Section A

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

1 (a) Explain what is meant by the term *Lewis acid*. [1]

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(b) The water molecule can react in various ways: as an acid, as a base, as a nucleophile, as an oxidising agent and as a reducing agent.

Study the following reactions and decide in which way water is reacting in each case.

Explain your answers fully.

(i) $2F_2 + 2H_2O \rightarrow 4HF + O_2$ [1]

(ii) $CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$ [1]

(iii) $H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$ [1]

(iv) $Li + H_2O \rightarrow LiOH + \frac{1}{2}H_2$ [1]

(v) $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$ [1]

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(c) The pK_a values of three acids are listed in Table 1.1.

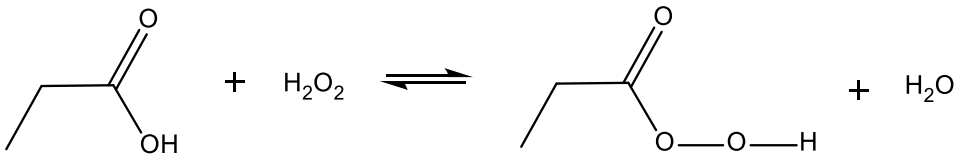
Table 1.1

acid	formula	pK_a
1	CH_3CH_2COOH	4.9
2	$CH_3CHClCOOH$	2.8
3	CH_2ClCH_2COOH	*z*

(i) Explain the difference in pK_a values between acid 1 and acid 2. [2]

(ii) Suggest a value for *z* and explain your answer. [1]

(iii) Peroxyacids are weak acids. One way to prepare peroxypropanoic acid is to treat the corresponding carboxylic acid with hydrogen peroxide.



acid 1 peroxypropanoic acid

Suggest why the pK_a of peroxypropanoic acid is higher than that of acid 1. [1]

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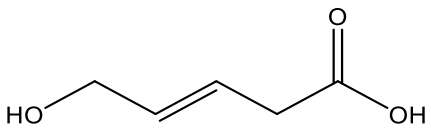
(d) **A**, **B** and **C** are isomers with the molecular formula $C_5H_6O_2$. All three compounds decolourise bromine water in the dark.

A produces effervescence in the presence of Na_2CO_3(aq) whereas **B** and **C** do not. **A** also reacts with hot acidified $KMnO_4$ to form **D**, $C_3H_2O_5$.

B forms a brick-red precipitate when heated with Fehling's solution.

C reacts with hot aqueous sodium hydroxide. Upon acidification, it forms $C_5H_8O_3$.



$C_5H_8O_3$

When **B** and **C** are separately reacted with hot acidified $KMnO_4$, they form the same mixture of **E**, $C_3H_4O_4$, and **F**, $C_2H_2O_4$. **F** undergoes further oxidation to give effervescence.

(i) Draw the structures of **D**, **E** and **F**. [3]

(ii) Deduce the structures of **A**, **B** and **C** with reasoning. [7]

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2 (a) The acid-base behaviour of aluminium oxide, Al_2O_3, shows similarities to that of magnesium oxide, MgO, on the one hand, and sulfur trioxide, SO_3, on the other.

Describe what these similarities are, and explain why aluminium oxide occupies this in-between position.

Write equations for all the reactions you choose to illustrate your answer. [5]

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(b) (i) Explain what is meant by the term *standard enthalpy change of atomisation of magnesium*. [1]

(ii) An experiment was carried out by adding 0.05 g of magnesium ribbon to 50 cm^3 of excess hydrochloric acid solution. The increase in temperature was 4.5 °C.

Reaction 1 is represented by the ionic equation as shown:

reaction 1 $\quad Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g) \quad \Delta H_1^{\ominus}$

Use data from the *Data Booklet* to calculate $\Delta H_1^{\ominus}$, the standard enthalpy change of reaction 1. [2]

(iii) Besides using an experimental method, another way to determine $\Delta H_1^{\ominus}$, the standard enthalpy change of reaction 1, is to construct an energy cycle.

Use the data in Table 2.1, together with data from the *Data Booklet*, calculate another value of $\Delta H_1^{\ominus}$. [4]

Table 2.1

	$\Delta H^{\ominus}$ / kJ mol^{-1}
standard enthalpy change of atomisation of Mg(s)	+148
standard enthalpy change of hydration of Mg^{2+}(g)	−1921
standard enthalpy change of hydration of H^{+}(g)	−1090

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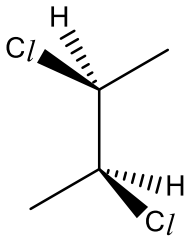
(c) 2,3-dichlorobutane exhibits stereoisomerism, one of which is enantiomerism. One enantiomer of 2,3-dichlorobutane is shown below.

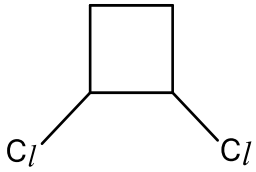


(i) Draw the other enantiomer. [1]

(ii) A molecule with *n* chiral centres can have a maximum of 2^n stereoisomers. 2,3-dichlorobutane has two chiral centres but it only has three stereoisomers.

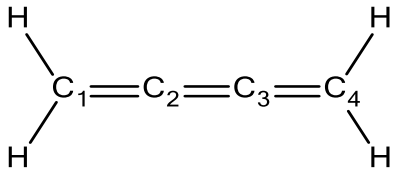
Draw the third stereoisomer of 2,3-dichlorobutane and explain why it has only three stereoisomers. [2]

(iii) The structure of 1,2-dichlorocyclobutane is shown below.



Suggest why 1,2-dichlorocyclobutane can exhibit cis−trans isomerism and draw the pair of cis−trans isomers. [2]

(iv) A cumulene is a hydrocarbon with three or more consecutive double bonds. The simplest molecule in this class is butatriene, C_4H_4.



With the aid of a labelled diagram, describe the orbitals that form the C_1=C_2 bond in butatriene and state the type of hybridisation involved. [3]

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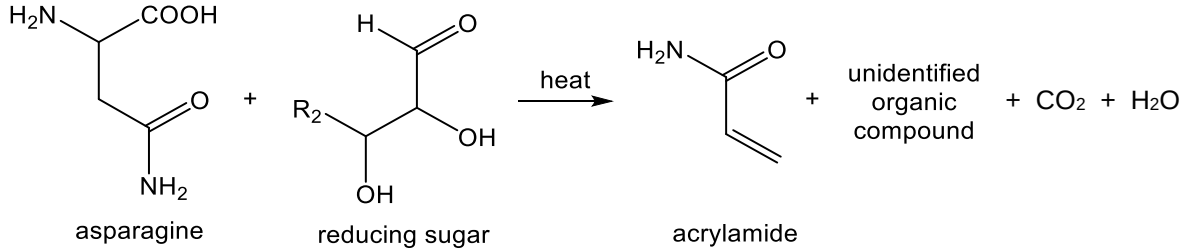
3 (a) The Maillard reaction is an important process that occurs between sugars with amino acids during cooking. Its occurrence is responsible for the golden brown colouration and crispy texture that makes food appealing and tasty.

In 2002, it was discovered that the Maillard reaction involving asparagine, an amino acid, forms acrylamide, a known carcinogen. Reaction 1 shows the chemical equation for the formation of acrylamide.



reaction 1

To determine the kinetics of reaction 1, three experiments were carried out and the results are shown in Table 3.1.

Table 3.1

experiment	concentration / mol dm^{-3}		initial rate / 10^{-3} mol dm^{-3} s^{-1}
	asparagine	reducing sugar	
1	0.100	0.500	2.46
2	0.100	0.625	3.08
3	0.200	0.750	3.69

(i) Deduce the order of reaction with respect to asparagine and the reducing sugar. Hence write the rate equation. [3]

(ii) The reducing sugar is at an initial concentration of 1.60 mol dm^{-3} and its half-life is 140 s.

Sketch a graph of the concentration of the reducing sugar against time for reaction 1. [2]

(iii) Determine the rate constant, *k*, for reaction 1. [1]

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(b) The reaction between the reducing sugar and aqueous sodium borohydride is a nucleophilic addition reaction.

Draw the mechanism for this reaction, assuming that sodium borohydride produces the hydride ion, **:**H^-, as the reacting species. In your answer, you may represent the reducing sugar as RCHO. [3]

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(c) The following mechanism in Fig. 3.1 has been proposed for the Maillard reaction involving asparagine.

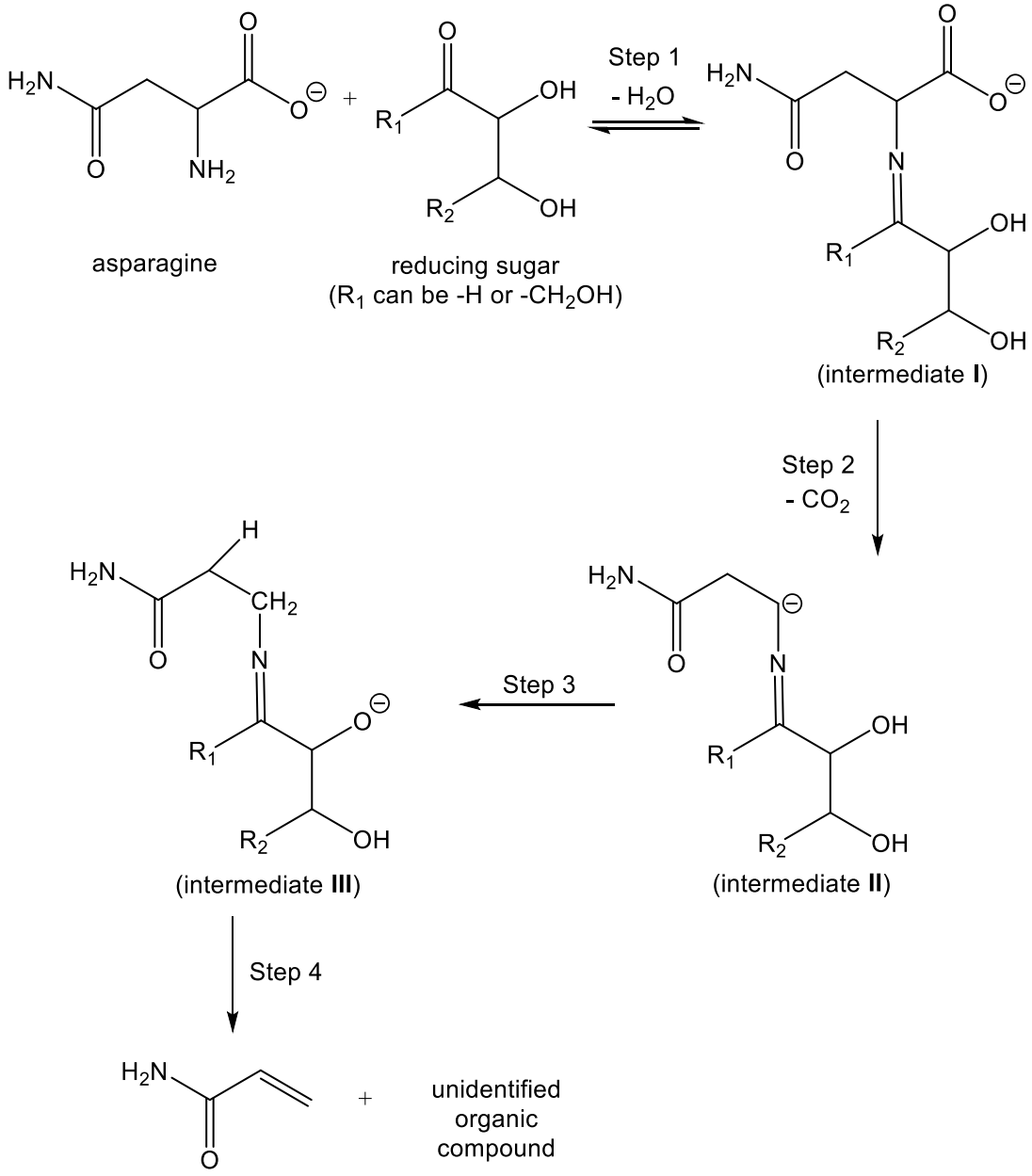

Fig. 3.1

(i) State the role of asparagine in step 1. [1]

(ii) Suggest and explain the effect on the rate of step 1 when R_1 is changed from –H to –CH_2OH. [1]

(iii) Draw the structure of the unidentified organic compound in step 4. [1]

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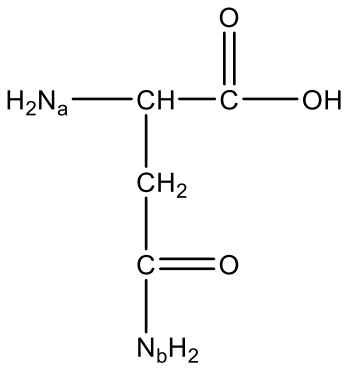
(d) Compare and explain the base strength of the atoms N_a and N_b in asparagine. [2]



asparagine

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(e) In the 2020 Olympic Games, winners received medals made from recycled gold, silver and bronze. These metals were recycled from electronic waste collected throughout Japan. In the recycling process, metal parts are physically removed from the plastics, and the metals are sorted by elements and levels of purity.

Low purity silver is refined using electrolysis to remove metal impurities such as gold and copper.

(i) The electrode potential for Au^+/Au is given below.

$$Au^+ + e^- \rightleftharpoons Au \qquad E^\ominus = +1.83\ V$$

Define the term *standard electrode potential of Au^+/Au*. [1]

(ii) Describe the electrode reactions that take place during this electrolysis, and explain in detail how each of the two impurity metals is removed from silver. [3]

(iii) The electrolytic refining of silver was carried out for 90 minutes using a current of 10.2 A.

Using data from the *Data Booklet*, calculate the expected mass of silver deposited in this process. [2]

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Section B

Answer **one** question from this section.

4 (a) (i) A glass rod was heated in a Bunsen burner flame and placed into a sample of hydrogen chloride gas.

The experiment was repeated using a sample of hydrogen iodide gas.

Use data from the *Data Booklet* to explain why a colour change was observed for hydrogen iodide but not hydrogen chloride. [2]

(ii) Hydrogen chloride can be oxidised to chlorine in the presence of CuC*l*.

Likewise, hydrogen cyanide can be oxidised to cyanogen in the presence of Cu according to the following equation.

$$2HCN + \tfrac{1}{2}O_2 \rightarrow (CN)_2 + H_2O$$

State the change in oxidation state of carbon which occurs during this reaction. [1]

(iii) Cyanogen can be converted to ethanedioic acid by heating with aqueous acid. State the type of reaction for this conversion. [1]

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To determine the solubility product, $K_{sp,}$ of calcium ethanedioate, CaC_2O_4, at 20 °C, an excess of solid calcium ethanedioate was shaken with Solution **A** which contains 100 cm^3 of 1.0×10^{-4} mol dm^{-3} sodium ethanedioate.

The resulting mixture was allowed to equilibrate at 20 °C in a water bath and then the mixture was filtered to obtain the filtrate, Solution **B**, which contains a saturated solution of calcium ethanedioate.

25.0 cm^3 of Solution **B** was titrated with 5.0×10^{-5} mol dm^{-3} of acidified potassium manganate(VII). 16.60 cm^3 of potassium manganate(VII) was required for complete reaction.

The reaction of ethanedioate ions and acidified potassium manganate(VII) ions is shown below.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(b) (i) The reaction between ethanedioate ions and acidified potassium manganate(VII) ions has a high activation energy, hence solution **B** was heated to 60 °C before titration.

Explain why the reaction has a high activation energy. [1]

(ii) Calculate the amount of ethanedioate ions in 25.0 cm^3 of Solution **B**. [2]

(iii) Calculate the amount of ethanedioate ions in 25.0 cm^3 of Solution **A.** [1]

(iv) Calculate the amount of ethanedioate ions which was precipitated out as calcium ethanedioate. [1]

(v) Write an expression for the solubility product, K_{sp}, of calcium ethanedioate and calculate its value at 20 °C, stating the units clearly in your answer. [3]

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(c) When a precipitate of calcium ethanedioate is formed, $\Delta G^{\ominus}_{ppt,}$ in J mol^{-1}, is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = RT \ln K_{sp}$$

(i) Given that the K_{sp} value of calcium ethanedioate at 25 ^{o}C is 2.70 x 10^{-9} mol^{2} dm^{-6}, calculate the $\Delta G^{\ominus}_{ppt}$ of calcium ethanedioate. [1]

(ii) The standard entropy change of the precipitation of calcium ethanedioate, $\Delta S^{\ominus}_{ppt}$, is +93.2 J mol^{-1} K^{-1}.

Calculate the standard enthalpy change of precipitation of calcium ethanedioate, $\Delta H^{\ominus}_{ppt}$. [1]

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(d) The precipitation of calcium ethanedioate is one of the reasons for the formation of kidney stones.

Given that the stomach has a pH of about 2.0 while the kidney has a pH of about 6.5, explain why stones are not formed in the stomach but stones can be formed in the kidney. [2]

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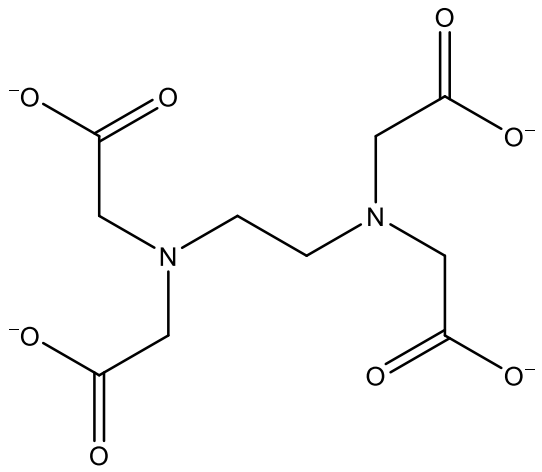
(e) Ethylenediaminetetraacetate, also known as EDTA has the structure shown below.



Suggest a reason why EDTA can be used as a treatment for kidney stones. [2]

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(f) Calcium ethanedioate decomposes at a temperature of 400 ^{o}C according to the equation shown below.

$$CaC_2O_4(s) \rightarrow CaO(s) + CO_2(g) + CO(g)$$

Explain why magnesium ethanedioate decomposes at a lower temperature than calcium ethanedioate. [2]

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5 (a) The equilibrium constant, K_p, of the following reaction is 1.64 at a certain temperature.

equation 1 $\quad I_2(s) + Br_2(g) \rightleftharpoons 2IBr(g) \qquad \Delta H < 0$

In a study, some bromine gas was introduced into a vessel with excess solid iodine at the same temperature and the reaction was allowed to take place until equilibrium was reached. The partial pressure of IBr(g) at equilibrium was found to be 0.80 atm. Assume that all the bromine is in the gaseous state and that the vapour pressure of iodine is negligible.

(i) State the K_p expression for equation 1.

Hence, calculate the partial pressure of Br_2 at equilibrium. [2]

(ii) Hence calculate the initial pressure of Br_2 in the container. [1]

(iii) Sketch a graph of rate against time, showing how the rates of the forward and reverse reactions change with time, from the point of mixing to the point after equilibrium is established. Label your graphs clearly. [2]

(iv) State and explain the effect on the rate of production and yield of IBr when temperature is decreased. [3]

(v) State and explain the effect on the equilibrium partial pressure of Br_2 when the pressure of the system is halved at constant temperature. [2]

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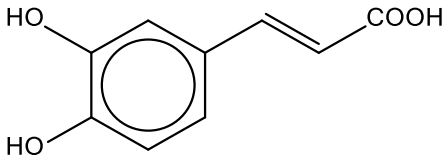
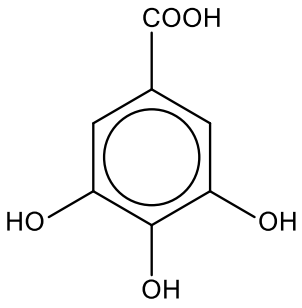
(b) Caffeic acid and gallic acid are organic compounds that can be found in coffee and tea leaves respectively.



caffeic acid



gallic acid

(i) Describe a chemical test to distinguish between the above two compounds and state the expected observations. [2]

(ii) Draw the structure of the major product that is formed when caffeic acid reacts with HBr. [1]

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(c) Buffer solutions are very important in many biological reactions as enzymes need a specific pH range to function properly. One of the most important buffer systems is carbonic acid, H_2CO_3, and bicarbonate, HCO_3^-, buffer system in blood.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

The above equilibrium has a K_a value of 7.90×10^{-7} mol dm^{-3} and is responsible for buffering the pH of the blood at 7.4.

(i) A blood buffer can be simulated by mixing 0.500 mol dm^{-3} H_2CO_3 and 2.00 mol dm^{-3} of $NaHCO_3$.

Show that the volumes of H_2CO_3 and $NaHCO_3$ required to make 200 cm^3 of this buffer solution with pH 7.4 are 34 cm^3 and 166 cm^3 respectively [3]

(ii) With the aid of an equation, explain how the buffer solution prepared in **c(i)** helps to maintain the pH at around 7.4 when a small amount of sodium hydroxide is added. [2]

(iii) Hence calculate the resultant pH of the above buffer solution when 0.003 mol of solid sodium hydroxide is added. [2]

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Additional answer space

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