1 The decomposition of hydrogen iodide to form iodine and hydrogen is an equilibrium reaction.

$$2HI(g) \rightleftharpoons I_2(g) + H_2(g)$$

The equilibrium was investigated by taking sealed tubes containing the same mass of hydrogen iodide and heating them at 700 K for some time. At this temperature, the equilibrium takes about two days to be established.

The tubes were rapidly cooled to room temperature, which maintained the equilibrium concentrations, because at this temperature the reaction is extremely slow.

Each tube was opened under an aqueous solution of potassium iodide, which dissolved the hydrogen iodide and the iodine. The amount of iodine was found by titration and the composition of the equilibrium mixture calculated. From the number of moles of each substance at equilibrium, and the volume of the tubes, the equilibrium concentrations were calculated.

(a) (i) How would the appearance of the contents of a tube change as it was cooled to room temperature?

(2)

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(ii) How could you show that equilibrium had been established?

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(b) The equilibrium concentrations of one experiment are shown in the table below.

$[HI]$ /mol dm^{-3}	$[H_2]$ /mol dm^{-3}	$[I_2]$ /mol dm^{-3}
0.00353	0.00048	0.00048

*(i) The volume of the tube in this experiment was 30 cm^3. Calculate the initial mass of hydrogen iodide. Show your working.

(5)

(ii) Write an expression for the equilibrium constant, K_c, at 700 K.

(1)

(iii) Calculate the value for this equilibrium constant.

(1)

(iv) Does this equilibrium constant have units? Explain your answer.

(1)

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(c) The equation for the reaction at 700 K can also be written

$$HI(g) \rightleftharpoons \tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g)$$

(i) Write the equilibrium constant, K_c', for this reaction.

(1)

(ii) Using the same equilibrium concentrations as below, calculate the equilibrium constant, K_c'.

Deduce the relationship between this value and the value calculated in part (b)(iii).

(2)

[HI] /mol dm^{-3}	[H_2] /mol dm^{-3}	[I_2] /mol dm^{-3}
0.00353	0.00048	0.00048

(d) Consider the following equilibrium reaction.

$$2HI(g) \rightleftharpoons I_2(s) + H_2(g)$$

For this reaction $K_p = \frac{P_{H_2}}{P_{HI}^2}$

Use the expression for K_p to explain the effect of an increase in total pressure on the position of the equilibrium.

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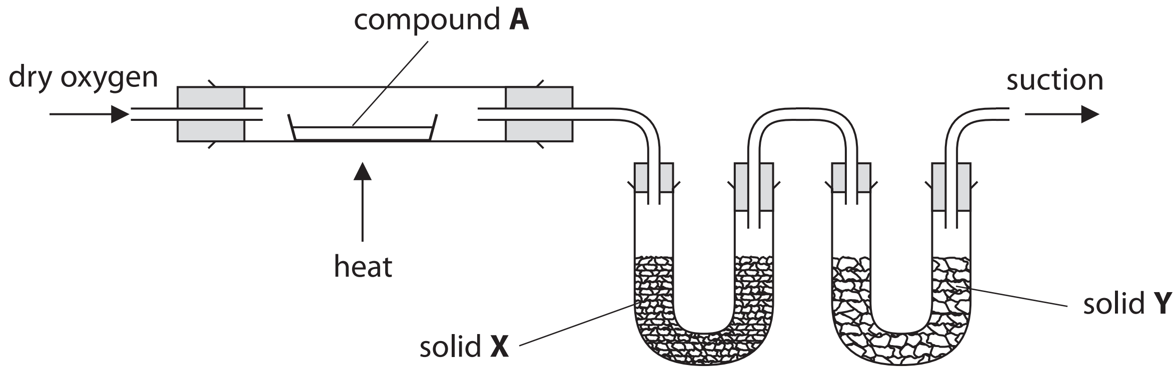
(Total for Question = marks)

2 A compound **A**, known to contain only the elements carbon, hydrogen and oxygen, was subjected to detailed analysis.

(a) A sample of **A** was burned completely in the apparatus shown below. Solid **X** absorbed the water formed in the combustion and solid **Y** absorbed the carbon dioxide.



(i) Explain why the oxygen must be dry.

(1)

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(ii) Suggest a suitable substance to use as solid **X**.

(1)

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(iii) Suggest a suitable substance to use as solid **Y**.

(1)

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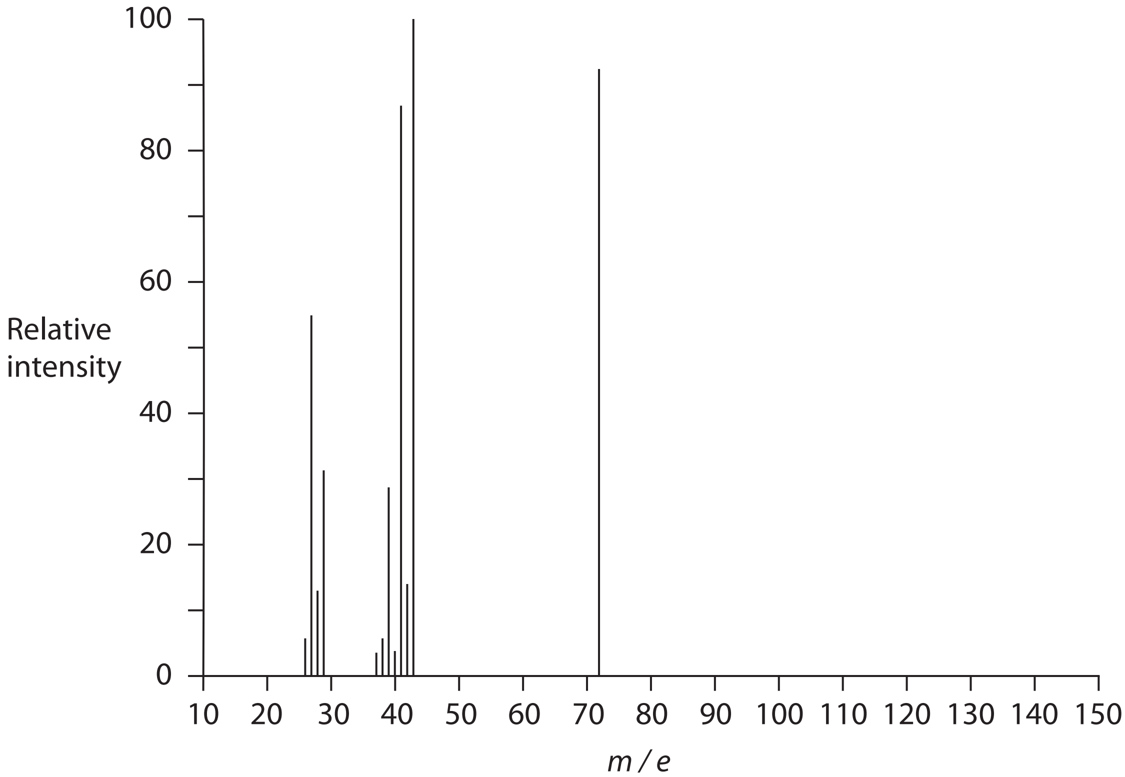
(iv) 3.60 g of compound **A** was burned completely. The mass of solid **X** increased by 3.60 g and the mass of solid **Y** increased by 8.80 g.

Use these data to calculate the empirical formula of compound **A**.
You **must** show your working.

(5)

(b) The mass spectrum of **A** is shown below.



(i) Identify the molecular ion peak and hence deduce the molecular formula of **A**.

(2)

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(ii) Given that **A** does **not** have a ring structure, suggest the **structural** formulae of three of the species that might cause the peak at *m/e* = 43 in the mass spectrum of **A**.

(3)

*(c) The low resolution nmr spectrum of **A** has three peaks in the ratio 6:1:1. Draw the structure of **A** and show how your structure is consistent with the nmr data.

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(Total for Question = marks)

3 (a) The following method was used to estimate the concentration of ethanol in an aqueous solution, **Q**, prepared by the fermentation of sucrose.

25 cm^3 of **Q** was measured using a pipette and transferred to a 250 cm^3 volumetric flask; the flask was made up to the mark with distilled water and mixed thoroughly, forming a diluted solution, **R**.

25 cm^3 samples of **R** were mixed with an equal volume of a 0.200 mol dm^{-3} potassium dichromate(VI) solution and excess dilute sulfuric acid.

The mixture was allowed to stand for several hours and then the amount of unreacted potassium dichromate(VI) was determined by titration against a 0.255 mol dm^{-3} iron(II) ammonium sulfate solution. The mean titre was 23.85 cm^3.

(i) Use the ionic half-equations below to write the full ionic equation for the reaction between potassium dichromate(VI) and iron(II) ammonium sulfate.

State symbols are not required.

(1)

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

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

(ii) Calculate the number of moles of potassium dichromate(VI) that remained **unreacted** after standing for several hours with solution **R**.

(2)

(iii) Calculate the number of moles of potassium dichromate(VI) that reacted with the ethanol while standing for several hours with solution **R**.

(2)

(iv) Write an ionic half-equation for the oxidation of ethanol to ethanoic acid.

Use your equation, and the half-equation for the reduction of dichromate(VI) ions, to show that 3 mol of ethanol are oxidized by 2 mol of potassium dichromate(VI).

(2)

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(v) Calculate the concentration of ethanol (in mol dm^{-3}) in solution **Q**.

(3)

*(b) The indicator used in this titration was barium diphenylamine sulfonate, which turns from deep purple to colourless at the end-point.

Identify the ion responsible for turning the indicator from deep purple to colourless at the end-point.

By considering the type of reaction involved when this ion reacts with barium diphenylamine sulfonate, suggest how barium diphenylamine sulfonate acts as an indicator in this titration. Note that complex formation does **not** occur. The detailed reactions of this particular indicator are **not** required.

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*(c) This method of determining ethanol concentration does not give very reliable results, although the titration is very accurate.

Suggest **one** reason why this might be the case, explaining how the measured concentration would differ from the actual concentration of the ethanol.

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(Total for Question = marks)

4 (a) When iron(II) sulfate is dissolved in water, the iron(II) ions are slowly oxidized to iron(III) ions by oxygen dissolved in the water.

(i) Write the two ionic half-equations for this redox reaction in **acid** conditions. State symbols are not required.

(1)

(ii) Hence write the overall ionic equation for the reaction. State symbols are not required.

(1)

(b) 6.90 g of iron(II) sulfate crystals ($FeSO_4{\cdot}7H_2O$) was dissolved in distilled water and the solution made up to 250 cm^3 in a volumetric flask. After 24 hours, 25.0 cm^3 portions of this solution were pipetted into a conical flask and titrated against acidified potassium manganate(VII) solution with a concentration of 0.0195 mol dm^{-3}. The mean titre was 24.90 cm^3.

(i) Write the ionic equation showing that 1 mol of manganate(VII) ions oxidizes 5 mol of iron(II) ions in acid conditions. State symbols are not required.

(1)

(ii) What is the colour of the solution in the conical flask at the end-point of the titration?

(1)

*(iii) Calculate the amount of Fe^{2+} ions in 250 cm^3 of the solution after it had been left to stand for 24 hours. Hence calculate the percentage of the iron(II) ions that had been oxidized between the preparation of the solution and the titration. The molar mass of $FeSO_4 \cdot 7H_2O$ is 277.9 g mol^{-1}.

(5)

(iv) Suggest, with an explanation, the appropriate number of significant figures to give for the answer to (b)(iii).

(1)

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(c) The most stable oxidation states in iron compounds are +2 and +3, but others do exist, for example in the ferrate(VI) ion, FeO_4^{2-}. The ionic half-equation for the conversion of ferrate(VI) to iron(III) is

$$FeO_4^{2-}(aq) + 8H^+(aq) + 3e^- \rightleftharpoons Fe^{3+}(aq) + 4H_2O(l) \qquad E^\ominus = +2.20\ V$$

(i) Ferrate(VI) decomposes in neutral or acid solution, but is stable in alkali. Suggest why this is so.

(1)

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(ii) Write the equation for the disproportionation of iron(III) into iron(II) and ferrate(VI) in aqueous solution. State symbols are not required.

(2)

(iii) Use standard electrode potential values to determine the thermodynamic feasibility of this disproportionation.

(2)

(Total for Question = marks)