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Diploma Programme
Programme du diplôme
Programa del Diploma

Chemistry
Higher level
Paper 2

Wednesday 22 May 2019 (afternoon)

Candidate session number

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.
- Answer all questions.
- Answers must be written within the answer 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]**.

23 pages

2219–6114
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Answer **all** questions. Answers must be written within the answer boxes provided.

1. Ethyne, C_2H_2, reacts with oxygen in welding torches.

(a) Write an equation for the complete combustion of ethyne. [1]

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(b) (i) Deduce the Lewis (electron dot) structure of ethyne. [1]

(ii) Compare, giving a reason, the length of the bond between the carbon atoms in ethyne with that in ethane, C_2H_6. [1]

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(iii) Identify the type of interaction that must be overcome when liquid ethyne vaporizes. [1]

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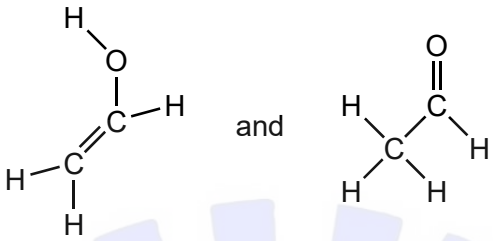
(Question 1 continued)

(c) Ethyne reacts with steam.

$$C_2H_2(g) + H_2O(g) \rightarrow C_2H_4O(g)$$

Two possible products are:



A **B**

(i) State the name of product **B**, applying IUPAC rules. [1]

. . . . . .

(ii) Determine the enthalpy change for the reaction, in kJ, to produce **A** using section 11 of the data booklet. [3]

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(iii) The enthalpy change for the reaction to produce **B** is –213 kJ.

Predict, giving a reason, which product is the most stable. [1]

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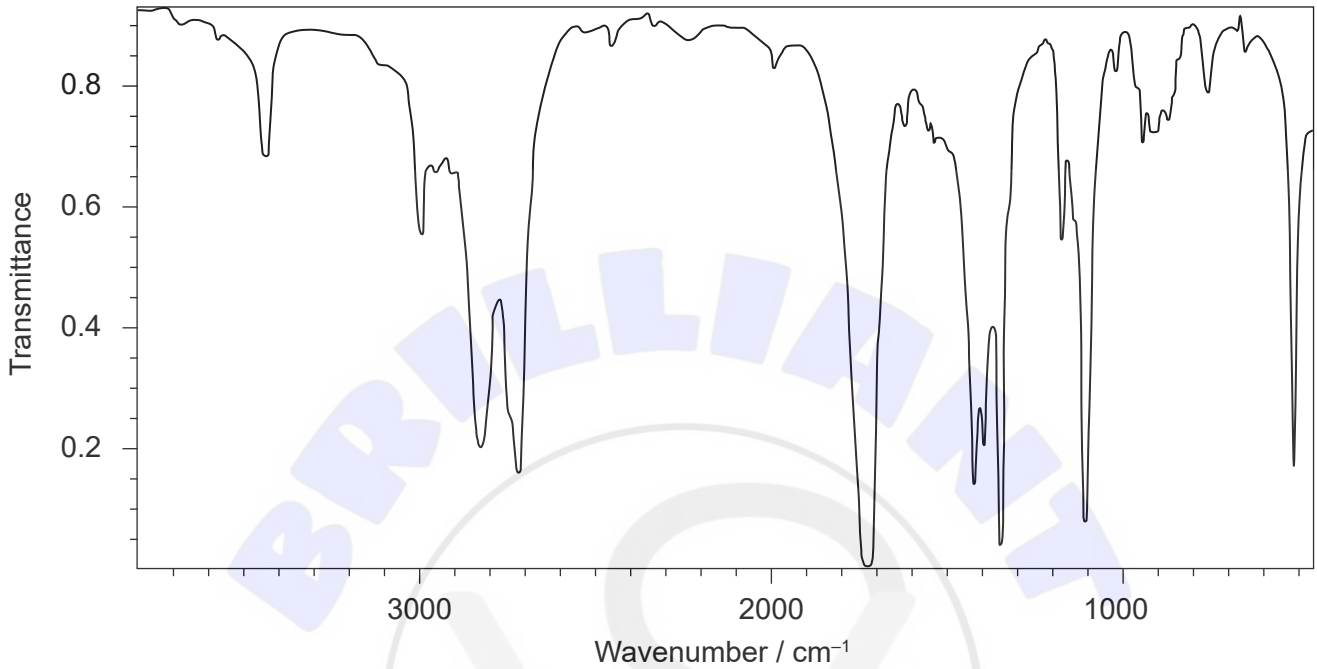
(Question 1 continued)

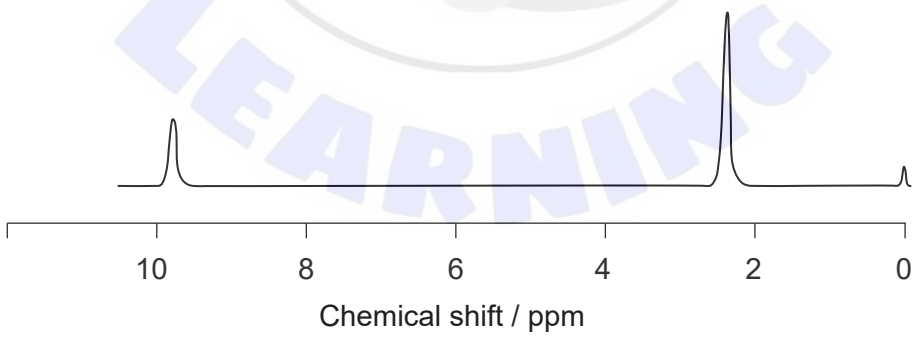
(iv) The IR spectrum and low resolution ^{1}H NMR spectrum of the actual product formed are shown.

IR spectrum



[Source: NIST Chemistry WebBook SRD 69
https://webbook.nist.gov/chemistry/ DOI: https://doi.org/10.18434/T4D303
http://webbook.nist.gov/cgi/inchi?Spec=C75070&Index=2&Type=IR
Acetaldehyde: Data compiled by: Coblentz Society, Inc.]

^{1}H NMR spectrum



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(Question 1 continued)

Deduce whether the product is **A** or **B**, using evidence from these spectra together with sections 26 and 27 of the data booklet. [2]

Identity of product:

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One piece of evidence from IR:

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One piece of evidence from ^{1}H NMR:

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(v) Deduce the splitting pattern you would expect for the signals in a high resolution ^{1}H NMR spectrum. [2]

2.3 ppm:

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9.8 ppm:

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(Question 1 continued)

(d) Product **B**, CH_3CHO, can also be synthesized from ethanol.

(i) Suggest the reagents and conditions required to ensure a good yield of product **B**. [2]

Reagents:

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Conditions:

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(ii) Deduce the average oxidation state of carbon in product **B**. [1]

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(iii) Explain why product **B** is water soluble. [3]

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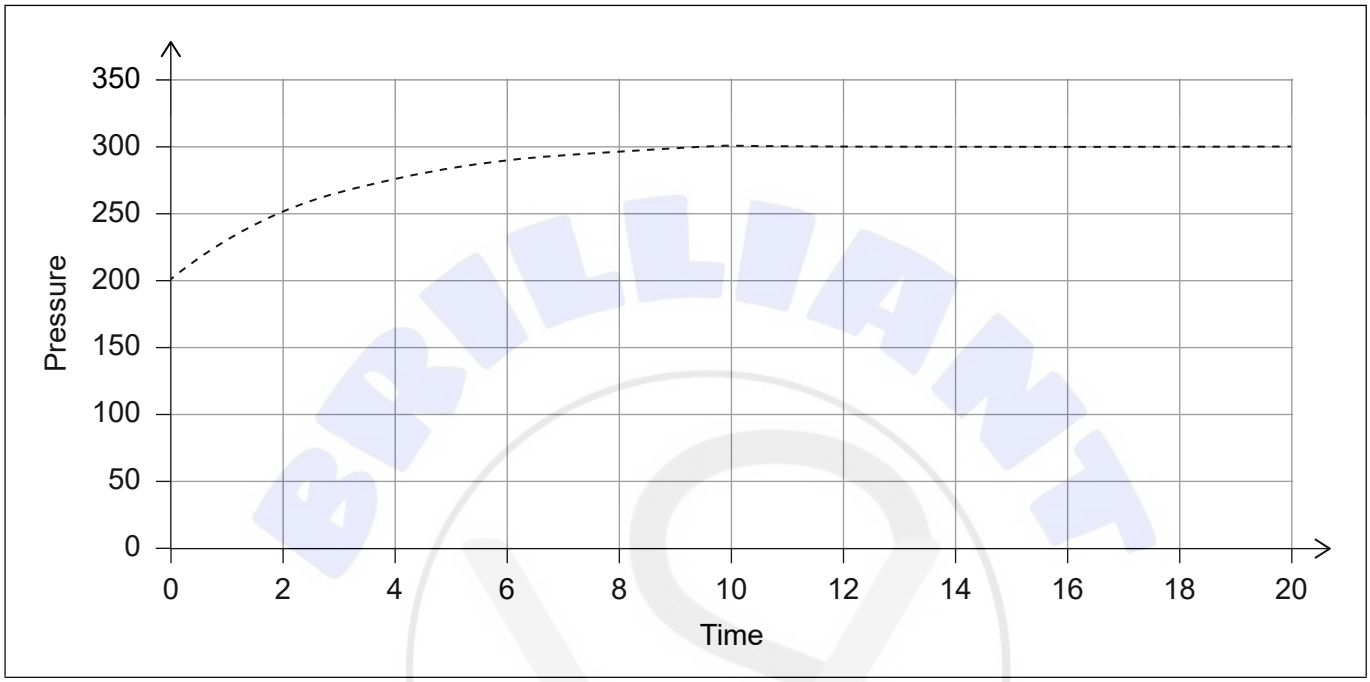
2. The thermal decomposition of dinitrogen monoxide occurs according to the equation:

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

The reaction can be followed by measuring the change in total pressure, at constant temperature, with time.

The x-axis and y-axis are shown with arbitrary units.



(a) Explain why, as the reaction proceeds, the pressure increases by the amount shown. [2]

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(b) Outline, in terms of collision theory, how a decrease in pressure would affect the rate of reaction. [2]

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(Question 2 continued)

(c) This decomposition obeys the rate expression:

$$-\frac{d[N_2O]}{dt} = k[N_2O]$$

(i) Deduce how the rate of reaction at $t = 2$ would compare to the initial rate. [1]

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(ii) It has been suggested that the reaction occurs as a two-step process:

Step 1: $N_2O(g) \rightarrow N_2(g) + O(g)$

Step 2: $N_2O(g) + O(g) \rightarrow N_2(g) + O_2(g)$

Explain how this could support the observed rate expression. [2]

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(d) The experiment is repeated using the same amount of dinitrogen monoxide in the same apparatus, but at a lower temperature.

Sketch, on the axes in question 2, the graph that you would expect. [2]

(e) The experiment gave an error in the rate because the pressure gauge was inaccurate. Outline whether repeating the experiment, using the same apparatus, and averaging the results would reduce the error. [1]

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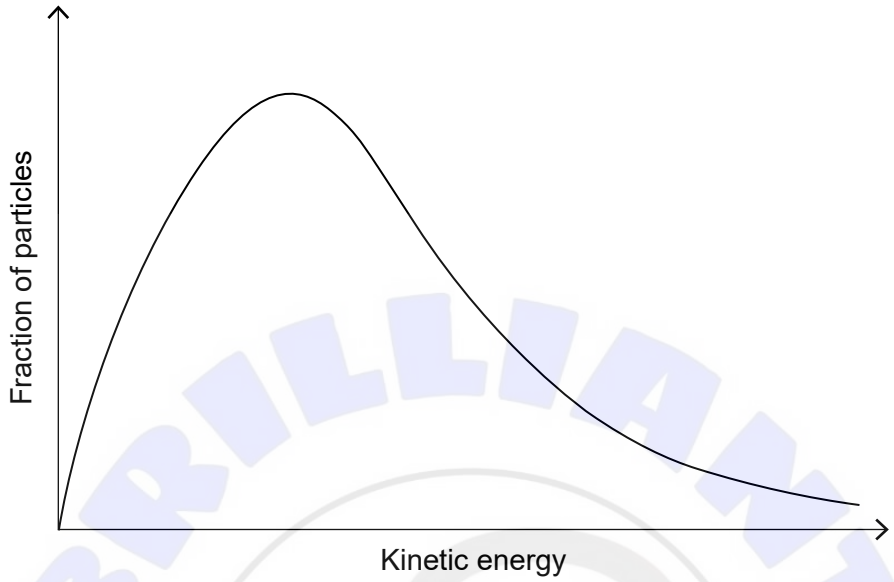
(Question 2 continued)

(f) The graph below shows the Maxwell–Boltzmann distribution of molecular energies at a particular temperature.



The rate at which dinitrogen monoxide decomposes is significantly increased by a metal oxide catalyst.

Annotate and use the graph to outline why a catalyst has this effect. [2]

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(Question 2 continued)

(g) (i) Determine the standard entropy change, in $J\,K^{-1}$, for the decomposition of dinitrogen monoxide. [2]

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

Species	$S^{\ominus}$ / $J\,mol^{-1}\,K^{-1}$
N_2O	220
N_2	193
O_2	205

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(ii) Dinitrogen monoxide has a positive standard enthalpy of formation, $\Delta H_f^{\ominus}$.

Deduce, giving reasons, whether altering the temperature would change the spontaneity of the **decomposition** reaction. [3]

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3. Dinitrogen monoxide, N_2O, causes depletion of ozone in the stratosphere.

(a) (i) Outline why ozone in the stratosphere is important. [1]

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(ii) Dinitrogen monoxide in the stratosphere is converted to nitrogen monoxide, NO(g).

Write **two** equations to show how NO(g) catalyses the decomposition of ozone. [2]

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(b) Different sources of N_2O have different ratios of $^{14}N : ^{15}N$.

(i) State **one** analytical technique that could be used to determine the ratio of $^{14}N : ^{15}N$. [1]

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(ii) A sample of gas was enriched to contain 2 % by mass of ^{15}N with the remainder being ^{14}N.

Calculate the relative molecular mass of the resulting N_2O. [2]

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(Question 3 continued)

(iii) Predict, giving **two** reasons, how the first ionization energy of ^{15}N compares with that of ^{14}N. [2]

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(c) Explain why the first ionization energy of nitrogen is greater than both carbon and oxygen. [2]

Nitrogen and carbon:

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Nitrogen and oxygen:

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(d) The Lewis (electron dot) structure of the dinitrogen monoxide molecule can be represented as:

(i) State what the presence of alternative Lewis structures shows about the nature of the bonding in the molecule. [1]

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(Question 3 continued)

(ii) State, giving a reason, the shape of the dinitrogen monoxide molecule. [1]

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(iii) Deduce the hybridization of the central nitrogen atom in the molecule. [1]

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4. Rhenium, Re, was the last element with a stable isotope to be isolated.

(a) The stable isotope of rhenium contains 110 neutrons.

State the nuclear symbol notation $^{A}_{Z}X$ for this isotope. [1]

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(b) Before its isolation, scientists predicted the existence of rhenium and some of its properties.

(i) Suggest the basis of these predictions. [2]

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(Question 4 continued)

(ii) A scientist wants to investigate the catalytic properties of a thin layer of rhenium metal on a graphite surface.

Describe an electrochemical process to produce a layer of rhenium on graphite. [2]

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(iii) Predict **two** other chemical properties you would expect rhenium to have, given its position in the periodic table. [2]

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(c) Describe how the relative reactivity of rhenium, compared to silver, zinc, and copper, can be established using pieces of rhenium and solutions of these metal sulfates. [2]

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(Question 4 continued)

(d) One chloride of rhenium has the empirical formula $ReCl_3$.

(i) State the name of this compound, applying IUPAC rules. [1]

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(ii) Calculate the percentage, by mass, of rhenium in $ReCl_3$. [2]

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(e) Rhenium forms salts containing the perrhenate(VII) ion, ReO_4^-.

(i) Suggest why the existence of salts containing an ion with this formula could be predicted. Refer to section 6 of the data booklet. [1]

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(ii) Deduce the coefficients required to complete the half-equation. [1]

$ReO_4^-(aq) + ____H^+(aq) + ____e^- \rightleftharpoons [Re(OH)_2]^{2+}(aq) + ____H_2O(l)$ $E^\ominus = +0.36\,V$

(iii) Predict, giving a reason, whether the reduction of ReO_4^- to $[Re(OH)_2]^{2+}$ would oxidize Fe^{2+} to Fe^{3+} in aqueous solution. Use section 24 of the data booklet. [1]

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5. Carbonated water is produced when carbon dioxide is dissolved in water under pressure. The following equilibria are established.

Equilibrium (1) $CO_2(g) \xrightleftharpoons{H_2O(l)} CO_2(aq)$

Equilibrium (2) $CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

(a) Carbon dioxide acts as a weak acid.

(i) Distinguish between a weak and strong acid. [1]

Weak acid:

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Strong acid:

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(ii) The hydrogencarbonate ion, produced in Equilibrium (2), can also act as an acid.

State the formula of its conjugate base. [1]

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(b) When a bottle of carbonated water is opened, these equilibria are disturbed.

State, giving a reason, how a decrease in pressure affects the position of Equilibrium (1). [1]

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(This question continues on the following page)

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(Question 5 continued)

(c) At 298 K the concentration of aqueous carbon dioxide in carbonated water is $0.200\,mol\,dm^{-3}$ and the pK_a for Equilibrium (2) is 6.36.

Calculate the pH of carbonated water. [3]

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(d) Soda water has sodium hydrogencarbonate, $NaHCO_3$, dissolved in the carbonated water.

(i) Identify the type of bonding in sodium hydrogencarbonate. [2]

Between sodium and hydrogencarbonate:

. . . . . .

Between hydrogen and oxygen in hydrogencarbonate:

. . . . . .

(ii) Predict, referring to Equilibrium (2), how the added sodium hydrogencarbonate affects the pH. (Assume pressure and temperature remain constant.) [2]

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(Question 5 continued)

(iii) $100.0\,cm^3$ of soda water contains $3.0 \times 10^{-2}\,g\ NaHCO_3$.

Calculate the concentration of $NaHCO_3$ in $mol\,dm^{-3}$. [2]

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(iv) The uncertainty of the $100.0\,cm^3$ volumetric flask used to make the solution was $\pm 0.6\,cm^3$.

Calculate the maximum percentage uncertainty in the mass of $NaHCO_3$ so that the concentration of the solution is correct to $\pm 1.0\,\%$. [1]

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(e) The reaction of the hydroxide ion with carbon dioxide and with the hydrogencarbonate ion can be represented by Equations 3 and 4.

Equation (3) $OH^-(aq) + CO_2(g) \rightarrow HCO_3^-(aq)$

Equation (4) $OH^-(aq) + HCO_3^-(aq) \rightarrow H_2O(l) + CO_3^{2-}(aq)$

Discuss how these equations show the difference between a Lewis base and a Brønsted–Lowry base. [2]

Equation (3):

. . . . . .

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Equation (4):

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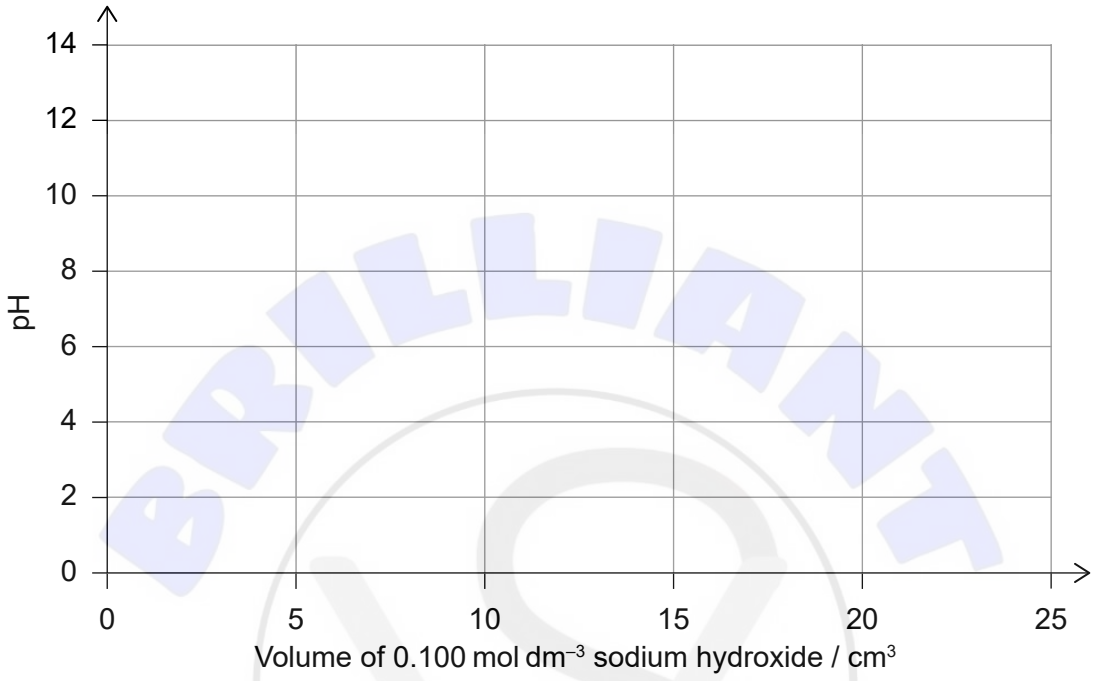
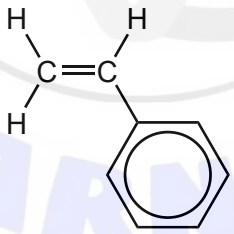
(Question 5 continued)

(f) Aqueous sodium hydrogencarbonate has a pH of approximately 7 at 298 K.

Sketch a graph of pH against volume when 25.0 cm^3 of 0.100 mol dm^{-3} NaOH (aq) is gradually added to 10.0 cm^3 of 0.0500 mol dm^{-3} $NaHCO_3$ (aq). [2]



6. Phenylethene can be polymerized to form polyphenylethene (polystyrene, PS).



(a) Draw the repeating unit of polyphenylethene. [1]

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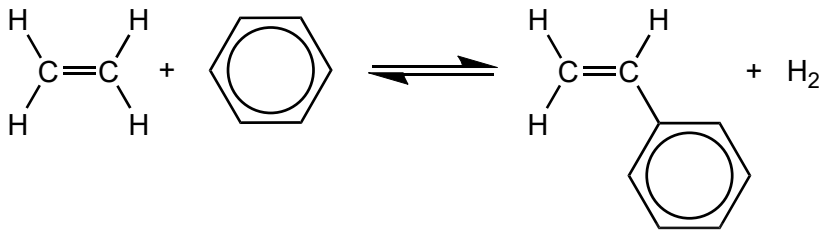
(Question 6 continued)

(b) Phenylethene is manufactured from benzene and ethene in a two-stage process. The overall reaction can be represented as follows with $\Delta G^{\ominus} = +10.0\,\text{kJ mol}^{-1}$ at 298 K.



Calculate the equilibrium constant for the overall conversion at 298 K, using section 1 of the data booklet. [2]

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(c) The benzene ring of phenylethene reacts with the nitronium ion, NO_2^+, and the C=C double bond reacts with hydrogen bromide, HBr.

Compare and contrast these two reactions in terms of their reaction mechanisms. [2]

Similarity:

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Difference:

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(Question 6 continued)

(d) The major product of the reaction with hydrogen bromide is $C_6H_5–CHBr–CH_3$ and the minor product is $C_6H_5–CH_2–CH_2Br$.

(i) Outline why the major product, $C_6H_5–CHBr–CH_3$, can exist in two forms and state the relationship between these forms. [2]

Two forms:

. . . . . .

. . . . . .

Relationship:

. . . . . .

(ii) The minor product, $C_6H_5–CH_2–CH_2Br$, can exist in different conformational forms (isomers).

Outline what this means. [1]

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(e) The minor product, $C_6H_5–CH_2–CH_2Br$, can be directly converted to an intermediate compound, **X**, which can then be directly converted to the acid $C_6H_5–CH_2–COOH$.

$$C_6H_5–CH_2–CH_2Br \rightarrow \mathbf{X} \rightarrow C_6H_5–CH_2–COOH$$

Identify **X**. [1]

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