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Baccalauréat International
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CHEMISTRY
HIGHER LEVEL
PAPER 2

Candidate session number

Monday 19 May 2014 (afternoon)

2 hours 15 minutes

Examination code

2 2 1 4 – 6 1 0 8

INSTRUCTIONS TO CANDIDATES

- Write your session number in the boxes above.
- Do not open this examination paper until instructed to do so.
- Section A: answer all questions.
- Section B: answer two questions.
- Write your answers in the boxes provided.
- A calculator is required for this paper.
- A clean copy of the ***Chemistry*** *Data Booklet* is required for this paper.
- The maximum mark for this examination paper is *[90 marks]*.

32 pages

SECTION A

*Answer **all** questions. Write your answers in the boxes provided.*

1. (a) Two chemistry students wished to determine the enthalpy of hydration of anhydrous magnesium sulfate. They measured the initial and the highest temperature reached when anhydrous magnesium sulfate, $MgSO_4(s)$, was dissolved in water. They presented their results in the table below.

mass of anhydrous magnesium sulfate / g	3.01
volume of water / cm^3	50.0
initial temperature / °C	17.0
highest temperature / °C	26.7

(i) Calculate the amount, in mol, of anhydrous magnesium sulfate. *[1]*

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(ii) Calculate the enthalpy change, ΔH_1, for anhydrous magnesium sulfate dissolving in water, in $kJ\,mol^{-1}$. State your answer to the correct number of significant figures. *[2]*

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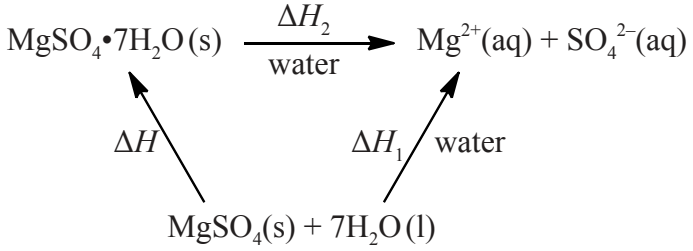
(This question continues on the following page)

(Question 1 continued)

(b) The students repeated the experiment using 6.16 g of solid hydrated magnesium sulfate, $MgSO_4 \cdot 7H_2O(s)$, and 50.0 cm^3 of water. They found the enthalpy change, ΔH_2, to be $+18\,kJ\,mol^{-1}$.

The enthalpy of hydration of solid anhydrous magnesium sulfate is difficult to determine experimentally, but can be determined using the diagram below.



(i) Determine the enthalpy change, ΔH, in $kJ\,mol^{-1}$, for the hydration of solid anhydrous magnesium sulfate, $MgSO_4$. *[1]*

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(ii) The literature value for the enthalpy of hydration of anhydrous magnesium sulfate is $-103\,kJ\,mol^{-1}$. Calculate the percentage difference between the literature value and the value determined from experimental results, giving your answer to **one** decimal place. (If you did not obtain an answer for the experimental value in (b)(i) then use the value of $-100\,kJ\,mol^{-1}$, but this is **not** the correct value.) *[1]*

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(This question continues on the following page)

(Question 1 continued)

(c) Another group of students experimentally determined an enthalpy of hydration of $-95\,kJ\,mol^{-1}$. Outline two reasons which may explain the variation between the experimental and literature values. *[2]*

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(d) Magnesium sulfate is one of the products formed when acid rain reacts with dolomitic limestone. This limestone is a mixture of magnesium carbonate and calcium carbonate.

(i) State the equation for the reaction of sulfuric acid with magnesium carbonate. *[1]*

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(ii) Deduce the Lewis (electron dot) structure of the carbonate ion, giving the shape and the oxygen-carbon-oxygen bond angle. *[3]*

Lewis (electron dot) structure:

Shape:

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Bond angle:

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(This question continues on the following page)

(Question 1 continued)

(iii) There are three possible Lewis structures that can be drawn for the carbonate ion, which lead to a resonance structure. Explain, with reference to the electrons, why all carbon-oxygen bonds have the same length. *[1]*

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(iv) Deduce the hybridization of the carbon atom in the carbonate ion. *[1]*

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2. Sodium thiosulfate solution, $Na_2S_2O_3(aq)$, and hydrochloric acid, $HCl(aq)$, react to produce solid sulfur as in the equation below.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$$

The following results to determine the initial rate were obtained:

Experiment	**$[S_2O_3^{2-}(aq)]$ / mol dm^{-3}**	**$[H^+(aq)]$ / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
1	0.200	2.00	0.036
2	0.200	1.00	0.036
3	0.100	1.00	0.018

(a) Deduce, with a reason, the order of reaction with respect to each reactant. *[2]*

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(b) State the rate expression for this reaction. *[1]*

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(c) Determine the value of the rate constant, k, and state its units. *[2]*

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(This question continues on the following page)

(Question 2 continued)

(d) State an equation for a possible rate-determining step for the reaction. *[1]*

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(e) Suggest how the activation energy, E_a, for this reaction may be determined. *[3]*

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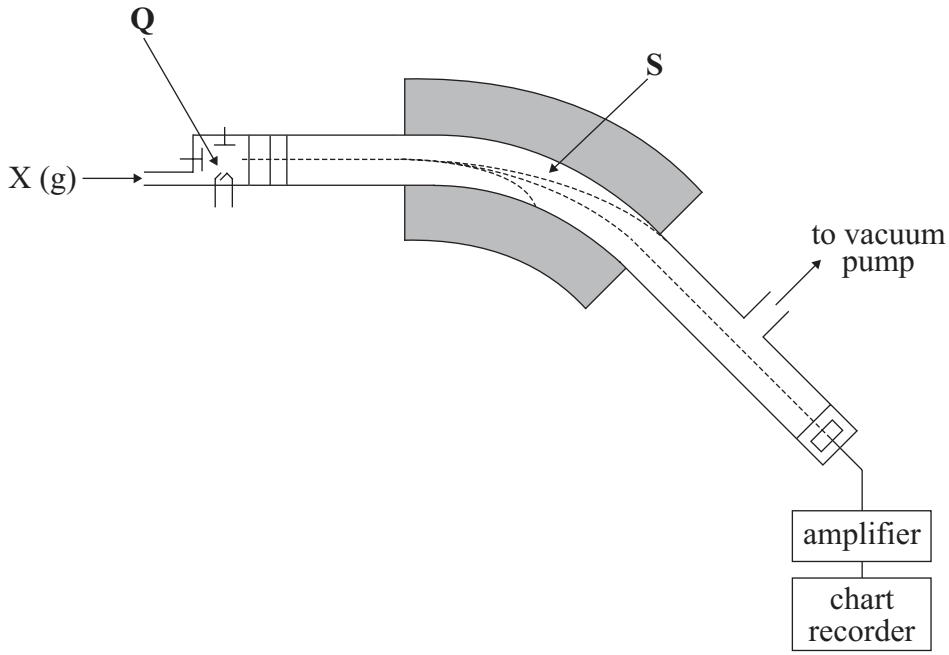
3. Magnesium has three stable isotopes, ^{24}Mg, ^{25}Mg and ^{26}Mg. The relative abundance of each isotope is 78.99%, 10.00% and 11.01%, respectively, and can be determined using a mass spectrometer.



(a) Describe the processes occurring at stage **Q** and stage **S**. *[4]*

Q:

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S:

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(b) Calculate, showing your working, the relative atomic mass, A_r, of magnesium, giving your answer to **two** decimal places. *[2]*

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4. Buta-1,3-diene can be hydrogenated to produce butane, according to the reaction below.

$$C_4H_6(g) + 2H_2(g) \rightarrow C_4H_{10}(g)$$

(a) State the conditions necessary for this reaction. *[2]*

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(b) Determine the standard enthalpy change of reaction, $\Delta H^{\ominus}$, in $kJ\,mol^{-1}$, at 298 K for the hydrogenation reaction, using Table 11 of the Data Booklet. *[1]*

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(c) Calculate the standard free energy change, $\Delta G^{\ominus}$, in $kJ\,mol^{-1}$, at 298 K for the hydrogenation reaction, using Table 11 of the Data Booklet. *[1]*

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(This question continues on the following page)

(Question 4 continued)

(d) (i) Determine the standard entropy change of the reaction, $\Delta S^{\ominus}$, at 298 K, in $kJ\,K^{-1}\,mol^{-1}$, using your answers from (b) and (c). *[2]*

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(ii) Explain why the standard entropy change for the hydrogenation of buta-1,3-diene has a negative sign. *[1]*

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(iii) Predict whether the hydrogenation reaction becomes more or less spontaneous as the temperature increases. *[1]*

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(iv) Determine the temperature, in K, at which the spontaneity changes. *[2]*

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(This question continues on the following page)

(Question 4 continued)

(v) Determine the standard entropy, $S^{\ominus}$, for hydrogen in $JK^{-1}mol^{-1}$, using Table 11 of the Data Booklet and your answer for (d)(i). *[2]*

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SECTION B

*Answer **two** questions. Write your answers in the boxes provided.*

5. (a) The oxides and chlorides of period 3 elements exhibit periodicity.

(i) State the changes in the acid-base nature of the oxides across period 3 (from Na_2O to Cl_2O_7), including equations for the reactions of Na_2O and SO_3 with water. *[3]*

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(ii) State whether or not molten aluminium chloride, Al_2Cl_6, and molten aluminium oxide, Al_2O_3, conduct electricity. Explain this behaviour in terms of the structure and bonding of the two compounds. *[3]*

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(iii) State the equation for the reaction of Cl_2 with water. *[1]*

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(This question continues on the following page)

(Question 5 continued)

(b) Chlorine gas, $Cl_2(g)$, is bubbled through separate solutions of aqueous bromine, $Br_2(aq)$, and potassium bromide, KBr(aq).

(i) Predict any changes that may be observed in each case. *[2]*

$Br_2(aq)$:

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KBr(aq):

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(ii) State the half-equations for the reactions that occur. *[2]*

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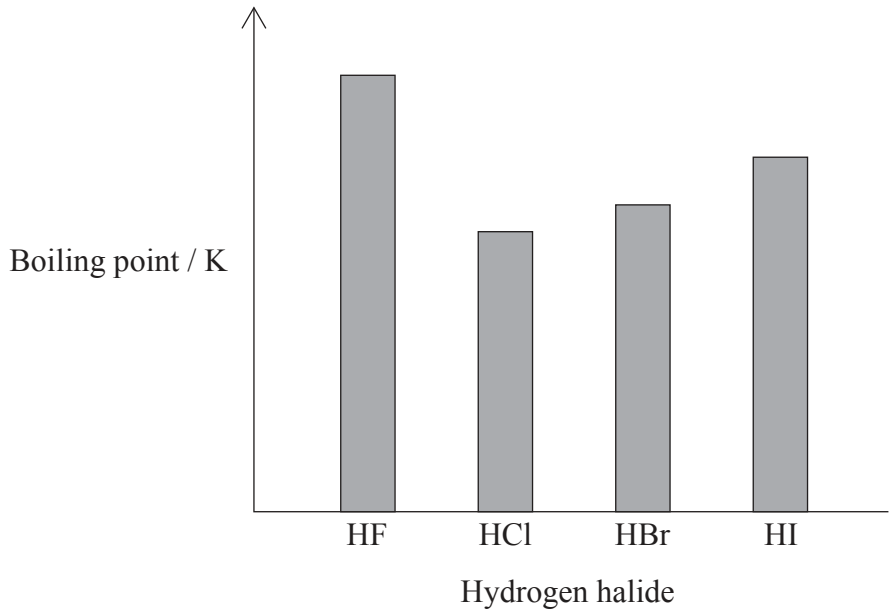
(Question 5 continued)

(c) The hydrogen halides do not show perfect periodicity. A bar chart of boiling points shows that the boiling point of hydrogen fluoride, HF, is much higher than periodic trends would indicate.



(i) Explain why the boiling point of HF is much higher than the boiling points of the other hydrogen halides. *[1]*

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(ii) Explain the trend in the boiling points of HCl, HBr and HI. *[2]*

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(This question continues on the following page)

(Question 5 continued)

(d) Transition metals form complex ions which are usually coloured.

(i) State the full electron configurations of Cr and Cr^{3+}. *[2]*

Cr:

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Cr^{3+}:

. . . . . .

(ii) Cr^{3+} ions and water molecules bond together to form the complex ion $[Cr(H_2O)_6]^{3+}$. Describe how the water acts and how it forms the bond, identifying the acid-base character of the reaction. *[3]*

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(iii) Explain why the $[Cr(H_2O)_6]^{3+}$ ion is coloured. *[3]*

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(This question continues on the following page)

(Question 5 continued)

(iv) Outline, including a relevant equation, whether the $[Cr(H_2O)_6]^{3+}$ ion is acidic, basic or neutral. *[1]*

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(e) Explain how the number of electrons in the outer main energy level of phosphorus, P, can be determined using the data of successive ionization energies. *[2]*

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6. Oxidation and reduction can be defined in terms of electron transfer or oxidation numbers.

(a) Alcohols with the molecular formula C_4H_9OH occur as four structural isomers. Three of the isomers can be oxidized with acidified potassium dichromate solution to form compounds with the molecular formula C_4H_8O.

(i) Deduce the half-equation for the oxidation of the alcohol C_4H_9OH. *[1]*

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(ii) Deduce the overall equation for the redox reaction. *[1]*

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(iii) Two of the isomers with the molecular formula C_4H_9OH can be oxidized further to form compounds with the molecular formula $C_4H_8O_2$. Deduce the structural formulas of these two isomers. *[2]*

(This question continues on the following page)

(Question 6 continued)

(iv) One isomer cannot be oxidized by acidified potassium dichromate solution. Deduce its structural formula, state its name and identify it as a primary, secondary or tertiary alcohol. *[3]*

Name: . . . . . .

Alcohol: . . . . . .

(v) All isomers of the alcohol C_4H_9OH undergo complete combustion. State an equation for the complete combustion of C_4H_9OH. *[2]*

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(b) A reactivity series can be experimentally determined by adding the metals W, X, Y and Z to solutions of these metal ions. The following reactions were observed:

$$W^{2+}(aq) + X(s) \rightarrow W(s) + X^{2+}(aq)$$
$$Y(s) + W^{2+}(aq) \rightarrow Y^{2+}(aq) + W(s)$$
$$Z^{2+}(aq) + W(s) \rightarrow Z(s) + W^{2+}(aq)$$
$$Y(s) + X^{2+}(aq) \rightarrow Y^{2+}(aq) + X(s)$$

(i) Deduce the order of reactivity of these four metals, from the least to the most reactive. *[1]*

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(This question continues on the following page)

(Question 6 continued)

(ii) A voltaic cell is made by connecting a half-cell of X in $XCl_2(aq)$ to a half-cell of Z in $ZCl_2(aq)$. Deduce the overall equation for the reaction taking place when the cell is operating. *[1]*

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(iii) The standard electrode potential for $Z^{2+}(aq) + 2e^- \rightleftharpoons Z(s)$ is +0.20 V. State which species is oxidized when this half-cell is connected to a standard hydrogen electrode. *[1]*

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(iv) Describe the standard hydrogen electrode including a fully labelled diagram. *[3]*

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(This question continues on the following page)

(Question 6 continued)

(c) A student carries out the electrolysis of aqueous potassium iodide, KI, using inert electrodes.

(i) State the half-equation for the reaction that occurs at each electrode. *[2]*

Positive electrode (anode):

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Negative electrode (cathode):

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(ii) Suggest, giving a reason, what would happen if the electrodes were changed to aluminium. *[2]*

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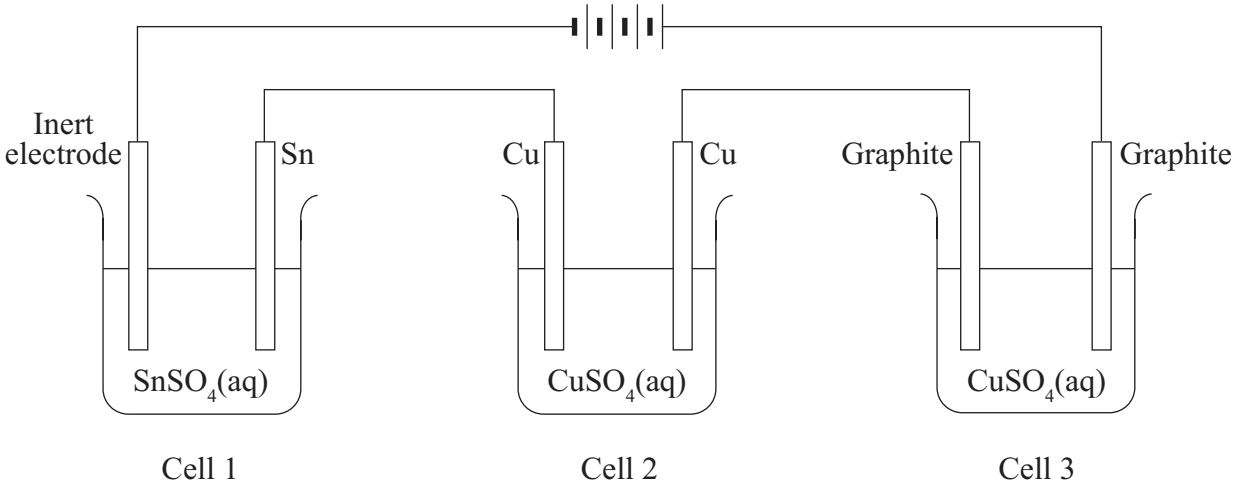
(Question 6 continued)

(d) Three electrolytic cells were set up in series (one cell after the other), as shown below. All of the solutions had a concentration of $1.00\,mol\,dm^{-3}$.



(i) Determine the mass of copper produced at one of the electrodes in cell 2 if the tin electrode in cell 1 decreased in mass by 0.034 g. *[2]*

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(ii) Compare the colour and the pH of the solutions in cells 2 and 3 after the current has been flowing for one hour. *[2]*

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(This question continues on the following page)

(Question 6 continued)

(iii) Explain your answer given for part (d) (ii). *[2]*

Colour:

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pH:

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7. (a) An equilibrium exists between nitrosyl chloride, NOCl, nitrogen oxide, NO, and chlorine, Cl_2.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

(i) Deduce the equilibrium constant expression for this reaction. *[1]*

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(ii) Explain the effect on the position of equilibrium and the value of K_c when pressure is decreased and temperature is kept constant. *[2]*

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(iii) 2.00 mol of NOCl was placed in a 1.00 dm^3 container and allowed to reach equilibrium at 298 K. At equilibrium, 0.200 mol of NO was present. Determine the equilibrium concentrations of NOCl and Cl_2, and hence calculate the value of K_c at this temperature. *[3]*

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(Question 7 continued)

(iv) The value of K_c is 1.60×10^{-5} at 318 K. State and explain whether the forward reaction is exothermic or endothermic. *[1]*

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(b) 20.0 cm^3 of hexane, C_6H_{14}, and 20.0 cm^3 of pentan-1-ol, $C_5H_{11}OH$, were placed separately into two closed containers at 298 K and allowed to reach equilibrium.

(i) Compare the two liquids in terms of their boiling points, enthalpies of vaporization and vapour pressures. *[2]*

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(ii) Explain your answer given for part (b)(i). *[2]*

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(This question continues on the following page)

(Question 7 continued)

(c) Ammonia is a weak base.

(i) Calculate the pH of a 1.50 mol dm^{-3} solution of ammonia at 298 K to **two** decimal places, using Table 15 of the Data Booklet. *[2]*

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(ii) A buffer solution is made using 25.0 cm^3 of 0.500 mol dm^{-3} hydrochloric acid, HCl(aq), and 20.0 cm^3 of 1.50 mol dm^{-3} ammonia solution, NH_3(aq).

Describe the meaning of the term *buffer solution*. *[2]*

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(This question continues on the following page)

(Question 7 continued)

(iii) Determine the pH of the buffer solution at 298 K. *[4]*

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(iv) A 1.50 mol dm^{-3} solution of ammonia is added to 25.0 cm^3 of a 0.500 mol dm^{-3} hydrochloric acid solution in a titration experiment.

Calculate the total volume of the solution at the equivalence point. *[1]*

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(This question continues on the following page)

(Question 7 continued)

(v) Calculate the pH of the solution at the equivalence point, using Table 15 of the Data Booklet. *[4]*

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(vi) Identify a suitable indicator for this titration, using Table 16 of the Data Booklet. *[1]*

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8. (a) Outline how electrical conductivity can be used to distinguish between a $0.200\,mol\,dm^{-3}$ solution of ethanoic acid, CH_3COOH, and a $0.200\,mol\,dm^{-3}$ solution of hydrochloric acid, HCl. *[1]*

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(b) $25.0\,cm^3$ of $0.200\,mol\,dm^{-3}$ ethanoic acid was added to $30.0\,cm^3$ of a $0.150\,mol\,dm^{-3}$ sodium hydrogencarbonate solution, $NaHCO_3(aq)$.

(i) State an equation for the reaction of ethanoic acid with a solution of sodium hydrogencarbonate. *[1]*

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(ii) Determine which is the limiting reagent. Show your working. *[2]*

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(This question continues on the following page)

(Question 8 continued)

(iii) Calculate the mass, in g, of carbon dioxide gas produced. *[2]*

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(c) The molar mass of a volatile organic liquid, **X**, can be determined experimentally by allowing it to vaporize completely at a controlled temperature and pressure. 0.348 g of **X** was injected into a gas syringe maintained at a temperature of 90 °C and a pressure of 1.01×10^5 Pa. Once it had reached equilibrium, the gas volume was measured as 95.0 cm^3.

(i) Determine the amount, in mol, of **X** in the gas syringe. *[3]*

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(ii) Calculate the molar mass of **X**. *[1]*

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(This question continues on the following page)

(Question 8 continued)

(d) Bromoethane, CH_3CH_2Br, undergoes a substitution reaction to form ethylamine, $CH_3CH_2NH_2$.

(i) Deduce the mechanism for the reaction using equations and curly arrows to represent the movement of electron pairs. *[3]*

(ii) Ethylamine can be produced in two stages starting with iodomethane. Deduce the reaction pathway and state any necessary conditions. *[3]*

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(iii) Bromoethane can also be converted to ethene. Identify the type of reaction and state which reagent(s) and conditions are necessary. *[3]*

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(This question continues on the following page)

(Question 8 continued)

(e) Many organic compounds exist as stereoisomers.

(i) Outline the meaning of the term *stereoisomers*. *[1]*

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(ii) Draw the structures of the two stereoisomers of dichloroethene, $C_2H_2Cl_2$. *[1]*

(iii) Explain why this type of stereoisomerism exists in $C_2H_2Cl_2$. *[1]*

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(This question continues on the following page)

(Question 8 continued)

(iv) Draw the structures of the two stereoisomers of 1-chloro-1-fluoroethane, C_2H_4FCl, showing the relationship between them. *[1]*

(v) Outline how the two isomers of C_2H_4FCl could be distinguished from each other. *[2]*

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