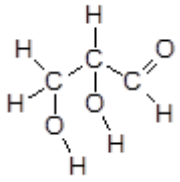
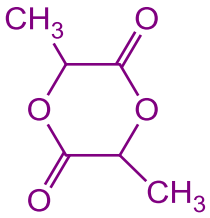
1.	Lactic acid (2-hydroxypropanoic acid), also known as milk acid, is a chemical compound that plays a role in several biochemical processes.		
	(a)	**(i)**	**A** is an isomer of lactic acid. It rotates plane-polarised light and reacts with Fehling's solution to give a reddish brown precipitate. 0.01 mol of **A** reacts with sodium to give 0.24 dm^3 of hydrogen gas under room temperature and pressure conditions. Suggest a structural formula of **A**, giving reasons for your answer.
			 **A is ;** **A has a chiral centre as it rotates plane–polarised light. ;** **A is an aldehyde since it reacts with Fehling's solution to give a reddish brown precipitate. ;** **Amount of hydrogen evolved with sodium per mol of A** **=** $\frac{0.24}{24} \div 0.01$ **= 1 mol** **Hence, there are two –OH group. ;**
		(ii)	Compare the acidity of isomer **A** and lactic acid. Explain your answer.
			A is less acidic than lactic acid. ; **A is an alcohol. The stability of its anion is lower than the stability of the anion of lactic acid as the anion is destabilised by the electron–donating alkyl group. ;** **Lactic acid is a much stronger acid as its anion forms two equivalent resonance structures with the negative charge on O delocalised over the carbon and two electronegative O atoms. ;**
			[7]
	(b)	Lactic acid can undergo a condensation reaction in the presence of hot concentrated sulfuric acid to form a cyclic diester **B**, $C_6H_8O_4$.	

2 Lactic acid (l) $\underset{\text{heat}}{\overset{\text{conc } H_2SO_4}{\rightleftharpoons}}$ Diester **B** (l) + 2 H_2O (l)

The system exists in *dynamic equilibrium*.

(i) Draw the structure of diester **B**.



;

(ii) Explain what is meant by the term *dynamic equilibrium*.

rate of forward reaction equals to rate of reverse reaction ;

(iii) Write an expression for the equilibrium constant, K_C, for the reaction, stating its units.

$$K_C = \frac{[B][H_2O]^2}{[Lactic\ acid]^2}$$;

units = mol dm^{-3} ;

(iv) In an experiment, 2.0 mol of lactic acid was allowed to reach equilibrium. Given that 95% of lactic acid has reacted at equilibrium and the total volume of the mixture remained constant at 200 cm^3, calculate the K_C for this reaction.

	2 lactic acid	⇌	B	+	2H_2O
initial mol	2		0		0
change in mol	-0.95(2)		+0.95		+0.95(2)
eqm mol	0.1		0.95		1.9

ICE table ;

$$K_C = \frac{\left(\frac{0.95}{0.2}\right)\left(\frac{1.9}{0.2}\right)^2}{\left(\frac{0.1}{0.2}\right)^2} = 1714.75 \approx 1710 \text{ mol dm}^{-3}$$;

(v) In the reverse reaction, i.e. the hydrolysis of the diester **B**,

Diester **B** (l) + 2 H_2O (l) ⟶ 2 Lactic acid (l)

the rate of reaction gradually increases at first, but subsequently it decreases. Explain why this is so.

The rate increases at first when the carboxylic acid is first formed

because it partially dissociates to give H^+ which catalyses the hydrolysis of ester. ;

The rate decreases as the reaction proceeds due to decrease in the concentration of the ester, leading to decrease in frequency of effective collisions. ;

[8]

(c) Lactic acid, along with ammonium hydrogen carbonate, $(NH_4)HCO_3$, is used in mosquito attractant.

Ammonium hydrogen carbonate is a solid which can decompose into ammonia, carbon dioxide and water.

(i) Write an equation, with state symbols, for the decomposition of ammonium hydrogen carbonate.

$(NH_4)HCO_3$ (s) → NH_3 (g) + CO_2 (g) + H_2O (*l*) ;

(ii) Using the enthalpy changes given in the table below, calculate the enthalpy change of reaction for the decomposition of $(NH_4)HCO_3$.

Compound	**Enthalpy change of formation / kJ mol^{-1}**
$(NH_4)HCO_3$ (s)	-853
NH_3 (g)	-46.0
CO_2 (g)	-394
H_2O (*l*)	-286

ΔH = (-46.0 – 394 – 286) – (-853) ;

= +127 kJ mol^{-1} ;

(iii) Predict, with a reason, the sign of ΔS for the decomposition of ammonium hydrogen carbonate.

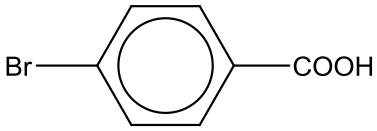
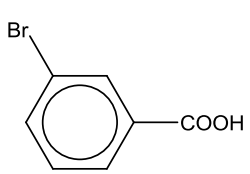
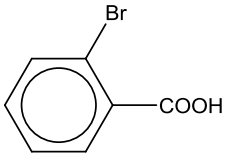
ΔS is positive. ;

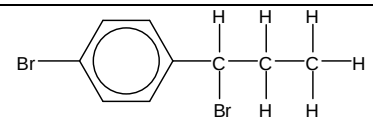
The system becomes more disorderly as there is an increase in number of moles of gases. ;

[5]

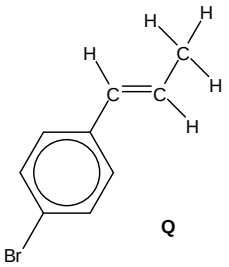
[Total: 20]

2. **(a)** Compound **P** is a halogen derivative with molecular formula $C_9H_{10}Br_2$. Reaction of

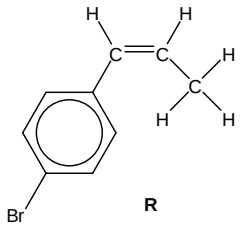
		P with ethanolic KOH gives rise to a mixture of two isomeric products, **Q** and **R**, with the molecular formula C_9H_9Br. Both **Q** and **R** decolourise hot acidified $KMnO_4$ and the reaction produces **S** (structure given below) and ethanoic acid, CH_3COOH. On treatment with excess ethanolic ammonia, **P** produces **T** ($C_9H_{12}NBr$) as the major product.  **S**	
		(i)	Draw all possible structural isomers of **S** that have the same chemical properties.
			  ; ;
		(ii)	Deduce the structures of **P**, **Q**, **R** and **T**. Explain your reasoning.
			P has C:H ≈ 1:1 ⇒ P is likely to contain a benzene ring **P undergoes elimination with ethanolic KOH to give Q and R** **⇒ Q and R are geometric isomers with only one C=C and one of the Br atoms in P is bonded to the benzene ring** **Q and R undergo oxidation with hot acidified $KMnO_4$ to give two carboxylic acids, S and CH_3COOH** **⇒ Q and R are alkenes and each of the C atom of the C=C bond is bonded to one R group and one H atom** **P undergoes nucleophilic substitution with NH_3 to give T ($C_9H_{12}NBr$)** **⇒ T is a primary amine**



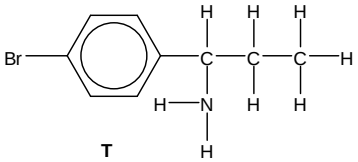
P



Q



R



T

1m for each deduction (capped at 2m)

1m for each structure

[8]

(b) Bromocyclohexane ($C_6H_{11}Br$) and benzoyl bromide (C_6H_5COBr) differ in their reactivity with aqueous sodium hydroxide. Describe and explain the differences.

Benzoyl bromide reacts with aqueous NaOH at <u>room temperature</u>, while bromocyclohexane reacts with aqueous NaOH only <u>on heating</u>. ;

Due to the presence of electronegative O attached to the carbonyl C, the carbonyl C in C_6H_5COBr is <u>more partially positive</u> compared to the C to which Br is attached in $C_6H_{11}Br$.

OR

The carbonyl carbon in C_6H_5COBr is sp^2–hybridised so that it is <u>less sterically hindered</u> than the sp^3–hybridised carbon to which the Br atom is attached in $C_6H_{11}Br$. ;

Thus, C_6H_5COBr undergoes nucleophilic substitution more readily.

[2]

(c) The kinetics of the reaction between bromocyclohexane and hot aqueous

sodium hydroxide was investigated.

1.0 mol dm^{-3} of bromocyclohexane was reacted with 0.01 mol dm^{-3} of aqueous sodium hydroxide. The pH of the reaction mixture was measured at regular time intervals using a data-logger. The data in the following table was obtained.

Time / min	pH	$[OH^-]$ / mol dm^{-3}
0	13.0	
2	12.9	
4	12.8	
6	12.6	
8	12.4	
10	11.9	

(i) Copy the table and fill in the $[OH^-]$ for each set of readings.

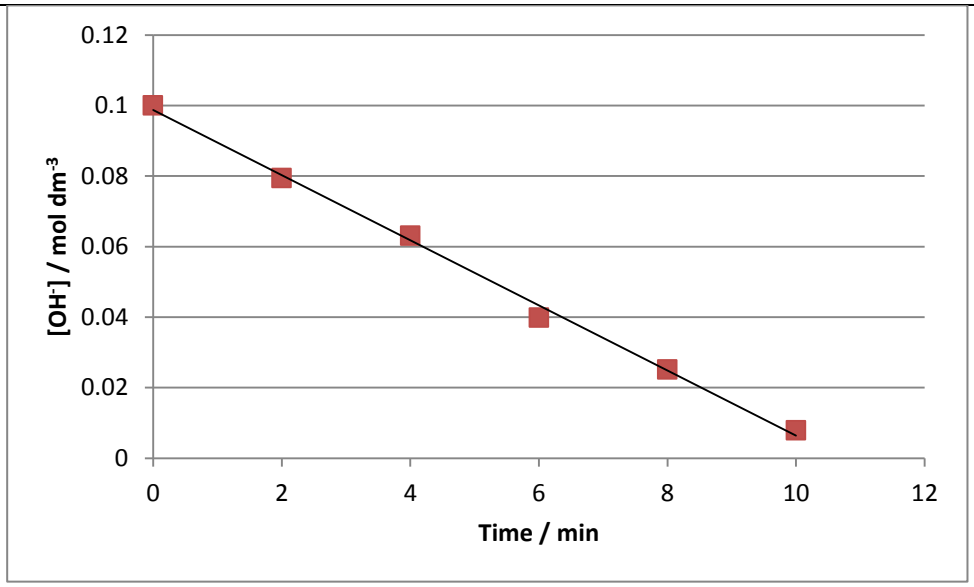
Time / min	pH	$[OH^-]$ / mol dm^{-3}
0	13.0	**0.100**
2	12.9	**0.0794**
4	12.8	**0.0631**
6	12.6	**0.0398**
8	12.4	**0.0251**
10	11.9	**0.00794**

All 6 values calculated correctly 2m

At least 3 values calculated correctly 1m

Less than 3 values calculated correctly 0m

(ii) Using a graphical method, prove that the reaction is zero order with respect to $[OH^-]$.



Graph ;

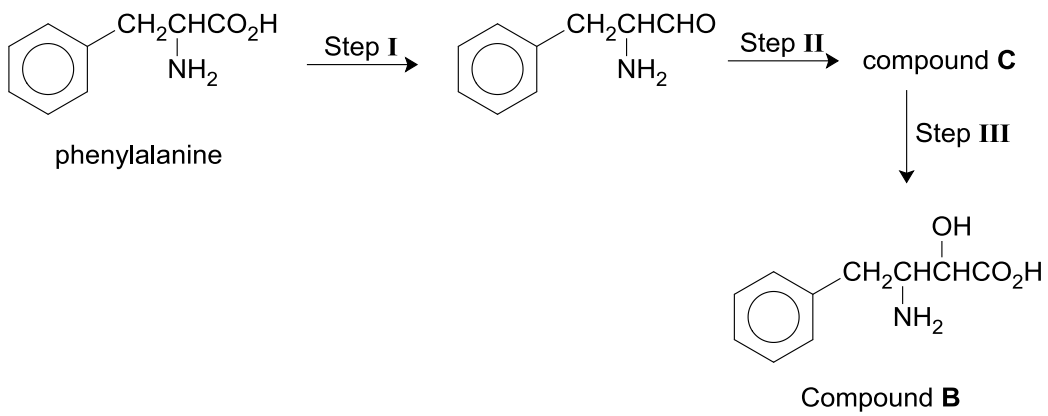
Since gradient is constant, the rate is independent of [OH^-]. ;

		(iii)	Given that the reaction is first order with respect to [bromocyclohexane], give the rate equation for the reaction.
			rate = k[bromocyclohexane] ;
		(iv)	The half-life of bromocyclohexane was found to be 75.3 min when 1.0 mol dm^{-3} of bromocyclohexane was reacted with 0.01 mol dm^{-3} of aqueous sodium hydroxide. Deduce the half-life of bromocyclohexane when 2.0 mol dm^{-3} of bromocyclohexane was reacted with 0.02 mol dm^{-3} of aqueous sodium hydroxide. Explain your reasoning.
			Since overall order of reaction is one, half life is constant. ; **75.3 min ;**
		(v)	Determine the rate constant of the reaction when 1.0 mol dm^{-3} of bromocyclohexane was reacted with 0.01 mol dm^{-3} of aqueous sodium hydroxide.
			k = ln 2 / 75.3 = 9.21 × 10^{-3} min^{-1} ;
		(vi)	Using your answer in **(c)(iii)**, propose the reaction mechanism for this reaction.
			 ;

			 ;
			[10]
			[Total: 20]

3.	**(a)**	Haemoglobin is a water soluble globular protein which is composed of two *α* polypeptide chains, two *β* polypeptide chains and an inorganic prosthetic haem group. Its function is to carry oxygen around in the blood and it is facilitated in doing so by the presence of the haem group.	
		(i)	State the transition metal cation present in the haem group.
			Fe^{2+} ;
		(ii)	Describe what is meant by the terms *primary*, *secondary*, *tertiary* and *quaternary* structures of proteins. In each case, you should state the type of bonding or interaction involved.
			The primary structure shows the unique sequence of how the amino acids are arranged. The amino acid residues in the polypeptide chains are joined together by the formation of peptide bonds. ; **In the secondary structure, hydrogen bonding is formed between the N-H of one peptide bond with the C=O of another peptide bond. ; ;** **In the tertiary structure, a polypeptide chain folds through the interactions of the side chains of the amino acids. ;** **The types of side chain interactions in tertiary structures are ionic interactions between $-CO_2^-$ and $-NH_3^+$ groups, hydrogen bonding between polar groups, van der waals' interactions between non-polar side chains and disulfide bridges between groups containing thiol (-SH groups). ; ;** **In the quaternary structure, the side chain of a folded polypeptide chain interacts with the side chain of another polypeptide chain through ionic interactions, hydrogen bonding, van der waals' interactions and disulfide bridges. ;**
			[8]

(b) Compound **B** can be synthesised from the naturally occurring amino acid phenylalanine by the following route:



phenylalanine

Compound **B**

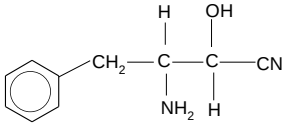
(i) State the reagents and conditions for Steps I, II and III and draw the structure of compound **C**.

Step I: LiA*l*H_4, dry ether followed by $K_2Cr_2O_7$, dil H_2SO_4, heat and distil ;

Step II: HCN (aq), trace amount of NaOH, 10-20ºC ;

Step III: dilute H_2SO_4 (aq), heat ;

Compound C:



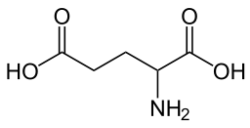
;

(ii) Compound **B** is an amino acid that is not involved in the building of proteins in the body. Explain why this is so.

Amino acids involved in the building of proteins in the body must be a 2-aminocarboxylic acid (contains an α-carbon). Compound B does not fulfil this structural requirement. ;

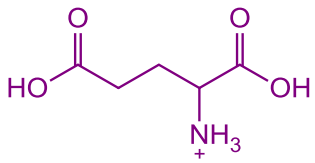
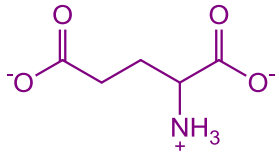
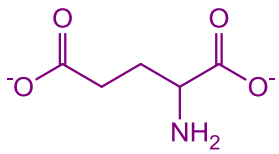
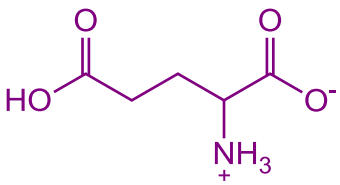
[5]

(c) Glutamic acid is a non-essential amino acid. All meats, poultry, fish, eggs and dairy products are excellent sources of glutamic acid. The structure of glutamic acid is shown below.



Glutamic acid

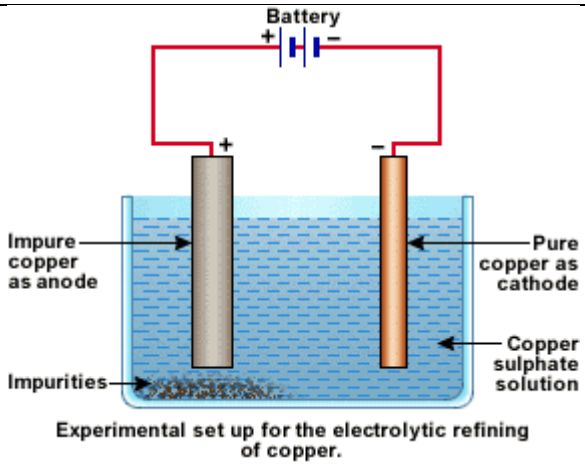
(i) Explain what is meant by the term pK_a as applied to a weak acid, H**A**.

			Hence, state the relationship between the pK_a value and the acidity of a compound.
			A weak acid partially dissociates. HA (aq) ⇌ H^+ (aq) + A^- (aq) **$pK_a = -lgK_a$;** **The larger the pK_a value, the lower the acidity of a compound. ;**
		(ii)	There are three pK_a values associated with glutamic acid: 2.1, 4.1 and 9.5. Make use of these pK_a values to draw the structures of the major species present in solutions of glutamic acid at the following pH values. **I.** pH 1 **II.** pH 7 **III.** pH 11
		pH = 1  pH=7  pH = 11  ***1m each***	
		(iii)	When two oppositely-charged electrodes are placed into an aqueous solution of glutamic acid at a particular pH, the glutamic acid migrates towards neither the anode nor the cathode. Draw the structure of glutamic acid under this condition and give the term used to describe chemical species that behave in this way.
			 **;** **zwitterion ;**

			[7]
			[Total: 20]

4.	**(a)**	Transition metals are often alloyed with one another to enhance their properties. For example, titanium can be alloyed with copper to form a strong and corrosion resistant material used in the aerospace and automobile industries.	
		(i)	Explain what is meant by the term *transition metal*.
			A transition metal is a d-block element which can form at least one stable ion with an incomplete d subshell. ;
		(ii)	State the electronic configuration of copper.
			$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$;
		(iii)	When 50 g of the titanium-copper alloy is completely oxidised, 34.4 g of CuO and a violet oxide of titanium, compound **D**, is obtained. The mass of oxygen measured in compound **D** is found to be 11.3 g. Determine the molecular formula of this oxide. Hence calculate the oxidation number of titanium in **D**.
			amount of Cu = amount of CuO = 34.4 / (63.5 + 16) = 0.4327 mol **mass of Ti = 50 – mass of Cu = 50 – 0.4327(63.5) = 22.52 g ;** **Table/ working ;** **Molecular formula = Ti_2O_3 ;** **Oxidation number = +3 ;** **correct answer without working – 0m**
		(iv)	On strong heating, compound **D** undergoes disproportionation to form two oxides. One of the oxides is a yellow solid and the other oxide is a white solid, compound **E.** Write a balanced equation for the disproportionation reaction.
			$Ti_2O_3 \rightarrow TiO + TiO_2$;
		(v)	State the full electronic configuration of Ti in compound **E**. Hence, explain why compound **E** is a white solid.

	Ti	O
mass	**22.52**	**11.3**
amount	**22.52 / 47.9 = 0.4701**	**11.3 / 16 = 0.7063**
ratio	**1**	**1.5**
simplest ratio	**2**	**3**

			$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$; **Ti in compound E has no 3d electron hence d-d transition is not possible ;**
		(vi)	A solution of $[Ti(H_2O)_6]^{3+}$ is violet while a solution of $[TiF_6]^{3-}$ is pale green. Explain the difference in colour.
			Different ligands split the energy level of d orbitals to different extent, ΔE. ; **The complex ions absorb light energy of different wavelengths for d-d transition ;** **hence transmitting different colours ;**
			[12]
	(b)	Pure copper can be obtained from copper ore by chemical reduction. The impure copper obtained can be purified using electrolysis.	
		(i)	Draw a labelled diagram to show how an impure sample of copper can be purified by electrolysis.
			 Experimental set up for the electrolytic refining of copper. **Correctly connecting the electrodes to the positive and negative terminals ;** **battery + correct electrolyte ;**
		(ii)	A 1.20 kg of impure copper sample was electrolysed using a current of 12 A. Calculate the time (in days) required for 850 g of pure copper to be deposited at the cathode.
			Amount of e = 2(850/63.5) = 26.77 mol ; **Q = It = nF** **12t = 26.77(96500)** **t = 215275 s = 2.49 days ;**

		(iii)	The impure copper sample contains other metals alloyed with it, one of which is zinc. Explain, using data from the *Data Booklet*, why zinc is not deposited at the cathode.
			Zn^{2+} + 2e ⇌ Zn -0.76 V ; **Since E^o of (Zn^{2+}/Zn) is more negative than E^o of (Cu^{2+}/Cu), Cu^{2+} is preferentially reduced and hence deposited at cathode. ;**
			[6]
	(c)	Like aluminium oxide, copper(II) oxide, CuO, is an amphoteric oxide. Write two equations to show how CuO reacts with separate solutions of dilute HC*l* and aqueous NaOH.	
		$CuO + HCl \rightarrow CuCl_2 + H_2O$; **$CuO + 2NaOH + H_2O \rightarrow Na_2Cu(OH)_4$;**	
			[2]
			[Total: 20]

5.	Nitrogen is a chemical element with a proton number of 7. Many industrially important compounds such as ammonia, nitric acid and cyanides contain nitrogen.		
	(a)	Explain the following observations clearly.	
		(i)	The third ionisation energy of nitrogen is lower than that of carbon.
			N^{2+} : $1s^2\ 2s^2\ 2p^1$ C^{2+} : $1s^2\ 2s^2$ **2p electron is further away from the nucleus ;** **2p electron is better shielded from the nucleus ;**
		(ii)	The bond angle of NH_3 is smaller than that of CH_4.
			NH_3 has 3 bond pairs and 1 lone pair, CH_4 has 4 bond pairs ; **Lone pair-bond pair repulsion is greater than bond pair-bond pair repulsion ;**
		(iii)	The melting point of $H_2NCH_2CONH_2$ is lower than that of H_2NCH_2COOH.
			H_2NCH_2COOH exists as a zwitterion held by strong electrostatic forces of attraction between oppositely-charged ions ; **$H_2NCH_2CONH_2$ is a simple molecular structure held by hydrogen bonds ;** **More energy required to overcome the stronger ionic bonds in the**

			zwitterion ;
			[7]
	(b)	Group II nitrates undergo thermal decomposition to form the metal oxide, nitrogen dioxide and oxygen. Magnesium nitrate decomposes at 330°C whereas barium nitrate decomposes at 600°C.	
		(i)	Explain why, going down Group II, the thermal stability of the nitrates increases.
			Down the group, **Charge density decreases as ionic radius increases;** **Nitrate ions become less distorted as polarising power of the group II ions decreases ;**
		(ii)	A sample containing 20 g of a mixture of magnesium nitrate and barium nitrate was heated at 350°C until no further change occurred. The remaining solid weighed 10.9 g. Calculate the percentage composition by mass of magnesium nitrate in the sample.
			$Mg(NO_3)_2$ → MgO + $2NO_2$ + ½ O_2 **Let mass of barium nitrate = x** **mass of magnesium nitrate = 20 – x** **mass of magnesium oxide = 10.9 – x** **amount of MgO = amount of $Mg(NO_3)_2$;** $\frac{10.9-x}{24.3+16}=\frac{20-x}{24.3+14(2)+6(16)}$ $\frac{10.9-x}{40.3}=\frac{20-x}{148.3}$ **1616.47 – 148.3x = 806 – 40.3x** **108x = 810.47** **x = 7.504** **mass of $Mg(NO_3)_2$ = 20 – 7.504 = 12.496 g ;** **% by mass =** $\frac{12.496}{20}\times 100\% = 62.48\% \approx 62.5\%$ **;**
			[5]
	(c)	A hydrocarbon **R**, C_5H_8, reacts with aqueous bromine in a mole ratio of 1 : 2. When	

R undergoes oxidation with hot acidified $KMnO_4$, **S**, $C_3H_4O_4$, is formed.

1 mole of **S** reacts with 1 mole of solid sodium carbonate to give effervescence. When **S** reacts with thionyl chloride, **T**, is formed along with the evolution of white fumes.

When **T** reacts with $CH_2(NH_2)_2$, a cyclic neutral compound **U**, $C_4H_6O_2N_2$, is formed.

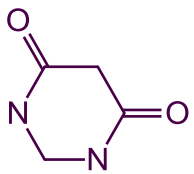
Deduce the structures of compounds **R** – **U**, explaining the chemistry involved.

Information	Deduction
A hydrocarbon R, C_5H_8, reacts with aqueous bromine in a mole ratio of 1 : 2.	**electrophilic addition ;** **R contains 2 C=C ;**
When R reacts with hot acidified $KMnO_4$, S, $C_3H_4O_4$, is formed.	**Loss of 2 C → C=C at terminal C ;**
1 mole of S reacts with 1 mole of solid sodium carbonate to give effervescence.	**acid-carbonate reaction ;** **2 carboxylic acid groups ;**
When S reacts with thionyl chloride, T, is formed along with the evolution of white fumes.	**T is a acyl chloride ;**
When T reacts with $CH_2(NH_2)_2$, a cyclic neutral compound U, $C_4H_6O_2N_2$, is formed.	**nucleophilic substitution ;** **cyclic diamide formed ;**

R : CH_2=CHCH_2CH=CH_2 ;

S: $CH_2(COOH)_2$;

T: $CH_2(COCl)_2$;

U:  ;

Deductions capped at 4m

[8]

[Total: 20]