## Section A

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

**1** The Group 17 elements and its halides can react with many transition metals.

**(a)** **(i)** Use the *Data Booklet* to describe the relative reactivity of the Group 17 elements as oxidising agents and relate this reactivity to relevant $E^{\ominus}$ values. [2]

**(ii)** The following reagents are contained in three bottles labelled A, B and C.

$NaBr(aq)$ $Cl_2(aq)$ $I_2(aq)$

Table 1.1 shows the results of tests that were carried out using the reagents in the bottles. In each test, equal volumes of the reagents were mixed and the resultant colour of the solution was recorded.

**Table 1.1**

| test | reagents mixed | colour of resultant solution |
|---|---|---|
| 1 | A and B | brown |
| 2 | C and B | orange |
| 3 | A and C | brown |

State the identity of the reagent in bottle A and write equations for any reactions that occur. [2]

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**(b)** Cobalt forms many complexes with ligands such as $H_2O$, $NH_3$ and $Cl^-$. The most common oxidation states of cobalt are +2 and +3.

Table 1.2 gives information about two octahedral cobalt(III) complexes **D** and **E**.

**Table 1.2**

| | complex | colour of aqueous ion |
|---|---|---|
| **D** | $[CoCl_2(NH_3)_4]^+$ | violet |
| **E** | $[Co(NH_3)_6]^{3+}$ | yellow |

**(i)** Define the term *complex*. [1]

**(ii)** The five d orbitals in a gas-phase transition metal ion are degenerate, but are split into two levels when the ion is in an octahedral complex.

Explain why the d orbitals are split into two levels in an octahedral complex, including which of the d orbitals are in each level. [2]

**(iii)** Draw the shapes of the d orbitals that occupy the higher energy level. [2]

**(iv)** The colour of the complexes is due to the absorption of light at specific wavelengths. The colour observed is the complement of the colour absorbed.

Suggest why the two complexes **D** and **E** have different colours. [1]

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**(c)** An electrochemical cell is set up using a $Co^{3+}$(aq)/$Co^{2+}$(aq) half-cell and a $[Ag(NH_3)_2]^+$(aq)/Ag(s) half-cell under standard conditions.

The electrode potential of the $[Ag(NH_3)_2]^+$(aq)/Ag(s) half-cell is –0.37 V.

When the cell discharges, the following reaction occurs.

$$Co^{3+}(aq) + Ag(s) + 2NH_3(aq) \longrightarrow Co^{2+}(aq) + [Ag(NH_3)_2]^+(aq)$$

**(i)** Write a half-equation for the oxidation of Ag to $[Ag(NH_3)_2]^+$. [1]

**(ii)** With the aid of the *Data Booklet*, calculate the $E^\ominus_{cell}$ and $\Delta G^\ominus$ for the above electrochemical reaction. [2]

**(iii)** Explain the effect on $E^\ominus_{cell}$ when $H^+$ is added to the $[Ag(NH_3)_2]^+$(aq)/Ag(s) half-cell. [2]

**(iv)** The Nernst equation can be used to determine the cell potential under non-standard conditions and is given as follows:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0592}{\text{n}} \log_{10} \text{Q}$$

where the value of Q is calculated using this expression $\dfrac{[Co^{2+}][Ag(NH_3)_2{}^{+}]}{[Co^{3+}][NH_3]^2}$

and n is the number of moles of electrons transferred per mole reaction.

When the electrochemical cell described in **(c)** discharges, the concentration of $Co^{3+}$ in the $Co^{3+}(aq)/Co^{2+}(aq)$ half-cell decreases from 1.00 mol dm$^{-3}$ to 0.75 mol dm$^{-3}$.

Show that the value of Q is 8.33 when $[Co^{3+}]$ is 0.75 mol dm$^{-3}$.

Hence, calculate the cell potential at this $Co^{3+}$ concentration. [3]

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**2** Inorganic compounds have various uses in the food and medical industry. For example, sodium hydroxide is used in the chemical peeling of fruits and vegetables, whereas magnesium compounds are used as food additives.

**(a)** Sodium hydroxide is formed in an explosive reaction between sodium metal and water, as shown in *reaction 1* in Table 2.1. The table also shows some other equations and their related standard enthalpy changes.

**Table 2.1**

| | | standard enthalpy change / kJ $mol^{-1}$ |
|---|---|---|
| *reaction 1* | $Na(s) + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq) + ½H_2(g)$ | $\Delta H_1^\ominus$ |
| *reaction 2* | $Na(s) \longrightarrow Na(g)$ | +107 |
| *reaction 3* | $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$ | –58 |
| *reaction 4* | $Na^+(g) + e^- + H^+(aq) \longrightarrow Na^+(aq) + ½H_2(g)$ | –850 |

**(i)** Deduce the sign of $\Delta S^\ominus$ for *reaction 1*. [1]

**(ii)** Hence, predict how an increase in temperature affects the spontaneity of *reaction 1*. Explain your answer. [1]

**(iii)** Write an equation to represent the first ionisation energy of sodium. [1]

**(iv)** Use the data in Table 2.1 and relevant data from the *Data Booklet* to draw an energy cycle to calculate the standard enthalpy change of *reaction 1*, $\Delta H_1^\ominus$. [3]

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**(b)** Magnesium sulfate is used as an additive to enhance the firmness of canned vegetables. It decomposes into magnesium oxide and sulfur trioxide according to the following equation.

$$MgSO_4 \xrightarrow{\Delta} MgO + SO_3 \qquad \Delta H^\ominus = +287.6\ \text{kJ mol}^{-1}$$
$$\Delta S^\ominus = +193\ \text{J mol}^{-1}\,\text{K}^{-1}$$

**(i)** Calculate $\Delta G^\ominus$ for the above reaction. [1]

**(ii)** Calculate the theoretical minimum temperature at which decomposition of $MgSO_4$ starts to occur. [2]

**(iii)** It has been found experimentally that magnesium sulfate starts to decompose at 1124 °C. Suggest a possible reason for the discrepancy between your calculated value in **(ii)** and the experimental value provided. [1]

**(iv)** The product of the above decomposition, magnesium oxide, is a white hygroscopic solid with a melting point 2850 °C.

Draw a labelled diagram to illustrate the arrangement of the lattice particles in solid magnesium oxide. Your diagram should show clearly the relative size of the different types of particles. [1]

**(v)** Magnesium oxide and silicon dioxide are both used as lining for furnaces. Using structure and bonding, explain why the melting point of magnesium oxide is higher than that of silicon dioxide. [3]

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**(c)** Magnesium carbonate is sparingly soluble in water. It is therefore commonly used as an additive in table salt to prevent it from clumping. Magnesium carbonate has a solubility of $1.26 \times 10^{-4}$ mol dm$^{-3}$ at 25 °C.

**(i)** Write the solubility product, $K_{sp}$, expression for magnesium carbonate, stating its units. [2]

**(ii)** Calculate a value for the solubility product, $K_{sp}$, for magnesium carbonate. [1]

**(iii)** When 0.0500 mol of solid $Na_2CO_3$ is added to a 1.0 dm$^3$ saturated solution of $MgCO_3$ at 25 °C, a precipitate forms in the solution.

Calculate the concentration of [$Mg^{2+}$] in the resultant solution. [2]

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**3** **(a)** Remifentanil ($C_{20}H_{28}N_2O_5$) is a synthetic opioid drug. It is given to patients during surgery to relieve pain and as an adjunct to an anesthetic.

A possible synthesis route of Remifentanil is shown in Fig. 3.1.

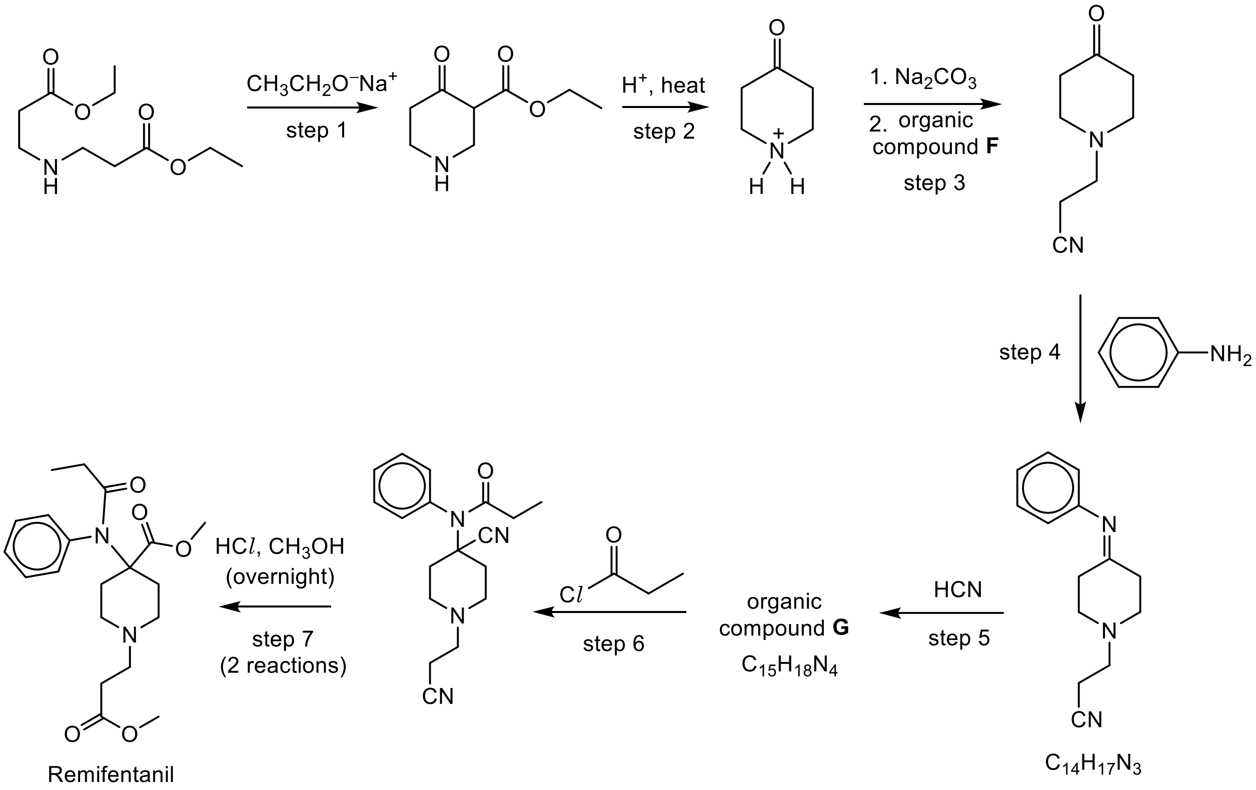
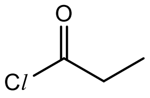
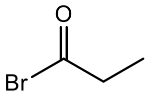


**Fig. 3.1**

**(i)** Name the types of reactions occurring in step 4 and step 7 (2 reactions occur in step 7). [3]

**(ii)** Draw the structure for the organic compound **G.** [1]

**(iii)** Suggest why step 5 is carried out at a temperature of about 10 °C. [1]

**(iv)** When the reagent  in step 6 is replaced by , it was found that the reaction was five times faster. Suggest an explanation for this observation. [1]

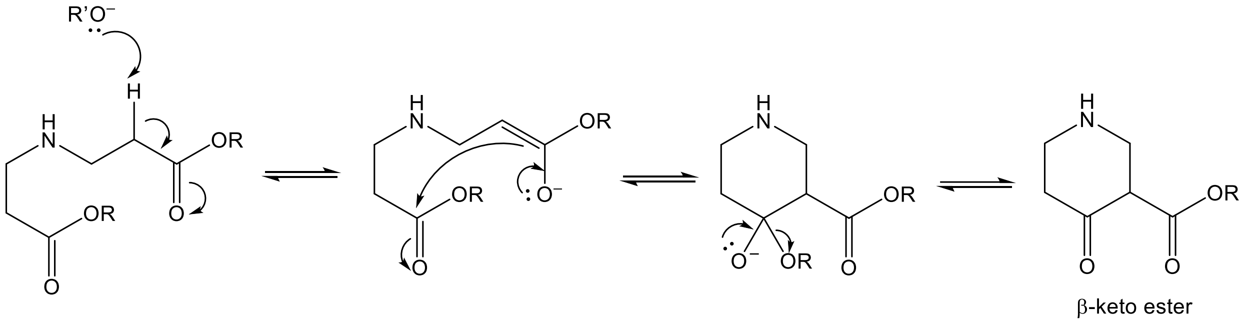
**(v)** Given that step 3 is a nucleophilic substitution reaction, suggest:

- why sodium carbonate was used and
- the structure of the organic compound **F**. [2]

**(b)** Step 1 of the reaction scheme in Fig. 3.1 involves the Dieckmann condensation.

This intramolecular condensation reaction occurs between 2 ester groups to give a cyclic β-keto ester.

Fig. 3.2 shows the mechanism for the Dieckmann condensation.

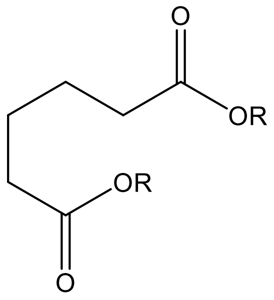


R and R' are alkyl groups

**Fig. 3.2**

**(i)** Suggest the role of R'O⁻ in the first step of the reaction. [1]

**(ii)** Suggest the structure of the organic product formed when the following compound undergoes the Dieckmann condensation. [1]



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**(c)** Under acidic conditions, ketones react with halogens to give substitution at the alpha($\alpha$)-carbon. Fig. 3.3 shows the mechanistic steps that occur with propanone as the organic reagent.

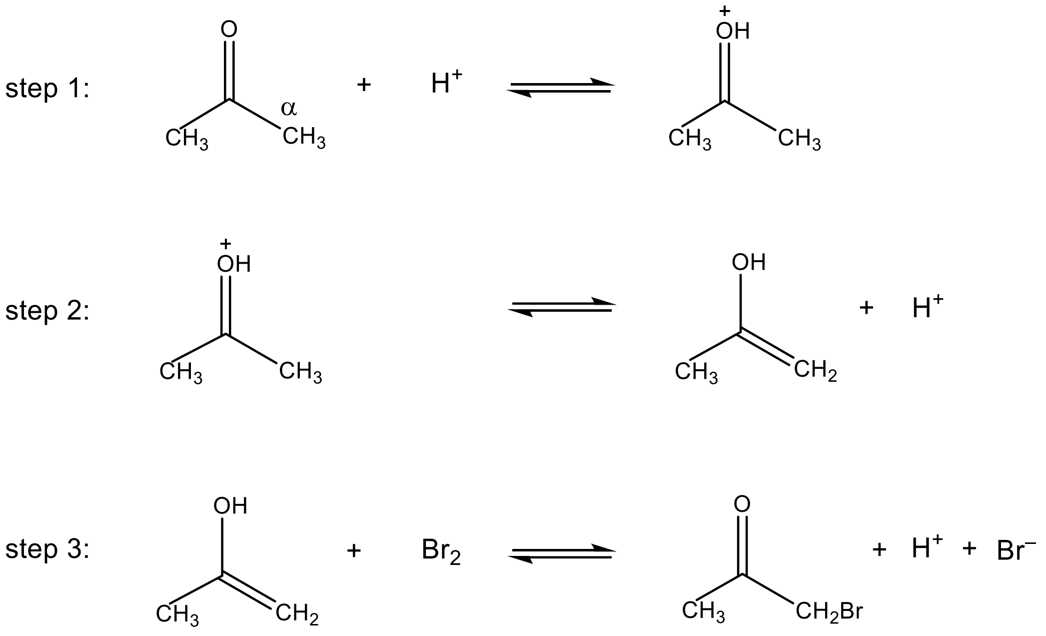

**Fig. 3.3**

**(i)** Write a balanced equation for the overall reaction that occurs when propanone is mixed with acidified $Br_2$. [1]

**(ii)** Briefly outline how the initial rate of the reaction in **(c)** could be measured. [2]

**(iii)** A student conducted an experiment and determined that the rate equation for the reaction in **(c)** is rate = $k$[propanone][$H^+$], but was unable to conclude whether step 1 or step 2 is the slow step. Suggest why. [1]

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**(d)** Groundwater contaminated with arsenite, $AsO_3^{3-}$, presents a grave concern in many developing countries. To protect public health, the World Health Organisation sets a permissible limit for **arsenic**(As) in drinking water; typically at 10 micrograms per $dm^3$ ($\mu g\ dm^{-3}$ or $10^{-6}$ g $dm^{-3}$). The level of arsenic toxicity is tested based on the amount of arsenite that is presented in the water source.

A 100 $cm^3$ sample of water is drawn from a polluted source. 50.00 $cm^3$ of 0.00110 mol $dm^{-3}$ acidified $Cr_2O_7^{2-}$ (aq) ions, which is in excess, is added to the solution. The two half-equations for the reaction that occurs are as shown:

$$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

An excess of iodide ions is then added to react with the remaining $Cr_2O_7^{2-}$, liberating iodine.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

The liberated iodine is then titrated against 0.0150 mol $dm^{-3}$ $Na_2S_2O_3$.

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$$

The end-point is reached when 21.20 $cm^3$ of $Na_2S_2O_3$ has been added.

**(i)** Construct the ionic equation for the reaction between arsenite ions, $AsO_3^{3-}$, and acidified dichromate(VI) ions, $Cr_2O_7^{2-}$. [1]

**(ii)** Determine the amount of arsenite, $AsO_3^{3-}$, in the 100 $cm^3$ sample of water. [3]

**(iii)** Hence calculate how many times the **arsenic** level in the water sample exceeds the permissible limit for drinking water. [2]

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**(e)** Aromatic compound **J** ($C_{10}H_{12}O_3$) gives a positive result with both Tollens' reagent and Fehling's solution. It forms a yellow precipitate when heated with alkaline aqueous iodine and produces white fumes when exposed to $SOCl_2$.

When **J** reacts with concentrated $H_2SO_4$ under hot conditions, it forms **K** ($C_{10}H_{10}O_2$), which does not exhibit stereoisomerism. Both **J** and **K** decolourise aqueous $Br_2$ but in different mole ratios, as shown in Table 3.1.

**Table 3.1**

| compound | moles of $Br_2$(aq) |
|---|---|
| **J** | 1 |
| **K** | 2 |

**K**, when heated with acidified potassium dichromate and subsequently treated with $PCl_5$, forms **L**($C_{10}H_8O_2$), which emits a sweet smell. Both **J** and **K** form a violet complex with neutral $FeCl_3$ but **L** does not.

Give the structure of compounds **J**, **K** and **L**. [3]

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## Section B

Answer **one** question from this section.

**4** Aromatic compounds serve as important building blocks in organic synthesis. They are widely used as starting materials to produce pharmaceuticals, dyes, fragrances, and many other chemicals.

**(a)** Both methylbenzene and phenol form nitro compounds with nitric acid under different conditions as shown in Fig. 4.1.

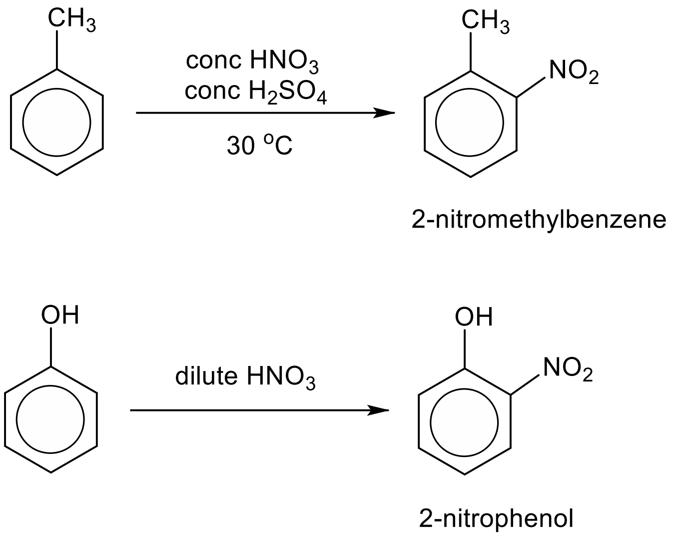

**Fig. 4.1**

**(i)** Explain why different conditions are needed for the formation of 2-nitrophenol and 2-nitromethylbenzene as shown in Fig. 4.1. [2]

**(ii)** Hence suggest the reagents and conditions required for a similar reaction of benzoic acid to form the corresponding nitro compound. [1]

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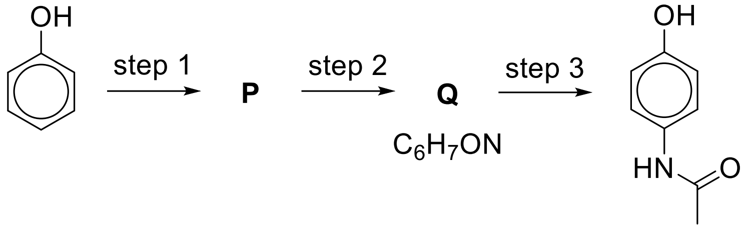
**(b)** Phenol is usually used for the synthesis of *paracetamol* which is a medication for treatment of pain and fever. *Paracetamol* can be prepared from phenol via a three-step synthesis as shown in Fig. 4.2.



paracetamol

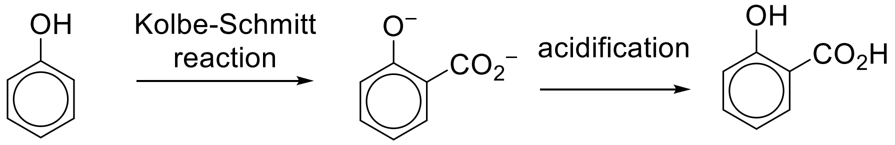
**Fig. 4.2**

**(i)** Suggest the structures of compounds **P** and **Q**, and the reagents and conditions for steps 1 and 2. [3]

**(ii)** A student suggested that ethanoyl chloride, $CH_3COCl$, could be used as a reagent for step 3. However, this reagent may form another compound **R** instead of paracetamol.

Suggest the structure of compound **R**. [1]

Aspirin can also be used for treatment of pain and fever. The industrial production of aspirin involves the conversion of phenol to salicylic acid by the Kolbe-Schmitt reaction. In the reaction, phenol is strongly heated with $CO_2$ and NaOH as shown in Fig. 4.3.



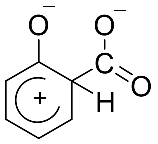
phenol anion of salicylic acid salicylic acid

**Fig. 4.3**

One suggested mechanism for the Kolbe-Schmitt reaction is similar to an electrophilic substitution reaction. The three steps of the mechanism are described below.

Step 1: Phenol undergoes acid-base reaction with hydroxide ion to form a phenoxide ion.

Step 2: $CO_2$ acts as an electrophile to react with phenoxide ion to form the following intermediate.



Step 3: The hydroxide ion reacts with the intermediate to form the anion of salicylic acid.

**(iii)** Suggest the mechanism for the reaction described above, showing all charges, dipoles and using curly arrows to show the movement of electron pairs in each step. [3]

**(c)** The reactions of the Period 3 chlorides with water vary across the Period.

**(i)** Describe the reactions of $MgCl_2$ and $PCl_5$ with water, suggesting the pH of the resulting solutions. Explain the reaction of these chlorides in water based on their structure and bonding. Write equations for all reactions that occur. [3]

**(ii)** Both $CCl_4$ and $SiCl_4$ are Group 14 chlorides. $SiCl_4$ fumes in moist air due to a vigorous reaction with water. However, $CCl_4$ does not react with water. Suggest a reason for the unreactivity of $CCl_4$ towards water. [1]

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**(d)** Upon heating, $PCl_5$ undergoes decomposition to form $PCl_3$ and $Cl_2$ as shown.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H > 0$$

A mixture of 0.0625 mol of $PCl_5$ and 0.0705 mol of $Cl_2$ were placed into a 2.0 $dm^3$ sealed vessel at 250 °C. After dynamic equilibrium was established, the total pressure in the vessel was 3.25 atm. You may assume that the gases behave ideally under the stated conditions.

**(i)** By calculating the total amount of gases in the vessel at equilibrium or otherwise, calculate the amount of $PCl_3$ formed at equilibrium at 250 °C. [2]

**(ii)** Calculate the equilibrium constant, $K_p$ at 250 °C, stating the units of $K_p$ clearly. [2]

**(iii)** State and explain how the $K_p$ value would change when the temperature of the vessel is increased. [2]

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**5** **(a)** The Group 2 carbonates are widely used in the construction and agriculture industry.

On heating, the Group 2 carbonates decompose as shown:

$MCO_3(s) \rightarrow MO(s) + CO_2(g)$ where M is the Group 2 element

**(i)** Describe and explain the trend in the thermal stabilities of the Group 2 carbonates. [2]

**(ii)** The graph in Fig. 5.1 represents the change in mass that occurs when 1.0 g of powdered calcium carbonate, $CaCO_3$, is heated at a certain temperature.

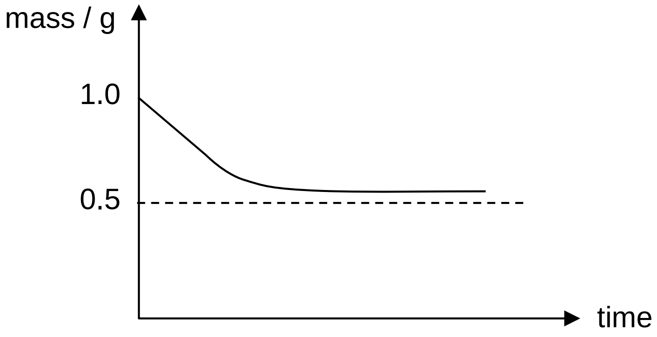

**Fig. 5.1**

Sketch, on the same axis, a graph that would be obtained by heating 1.00 g of magnesium carbonate, $MgCO_3$, at the same temperature.
Your answer should illustrate clearly the relative ease of thermal decomposition of the two carbonates and the relative mass of residue formed.

Include any relevant calculations.
[$M_r$: $MgCO_3$, 84.3 ; $CaCO_3$, 100.1] [2]

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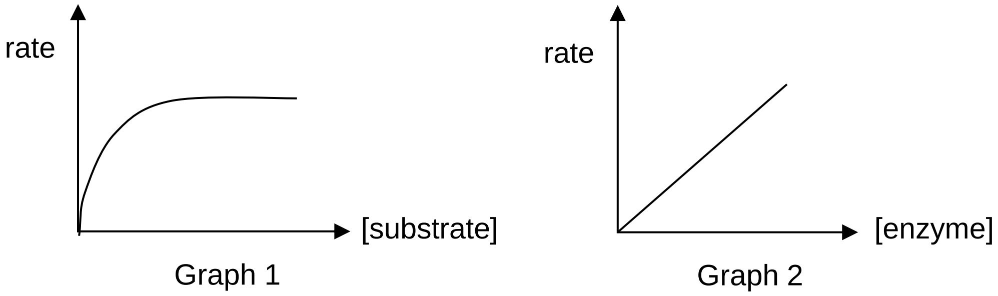
**(b)** The biological process of forming proteins from amino acids is enzyme catalysed.

Graph 1 in Fig. 5.2 shows how the rate of an enzyme catalysed reaction varies with substrate(reactant) concentration for a given enzyme concentration.

Graph 2 in Fig. 5.2 shows how the rate of an enzyme catalysed reaction varies with enzyme concentration when the enzyme concentration is significantly lower than the substrate concentration.



Graph 1

Graph 2

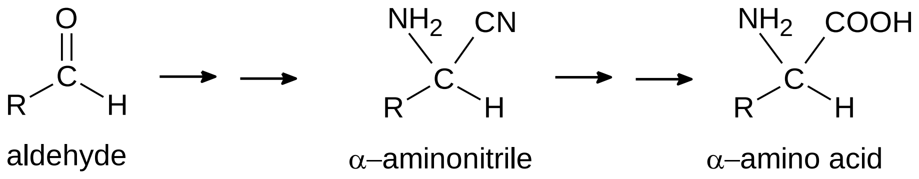
**Fig. 5.2**

**(i)** Explain why Graph 1 in Fig. 5.2 levels off at high [substrate]. [1]

**(ii)** State the relationship between reaction rate and enzyme concentration as shown in Graph 2. Suggest a reason for this. [1]

**(c)** The Strecker Synthesis is a laboratory method of forming amino acids from aldehydes.

Fig. 5.3 shows an overview of this multi-step synthesis that involves forming an α-aminonitrile, which is then subsequently carefully hydrolysed to form the amino acid.

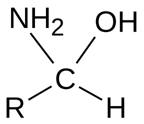


$\longrightarrow\ \longrightarrow$ denotes series of steps

**Fig. 5.3**

**(i)** In the conversion of the aldehyde to an α-aminonitrile shown in Fig. 5.3, the first 2 steps involve a nucleophilic addition which occurs as described:

- nucleophilic attack of ammonia on the carbonyl carbon to yield a dipolar ion consisting of both a positive and a negative charge;
- internal proton transfer to form a neutral molecule with the structure below.

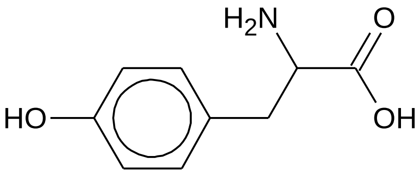


Draw the mechanism described in the 2 steps above, showing clearly the structure of the dipolar ion. Include curly arrows and relevant dipoles in your answer. [3]

**(ii)** By considering the information given in **(c)(i)**, explain why the product formed is likely a racemic mixture. [1]

**(iii)** Suggest why the α-aminonitrile had to be "carefully hydrolysed" to form the amino acid. [1]

**(iv)** Draw the **skeletal** formula of the aldehyde that can be used to form the amino acid *tyrosine* via the Strecker Synthesis. [1]

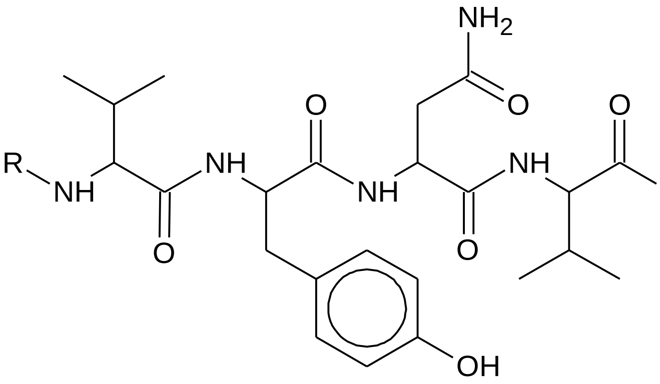


*tyrosine*

**(v)** *Tyrosine* has three p$K_a$ values associated with it: 2.2, 9.1 and 10.0.

Given that p$K_a$ = 10.0 is for the phenolic R group, draw the structure of the predominant species of tyrosine at pH 7. [1]

**(d)** Fig. 5.4 shows a part of the protein structure of human insulin.



R and R’ represent the rest of the molecule.

**Fig. 5.4**

**(i)** State the reagents and conditions required to completely hydrolyse a protein molecule into its constituent amino acids. [1]

**(ii)** The insulin molecule is hydrolysed using the reagent and conditions given in **(i)**. Draw the structure of a species in the resulting reaction mixture that is formed from one of the amino acids other than tyrosine. [1]

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**[Turn over**

**(e)** Compound **X** has molecular formula $C_7H_{13}NO_2$. On boiling **X** with aqueous sodium hydroxide, ethylamine is formed.

**(i)** Ethylamine dissolves readily in dilute acid at room conditions whereas compound **X** does not.

Suggest the nitrogen-containing functional group that could be present in **X.** Explain the observed difference in acid-base nature of the nitrogen-containing functional groups. [2]

**(ii)** Compound **X** is optically active. Compound **Y**, $C_7H_{17}NO$, which is also optically active, is formed when **X** reacts with $LiAl\mathit{l}H_4$. On heating with $A\mathit{l}_2O_3$, **Y** forms two different compounds which readily decolourise aqueous bromine.

Suggest possible structures for **X** and **Y**, stating the type of reaction that has occurred for each. [3]

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