TEMASEK JUNIOR COLLEGE

2022 JC2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME

WORKED SOLUTIONS

CENTRE NUMBER | S | | | | |

INDEX NUMBER | | | | |

Chemistry **9729/03**

Paper 3 Free Response Questions **14 September 2022**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do **NOT** open this booklet until you are told to do so.

Write your name, civics class, centre number and index number on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use		
Paper 3	Q1	/18
	Q2	/20
	Q3	/22
	Q4	/20
	Q5	/20
	Total	/80

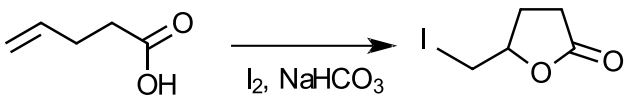
This document consists of **23** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

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

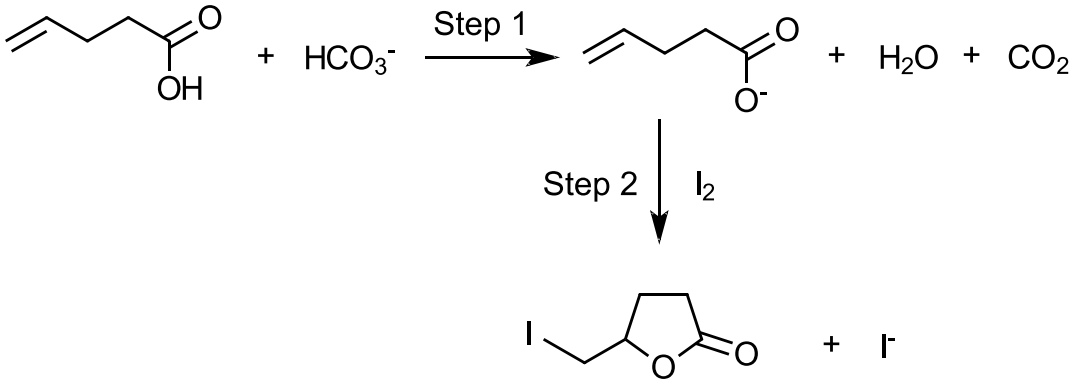
An example of the iodolactonisation is the reaction of 4-pentenoic acid as shown in Fig 1.1.



Compound X

Fig 1.1

Two simplified steps in the iodolactonisation mechanism are given in Fig 1.2.



Compound X

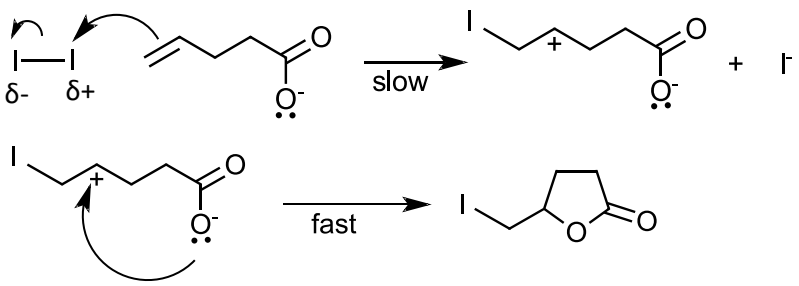
Fig 1.2

(i) Suggest the role of HCO_3^- in step **1**. [1]

It acts as a Bronsted-Lowry base to abstract H^+ from the carboxylic acid.[1]

(ii) Suggest the mechanism for reaction taking place in **Step 2.** Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

- **Electrophilic addition**



Name of mechanism [1]

Mechanism [2]

(iii) Sketch a well-labelled reaction pathway diagram for the reaction in **Step 2**, given that the reaction is exothermic. [2]

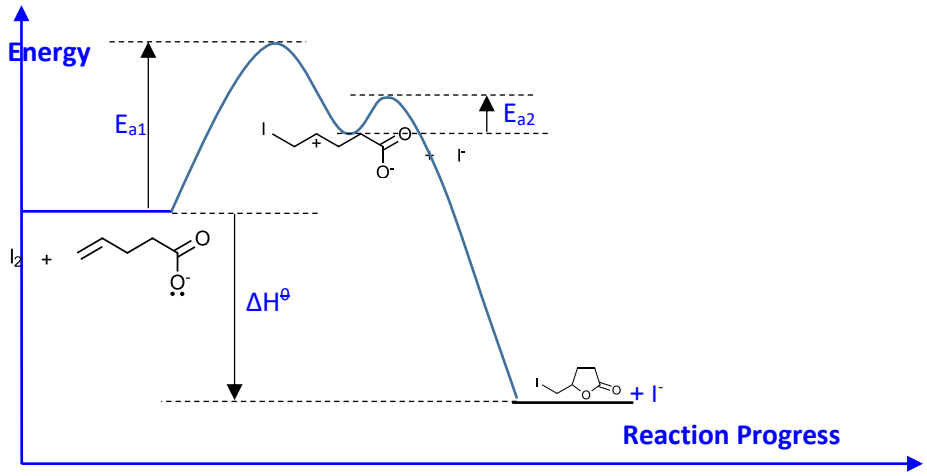
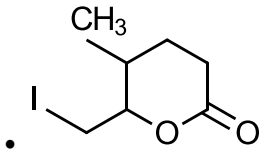


Diagram & labelling:[1]

E_{a1}, E_{a2} & ΔH^{θ}: [1]

(iv) Suggest the structural formulae of the final organic product formed when CH_2=CHCH(CH_3)CH_2CH_2COOH undergoes iodolactonisation in a similar process in Fig 1.1. [1]



(b) Carbon monoxide is one of the most widespread and dangerous industrial hazards. The formation of carboxyhaemoglobin, $Hb(CO)_4$, takes place much more readily than the formation of oxyhaemoglobin, $Hb(O_2)_4$.

$Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq)$ **… (1)**

$Hb(aq) + 4CO(aq) \rightleftharpoons Hb(CO)_4(aq)$ **… (2)**

A treatment method for carbon monoxide poisoning is to provide the patient with pure oxygen gas over a period of time.

With reference to the equations given above, explain why this is a suitable treatment method. [2]

Providing O_2 forms $Hb(O_2)_4(aq)$, which ✓ **shifts the position of 1st equilibrium to the right,** ✓ **removing Hb(aq)** from the bloodstream.

By Le Chatelier's Principle, the ✓ **position of 2nd equilibrium will shift left to** ✓ **increase amount of Hb(aq),** thus reducing the amount of $Hb(CO)_4(aq)$ in the body.

2✓: [1]

(c) The water-gas shift reaction is used to produce hydrogen gas industrially by reacting carbon monoxide with water vapour.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

An evacuated tank was initially filled with 0.0197 atm of CO and 0.0394 atm of H_2O at 600 K. It was sealed and left to stand. At equilibrium, the partial pressure of CO_2 was found to be 0.0191 atm.

(i) Calculate the value of K_p at 600 K. [2]

	CO (g)	+ H_2O (g)	⇌ CO_2 (g)	+ H_2 (g)
Initial P / atm	0.0197	0.0394	0	0
Δ in P / atm	–0.0191	–0.0191	+0.0191	+0.0191
Eqm P / atm	**0.0006**	**0.0203**	**0.0191**	**0.0191**

Working [1]

$$K_p = \frac{(0.0191)(0.0191)}{(0.0006)(0.0203)} = 30.0$$

Answer [1]

Table 1.1 shows how the value of K_p varies with temperature.

Table 1.1

T / K	300	900	1500
value of K_p	1.170×10^5	1.978	0.2195

(ii) The Gibbs free energy, $\Delta G^\ominus$ (in J mol^{-1}), and the equilibrium constant, K_p, of a reaction are related by the following equation:

$$\Delta G^\ominus = - RT \ln K_p,$$

where R is the molar gas constant and T is the temperature in Kelvins.

Using the given values of K_p, calculate the values of $\Delta G^\ominus$ at 300 K and 900 K. Hence, determine the value of $\Delta S^\ominus$ for the water-gas shift reaction.

(Assume that both $\Delta H^\ominus$ and $\Delta S^\ominus$ are independent of temperature.) [3]

$\Delta G^\ominus_{(300)} = - RT \ln K_{p\,(300)}$

$= - (8.31)(300) \ln (117000) = - 29090$ J mol^{-1} **[√]**

$\Delta G^\ominus_{(900)} = - RT \ln K_{p\,(900)}$

$= - (8.31)(900) \ln (1.978) = - 5101$ J mol^{-1} **[√]**

$\Delta G^\ominus_{(300)} = \Delta H^\ominus - (300)\Delta S^\ominus = - 29090$ J mol^{-1} ----- (1) **allow ecf [√]**

$\Delta G^\ominus_{(900)} = \Delta H^\ominus - (900)\Delta S^\ominus = - 5101$ J mol^{-1} ----- (2) **allow ecf [√]**

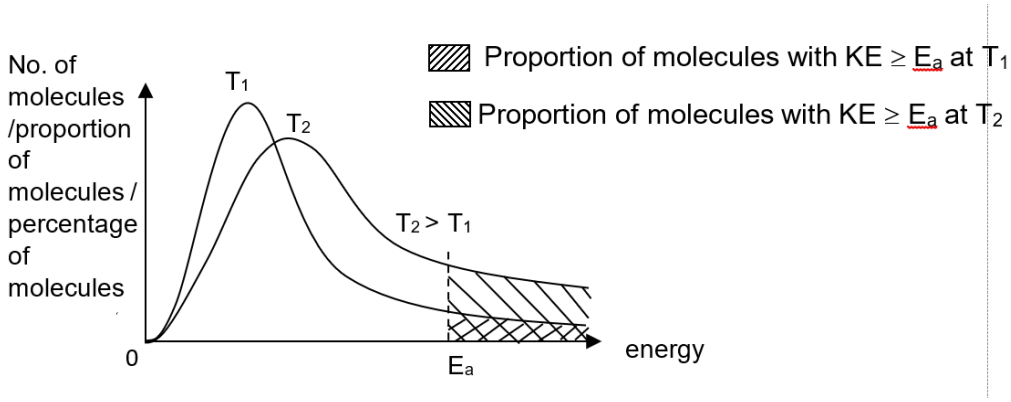
(1) – (2): $\Delta S^\ominus = - 40.0$ J K^{-1} mol^{-1} (3 sf) **allow ecf [1] include unit**

(iii) Comment on the magnitude of the calculated value of $\Delta S^\ominus$. [1]

The magnitude is **small** as there is **no change in the amount of gaseous molecules** when reactants changed to products. Hence, there is little change in the number of ways that energy can be distributed over the molecules.

(iv) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of water-gas shift reaction. [3]

Boltzmann distribution diagram: **[1]**



At higher temperatures, **the proportion of molecules with kinetic energy greater than or equal to activation energy increases [√]**.

Frequency of effective collision increases [√],

rate constant increases [√],

rate increases [√].

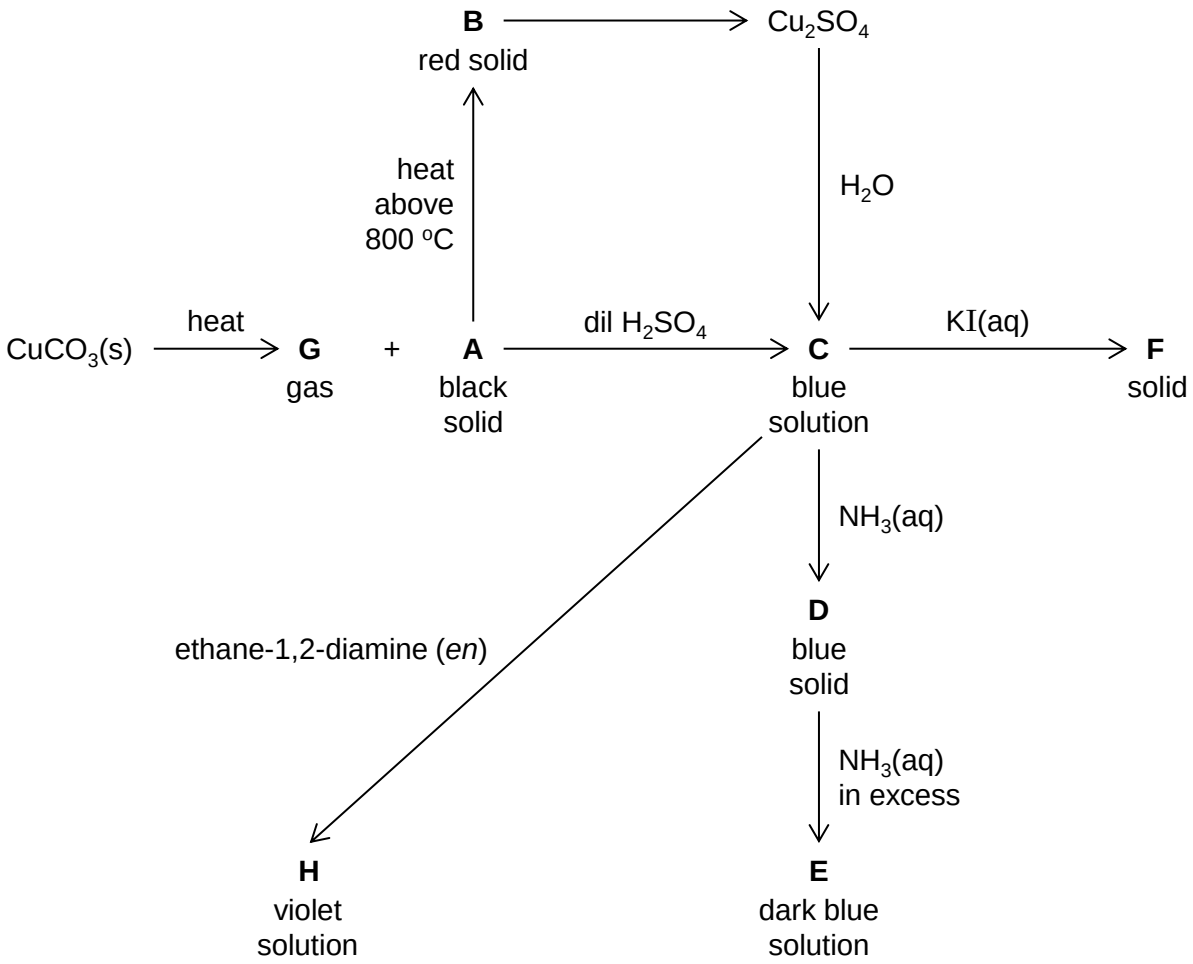
2√: [1]

[Total:18]

DO NOT WRITE IN THIS MARGIN

2 Copper is a typical transition element with more than one oxidation state. Many of its compounds have colours in the blue-green-yellow part of the visible spectrum.

The following reaction scheme shows the chemistry of some copper-containing species.



(a) (i) **A** and **B** are both compounds of copper and oxygen only.

Cu_2SO_4 can be made from **B** under certain anhydrous conditions. The oxidation number of copper in **B** is the same as in Cu_2SO_4.

Identify gas **G**, and write the formula of the copper-containing species in **A** to **C**. [2]

G: CO_2 **A**: CuO **B**: Cu_2O **C**: $[Cu(H_2O)_6]^{2+}$

1 tick for each answer.

4 ticks − [2]

2 to 3 ticks − [1]

(ii) Suggest, with reason, the colour of solid **F**. [2]

Oxidation of copper in **F**, CuI = +1

Electronic configuration of Cu^+: [Ar] $3d^{10}$

The d orbitals of Cu^+ ion are **fully filled**.

No electrons can undergo d-d transition from the lower energy group of d orbitals to the higher energy group. *OR* **No d-d electronic transition can occur**. **[1]**

Thus, solid **F** is expected to be **white** *OR* **grey-white**. **[1]**

(b) Explain the transformations from **C** to **E** in terms of the competing equilibria and the type of reaction that has occurred. Include equations and the formulae of all copper-containing species. [4]

- ✓ When $NH_3(aq)$ is added dropwise to **C**, a blue precipitate **D**, **$Cu(OH)_2(H_2O)_4$** *OR* **$Cu(OH)_2$**, is formed. **NH_3 acts as a base**.
- ✓ $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
- ✓ When excess $NH_3(aq)$ is added, **E**, which contains the dark blue complex, **$[Cu(NH_3)_4(H_2O)_2]^{2+}$**, is formed **$NH_3$ acts as a ligand** here.
- ✓ By Le Chatelier's Principle, **concentration of $[Cu(H_2O)_6]^{2+}$ decreases**, and **position of equilibrium (1) shifts left**, causing **D** to dissolve.

4 ticks − [2]

2 to 3 ticks − [1]

$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(H_2O)_4(s) + 2H_2O(l)$ −−−− (1)

OR **$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$ −−−− (1) [1]**

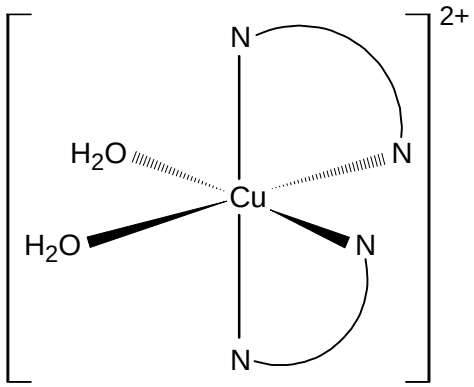
$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$ [1]

(Note: equation does not start with $Cu(OH)_2(H_2O)_4$)

(c) Like many organic compounds, transition metal complexes also exhibit stereoisomerism, namely *cis-trans* isomerism and enantiomerism.

For example, $[Cu(en)_2(H_2O)_2]^{2+}$, the complex ion present in **H**, has three stereoisomers, **X**, **Y** and **Z**. One of these stereoisomers, **X**, is shown below.

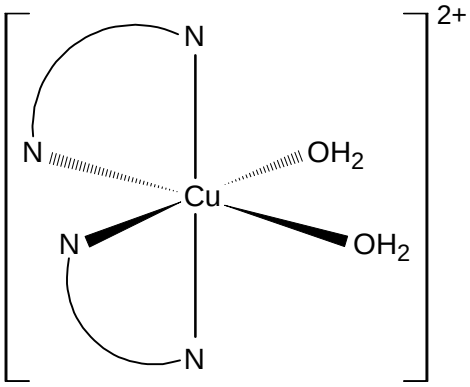
(N⌒N represents the *en* ligand.)



X

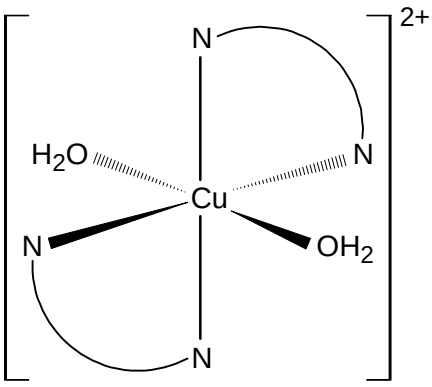
X and **Z** are *cis-trans* isomers, while **Y** is an enantiomer of **X**.

Draw and label clearly the three-dimensional diagrams of **Y** and **Z**. You should use N⌒N to represent the *en* ligand. [3]



[1]

Y



[1]

Z

(*trans*-isomer of X)

Correct labels for Y and Z − [1]

(d) Selective precipitation is a technique of separating ions in an aqueous solution by using a reagent that precipitates one or more of the ions, while leaving other ions in solution. In the case of Cu^{2+} ions, the separation is achieved by adjusting the pH so that only Cu^{2+} ions are precipitated.

In an experiment, a student adds sodium hydroxide gradually to a solution containing 0.100 mol dm^{-3} Cu^{2+} ions and 0.100 mol dm^{-3} Fe^{2+} ions.

Relevant K_{sp} values are given in Table 2.1.

Table 2.1

metal hydroxide	K_{sp} / mol^3 dm^{-9}
$Cu(OH)_2$	2.2×10^{-20}
$Fe(OH)_2$	8.0×10^{-16}

Determine the pH at which maximum separation of the two cations is achieved. [2]

$$K_{sp}\ of\ Fe(OH)_2 = [Fe^{2+}][OH^-]^2$$
$$8.0 \times 10^{-16} = (0.100)[OH^-]^2$$
$$[OH^-] = 8.944 \times 10^{-8}\ mol\ dm^{-3}$$

Calculation of [OH^-] at max separation − [1]

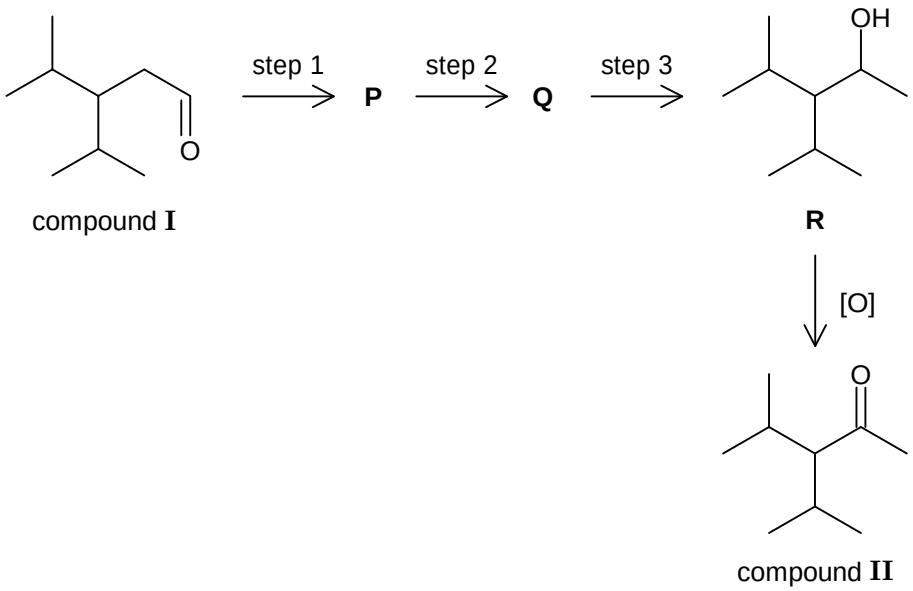
∴ pH at maximum separation = $14 - [-\log_{10}(8.944 \times 10^{-8})]$ = **6.95** **[1]**

Explanation:

$Cu(OH)_2$ would first be precipitated as a lower concentration of OH^- is needed for precipitation. Maximum separation is achieved when the *maximum amount of $Cu(OH)_2$ has precipitated i.e.* just before $Fe(OH)_2$ is precipitated i.e. a saturated solution of $Fe(OH)_2$.

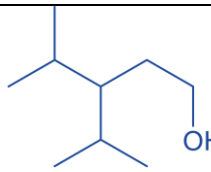
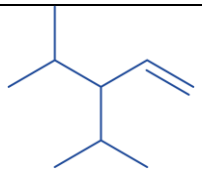
(e) **(i)** Compound **II** can be converted from compound **I** in four steps.

State the reagents and conditions you would use for steps 1−3 and give the structures of compounds **P** and **Q**.



compound **I** **R** compound **II**

[5]

step	reagents & conditions	compound
1	LiA*l*H$_4$ in dry ether, r.t.p. *OR* NaBH$_4$ in ethanol, r.t.p. *OR* H_2, Ni, high temperature and pressure *OR* H_2, Pd or Pt, r.t.p. **[1]**	 **[1]** **P**
2	excess conc H_2SO_4, 170 °C *OR* A*l*$_2$O$_3$, 400 °C **[1]**	 **[1]** **Q**
3	cold, conc H_2SO_4, followed by $H_2O(l)$, heat *OR* $H_2O(g)$, conc H_3PO_4, high temperature and pressure **[1]**	–

(ii) Suggest how compounds **II** and **R** could be distinguished from one another by means of a simple chemical test. [2]

Appropriate chemical test: [1]

Observation for both compounds: [1]

Possible Tests:

		Observations

	To each compound separately, add	**II** (ketone)	**R** (secondary alcohol)
1	**2,4-dinitrophenylhydrazine**. **Accept 2,4-DNPH *OR* Brady's reagent.**	**Orange ppt**	**No ppt**
2	solid **PCl_5**	**No white fumes**	**White fumes** (of HCl)
3	**Na(s)**	**No effervescence**	**Effervescence**. H_2 gas evolved "pops" with a lighted splint
4	**$K_2Cr_2O_7$(aq), dil H_2SO_4** and **heat** in a water bath. **Accept acidified $K_2Cr_2O_7$.**	**Orange** solution does **not turn green**.	**Orange** solution **turns green**.
5	**$KMnO_4$(aq), dil H_2SO_4** and **heat** in a water bath. **Accept acidified $KMnO_4$.**	**Purple** solution is **not decolourised**.	**Purple** solution is **decolourised**.

[Total: 20]

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

3 **(a)** The reaction of $SiBr_4$ with moist ethoxyethane produces two oxybromides with the formula $Si_3O_2Br_8$ (M_r = 755.5) and Si_2OBr_6 (M_r = 551.6).

When 0.192 g of one of the oxybromides reacts with excess water, all the bromine atoms are converted to bromide ions. Excess silver nitrate is added and 0.392 g of cream precipitate is obtained.

(i) Determine, with the aid of calculations, the identity of the oxybromide which reacted with excess water. [2]

Cream ppt is AgBr, M_r = 187.8

Amt of ppt formed = 0.392/187.8 = 0.002087 mol

Amt of $Si_3O_2Br_8$ used = 0.192/755.5 = 2.541 x 10^{-4} mol (8.2 Br atoms)

Amt of Si_2OBr_6 used = 0.192/551.6 = 3.481 x 10^{-4} mol (5.99 Br atoms)

Hence, the oxybromide is Si_2OBr_6 [1]

working [1]

(ii) The cream precipitate was only sparingly soluble in excess aqueous ammonia. However, on addition of aqueous sodium cyanide, the precipitate completely dissolves.

The numerical values of the stability constant, K_{stab}, for the relevant complex ions are given below.

Complex	Stability constant / K_{stab}
$[Ag(NH_3)_2]^+$	1.7 x 10^7

$[Ag(CN)_2]^-$	1.0×10^{21}

With reference to the table above, briefly explain the observations above as fully as you can. [3]

Cream ppt AgBr is sparingly soluble in water and exists in equilibrium with its aqueous ions

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ … (1)

In the presence of aqueous NH_3, free Ag^+ forms a complex ion, $[Ag(NH_3)_2]^+$. However since AgBr has moderate K_{sp} value, ionic product $[Ag^+][Br^-]$ decreases but remains larger than K_{sp}(AgBr), so the ppt is remains insoluble. [1]

When cyanide ions are added, ✓ Ag^+ forms a more stable complex due to larger K_{stab} value. Hence ✓ conc of Ag^+ decrease to a greater extent. [1]

By Le Chatelier's principle, ✓ position of equilibrium (1) shifts to right to increase conc of Ag^+ ions. ✓ Ionic product decreases below K_{sp}, hence cream ppt dissolves. [1]

(b) Polypeptide chain **Y** has a sequence of 8 α-amino acids. 2 enzymes, **E1** and **E2**, are added to separate samples of **Y** and the following fragments are obtained.

Fragments after reaction with **E1**	Fragments after reaction with **E2**
val-gln-phe	cys-phe-val
cys-phe	gln-lys-asp
gln-lys-asp	gln-phe

E1 hydrolyse the peptide bond at the carboxylic acid end of phenylalanine (phe) while **E2** hydrolyse the peptide bond at the amino end of glutamine (gln).

(i) Under specific conditions, the dipeptide cys-phe exists as a zwitterion. Explain

• the term "zwitterion"; and

• one physical property of the cys-phe dipeptide to support its existence as a zwitterion. [2]

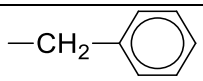
• A zwitterion is a dipolar compound that contains both cationic and anionic groups and is electrically neutral. [1]

1 physical property **[1]***:*

High melting point: in the solid state, dipeptide exist as zwitterions in which both the anion and cation are held in the same unit (an internal salt). A large amount of energy is required to overcome the strong electrostatic forces of attraction or ionic bonds between the zwitterions.

Soluble in water: formation of ion-dipole interactions between water and zwitterions release sufficient energy to overcome the ionic bonds between the zwitterions and hydrogen bonds between water molecules.

The table below shows the R group of some α-amino acids and the pK_a values of respective functional groups.

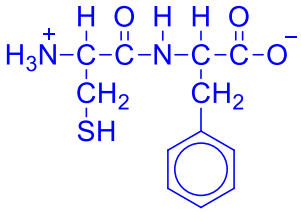
Amino acid	Structure of R-group	pK_a of α-amino group	pK_a of α-carboxylic group	pK_a of R group
cys	$-CH_2SH$	10.28	1.91	8.14
phe		9.09	2.18	-

(ii) Draw the zwitterion of cys-phe and determine a pH at which the cys-phe exists as a zwitterion as the predominant species. [2]

At 1st equivalence point, the α-COOH of Phe is deprotonated, giving a zwitterion

Hence isoelectric point, pI = ½ (2.18+8.14) = 5.16 [1] (accept between 2.18 and 8.14)

Structure of zwitterion is



[1]

(iii) Deduce the sequence of the amino acids in polypeptide chain **Y**. [2]

E1 hydrolyse the peptide bond at the carboxylic acid end of phe, so 2 possible structures are:

val-gln-phe-cys-phe-gln-lys-asp

cys-phe-val-gln-phe-gln-lys-asp

E2 hydrolyse the peptide bond at the amino end of gln, so 2 possible structure are:

cys-phe-val-gln-lys-asp-gln-phe

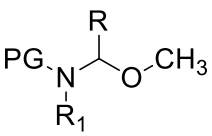
cys-phe-val-gln-phe-gln-lys-asp

logical reasoning / working **[1]**

Hence the correct sequence of amino acids in Y is

• **cys-phe-val-gln-phe-gln-lys-asp [1]**

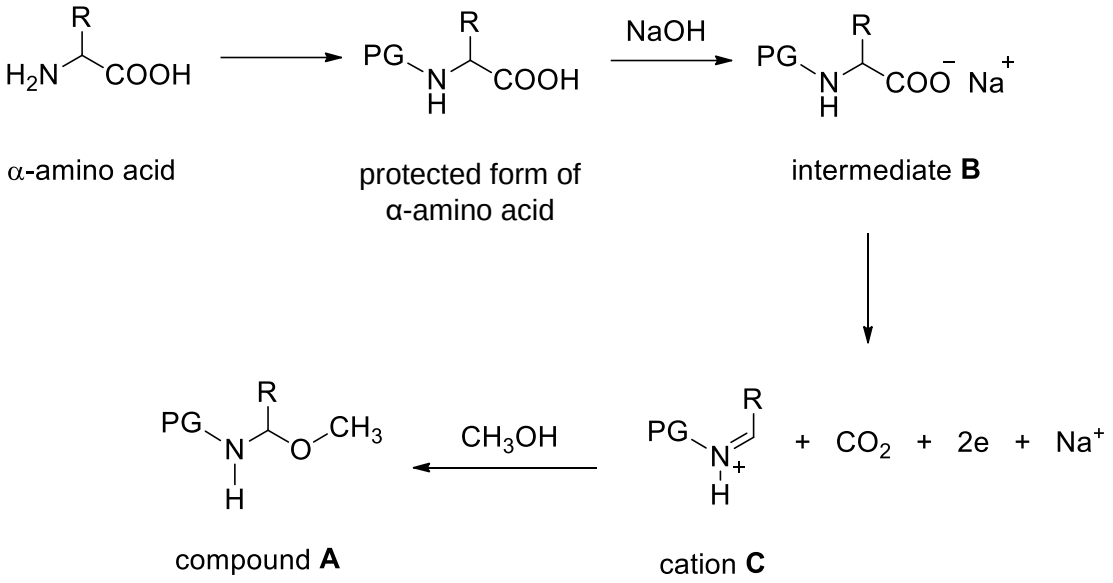
Compound **A** is formed from the electrolysis from α-amino acids in methanol solvent,



compound **A**

where R is alkyl, R_1 is alkyl or hydrogen and PG is the protecting group, $CH_3CO–$.

The α-amino acids are first converted to its protected form, followed by reaction with sodium hydroxide to form an intermediate, **B**.



α-amino acid

protected form of α-amino acid

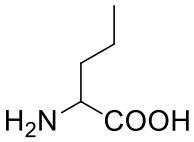
intermediate **B**

compound **A**

cation **C**

At the anode, the anion in intermediate **B** undergoes decarboxylation to form cation **C**. No other reactions occur at the anode.

Norvaline is an α-amino acid which is used in dietary supplement for bodybuilding. It undergoes the electrolysis reaction above.



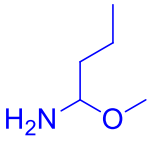
norvaline

(c) State the reagent and condition to convert norvaline to its protected form. [1]

CH_3COCl, room temp [1]

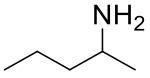
(d) Compound **A** undergoes hydrolysis to form amine **X**.

(i) Draw the structure of amine **X**, when norvaline undergoes the electrolysis reaction above, followed by hydrolysis. [1]



[1]

(ii) Explain the difference in basicity of amine **X** and 2-aminopentane. [2]



2-aminopentane

Amine X is less basic than 2-aminopentane. [1]

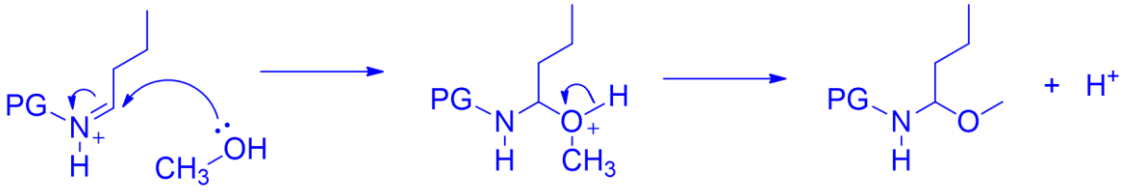
The presence of the electron withdrawing oxygen atom reduces the electron density on the nitrogen atom in amine X. The lone pair electrons are less available to accept / dative bond with H^+.[1]

(e) Cation **C** subsequently reacts with methanol, as a nucleophile to give **A** in 2 steps.

Step 1: methanol attacks the electron deficient carbon in cation **C**, to form another cation intermediate.

Step 2: the intermediate undergoes deprotonation to give **A**.

Starting with the appropriate structure of **C** which is produced from norvaline, use appropriate curly arrows to show how the **A** is formed at the anode. Show clearly the charges and lone pair of electrons as well as structure of intermediate formed. [2]



1 mark for each step + charges + lone pair e and curly arrows

(f) **(i)** The standard reduction potential of CO_2/CH_3OH is +0.45 V, measured against the standard hydrogen electrode.

Write the ion-electron half reaction for the complete oxidation of methanol. [1]

$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e$

(ii) With reference to the reaction occurring at the anode for the electrolysis, suggest a suitable standard reduction potential value for (cation **C**)/(compound **B**) and explain your answer. [2]

• **+0.40 V** *(any value less positive than +0.45 V. Accept only 1 value, reject if range is given instead)*

At the anode, both CH_3OH and anion intermediate B can be oxidised. Since B • is preferentially oxidised at the anode instead of CH_3OH, its E^o value has to be less positive, implying that B is more easily oxidised than CH_3OH at the anode.

(g) The efficiency of the electrolysis reaction of compound **A** is around 95%.

A current of 0.1 A was applied to the electrolytic cell consisting of *N*-protected norvaline for 1 hour.

Calculate the mass of compound **A** produced at the anode when norvaline undergoes the electrolysis reaction. [M_r of **A**: 145.0] [2]

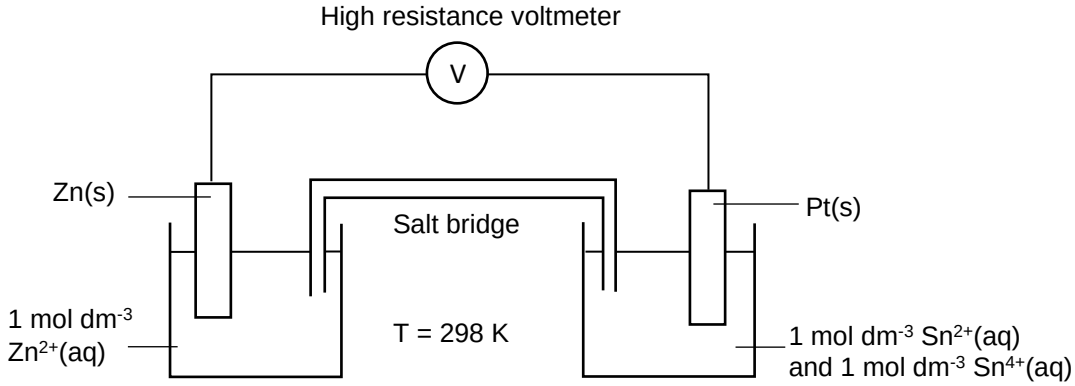
[Total: 22]

Section B

Answer **one** question from this section.

4 **(a)** An electrochemical cell consists of a half-cell containing Sn^{4+}/Sn^{2+} and another half-cell containing Zn^{2+}/Zn.

(i) Draw a fully labelled diagram of the experimental setup used to measure the standard potential of this cell. [2]



- ✓ **voltmeter labelled (or circled V)**
- ✓ **Zn electrode and Pt electrode**
- ✓ **1 mol dm^{-3} Zn^{2+}**
- ✓ **1 mol dm^{-3} each for Sn^{2+} and Sn^{4+}**
- ✓ **298 K**

Note: Salt bridge must be labelled (must touch solution)

(ii) Use data from the Data Booklet to calculate a value for the standard cell potential. [1]

$E^{\ominus}_{Zn^{2+}/Zn}$ = -0.76V = $E^{\ominus}_{oxid}$

$E^{\ominus}_{Sn^{4+}/Sn^{2+}}$ = +0.15V = $E^{\ominus}_{red}$

$E^{\ominus}_{cell}$ = $E^{\ominus}_{red}$ – $E^{\ominus}_{oxid}$

= +0.15 – (-0.76)

= + 0.91 V [1]

E values either quoted or shown in working. Sign must be shown.

(iii) Explain how the cell potential will change when a small amount of sodium carbonate is added to the Zn^{2+}/Zn half-cell. [2]

Formation of insoluble zinc carbonate causes the $[Zn^{2+}]$ to decrease. The position of equilibrium of $Zn^{2+} + 2e^- \rightleftharpoons Zn$ shifts to the left, favouring oxidation. [1]

$E_{Zn^{2+}/Zn}$ or E_{oxid} becomes more negative, hence E_{cell} becomes more positive. [1]

(iv) Thermal decomposition of zinc carbonate is an endothermic reaction. Explain why the decomposition reaction is spontaneous at high temperature. [1]

$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

ΔH is positive for endothermic reaction.

ΔS is positive due to the increase in number of moles of gases, hence greater disorder.

ΔG = ΔH – TΔS is negative at high temperature. [1]

(v) Using relevant data from the *Data Booklet*, explain the relative thermal stability of zinc carbonate and calcium carbonate. [2]

- ✓ **Ionic radii: Zn^{2+} - 0.074nm, Ca^{2+} - 0.099nm**
- ✓ **Order of thermal stability $ZnCO_3 < CaCO_3$**

2 points [1]

Zn^{2+} has the highest charge density. Zn^{2+} polarises the carbonate ion and weakens the C-O bond to the greater extent. Less energy is needed to break the C-O bond. [1]

(b) An oxide of tin, **G**, contains the metal in both oxidation states II and IV. **G** was dissolved in excess $H_2SO_4(aq)$ to produce solution **H**, which contains a mixture of tin(II) sulfate and tin(IV) sulfate. Solution **H** was divided into two portions.

A 25.0 cm^3 of one potion required 17.40 cm^3 of 0.0150 mol dm^{-3} $KMnO_4$ to reach the end-point.

An excess of powdered zinc was added to another portion of **H**. The mixture was stirred until the reaction was complete, and then filtered. 25.0 cm^3 of the filtrate required 26.10 cm^3 of 0.0150 mol dm^{-3} $KMnO_4$ to reach the end-point.

The equation for the titration reaction is as follows.

$$2MnO_4^- + 16H^+ + 5Sn^{2+} \rightarrow 2Mn^{2+} + 8H_2O + 5Sn^{4+}$$

(i) Deduce the Sn^{2+}/ Sn^{4+} ratio in the oxide **G**, and hence suggest the formula of **G**. [3]

No. of moles of MnO_4^- reacted with Sn^{2+} = $\frac{17.40}{1000} \times 0.015$ = 2.61 x 10^{-4} mol

No. of moles of Sn^{2+} = $\frac{5}{2} \times 2.61 \times 10^{-4}$= 6.53 x 10^{-4} mol

No. of moles of MnO_4^- reacted with Sn^{2+} reduced from Sn^{4+}

= $\frac{26.10}{1000} \times 0.015$ - 2.61 x 10^{-4}

= 1.31 x 10^{-4} mol

No. of moles of Sn^{4+} = = $\frac{5}{2} \times 1.31 \times 10^{-4}$= 3.28 x 10^{-4} mol

working [1]

Alternative

volume of MnO^{4-} reacted with Sn^{2+} originally present : Sn^{2+} reduced from Sn^{4+}

= 17.40 : (26.10 – 17.40)

= 17.40 : 8.70 [1]

Sn^{2+}/ Sn^{4+} = $\frac{6.53 \times 10^{-4}}{3.28 \times 10^{-4}} = \frac{2}{1}$ [1] or use volume ratio

Formula of G is Sn_3O_4 [1]

(ii) Tin(IV) oxide, SnO_2, reacts separately with both acids and alkalis. Write separate equations for the reaction of tin(IV) oxide with

- hydrochloric acid
- sodium hydroxide [2]

$SnO_2 + 4HCl \rightarrow SnCl_4 + 2H_2O$ [1]

$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O$ [1]

(c) Halogenoalkanes react with lithium to give organolithium compounds.

These organolithium compounds can react with carbonyl compounds to form alcohols, as shown in Fig. 4.1.

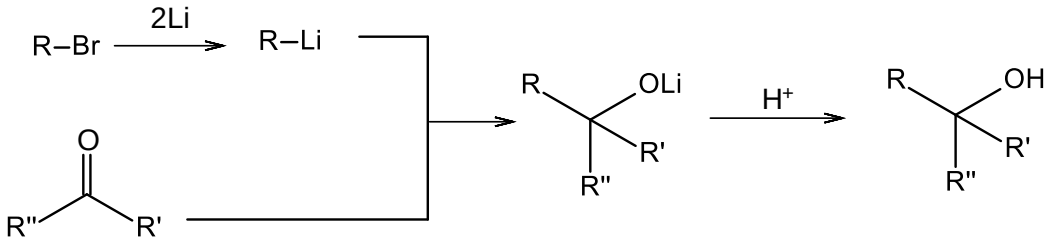
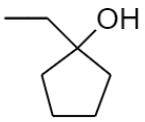


Fig. 4.1

(R is alkyl, R' and R'' are either alkyl or H)

(i) Draw the skeletal formula of the organic product formed when bromoethane is reacted with lithium, followed by cyclopentanone in a similar synthetic route as shown in Fig. 4.1. [1]



[1]

(ii) Compound **J**, $C_{10}H_{14}NBr$, decolourises aqueous bromine to give a white precipitate **K**, $C_{10}H_{12}NBr_3$.

J reacts with hot alcoholic NaOH to form isomers **L** and **M**, with the formula $C_{10}H_{13}N$. When heated with acidified $KMnO_4$, **L** gives effervescence, whereas **M** gives **N** as one of the products. Reacting the **N** with bromomethane according to the sequence in Fig. 4.1 gives 2-methylpropan-2-ol.

Heating **J** gives **P**, $C_{10}H_{13}N$ as the organic product.

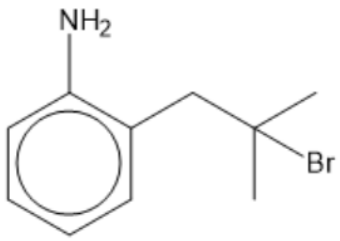
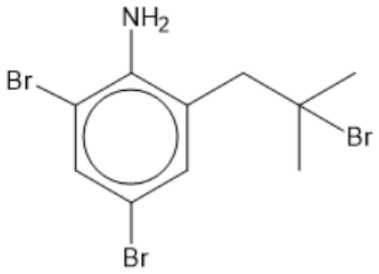
Suggest the possible structures of **J**, **K**, **L**, **M** and **P**. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional groups present in each compound. [6]

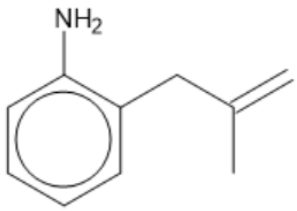
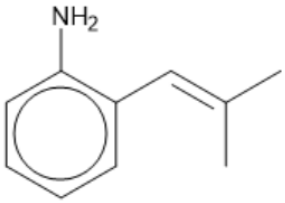
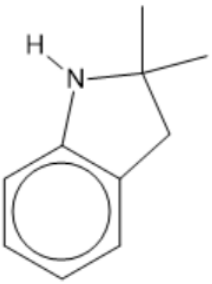
- ✓ **J has a high C:H ratio, J contains benzene.**
- ✓ **J undergoes electrophilic substitution with aqueous bromine to form K. J is a phenylamine (not phenol since J does not contain O).**

- ✓ 1 of the 2,4,6 positions of the phenylamine contains a substituent and is not available for substitution by Br.
- ✓ J undergoes elimination with alcoholic NaOH to form L and M which are alkenes.
- ✓ L and M undergoes oxidation/ oxidative cleavage with $KMnO_4$. L contains a terminal alkene.
- ✓ Following the reaction scheme in Fig. 4.1, N is propanone.
- ✓ J undergoes nucleophilic substitution to form P, $-NH_2$ and the bromoalkyl substituents should be adjacent to each other on the benzene.

Every 2 √ [1]

max [3]

J √	K √
	

L √	M √	P [1]
		

structures [3]

5 **(a)** In 1944, T. Ellingham published plots of Gibbs free energy change, ΔG, against temperature, T, for several reactions. Today, such plots are called Ellingham diagrams.

At present, titanium is more commonly produced by reducing titanium tetrachloride with magnesium. Titanium tetrachloride is a colourless liquid that boils at 400 K. To optimise this reduction process, it is necessary to know how ΔG of the reaction changes with T.

Fig. 5.1 shows the variation in ΔG with T for the following reactions:

Reaction 1: $\frac{1}{2}Ti + Cl_2 \longrightarrow \frac{1}{2}TiCl_4$

Reaction 2: $Mg + Cl_2 \longrightarrow MgCl_2$

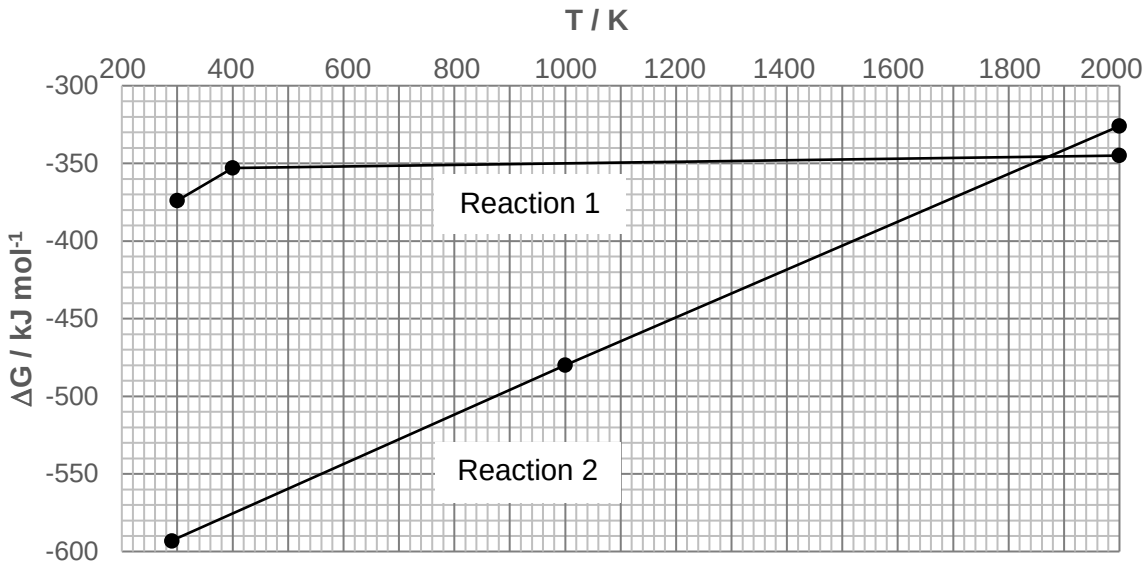


Fig. 5.1

(i) With reference to the gradient of the graph for Reaction 2, deduce the sign of ΔS.

Hence, explain why the graph for Reaction 2 becomes more positive with increasing temperature. [2]

√ **For graph of ΔG against T, y–intercept gives ΔH and the gradient gives $-\Delta S$. Since the gradient for reaction 2 is positive, ΔS is** negative.

√ This is because there is a decrease in disorder due to decrease in the number of moles of gas molecules from 1 to 0.

√ **Since ΔH and ΔS are both negative, $-T\Delta S$ becomes more positive with increasing temperature and hence the graph for reaction 2 becomes more positive**

3 √ = 2m; 2 √ = 1m

Industrially, the reduction of titanium tetrachloride by magnesium is carried out at 1100 K in an atmosphere of argon:

$$\frac{1}{2}TiCl_4 + Mg \longrightarrow \frac{1}{2}Ti + MgCl_2$$

(ii) Suggest a reason for the reduction to be carried out in an atmosphere of argon. [1]

To prevent the hot titanium extracted from oxidising to TiO_2

Note: traces of oxygen in the titanium tend to make the metal brittle.

Similar to enthalpy change of reaction, the Gibbs free energy, ΔG, of a reaction can be calculated using the following expression.

$$\Delta G = \sum \Delta G \text{ (products)} - \sum \Delta G \text{ (reactants)}$$

With reference to Figure 5.1,

(iii) evaluate ΔG for the reduction of $TiCl_4$ by Mg at 1100 K. [1]

$\frac{1}{2}Ti + Cl_2 \longrightarrow \frac{1}{2}TiCl_4$ ΔG at 1110 K = –350

$Mg + Cl_2 \longrightarrow MgCl_2$ ΔG at 1110 K = –465

ΔG = –465 – (–350)

= –115 kJ mol^{-1}

(iv) state the temperature above which it is **not** feasible to reduce $TiCl_4$ with Mg. [1]

1870 K (at T higher than 1870 K, $\Delta G > 0$)

Accept 1860-1880 K

Cobalt(II) chloride has been extensively used as a catalyst for various organic transformations.

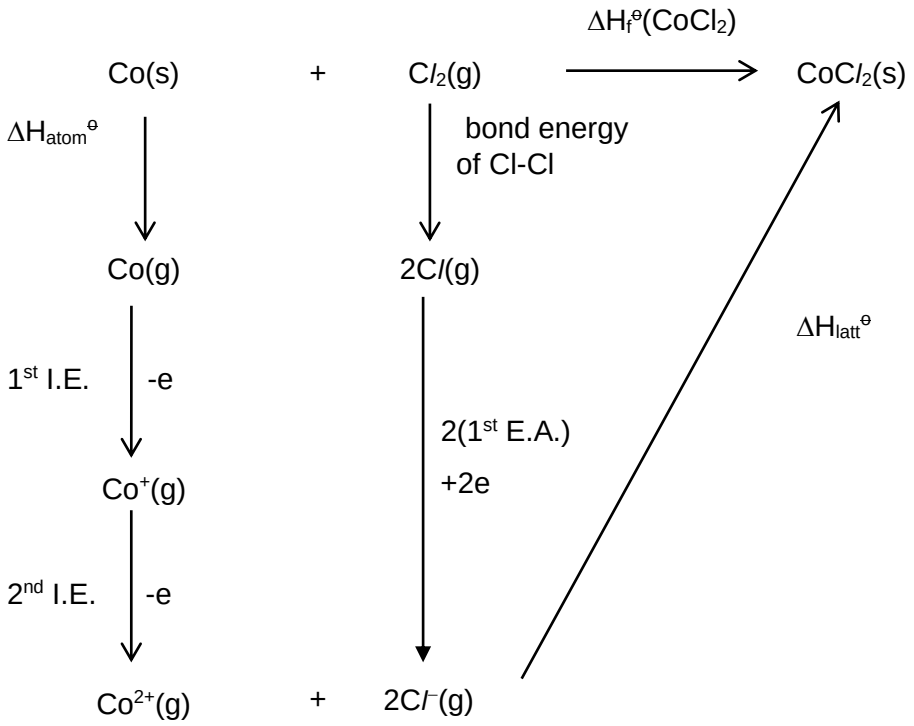
(b) Using the data in Table 5.1 and relevant data from the *Data Booklet*, construct a Born–Haber cycle to determine the standard enthalpy change of formation of cobalt(II) chloride.

Table 5.1

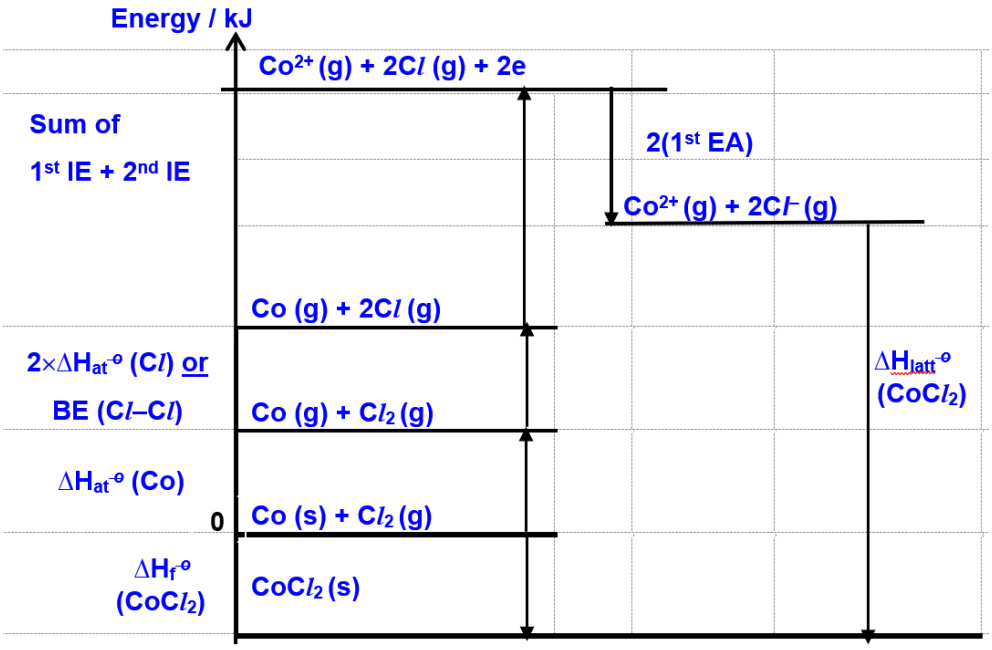
Enthalpy term	ΔH / kJ mol^{-1}
Lattice energy of $CoCl_2$	-2624
Standard enthalpy change of atomisation of cobalt	+427
First electron affinity for chlorine	-364

[3]

DO NOT WRITE IN THIS MARGIN



OR



By Hess' Law,

$\Delta H_f^{\ominus}(CoCl_2) = +427 + 244 + 757 + 1640 + 2(-364) + (-2624)$

$= \underline{-284\ kJ\ mol^{-1}}$

1m – labelled Born-Haber cycle (axis, zero point, all enthalpy terms/value)

1m – balanced equations with state symbols

1m – calculated value with sign and units *(do not award if no units/sign)*

(c) Cobalt(II) chloride is known to be a useful catalyst for the synthesis of α-aminonitriles by a one-pot 3-component condensation as shown:

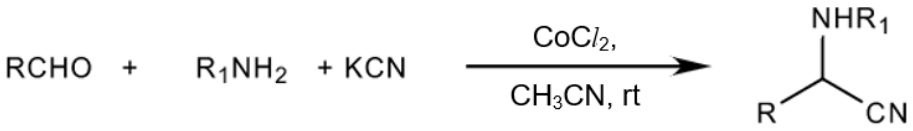
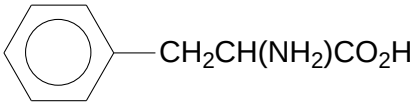


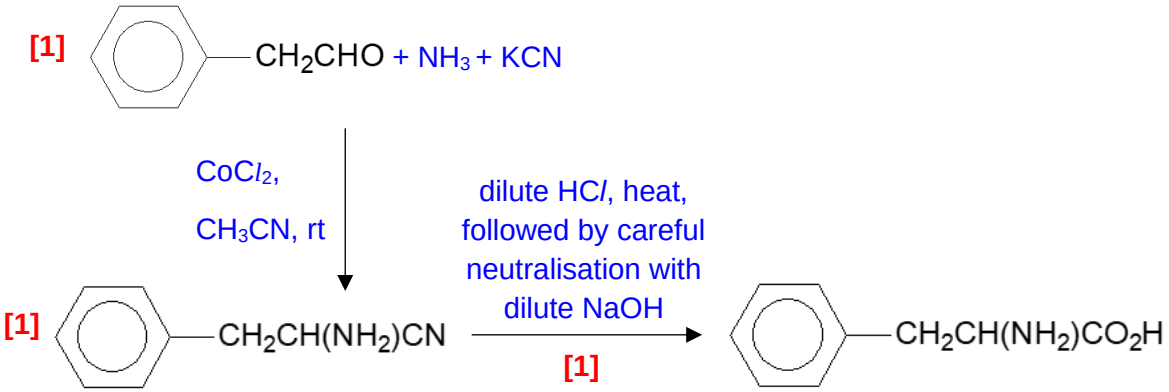
Fig. 5.2

Using the information in Fig. 5.2, propose a pathway to synthesize the following α–amino acid:



phenylalanine

Suggest the structures of the aldehyde that can be used as starting material and the intermediate. State the reagents and conditions for each step clearly. [3]



(d) Compound **Q**, $C_5H_{10}O_3$, does not react with 2,4–DNPH but reacts with warm alkaline aqueous iodine to give a yellow precipitate.

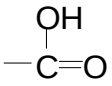
On treatment with hot concentrated sulfuric acid, compound **Q** forms a mixture of three isomeric compounds **R, S** and **T**, with the formula $C_5H_8O_2$, two of which are cis-trans isomers of each other.

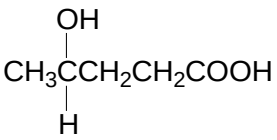
Compound **R** is a sweet-smelling liquid. Both **S** and **T** undergo reaction with acidified potassium manganate (VII) to give **U**, $C_3H_4O_4$, and ethanoic acid. 1 mole of **U** liberates 1 mole of CO_2 on reaction with excess sodium carbonate.

Identify the five compounds **Q** – **U**, explaining the chemistry of the reactions described.

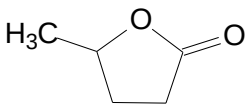
[9]

Observation	Type of reaction	Deduction
Q does not react with 2,4–DNPH.	√ does not undergo condensation	√ **Q** does not contain aldehyde or ketone functional group.
Q reacts with alkaline I_2(aq) to give yellow ppt.	√ oxidation	√ **Q** contains $CH_3CH(OH)$– *(reject if answer suggested methyl ketone structure)*

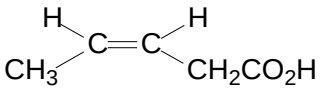
Q reacts with concentrated H_2SO_4 to give **R**, which is a sweet–smelling liquid	√ (Intramolecular) condensation	√ **R** is an **ester.** √ **Q** contains both the –OH and –COOH group
Q reacts with concentrated H_2SO_4 to give **S** and **T**, with the formula $C_5H_8O_2$	√ elimination	√ **S** and **T** contains C=C with √ two different substituents about each sp^2 C (**S** and **T** exhibits cis-trans isomerism)
S and **T** reacts with $KMnO_4$ to give **U**, $C_3H_4O_4$ and ethanoic acid	√ oxidation	√ The C=C in **S/T** is cleaved, there is no terminal C=C as no CO_2 is produced.
1 mole of **U** reacts with excess Na_2CO_3 to give 1 mole of CO_2.	√ acid–base reaction	**U** contains **2**  √ **U** is a dicarboxylic acid.



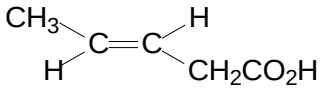
Q



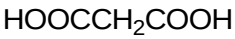
R



S



T



U

Structures: [1] each for **Q**, **R**, and **U;** [1] for both **S** and **T** (120° about sp^2 C)

Deductions:

[5]: 13 – 14 √

[4]: 10 – 12 √

[3]: 7 – 9 √

[2]: 4 – 6 √

[1]: 2 – 3 √

[Total: 20]