]

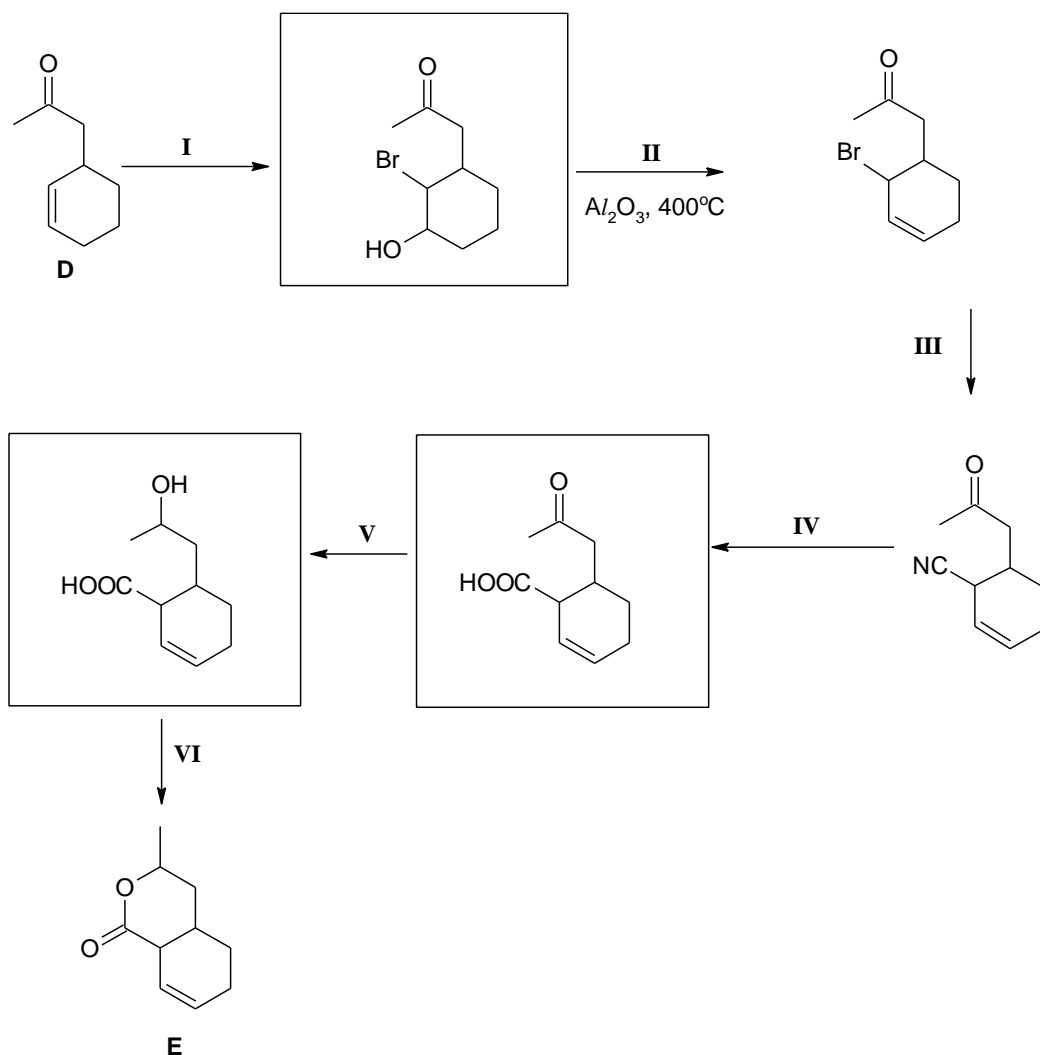
[Total: 9]

- 6 Lactones are cyclic esters. They are formed by intramolecular esterification of the corresponding hydroxycarboxylic acids.

(a) (i) The reaction scheme below shows how lactone **E** is synthesised from compound **D**.



Complete the reaction scheme by giving the structural formulae of the intermediate organic products in the spaces provided and stating the reagents and conditions for steps **I**, **III**, **IV**, **V** and **VI**.



Step	Reagents and conditions
I	$\text{Br}_2(\text{aq})$
III	NaCN/KCN in ethanol, heat
IV	$\text{H}_2\text{SO}_4(\text{aq})$, heat
V	NaBH_4 in methanol
VI	concentrated H_2SO_4 , heat

[8]

- (ii) Suggest a simple chemical test to distinguish compound **D** from **E**.

Reagents and conditions: 2,4-dinitrophenylhydrazine

Observations:

For compound **D**, orange ppt is formed.

For compound **E**, no orange ppt is formed (or no observable change)

Or

Reagents and conditions: $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{H}_2\text{SO}_4(\text{aq})$, heat

Observations:

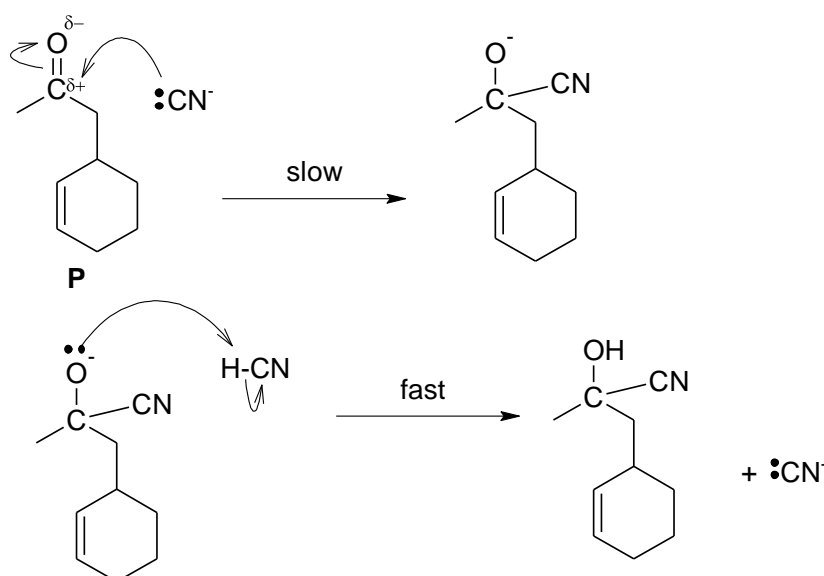
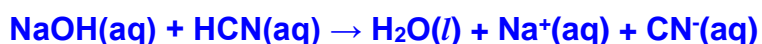
For compound **D**, orange solution remains (or no observable change)

For compound **E**, orange solution turned green.

[2]

- (iii) Name and outline the mechanism when compound **D** is treated with HCN in the presence of aqueous NaOH at 10°C .

Name of mechanism: Nucleophilic Addition



[3]

- (b) Lactones with three- or four-membered rings are very reactive compared to five- or six-membered rings, making their isolation difficult.

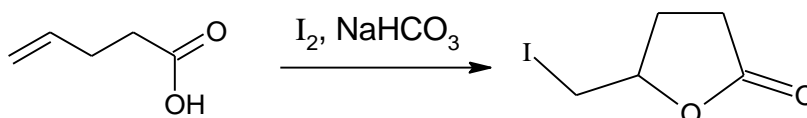
Suggest why lactones with three- or four-membered rings are very reactive.

Three- or four-membered rings have significant ring/angle strain.

[1]

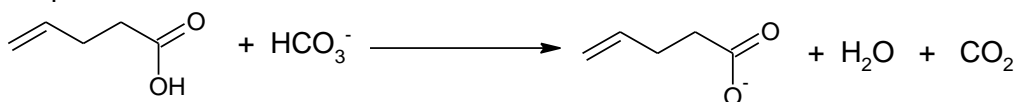
- (c) Iodolactonisation reaction was first reported by M. J. Bougalt in 1904 and has since become one of the most effective ways to synthesise lactones.

An example of the iodolactonisation is the reaction of 4-pentenoic acid as shown below.

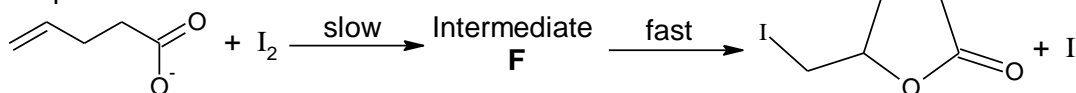


Two simplified steps in the iodolactonisation mechanism are given below.

Step 1



Step 2



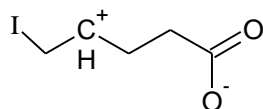
- (i) Suggest the role of HCO_3^- in step 1 of the mechanism.

It acts as a base to abstract H^+ from the carboxylic acid.

[1]

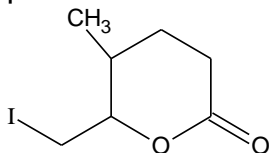
- (ii) The type of reaction in Step 2 of the mechanism is electrophilic addition.

Draw the structure of intermediate **F**.



[1]

- (iii) Suggest the structural formulae of the final organic product formed when $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{COOH}$ undergoes iodolactonisation in a similar process as above.



[1]

[Total: 17]

End of Paper