UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
Cambridge International Level 3 Pre-U Certificate
Principal Subject

CANDIDATE NAME

CENTRE NUMBER | CANDIDATE NUMBER

CHEMISTRY **9791/03**

Paper 3 Part B Written **May/June 2010**

2 hours 15 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen in the spaces provided.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Do **not** write in any Barcodes.

Answer **all** questions.
You may lose marks if you do not show your working or if you do not include appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
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Total	

This document consists of **15** printed pages and **1** blank page.

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UNIVERSITY of CAMBRIDGE International Examinations

[Turn over

1 Fig. 1.1 shows the pH changes during the addition of 0.200 mol dm^{-3} HNO_3 to 20.0 cm^3 of a solution of sodium carbonate, Na_2CO_3.

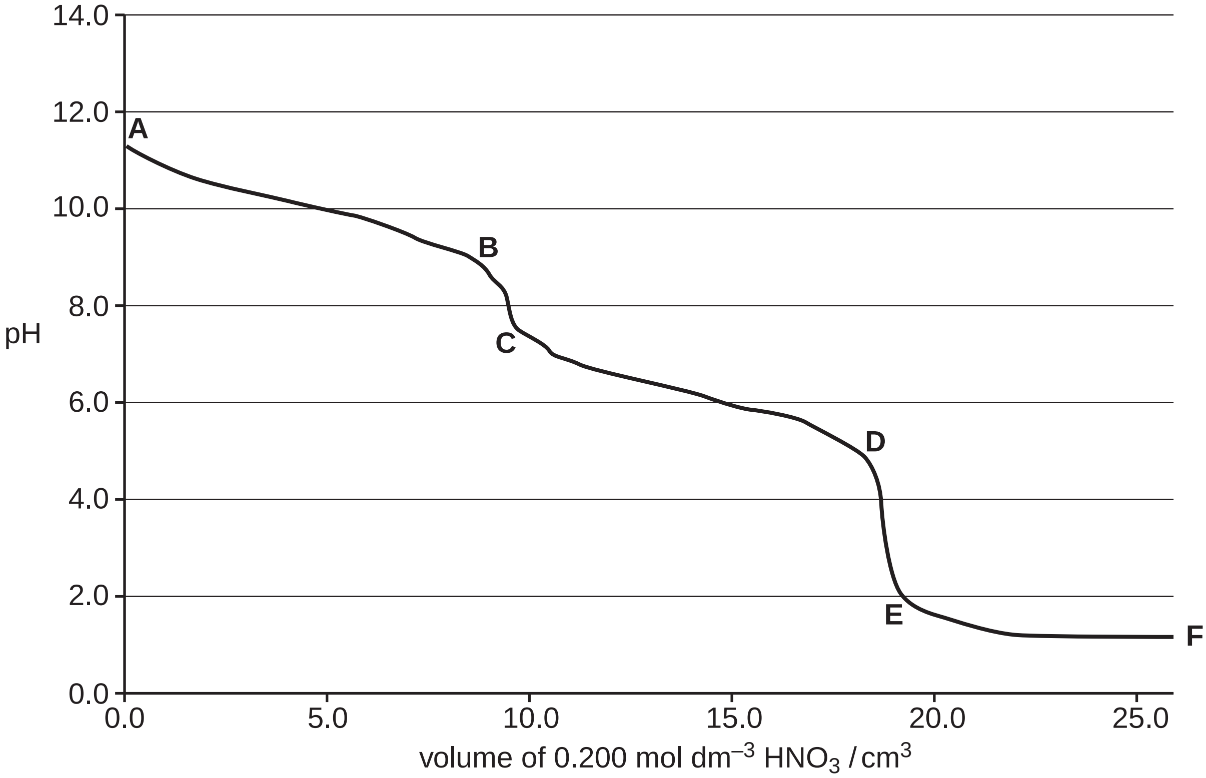


Fig. 1.1

(a) Write **ionic** equations for the reactions which occur in the solution between point **A** and point **B** on the graph and between point **C** and point **D** on the graph.

(i) ionic equation for the reaction occurring between **A** and **B**

....[1]

(ii) ionic equation for the reaction occurring between **C** and **D**

....[1]

(b) Table 1.1 gives some information about seven different indicators.

Table 1.1

indicator	pK_a	acid form	base form
thymol blue	1.6	yellow	blue
methyl yellow	3.3	red	yellow
chlorophenol red	6.0	yellow	red
bromothymol blue	7.1	yellow	blue
cresol purple	8.3	yellow	purple
thymolphthalein	9.9	colourless	blue
alizarin yellow	11.0	yellow	red

(i) From the information given in Table 1.1 choose the indicator that would be most suitable for determining the end-point occurring between points **D** and **E** on the graph.

....[1]

(ii) Explain your choice.

....

....[1]

(iii) What colour change will be seen with this indicator at the end-point?

....[1]

(c) Calculate the concentration, in $g\,dm^{-3}$, of sodium carbonate present in the original solution, given that the end-point between **D** and **E** occurs after 18.80 cm^3 of HNO_3 have been added.

.... $g\,dm^{-3}$ [3]

(d) **(i)** Write an equation for the dissociation of water.

....[1]

(ii) Use the equation in **(d)(i)** to write an expression for the equilibrium constant, K_c, for this reaction. Use this expression to show that $K_w = [H^+][OH^-]$. Justify and explain your reasoning.

....

....[3]

(iii) At 373 K the ionic product of water, K_w, has a value of $51.3 \times 10^{-14}\,mol^2\,dm^{-6}$. Use this information to calculate the pH of water at 373 K. Give your answer to 3 significant figures.

....[3]

(iv) At 298 K the pH of water is 7.00. Use this information to state whether the dissociation of water is endothermic or exothermic and explain your answer.

....

....

....[2]

(e) Calculate the final pH, at 298 K, after a 5.00 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added separately to

(i) 100 cm^3 of a solution of 1.00×10^{-4} mol dm^{-3} hydrochloric acid.

pH = ... [4]

(ii) 100 cm^3 of a solution that contains 0.100 mol dm^{-3} ethanoic acid and 0.100 mol dm^{-3} sodium ethanoate.
(K_a for ethanoic acid is 1.70×10^{-5} mol dm^{-3} at 298 K)

pH = ... [4]

[Total: 25]

2 2-bromobutane reacts with potassium hydroxide by either elimination or nucleophilic substitution depending on a combination of factors.

(a) State the conditions needed to bring about each of these reactions.

(i) elimination

....

....

(ii) nucleophilic substitution

....

....[3]

(b) 2-bromobutane is a *chiral* molecule and, when it is prepared by the reaction between but-1-ene and hydrogen bromide, a *racemate* is formed. The enantiomers in the *racemate* can be converted to *diastereoisomers* by covalent derivatisation with suitable *chiral* reagents. Pure samples of each of the enantiomers can then be obtained by simple separation techniques as the *diastereoisomers* have different physical and chemical properties.

Give definitions of each of the words in italics.

(i) *chiral* ....

....

....[1]

(ii) *racemate* ....

....

....[1]

(iii) *diastereoisomers* ....

....

....[1]

(iv) Draw suitable diagrams of the two different enantiomers of 2-bromobutane.

[2]

(c) When R-(–)-2-bromobutane undergoes nucleophilic substitution with potassium hydroxide under appropriate conditions the reaction proceeds predominantly by the S_N2 mechanism. When the progress of the reaction is followed in a polarimeter the optical activity is seen to change gradually from –23.1° via zero to +13.5°.

(i) Draw a curly-arrow mechanism for the reaction that is taking place. Show the 3-D structures of the reactant and product clearly.

[4]

(ii) Give the systematic name of the organic product.

....[2]

(d) The kinetics of the reaction of a different bromoalkane (RBr) with aqueous alkali were investigated at 323 K. The results are shown in Table 2.1.

Table 2.1

experiment	[RBr] / mol dm^{-3}	[OH^-] / mol dm^{-3}	initial rate / mol dm^{-3}s^{-1}
1	0.05	0.10	4.0×10^{-4}
2	0.15	0.10	1.2×10^{-3}
3	0.10	0.20	1.6×10^{-3}

(i) Deduce the order of reaction with respect to RBr and with respect to the hydroxide ion, OH^-.

Give reasons for each of your answers.

....

....

....

....

....[4]

(ii) Write the rate equation for the reaction.

....[1]

(iii) Calculate the value of the rate constant, *k*, at 323 K and give its units.

....[3]

(iv) Draw the skeletal formula of RBr, which is an isomer of 2-bromobutane.

[1]

[Total: 23]

3 The elements of Group 14 can all form monoxides and dioxides. The stabilities of the monoxides, with respect to disproportionation into the element and the dioxide, vary. The equations for the disproportionation reactions are given in Table 3.1 together with some thermodynamic data for the reactions.

Table 3.1

disproportionation equation	$\Delta_r S^{\ominus}$ (298 K) / J K^{-1} mol^{-1}	$\Delta_r H^{\ominus}$ (298 K) / kJ mol^{-1}	$\Delta_r G^{\ominus}$ (298 K) / kJ mol^{-1}
$2CO(g) \rightarrow C(s) + CO_2(g)$	–175.9	–172.5	–120.1
$2SiO(g) \rightarrow Si(s) + SiO_2(s)$	–362.9	–711.5	–603.4
$2GeO(s) \rightarrow Ge(s) + GeO_2(s)$		–126.8	
$2SnO(s) \rightarrow Sn(s) + SnO_2(s)$	–9.200	–9.100	–6.360
$2PbO(s) \rightarrow Pb(s) + PbO_2(s)$	–4.000	+157.2	+158.4

(a) Explain why the entropy change for the disproportionation of

(i) SiO is so much bigger than for CO,

....

....

....[2]

(ii) PbO is so close to zero.

....

....

....[2]

(b) Table 3.2 gives the standard molar entropies for germanium and its oxides.

Table 3.2

name	standard molar entropy at 298 K, $S^{\ominus}$(298 K) / J K^{-1} mol^{-1}
germanium, Ge(s)	31.1
germanium monoxide, GeO(s)	50.0
germanium dioxide, GeO_2(s)	55.3

(i) Calculate the standard entropy change, $\Delta_r S^{\ominus}$(298 K), for the disproportionation of germanium monoxide.

.... [2]

(ii) Calculate the standard free energy change, $\Delta_r G^{\ominus}$(298 K), for the same reaction.

.... [2]

(c) Use data from Table 3.1 to calculate

(i) the value of the equilibrium constant, K_p, for the disproportionation of carbon monoxide, CO,

.... [2]

(ii) the temperature above which the disproportionation of carbon monoxide ceases to be favourable.

.... [2]

(d) Explain why carbon monoxide does not spontaneously disproportionate at room temperature.

....

....[1]

[Total: 13]

4 The complex compound diamminedichloroplatinum(II) has two isomeric forms, one of which can be prepared from potassium tetrachloroplatinate(II) as shown in the reaction sequence in Fig. 4.1.

$$K_2[PtCl_4] \rightarrow K_2[PtI_4] \rightarrow \mathbf{X} \rightarrow [Pt(H_2O)_2(NH_3)_2](NO_3)_2 \rightarrow \text{diamminedichloroplatinum(II)}$$

Fig. 4.1

Compound **X** has the composition by mass Pt 40.37%, I 52.59%, N 5.80% and H 1.24% and a relative molecular mass of 483.

(a) Calculate the molecular formula of **X**, draw its two possible structures and indicate the ligand-platinum-ligand bond angle.

[6]

(b) Cobalt forms both octahedral and tetrahedral complexes. Give the identities of one complex ion of cobalt with each shape and, in each case, state the ligand-cobalt-ligand bond angle.

octahedral tetrahedral

bond angle .... bond angle .... [3]

(c) With reference to the **3-D orientation** of d orbitals in an octahedral transition metal complex explain why such complexes are usually coloured.

....

....

....

....

....

....[4]

[Total: 13]

5 Cyanoacrylate is the generic name for cyanoacrylate based fast-acting glues such as ethyl 2-cyanoacrylate. The skeletal formula of ethyl 2-cyanoacrylate is given in Fig. 5.1.

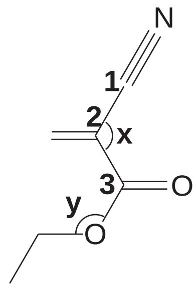


Fig. 5.1

(a) Give the molecular formula of ethyl 2-cyanoacrylate.

....[1]

(b) Give the bond angles labelled **x** and **y**.

bond angle **x** ....

bond angle **y** .... [2]

(c) Write the **names** of the functional group levels of the carbon atoms numbered **1**, **2**, and **3**.

1 ....

2 ....

3 .... [2]

(d) Ethyl 2-cyanoacrylate rapidly undergoes addition polymerisation in the presence of a suitable nucleophile to form long, strong chains which join the bonded surfaces together. The presence of moisture can therefore cause the glue to set, so exposure to moisture in the air can cause a tube or bottle of glue to become unusable over time.

(i) Explain what is meant by the term *nucleophile.*

....

....[2]

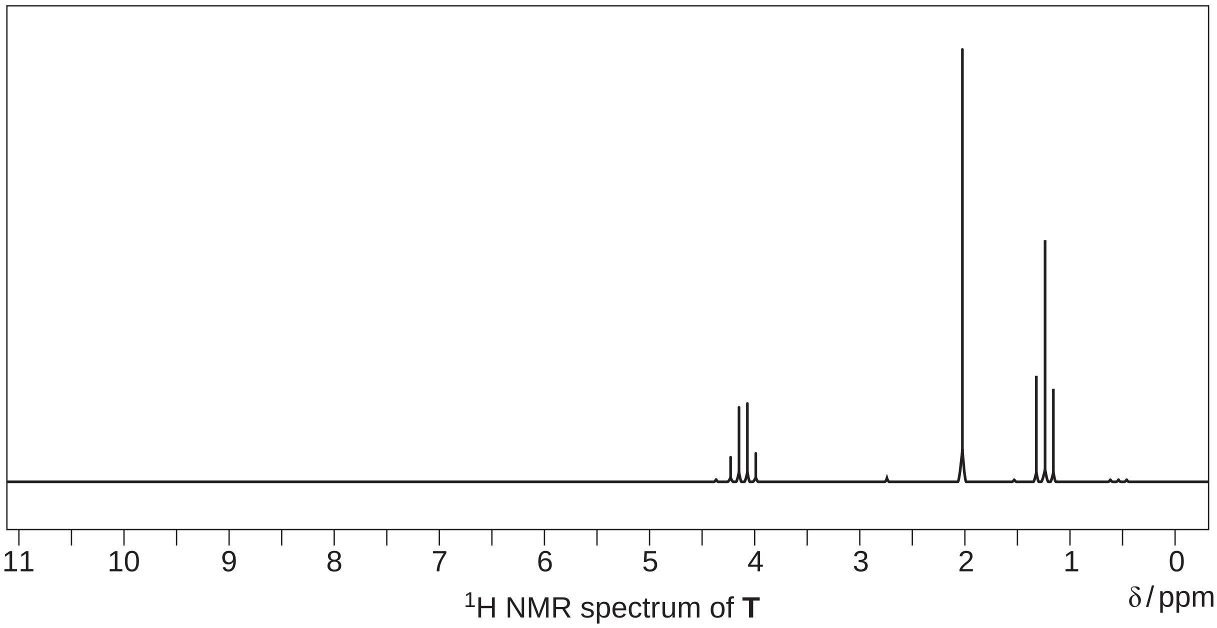
(ii) Draw the structure of part of the polymer chain that would be formed, showing **three** repeat units.

[2]

(e) The reduction of ethyl 2-cyanoacrylate with $LiAlH_4$ in ether produces two compounds, **Q** and **R**. **Q** reacts with ethanoyl chloride in a 1:2 molar ratio to form **S**. **R** reacts with ethanoyl chloride in a 1:1 ratio to form **T**. The ^{1}H NMR spectrum of **T** is shown in Fig. 5.2 and the ^{13}C NMR spectrum of **T** is shown in Fig. 5.3.

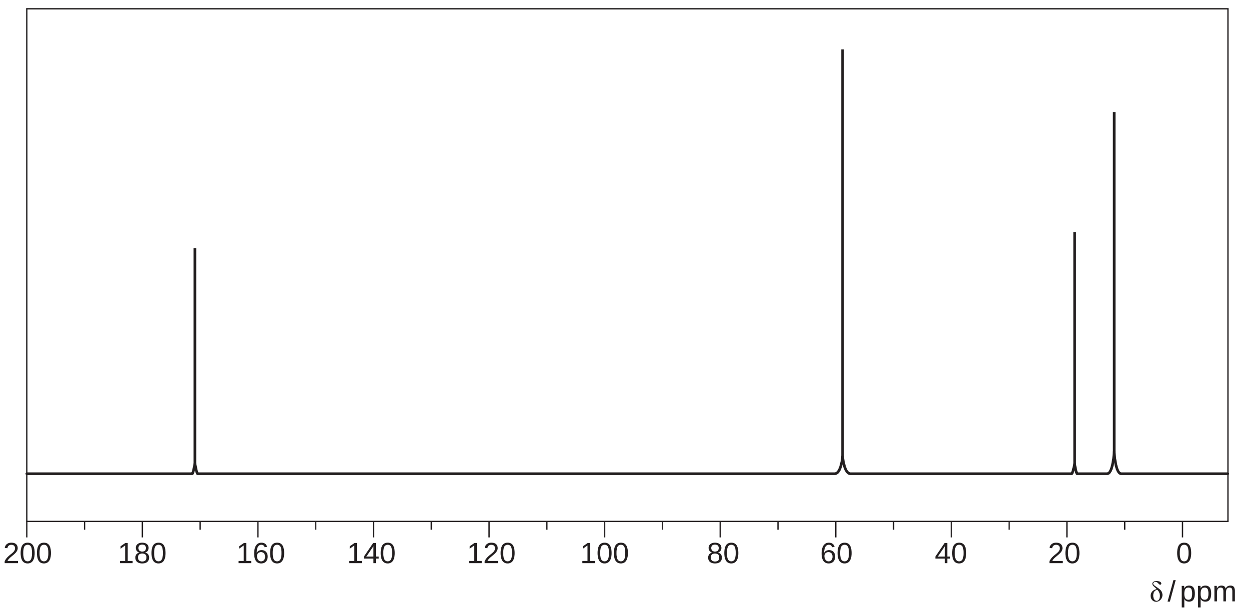
If ethyl 2-cyanoacrylate is instead reduced with hydrogen using a nickel catalyst then there is only a single product, **U**. The ^{1}H NMR spectrum of **U** has six signals, one of which disappears on shaking with D_2O.

Draw the structural formula of each of the compounds **Q**, **R**, **S**, **T** and **U**. Explain the reactions and the forms of the spectra in Fig. 5.2 and Fig. 5.3. This should include the identification of the atoms or groups of atoms responsible for each signal.



^{1}H NMR spectrum of **T**

Fig. 5.2



^{13}C NMR spectrum of **T**

Fig. 5.3

Structural formulae

Q

R

S

T

U

[5]

Explanations

Reactions of **Q** and **R** with ethanoyl chloride ....

....

....

....[3]

^{1}H NMR of **T** ....

....

....

....[3]

^{13}C NMR of **T** ....

....

....

....[3]

^{1}H NMR of **U** ....

....

....

....[3]

[Total: 26]

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