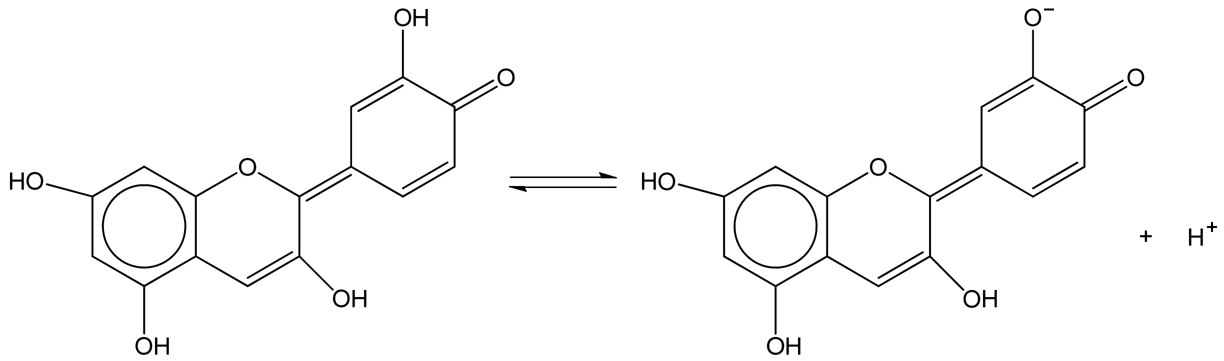
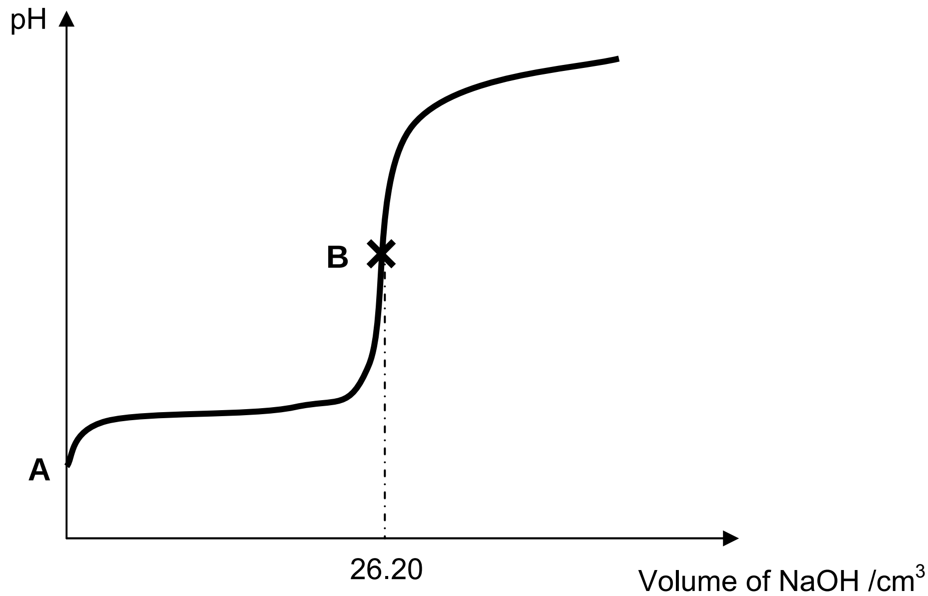
1 Use of the *Data Booklet* is relevant to this question.

Cyanidin is a natural pH indicator that can be found in many red berries, including grapes, blackberry and cherry. Aqueous solutions of cyanidin change colour with pH, appearing red at pH < 3, violet at pH 7-8, and blue at pH > 11. In addition, cyanidins are antioxidants that can scavenge free radicals and counteract ageing caused by oxidative damage in our body tissues and cells.



Cyanidin

Cyanidin (CyH) is a *weak monoprotic acid*. In one experiment, 25.0 cm^3 of cyanidin was titrated against 0.10 mol dm^{-3} of dilute NaOH at 25°C. The following titration curve was obtained using a data logger.



(a)(i) Explain what is meant by a *weak monoprotic acid*, with reference to CyH.

(ii) Calculate the molar concentration of the cyanidin solution.

(iii) Given that the solution of cyanidin is only 0.8% dissociated into ions, calculate the value of K_a for cyanidin, stating clearly its units.

(iv) Explain, with the aid of an appropriate equation, why the pH at end-point **B** is greater than 7.

(v) Calculate the pH value at end-point **B**. Hence, state the colour change observed at the end-point.

[10]

(b) An aqueous solution of cyanidin CyH and Cy^- can act as a buffer.

(i) Copy the titration curve onto your answer script and label
I – the buffer region
II – the point corresponding to maximum buffer capacity by indicating the pH and volume of NaOH used.

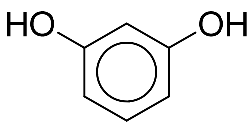
(ii) Explain, with the help of equations, how an aqueous mixture of CyH and Cy^- can control pH when relatively small amounts of acid or base are added to the solution.

(iii) In a sample of cherry juice at 25°C, the concentration ratio of Cy^- to CyH was found to be 3 to 1. Using the K_a value determined above, calculate the pH value of the cherry juice.

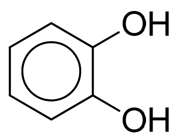
(iv) Sam tried to dilute the same cherry juice sample by adding 100 cm^3 of deionized water at 25°C. Predict the pH of the resulting sample.

[6]

(c) Cyanidin can be synthesized via a number of steps from either of the two molecules shown below:



Molecule P



Molecule Q

(i) Which molecule **P** or **Q** will have a higher boiling point? Explain your answer.

(ii) Draw the structures of all the possible organic products when **P** and **Q** react separately with chlorine in trichloromethane.

[4]

[Total: 20]

2 This question is about elements and their compounds in Period 3, Group IV and Group VII.

(a) The elements in Period 3 range from metals on the left of the Periodic Table to non-metals on the right. By describing one **physical** property of the element and one **chemical** property of its chloride, explain why phosphorus can be regarded as a non-metal. Write equation(s) where relevant.

[2]

(b) **(i)** The element aluminium and its compounds have some properties characteristic of metals, and some of non-metals. Aluminium hydroxide, for example, is known to be *amphoteric*. Explain the meaning of the word in italics.

Aluminium sulfate and calcium oxide are sometimes added to water supplies to co-precipitate suspended solids and bacteria. A small amount of aluminium-containing ions remains in solution and its presence in drinking water may contribute to the mental illness known as Alzheimer's disease.

(ii) Write a balanced equation for the reaction that occurs when aluminium sulfate and calcium oxide are added to water, given that aluminium hydroxide is one of the products formed.

(iii) Explain why adding too much calcium oxide would increase the probability of contracting Alzheimer's disease. Write equations for all reactions that occur.

[4]

(c) Explain each of the following as fully as you can. Justify your answers with relevant data from the *Data Booklet*. Write balanced equations, including state symbols, for any reaction that occurs.

(i) HCl can be prepared by adding concentrated sulfuric acid to solid sodium chloride. However the yield of HI is very low when concentrated sulfuric acid is added to solid sodium iodide.

(ii) When a hot glass rod is plunged into a gas jar of gaseous HI, some violet vapour is seen. On repeating the experiment with HBr, no change is observed.

[5]

(d) Tetraethyl-lead (IV), $Pb(C_2H_5)_4$, is an example of an organometallic compound. It can be used as an antiknock agent in petrol. At the high temperature in a car engine, the Pb-C bond in $Pb(C_2H_5)_4$, breaks to yield lead atoms and ethyl radicals.

(i) By using the VSEPR theory, predict the shape of the $Pb(C_2H_5)_4$ molecule.

(ii) Using only the data provided below, draw an *energy level* diagram to calculate ΔH_1, the enthalpy change of the following reaction:

$$2C(g) + 5H(g) \rightarrow CH_3CH_2\bullet(g)$$

Data:

Enthalpy change of atomization of C(s), ΔH_2	$+717$ kJ mol^{-1}
Enthalpy change of atomization of $H_2(g)$, ΔH_3	$+218$ kJ mol^{-1}
Enthalpy change of formation of $CH_3CH_3(g)$, ΔH_4	-85 kJ mol^{-1}
Bond dissociation energy of the first C-H bond in $CH_3CH_3(g)$, ΔH_5	$+435$ kJ mol^{-1}

(iii) Hence, with the aid of the data in **(ii)** and additional data given below, draw an energy cycle to calculate the Pb-C bond energy in $Pb(C_2H_5)_4$.

Data:

Enthalpy change of atomization of Pb(s), ΔH_6	$+195$ kJ mol^{-1}
Enthalpy change of formation of $Pb(C_2H_5)_4(g)$, ΔH_7	$+264$ kJ mol^{-1}

[7]

(e) The ethyl radical formed in **(d)** reacts readily with chlorine gas to give chloroethane. Another possible product is 1, 2-dichloroethane.

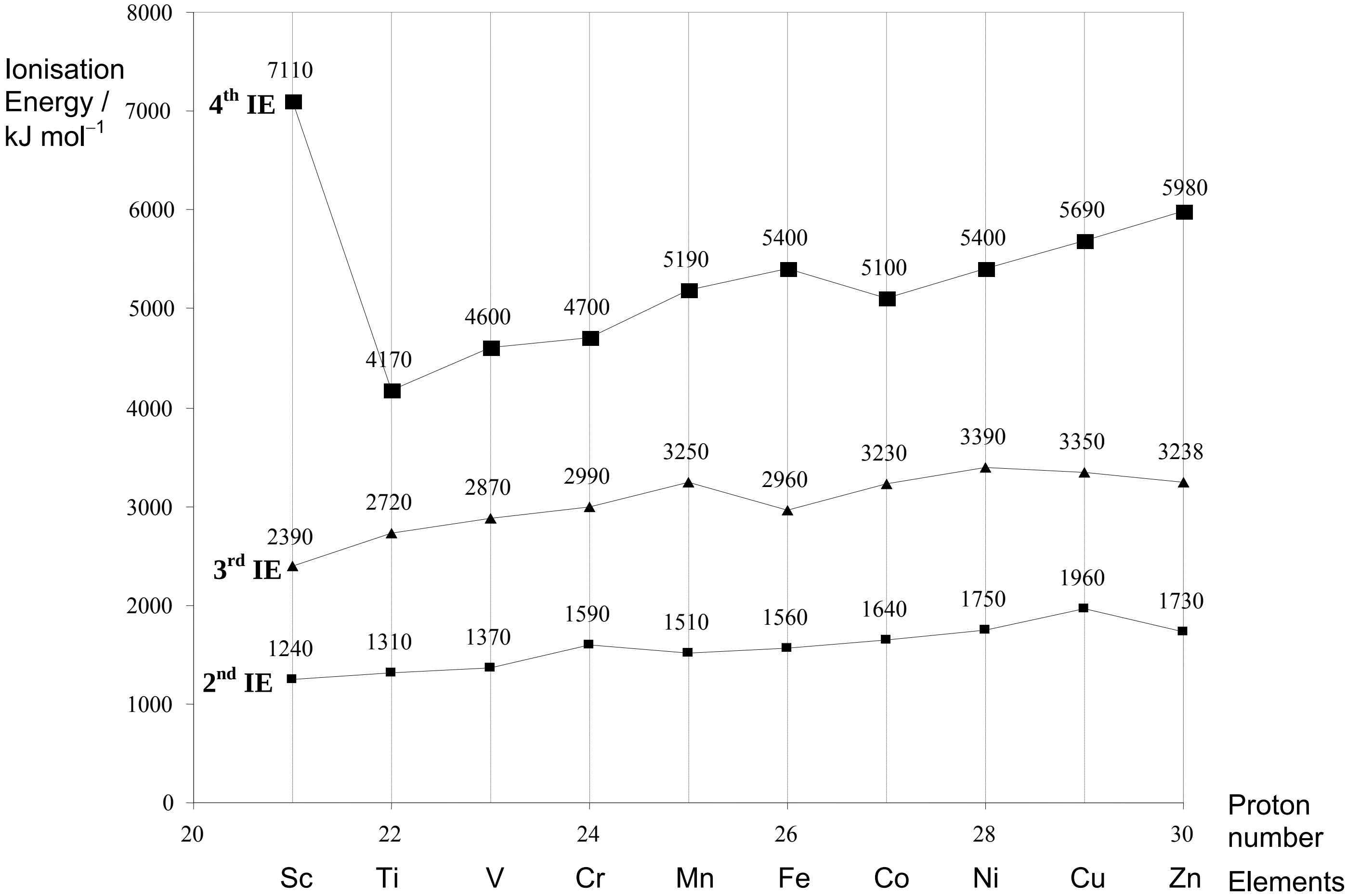
Outline the steps in the mechanism to show the formation of 1, 2-dichloroethane, starting from chlorine gas and ethyl radical.

[2]

[Total: 20]

3 This question is about transition elements and their compounds.

(a) The graph below shows the second to fourth ionisation energies for the first row d–block elements scandium to zinc.



(i) Explain what is meant by the term *transition element*.

(ii) Give an equation each to represent the second ionisation energy of chromium and the fourth ionisation energy of iron respectively.

(iii) Explain briefly why the second ionisation energy of chromium is higher than that of manganese.

(iv) Explain briefly why the fourth ionisation energy of cobalt is lower than that of iron.

[6]

(b) *The use of the Data Booklet is relevant to this question.*

In one experiment, when aqueous iron(III) sulphate is boiled with an excess of potassium cyanide, a red solution **A** is obtained. In another experiment, when aqueous iron(III) sulphate is added to aqueous potassium iodide, a brown solution **B** is obtained.

Solution **B** is found to catalyse the reaction between iodide and peroxodisulphate, $S_2O_8^{2-}$, whereas solution **A** does not affect the rate of this reaction.

When aqueous sodium thiosulfate is added to solution **B** followed by aqueous sodium hydroxide, the brown colour is discharged and a green precipitate is observed. On standing, the green precipitate turns red-brown.

Explain these observations as fully as you can, with the aid of equations and reference to relevant $E^{\ominus}$ values.

[9]

(c) Cobalt is one of the transition elements which is capable of complex ion formation.

(i) Ethylenediamine, $NH_2CH_2CH_2NH_2$, is a ligand that can form a complex with Co^{3+} ions in the mole ratio of 3:1. Deduce the formula of the cobalt-containing complex ion and state its shape.

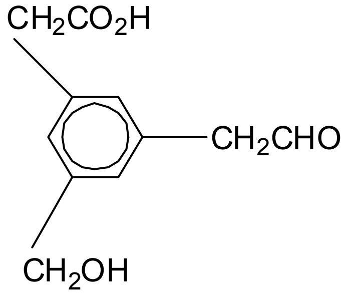
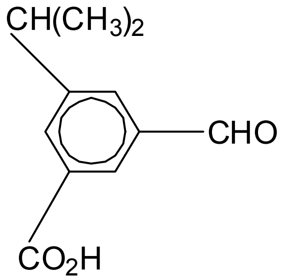
(ii) $[Co(NH_3)_6]^{3+}$ appears yellow-brown while $[CoF_6]^{3-}$ appears blue. Account for the difference in colour.

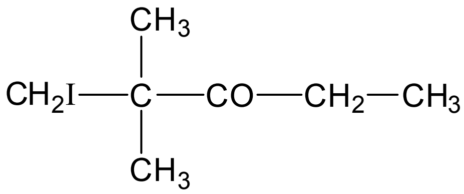
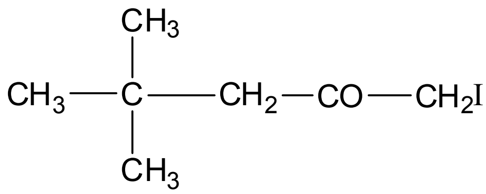
[5]

[Total: 20]

4 (a) Suggest methods by which the following pairs of compounds could be distinguished from each other by simple chemical tests.

For each case, **no more than two steps** should be used.

(i)  and 

(ii)  and 

(iii) $CH_3CH_2CH{=}CHCH_2C(CH_2CH_3){=}CH_2$ and $CH_3CH_2CH_2CH{=}CHCH{=}CHCH_2CH_3$

[7]

(b) **D** ($C_{10}H_8O_2$) is a neutral compound. On heating with aqueous NaOH followed by acidification, **D** yields only one organic product, **E** ($C_{10}H_{10}O_3$), which is soluble in aqueous Na_2CO_3. When **E** is treated with H_2 and Ni, **F** ($C_{10}H_{12}O_3$) is formed. Unlike **E**, **F** does not display cis-trans isomerism.

1 mol of **F** is found to decolorize exactly 2 mol of aqueous Br_2. Upon reaction with $LiAlH_4$ in dry ether, **F** forms the compound **G**. **G** is no longer soluble in Na_2CO_3. When **G** is passed over hot Al_2O_3, **H** is produced.

H reacts with gaseous HC*l* to give the major product, **I**, which exists as optical isomers. On warming **I** with aqueous $AgNO_3$, a white precipitate is formed together with an organic product which does not change the colour of acidified $K_2Cr_2O_7$ solution.

Deduce the structures of all the lettered compounds (**D** to **I**) and explain the reactions involved.

[13]

[Total: 20]

5 **(a)** Sucrose is the most common natural food sweetener, often known as table sugar. In acidic solutions, sucrose is readily hydrolysed to a 1:1 mixture of glucose and fructose. The reaction is catalysed by aqueous H^+ ions.

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+(aq)} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

A series of experiments was carried out at 25°C to investigate the kinetics of this reaction, using 0.79 mol dm^{-3} sucrose solution and 1.25 mol dm^{-3} hydrochloric acid.

The following data were obtained:

Expt	Volume of sucrose /cm^3	Volume of HC*l* /cm^3	Volume of water /cm^3	Initial rate of reaction /mol dm^{-3} min^{-1}
1	20	20	10	1.25×10^{-3}
2	20	30	0	1.88×10^{-3}
3	10	30	10	9.38×10^{-4}
4	40	20	10	**?**

(i) Using the data given above, determine the order of reaction with respect to sucrose and HC*l*.

Hence, determine the rate equation and calculate a value for the rate constant of the reaction, stating its units.

(ii) Using your answer in **(i)**, deduce the initial rate of reaction for Experiment **4**.

[6]

(b) In bacteria, sucrose is broken down into glucose and fructose by the enzyme, *invertase*. A few experiments were carried out to measure the initial rate of the enzyme-catalysed hydrolysis reaction for different concentrations of sucrose.

(i) Sketch a graph to show how the initial rate of this enzyme-catalysed hydrolysis reaction varies with the concentration of sucrose. Label your graph as **Graph 1**.

(ii) Explain the shape of **Graph 1**, making reference to the order of reaction with respect to sucrose.

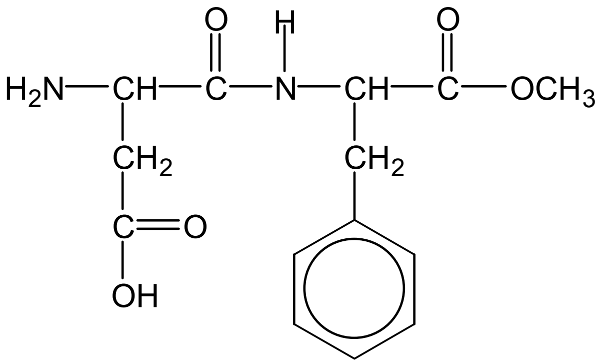
(iii) On the same axes in **(b)(i)**, sketch another graph to show how the initial rate will vary with the concentration of sucrose if the reaction mixtures were contaminated with *trace* amounts of Ag^+ ions. Label this graph as **Graph 2**.

(iv) What causes the shape of **Graph 2** to be different from **Graph 1**? Explain your answer.

[7]

(c) Aspartame, an artificial sweetener, is about 200 times sweeter than sucrose.

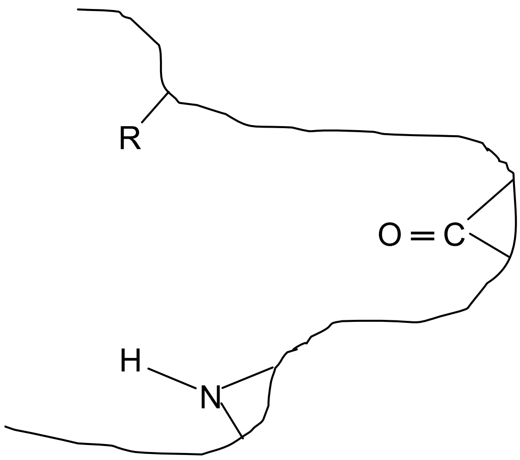
The structure of aspartame is as follows:



(i) Predict and explain whether aspartame is soluble in water, making reference to its structure and bonding.

(ii) Draw the structural formulae of all the organic products formed when aspartame is boiled with aqueous KOH, labelling with an asterisk any chiral carbon atom in each product.

(iii) Scientists believe that molecules which promote the sensation of sweetness fit into a receptor site in the taste buds on the tongue, which is essentially a protein molecule. A simplified diagram of the receptor site is shown below.



R = non-polar group

State **two** different types of interactions that can be formed between an aspartame molecule and the receptor protein. Illustrate your answer with labelled diagrams.

[7]

[Total: 20]