Diploma Programme
Programme du diplôme
Programa del Diploma

# Chemistry
# Higher level
# Paper 2

Friday 13 November 2015 (afternoon)

Candidate session number

| | | | | | | | | | |
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| | | | | | | | | | |

2 hours 15 minutes

**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]**.

8815 – 6102

28 pages

## Section A

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

**1.** A student used the technique of titration to determine the concentration of ascorbic acid ($C_6H_8O_6$) in a sample of orange juice. Excess potassium iodide, $KI(aq)$, was added to acidified orange juice. The resulting solution was titrated with potassium iodate, $KIO_3(aq)$, in the presence of starch as an indicator. The end-point of the titration was shown by a blue-black colour.

Step 1 $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$

Iodine is only slightly soluble in water; but in the presence of excess iodide ions, $I^-(aq)$, it forms the soluble tri-iodide ion, $I_3^-(aq)$.

Step 2 $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$

Ascorbic acid reacts with tri-iodide ions as follows.

Step 3 $C_6H_8O_6(aq) + I_3^-(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 3I^-(aq)$

(a) (i) Deduce the changes in oxidation number of iodine in step 1. [2]

$IO_3^-$ to $I_2$:

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$I^-$ to $I_2$:

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(ii) Identify the oxidizing and reducing agents in step 1. [1]

Oxidizing agent:

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Reducing agent:

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**(Question 1 continued)**

(b) Calculate the mass, in g, of potassium iodate, $KIO_3(s)$, which was required to prepare $0.250\,dm^3$ of a $2.00 \times 10^{-3}\,mol\,dm^{-3}$ solution. [2]

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(c) The concentration of $KIO_3$ used in the titration was $2.00 \times 10^{-3}\,mol\,dm^{-3}$.
The titration produced the following results.

| | **Titration 1** | **Titration 2** | **Titration 3** |
|---|---|---|---|
| Final volume of $KIO_3$ ($\pm$ 0.05 $cm^3$) | 7.10 | 14.40 | 21.60 |
| Initial volume of $KIO_3$ ($\pm$ 0.05 $cm^3$) | 0.00 | 7.10 | 14.40 |
| Volume added of $KIO_3$ ($\pm$ 0.10 $cm^3$) | 7.10 | 7.30 | 7.20 |
| Mean volume added of $KIO_3$ ($\pm$ 0.10 $cm^3$) | 7.20 | | |

(i) Calculate the percentage uncertainty associated with the mean volume of $KIO_3(aq)$. [1]

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(ii) The colour of orange juice interfered with the blue-black colour at the equivalence point. State the name of this type of error and suggest how this can be minimized. [2]

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**(This question continues on the following page)**

**(Question 1 continued)**

(iii) Determine the amount, in mol, of $KIO_3(aq)$, in the mean volume. [1]

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(d) Determine the amount, in mol, of ascorbic acid, $C_6H_8O_6(aq)$, in the sample of acidified orange juice. [2]

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(e) Calculate the mass, in g, of ascorbic acid, $C_6H_8O_6(aq)$, present in the sample of acidified orange juice. [1]

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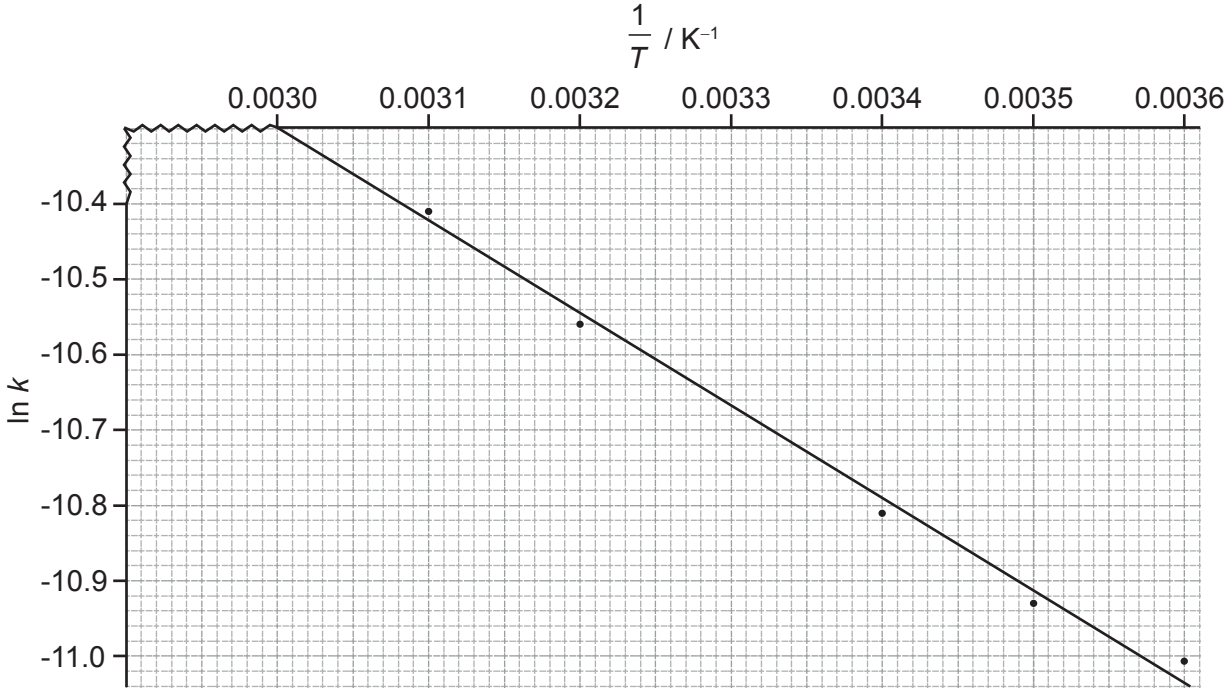
**(This question continues on the following page)**

**(Question 1 continued)**

(f) The student found by further experimentation that oxidation of ascorbic acid follows first-order kinetics. The graph of ln $k$ against $\frac{1}{T}$ is shown below.
Determine the activation energy to **three** significant figures, including units. [3]

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**2.** (a) State the **full** electron configurations of copper, Cu, and copper(II) ion, $Cu^{2+}$. [2]

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(b) $Cu^{2+}(aq)$ reacts with ammonia to form the complex ion $[Cu(NH_3)_4]^{2+}$.
Explain this reaction in terms of acid-base theory, and outline the bonding in the complex formed between $Cu^{2+}$ and $NH_3$. [3]

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(c) Explain why complexes of $Zn^{2+}(aq)$ are colourless whereas complexes of $Cu^{2+}(aq)$ are coloured. [4]

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**3.** Propane, $C_3H_8(g)$, undergoes complete combustion to form carbon dioxide, $CO_2(g)$, and water, $H_2O(g)$.

(a) State an equation for the complete combustion of propane, $C_3H_8(g)$. [1]

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(b) Calculate the standard enthalpy change for the reaction in part (a) using bond enthalpy values given in table 10 of the data booklet. [3]

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**4.** (a) The monomers hexanedioic acid and 1,6-diaminohexane react together to form a synthetic polymer.

Deduce the structural formula of each monomer. [2]

(b) State the type of polymerization reaction that occurs between these two monomers and identify the structural feature needed in the monomers. [2]

Type:

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Structural feature:

. . . . . .

. . . . . .

(c) Draw the structure of the linkage formed in this polymer, and identify the other product of this polymerization reaction. [2]

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**5.** (a) (i) Define the term electronegativity. [1]

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(ii) Suggest why the noble gases are generally not assigned electronegativity values. [1]

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(b) Explain why the melting points of the group 1 metals (Li $\rightarrow$ Cs) decrease down the group whereas the melting points of the group 7 elements (F $\rightarrow$ I) increase down the group. [3]

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(c) Outline **one** reason why the sodium ion, $Na^+$, has a smaller radius than the sodium atom. [1]

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## Section B

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

**6.** Iron (III) oxide is the main source of iron but the decomposition of $Fe_2O_3(s)$ into its elements is extremely difficult due to a large positive value of $\Delta G^{\ominus}$.

(a) Consider the following reactions:

$$Fe_2O_3(s) \rightarrow 2Fe(s) + \frac{3}{2}O_2(g) \qquad \Delta G^{\ominus} = +742\,kJ\,mol^{-1}$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta G^{\ominus} = -257\,kJ\,mol^{-1}$$

Suggest, with a reason, whether it is possible to produce iron by reacting $Fe_2O_3$ with CO. [2]

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(b) The thermite reaction is one of the most exothermic reactions.

$$Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(l) + Al_2O_3(s) \qquad \Delta H^{\ominus} = -825.2\,kJ$$

| Species | $S^{\ominus}$ / J K$^{-1}$ mol$^{-1}$ | $\Delta G_f^{\ominus}$ / kJ mol$^{-1}$ |
|---|---|---|
| Al (s) | +28.3 | 0 |
| $Al_2O_3$ (s) | +50.9 | −1582 |
| Fe (l) | +34.8 | +10.0 |
| $Fe_2O_3$ (s) | +87.5 | −742 |

(i) Calculate the standard free energy change, $\Delta G^{\ominus}$, in kJ mol$^{-1}$, by using values of the standard free energy change of formation, $\Delta G_f^{\ominus}$, from the table above. [2]

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**(Question 6 continued)**

(ii) Calculate the standard entropy change, $\Delta S^{\ominus}$, in $JK^{-1}mol^{-1}$, by using values of standard entropy, $S^{\ominus}$, from the table. [1]

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(iii) Calculate the standard free energy change, $\Delta G^{\ominus}$, for the reaction using $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values at 25°C. [2]

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(c) (i) Deduce the type of hybridization shown by the nitrogen atoms in $NF_4^+$, $N_2H_2$ and $N_2H_4$. [3]

| | $NF_4^+$ | $N_2H_2$ | $N_2H_4$ |
|---|---|---|---|
| **Hybridization** | . . . . . | . . . . . | . . . . . |

(ii) Describe how sigma (σ) and pi (π) bonds form. [2]

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**(Question 6 continued)**

(iii) Draw the Lewis (electron dot) structures of $SF_4$ and $SF_6$. Use the valence shell electron pair repulsion (VSEPR) theory to predict the name of the shape of each molecule. [4]

(d) (i) List the following compounds in order of **increasing** boiling point: $CH_3CHO$, $CH_3CH_2CH_3$, $CH_3COOH$, $CH_3CH_2OH$. [2]

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(ii) Explain the order of boiling points in the compounds listed in part (d) (i), in terms of intermolecular forces. [4]

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**(Question 6 continued)**

(e) In the operation of a mass spectrometer, the first stage is vaporization and the last is detection. State the names of the other three stages and outline what happens in each one. [3]

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**7.** (a) The following reaction is used in industry to obtain hydrogen from natural gas by partial oxidation with steam.

$$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g) \qquad \Delta H^{\ominus} = +206\,kJ$$

(i) Describe the effect, if any, of each of the following changes on the equilibrium amount of hydrogen, giving a reason in each case. [4]

Increasing the pressure, at constant temperature:

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Increasing the temperature, at constant pressure:

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(ii) Discuss the effects of adding a solid catalyst to the mixture of methane and steam, at constant pressure and temperature. [3]

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(iii) Deduce the equilibrium constant expression, $K_c$, for the reaction. [1]

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**(Question 7 continued)**

(iv) Identify which of the changes in part (a) (i) will affect the value of $K_c$ and whether the value will increase or decrease. [1]

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(b) The equilibrium constant, $K_c$, for the reaction

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$

was found to be 10.0 at 420°C.

1.00 mol of CO (g) and 1.00 mol of $H_2O$ (g) are mixed in a 1.00 $dm^3$ container at 420°C. Calculate the equilibrium concentration of each component in the mixture, showing your working. [3]

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**(Question 7 continued)**

(c) The oxidation of nitrogen monoxide takes place as follows:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The following experimental data was obtained at 101.3 kPa and 298 K.

| Experiment | Initial [NO] / mol dm$^{-3}$ | Initial [$O_2$] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | $2.30 \times 10^{-2}$ | $1.15 \times 10^{-2}$ | $1.05 \times 10^{-3}$ |
| 2 | $2.30 \times 10^{-2}$ | $2.30 \times 10^{-2}$ | $2.09 \times 10^{-3}$ |
| 3 | $4.60 \times 10^{-2}$ | $4.60 \times 10^{-2}$ | $1.68 \times 10^{-2}$ |

(i) Deduce the orders of reaction with respect to $O_2$ and NO. [2]

Order with respect to $O_2$:

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Order with respect to NO:

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(ii) State the rate expression for the reaction. [1]

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(iii) Calculate the value of the rate constant, *k*, and include its units. [2]

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**(Question 7 continued)**

(iv) Suggest a mechanism that is consistent with the rate expression, indicating the rate-determining step. [3]

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(d) Consider the following spontaneous reactions.

$$Fe(s) + Ni^{2+}(aq) \rightarrow Fe^{2+}(aq) + Ni(s)$$
$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$$
$$Ni(s) + Pb^{2+}(aq) \rightarrow Ni^{2+}(aq) + Pb(s)$$

(i) Deduce the order of **increasing** reactivity of the metals based on the reactions above. [2]

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(ii) Identify the strongest oxidizing agent in the reactions above. [1]

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**(Question 7 continued)**

(e) Deduce the half-equations for the formation of the major product at the positive electrode (anode) when the following aqueous solutions are electrolysed. [2]

Dilute sodium chloride:

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Concentrated sodium chloride:

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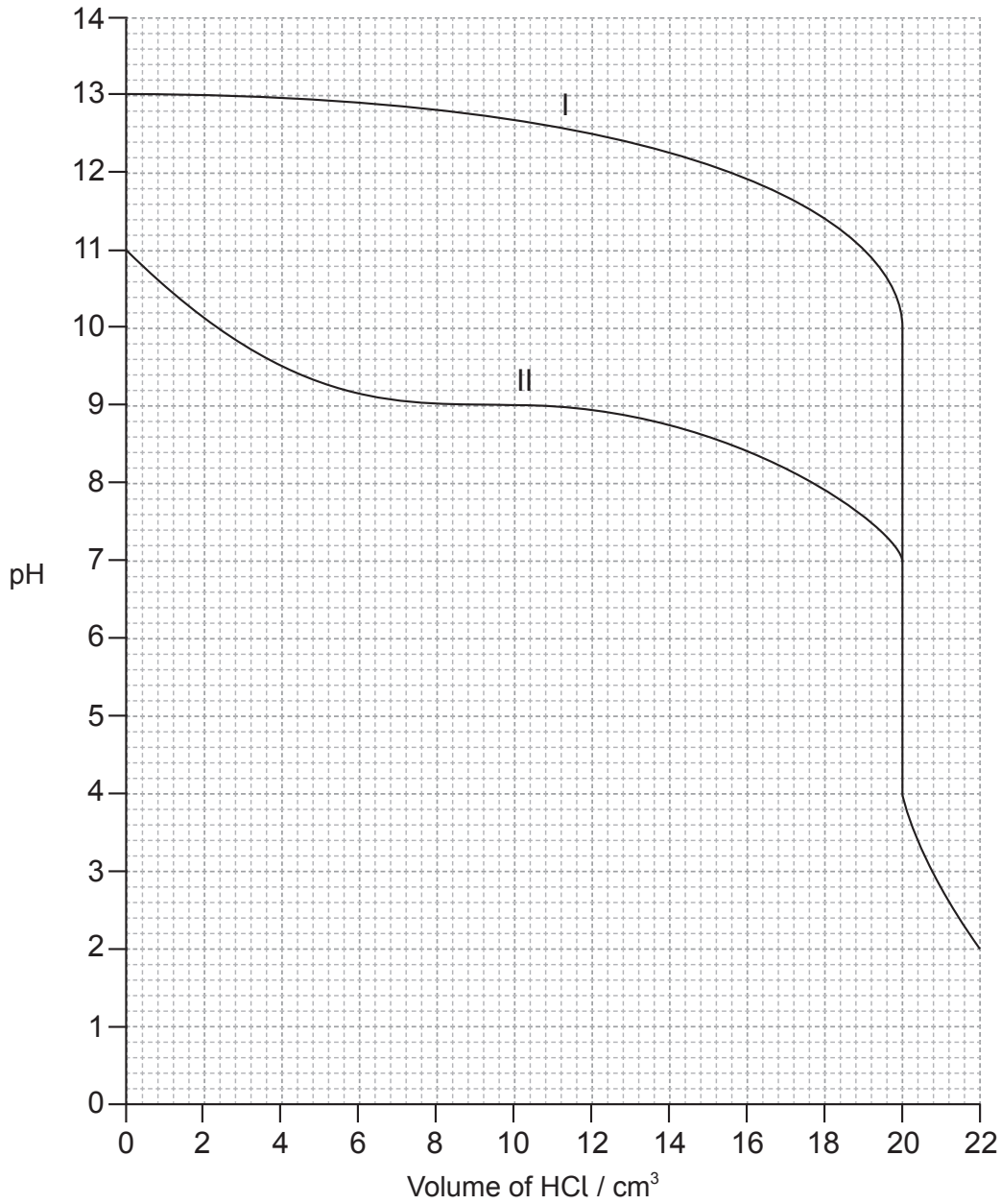
Please **do not** write on this page.

Answers written on this page
will not be marked.

**8.** (a) 20.0 $cm^3$ aqueous solutions of two bases, each with a concentration of 0.100 $mol\,dm^{-3}$ were separately titrated with 0.100 $mol\,dm^{-3}$ hydrochloric acid, HCl (aq), and the following graph was obtained.

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**(Question 8 continued)**

(i) Deduce the pH at the equivalence points for base I and base II. [2]

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(ii) Suggest why the titration curve for base I is different from base II. [1]

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(iii) State the formulas of **two** possible bases which could be used as base I. [1]

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(iv) Calculate, using data from the graph, the dissociation constant, $K_b$, of base II, showing your working. [3]

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(v) Suggest an indicator that can be used for both titrations. [1]

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**(This question continues on the following page)**

**(Question 8 continued)**

(b) (i) State what is meant by the term buffer solution. [2]

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(ii) Calculate the pH of a solution prepared by mixing 40.0 $cm^3$ of 0.200 $mol\,dm^{-3}$ $NH_3(aq)$ and 40.0 $cm^3$ of 0.100 $mol\,dm^{-3}$ $HCl(aq)$, showing your working. ($pK_b$ $NH_3 = 4.75$ at 298 K) [3]

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(c) The equations of two acid-base reactions are given below.

Reaction **A** $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

Reaction **B** $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

(i) Explain whether $HCO_3^-(aq)$ behaves as an acid or a base in each of the reactions **A** and **B**. [2]

Reaction **A**:

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Reaction **B**:

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**(This question continues on the following page)**

**(Question 8 continued)**

(ii) Deduce **two** conjugate acid-base pairs from reactions **A** and **B**. [2]

| | **Acid** | **Base** |
|---|---|---|
| **Conjugate acid-base pair 1** | . . . . . | . . . . . |
| **Conjugate acid-base pair 2** | . . . . . | . . . . . |

(d) Nitric acid, $HNO_3$, and nitrous acid, $HNO_2$, are described as strong and weak acids respectively.

(i) Distinguish between *strong* and *weak* acids. [1]

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(ii) A 1.00 g sample of solid magnesium carbonate, $MgCO_3$, is added to separate solutions of $HNO_3$ and $HNO_2$ of the same concentration and temperature. State **one** similarity and **one** difference in the observations made in these reactions. [2]

Similarity:

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Difference:

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**(This question continues on the following page)**

**(Question 8 continued)**

(iii) A solution of $HNO_3$ has a pH of 1, while a solution of $HNO_2$ has a pH of 5. Determine the ratio of the hydrogen ion concentration in $HNO_3$:$HNO_2$. [1]

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(e) (i) State the acid-base character of the oxides of the period 3 elements Na to Ar. [2]

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(ii) State balanced equations to illustrate the acid-base character of sodium oxide and sulfur trioxide. [2]

Sodium oxide:

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Sulfur trioxide:

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**9.** (a) A 0.842 g sample of a liquid halogenoalkane, RBr(l), was heated under reflux with $1.35 \times 10^{-2}$ mol of aqueous sodium hydroxide, NaOH(aq). After cooling the mixture, the excess NaOH was titrated with hydrochloric acid, HCl(aq), and required $7.36 \times 10^{-3}$ mol of the acid.

(i) State the equation for the substitution reaction of the halogenoalkane with sodium hydroxide. [1]

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(ii) Calculate the amount, in mol, of sodium hydroxide that reacted with the halogenoalkane. [1]

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(iii) Calculate the molar mass of the halogenoalkane. [1]

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(iv) Given that each molecule of the halogenoalkane contains one bromine atom, determine its molecular formula. [1]

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**(This question continues on the following page)**

**(Question 9 continued)**

(v) Deduce the structural formulas of **four** structural isomers of the halogenoalkane based on the molecular formula **and** label each isomer as primary, secondary or tertiary. [4]
(If you have not been able to determine the molecular formula in part (a) (iv), use $C_5H_{11}Br$ to deduce the four structural isomers.)

(b) The reaction between a primary halogenoalkane drawn in part (a) (v) and potassium cyanide follows a $S_N2$ mechanism.

(i) State the importance of this reaction in organic synthesis. [1]

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**(This question continues on the following page)**

**(Question 9 continued)**

(ii) Explain the mechanism of the reaction using curly arrows to represent the movement of electron pairs. [4]

(iii) The organic product obtained in part (b) (ii) can be reduced to form an amine. State an equation for this reaction and a suitable catalyst. [2]

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(c) The reaction between the primary halogenoalkane, obtained in part (a) (v), and hot, concentrated alcoholic NaOH is an example of an elimination reaction.

(i) Explain the mechanism of the elimination reaction using curly arrows to represent the movement of electron pairs. [4]

**(This question continues on the following page)**

**(Question 9 continued)**

(ii) Under certain conditions, the major product obtained in the elimination reaction can undergo polymerization. Identify the type of polymerization and draw a section of the polymer consisting of **two** repeating units. [2]

Type of polymerization:

. . . . . .

Section of polymer:

(d) Ethane can react with chlorine. Explain the free-radical mechanism of this reaction, including any necessary reaction conditions. [4]

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