

Chemistry
Higher level
Paper 2

Thursday 11 May 2017 (afternoon)

Candidate session number

2 hours 15 minutes

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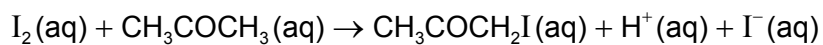
Instructions to candidates

- 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 **[95 marks]**.



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

1. The rate of the acid-catalysed iodination of propanone can be followed by measuring how the concentration of iodine changes with time.



The general form of the rate equation is:

$$\text{Rate} = [\text{H}_3\text{CCOCH}_3(\text{aq})]^m \times [\text{I}_2(\text{aq})]^n \times [\text{H}^+(\text{aq})]^p$$

The reaction is first order with respect to propanone.

- (a) (i) Suggest how the change of iodine concentration could be followed. [1]

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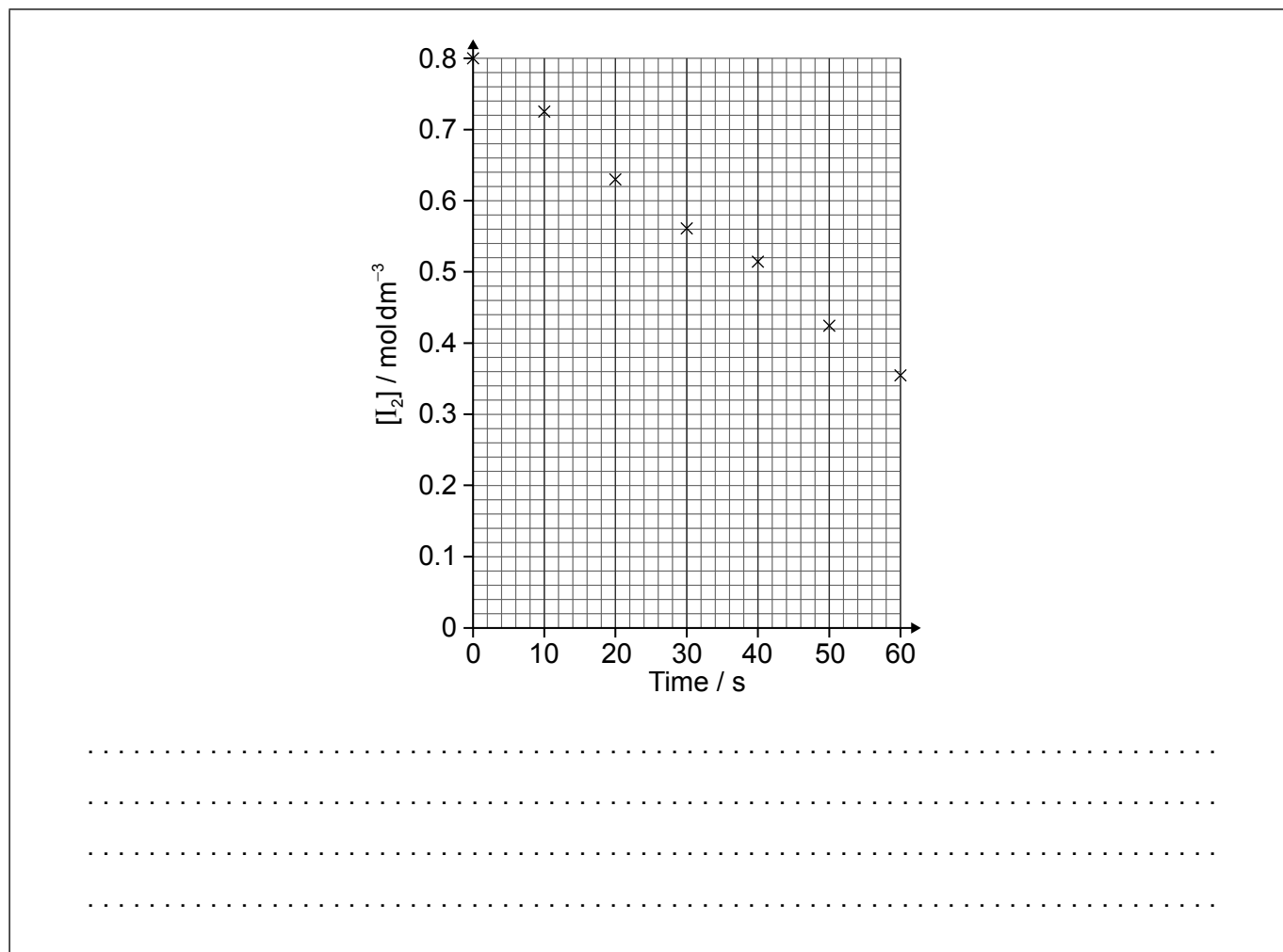


(Question 1 continued)

- (ii) A student produced these results with $[H^+] = 0.15 \text{ mol dm}^{-3}$. Propanone and acid were in excess and iodine was the limiting reagent.

Determine the relative rate of reaction when $[H^+] = 0.15 \text{ mol dm}^{-3}$.

[2]



(This question continues on the following page)



(Question 1 continued)

- (b) The student then carried out the experiment at other acid concentrations with all other conditions remaining unchanged.

$[\text{H}^+] / \text{mol dm}^{-3}$	Relative rate of reaction
0.05	0.0025
0.10	0.0051
0.20	0.0100

Determine the relationship between the rate of reaction and the concentration of acid and the order of reaction with respect to hydrogen ions.

[2]

Relationship:

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Order of reaction with respect to $[\text{H}^+]$:

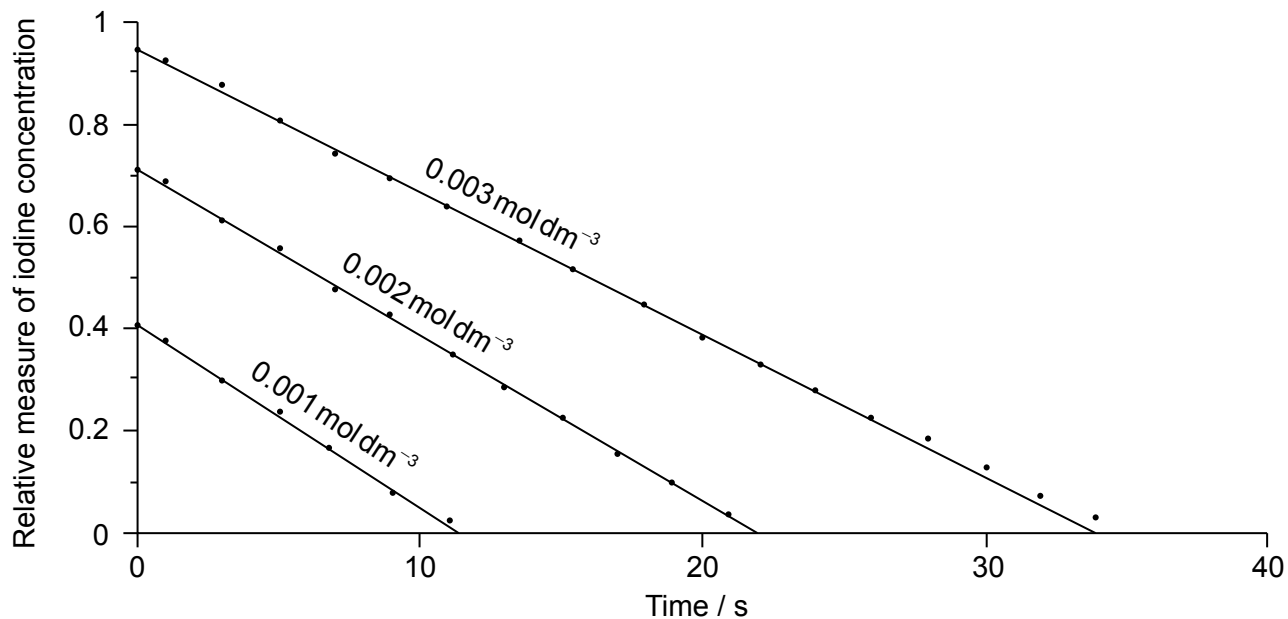
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(Question 1 continued)

(c) When the concentration of iodine is varied, while keeping the concentrations of acid and propanone constant, the following graphs are obtained.



Deduce, giving your reason, the order of reaction with respect to iodine.

[2]

Order with respect to iodine:

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Reason:

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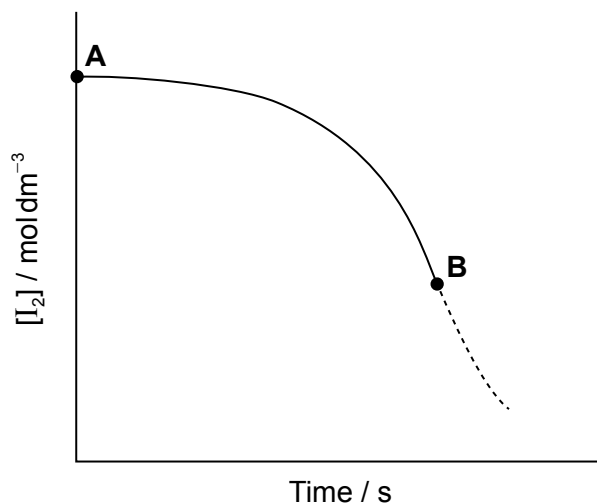


28EP05

Turn over

(Question 1 continued)

(d) When the reaction is carried out in the absence of acid the following graph is obtained.



Discuss the shape of the graph between A and B.

[2]

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2. Titanium and vanadium are consecutive elements in the first transition metal series.

(a) Describe the bonding in metals.

[2]

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(Question 2 continued)

- (b) Titanium exists as several isotopes. The mass spectrum of a sample of titanium gave the following data:

Mass number	% abundance
46	7.98
47	7.32
48	73.99
49	5.46
50	5.25

Calculate the relative atomic mass of titanium to two decimal places.

[2]

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- (c) State the number of protons, neutrons and electrons in the ${}^{48}_{22}\text{Ti}$ atom.

[1]

Protons:

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Neutrons:

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Electrons:

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(Question 2 continued)

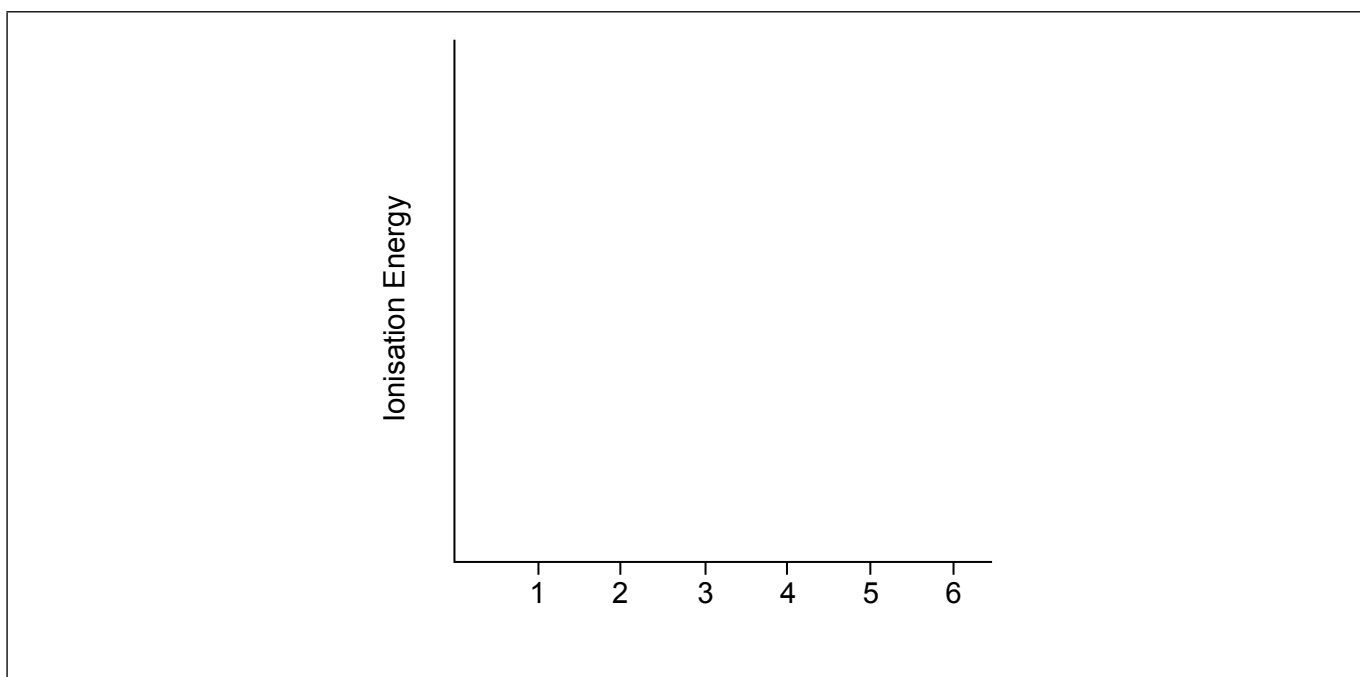
- (d) (i) State the full electron configuration of the ${}_{22}^{48}\text{Ti}^{2+}$ ion. [1]

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- (ii) Suggest why the melting point of vanadium is higher than that of titanium. [1]

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- (iii) Sketch a graph of the first six successive ionization energies of vanadium on the axes provided. [1]



- (iv) Explain why an aluminium-titanium alloy is harder than pure aluminium. [2]

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(Question 2 continued)

- (e) Describe, in terms of the electrons involved, how the bond between a ligand and a central metal ion is formed. [1]

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- (f) Outline why transition metals form coloured compounds. [4]

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- (g) (i) State the type of bonding in potassium chloride which melts at 1043K. [1]

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- (ii) A chloride of titanium, TiCl_4 , melts at 248K. Suggest why the melting point is so much lower than that of KCl. [1]

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(Question 2 continued)

(h) TiCl_4 reacts with water and the resulting titanium(IV) oxide can be used as a smoke screen.

(i) Formulate an equation for this reaction. [2]

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(ii) Suggest **one** disadvantage of using this smoke in an enclosed space. [1]

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28EP11

Turn over

3. Vanadium has a number of different oxidation states.

(a) Determine the oxidation state of vanadium in each of the following species. [2]

V_2O_5 :
VO^{2+} :

(b) Electrode potentials for the reactions of vanadium and other species are shown below.

$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	-0.26 V
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34 V
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.0 V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76 V
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13 V
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.17 V
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80 V
$\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$	+1.36 V

(i) Identify, from the table, a non-vanadium species that can reduce $VO^{2+}(aq)$ to $V^{3+}(aq)$ but no further. [1]

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(ii) Identify, from the table, a non-vanadium species that could convert $VO_2^+(aq)$ to $V^{2+}(aq)$. [1]

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(This question continues on the following page)



(Question 3 continued)

- (c) (i) Formulate an equation for the reaction between $\text{VO}^{2+}(\text{aq})$ and $\text{V}^{2+}(\text{aq})$ in acidic solution to form $\text{V}^{3+}(\text{aq})$.

[1]

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- (ii) Comment on the spontaneity of this reaction by calculating a value for ΔG^\ominus using the data given in (b) and in section 1 of the data booklet.

[3]

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will not be marked.



4. Millerite, a nickel sulfide mineral, is an important source of nickel. The first step in extracting nickel is to roast the ore in air.

(a) Formulate an equation for the oxidation of nickel(II) sulfide to nickel(II) oxide. [1]

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(b) The nickel obtained from another ore, nickeliferous limonite, is contaminated with iron. Both nickel and iron react with carbon monoxide gas to form gaseous complexes, tetracarbonylnickel, $\text{Ni}(\text{CO})_4(\text{g})$, and pentacarbonyliron, $\text{Fe}(\text{CO})_5(\text{g})$. Suggest why the nickel can be separated from the iron successfully using carbon monoxide. [1]

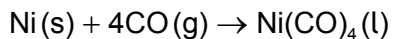
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(Question 4 continued)

(c) The reaction for the formation of liquid tetracarbonylnickel is shown below:



(i) Calculate the standard entropy change, ΔS^\ominus , of the reaction, in JK^{-1} , using the values given. [2]

	$S^\ominus / \text{JK}^{-1}\text{mol}^{-1}$
Ni(s)	29.9
CO(g)	197.6
Ni(CO) ₄ (l)	313.4

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(ii) Calculate a value for ΔH^\ominus in kJ. [1]

	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
CO(g)	-110.5
Ni(CO) ₄ (l)	-633.0

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(Question 4 continued)

- (iii) Use your answers to (c)(i) and (c)(ii), to determine the temperature, in °C, at which the decomposition of liquid tetracarbonylnickel to nickel and carbon monoxide becomes favourable.

(If you did not get answers to (c)(i) and (c)(ii), use -500 J K^{-1} and -200 kJ respectively but these are not the correct answers.)

[3]

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- (d) Suggest why experiments involving tetracarbonylnickel are very hazardous.

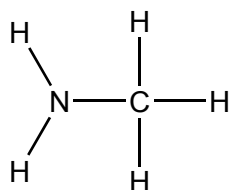
[1]

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5. Two hydrides of nitrogen are ammonia and hydrazine, N_2H_4 . One derivative of ammonia is methanamine whose molecular structure is shown below.



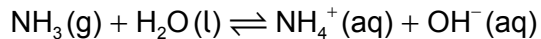
- (a) Estimate the H–N–H bond angle in methanamine using VSEPR theory. [1]

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- (b) State the electron domain geometry around the nitrogen atom and its hybridization in methanamine. [2]

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- (c) Ammonia reacts reversibly with water.



- Explain the effect of adding $H^+(aq)$ ions on the position of the equilibrium. [2]

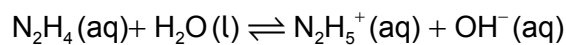
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(Question 5 continued)

- (d) (i) Hydrazine reacts with water in a similar way to ammonia. (The association of a molecule of hydrazine with a second H⁺ is so small it can be neglected.)



$$pK_b(\text{hydrazine}) = 5.77$$

Calculate the pH of a 0.0100 mol dm⁻³ solution of hydrazine. [3]

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- (ii) Suggest a suitable indicator for the titration of hydrazine solution with dilute sulfuric acid using section 22 of the data booklet. [1]

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- (e) Outline, using an ionic equation, what is observed when magnesium powder is added to a solution of ammonium chloride. [2]

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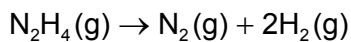
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(Question 5 continued)

- (f) Determine the enthalpy change of reaction, ΔH , in kJ, when 1.00 mol of gaseous hydrazine decomposes to its elements. Use bond enthalpy values in section 11 of the data booklet. [3]



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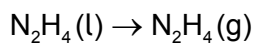
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- (g) The standard enthalpy of formation of $\text{N}_2\text{H}_4(\text{l})$ is $+50.6 \text{ kJ mol}^{-1}$. Calculate the enthalpy of vaporization, ΔH_{vap} , of hydrazine in kJ mol^{-1} .



(If you did not get an answer to (f), use -85 kJ but this is not the correct answer.) [2]

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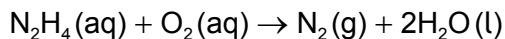
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(Question 5 continued)

(h) Hydrazine is used to remove oxygen from water used to generate steam or hot water.



The concentration of dissolved oxygen in a sample of water is $8.0 \times 10^{-3} \text{ g dm}^{-3}$.

(i) Calculate, showing your working, the mass of hydrazine needed to remove all the dissolved oxygen from 1000 dm^3 of the sample. [3]

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(ii) Calculate the volume, in dm^3 , of nitrogen formed under SATP conditions. (The volume of 1 mol of gas = 24.8 dm^3 at SATP.) [1]

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6. This question is about carbon and chlorine compounds.

(a) Ethane, C_2H_6 , reacts with chlorine in sunlight. State the type of this reaction and the name of the mechanism by which it occurs. [1]

Type of reaction:

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Mechanism:

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(b) (i) Formulate equations for the two propagation steps and one termination step in the formation of chloroethane from ethane. [3]

Two propagation steps:

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One termination step:

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(ii) Deduce the splitting patterns in the 1H NMR spectrum of C_2H_5Cl . [1]

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(Question 6 continued)

(iii) Explain why tetramethylsilane (TMS) is often used as a reference standard in ^1H NMR.

[2]

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(Question 6 continued)

- (c) (i) One possible product, **X**, of the reaction of ethane with chlorine has the following composition by mass:

carbon: 24.27%, hydrogen: 4.08%, chlorine: 71.65%

Determine the empirical formula of the product.

[2]

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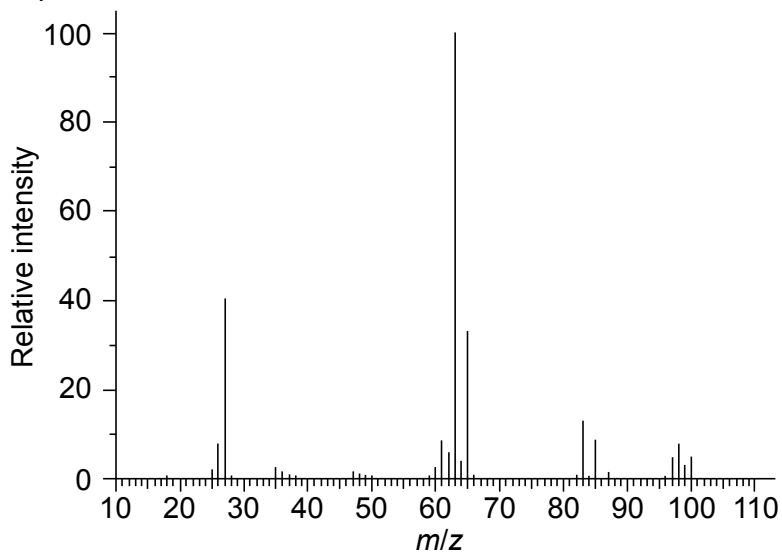
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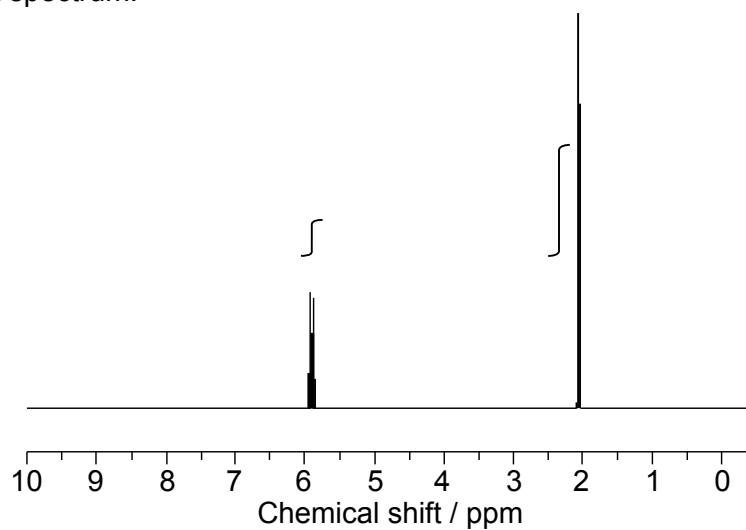
(Question 6 continued)

- (ii) The mass and ^1H NMR spectra of product **X** are shown below. Deduce, giving your reasons, its structural formula and hence the name of the compound. [3]

Mass spectrum:



^1H NMR spectrum:



[Source: <http://sdfs.db.aist.go.jp>]

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28EP25

Turn over

(Question 6 continued)

- (iii) When the product **X** is reacted with NaOH in a hot alcoholic solution, C₂H₃Cl is formed. State the role of the reactant NaOH other than as a nucleophile. [1]

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- (d) Chloroethene, C₂H₃Cl, can undergo polymerization. Draw a section of the polymer with three repeating units. [1]

7. Benzene is an aromatic hydrocarbon.

- (a) Discuss the physical evidence for the structure of benzene. [2]

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- (b) State the typical reactions that benzene and cyclohexene undergo with bromine. [1]

Benzene:
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Cyclohexene:
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(Question 7 continued)

- (c) State the reagents used to convert benzene to nitrobenzene and the formula of the electrophile formed. [2]

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- (d) Explain the mechanism for the nitration of benzene, using curly arrows to show the movement of electron pairs. [4]

- (e) State the reagents used in the two-stage conversion of nitrobenzene to aniline. [2]

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8. There is concern about damage done to the ozone layer in the stratosphere by jet-propelled aircraft.

(a) Formulate two equations to show how nitrogen(II) oxide, NO, catalyses the destruction of ozone. [2]

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(b) Suggest why the loss of ozone is an international environmental concern. [2]

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