TEMASEK JUNIOR COLLEGE

2022 JC2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME		CIVICS CLASS	
CENTRE NUMBER	S	INDEX NUMBER	

Chemistry **9729/03**

Paper 3 Free Response **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

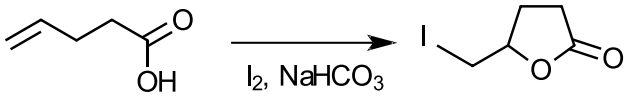
This document consists of **28** printed pages.

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.

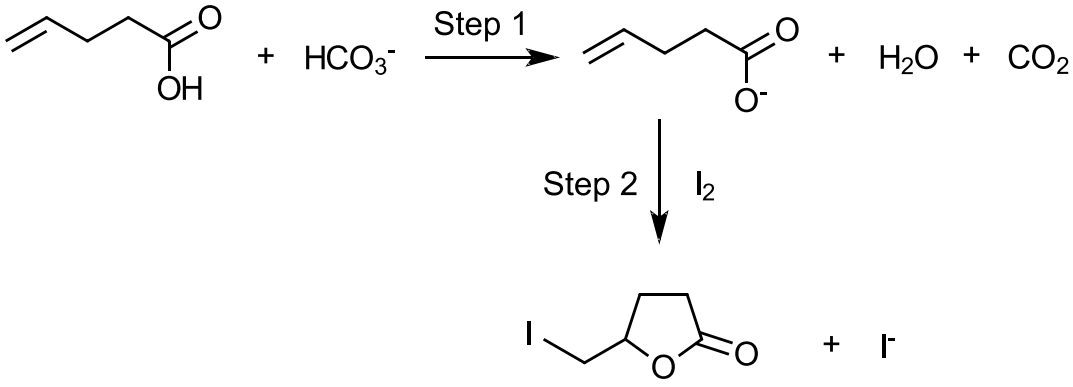
An example of the iodolactonisation is the reaction of 4-pentenoic acid as shown in Fig 1.1.



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]

(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]

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

(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]

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(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, $Hb(O_2)_4$.

$$Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq)$$

$$Hb(aq) + 4CO(aq) \rightleftharpoons Hb(CO)_4(aq)$$

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]

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(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]

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]

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

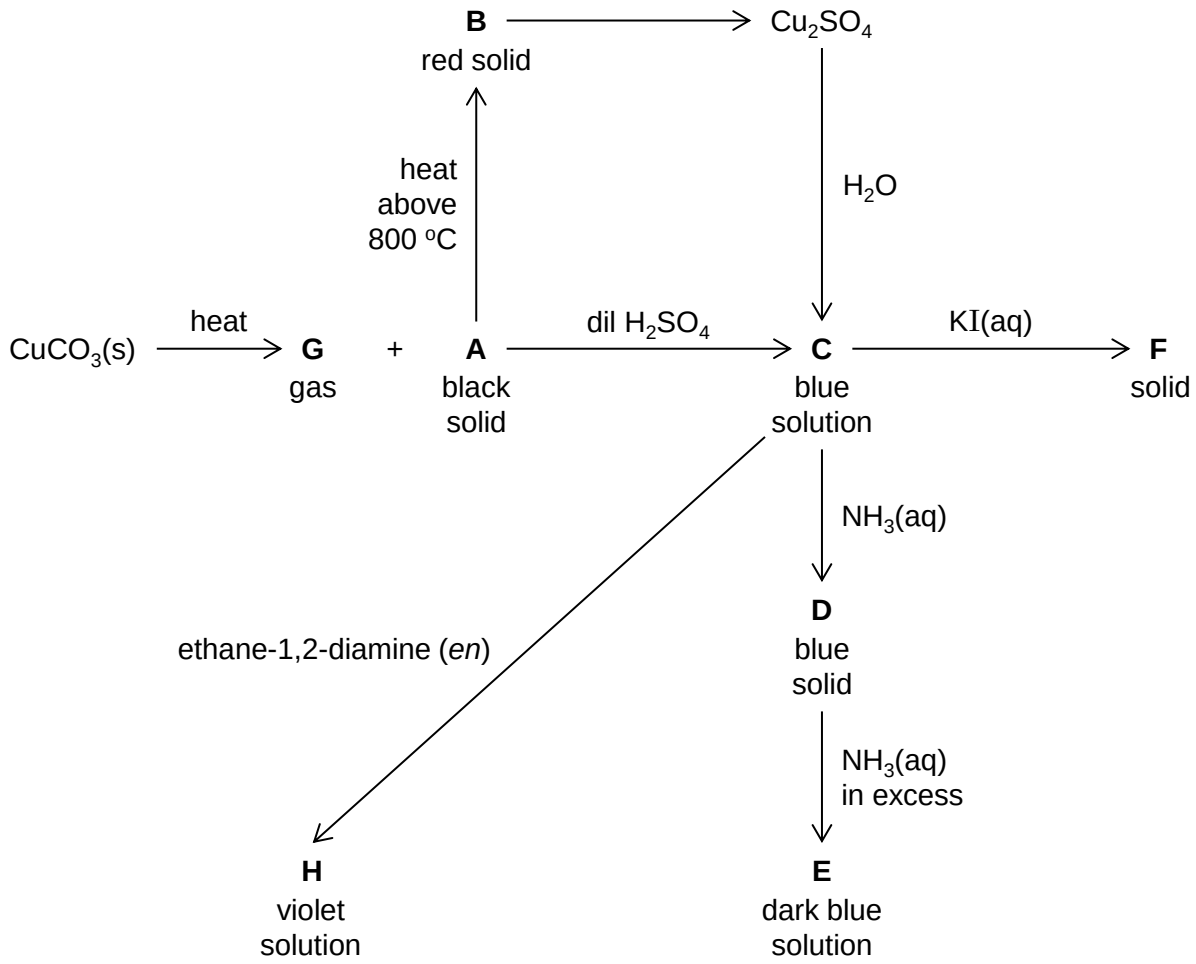
(iv) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of water-gas shift reaction. [3]

[Total:18]

[Turn over

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]

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

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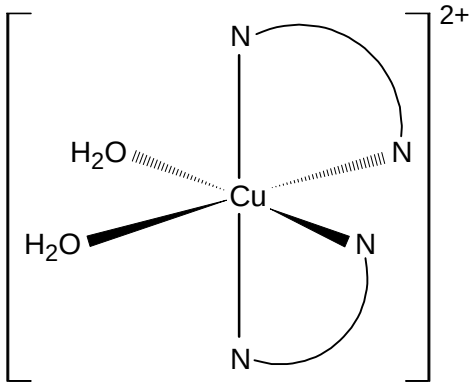
(b) Explain the transformations from **C** to **E** in terms of the competing equilibria and the type of reaction that has occurred. Include equations and the formulae of all copper-containing species. [4]

(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]

(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]

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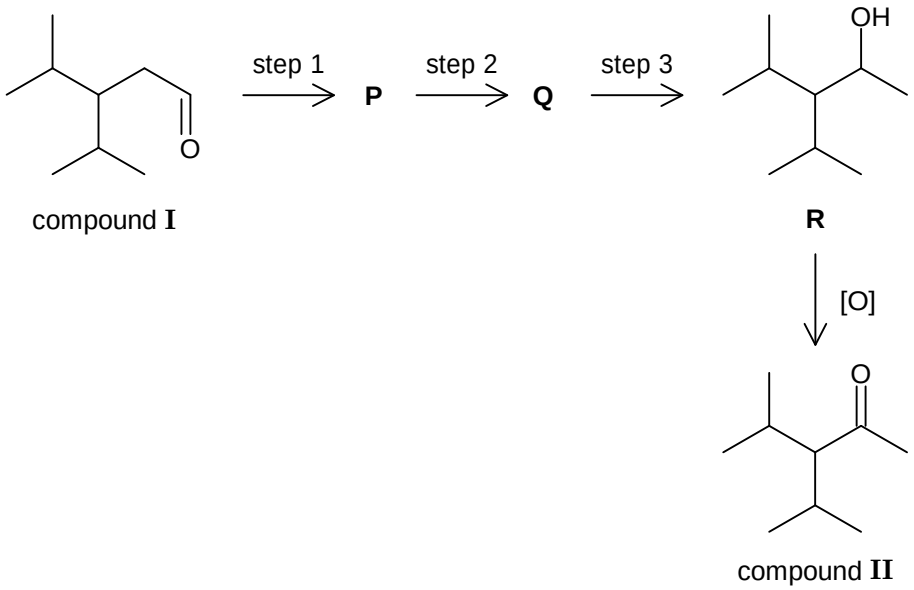
(e) Compound **II** can be converted from compound **I** in four steps.



(i) State the reagents and conditions you would use for steps 1−3 and give the structures of compounds **P** and **Q**. [5]

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

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[Total: 20]

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]

(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}
$[Ag(NH_3)_2]^+$	1.7×10^7
$[Ag(CN)_2]^-$	1.0×10^{21}

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

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(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.

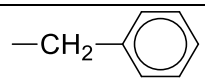
Fragments after reaction with **E1**	Fragments after reaction with **E2**
val-gln-phe	cys-phe-val
cys-phe	gln-lys-asp
gln-lys-asp	gln-phe

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]

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]

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

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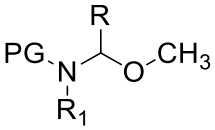
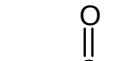
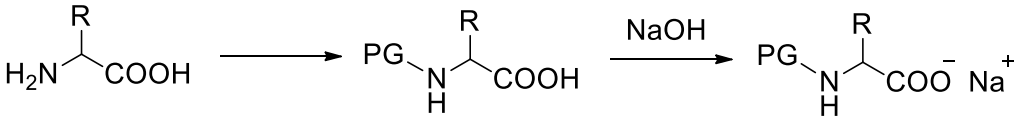
Compound **A** is formed from the electrolysis from α-amino acids in methanol solvent,



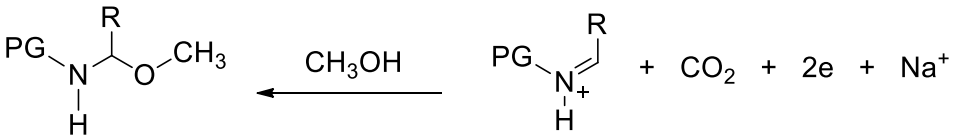
compound **A**

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

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



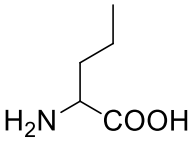
α-amino acid | protected form of α-amino acid | intermediate **B**



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]

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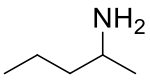
(d) Compound **A** undergoes hydrolysis to form amine **X**.

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

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



2-aminopentane

(e) Cation **C** subsequently reacts with methanol, which acts 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]

(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]

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

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(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]

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[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]

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

(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]

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

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

(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]

(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]

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(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.

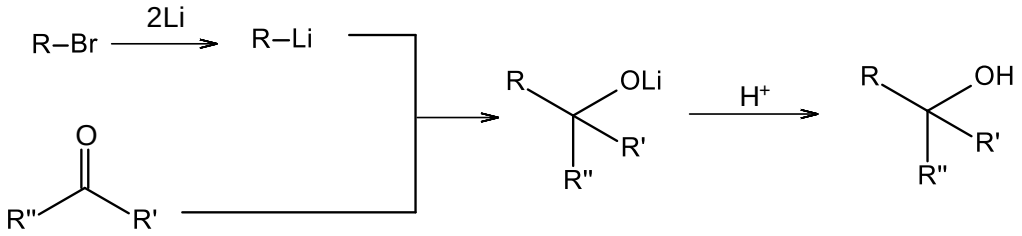

Fig. 4.1

(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]

(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]

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[Total: 20]

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: $Mg + Cl_2 \longrightarrow MgCl_2$

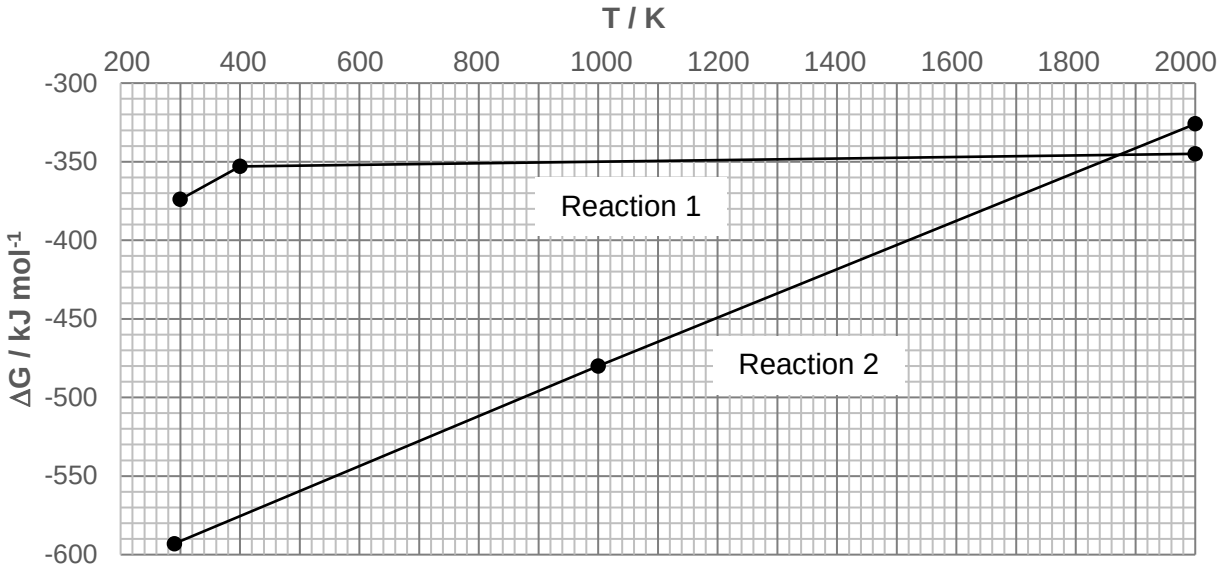


Fig. 5.1

(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]

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]

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 Fig. 5.1,

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

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

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]

(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:

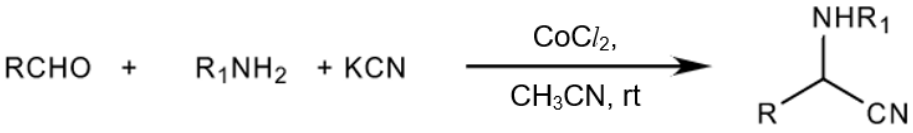
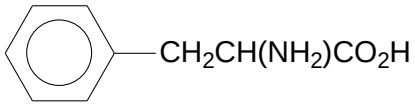


Fig. 5.2

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]

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(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]

[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.