Cambridge Assessment International Education
Cambridge Pre-U Certificate

CANDIDATE NAME	

CENTRE NUMBER		CANDIDATE NUMBER	

CHEMISTRY (PRINCIPAL) **9791/03**

Paper 3 Part B Written **May/June 2019**

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.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.
Electronic calculators may be used.
You may lose marks if you do not show your working, if you do not use appropriate units or if you do not give your answer to appropriate significant figures.
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	
2	
3	
4	
5	
Total	

This syllabus is regulated for use in England, Wales and Northern Ireland as a Cambridge International Level 3 Pre-U Certificate.

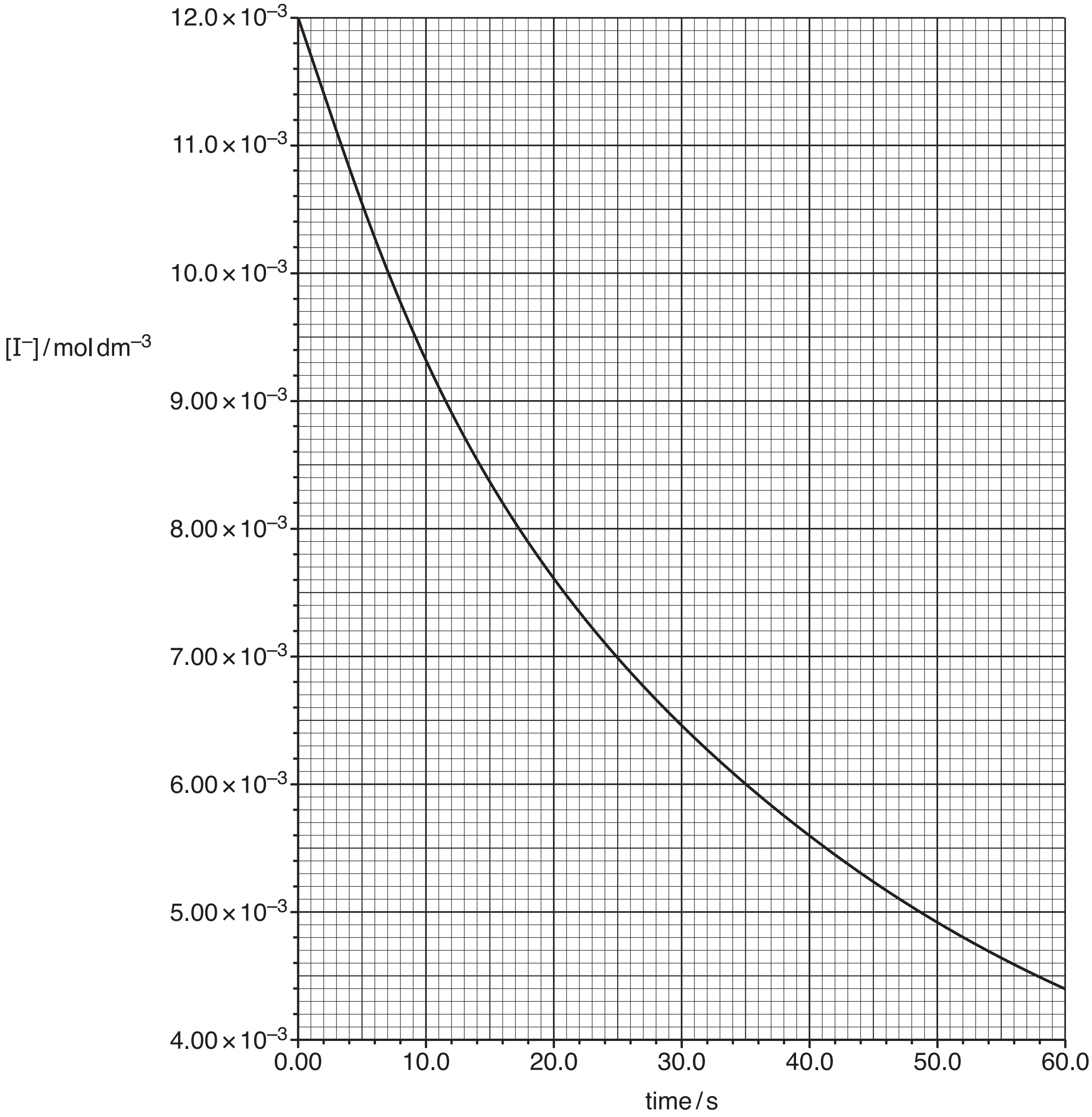
This document consists of **18** printed pages and **2** blank pages.

DC (ST/CT) 166956/4

1 The reaction between iron(III) ions, Fe^{3+}(aq), and iodide ions, I^-(aq), occurs as shown.

$$Fe^{3+}(aq) + I^-(aq) \rightarrow Fe^{2+}(aq) + \tfrac{1}{2}I_2(aq)$$

The rate of this reaction can be followed by the change in the I^-(aq) concentration as given in the graph.



The initial concentration of Fe^{3+}(aq) is 0.150 mol dm^{-3}.

(a) **(i)** Use the graph to calculate the initial rate of reaction and the rate of reaction at 20 s. Show your working on the graph.

initial rate = ... mol dm^{-3} s^{-1}

rate at 20 s = ... mol dm^{-3} s^{-1}
[4]

(ii) Use the values for the rate of reaction and the values for [I$^-$] at t = 0 and t = 20 s to determine the order of reaction with respect to the concentration of iodide ions. Show your working.

order = ... [3]

(iii) Explain why it is important that the concentration of Fe^{3+}(aq) is in large excess compared to the concentration of I$^-$(aq) in this experiment.

....

....

.... [1]

(b) The table shows some results for the same reaction performed at a different temperature.

experiment	[I$^-$] / mol dm^{-3}	[Fe^{3+}] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.080	0.040	5.38×10^{-3}
2	0.160	0.020	1.075×10^{-2}

Use the data in the table to deduce the order of reaction with respect to the concentration of Fe^{3+}(aq). Explain your answer.

....

....

.... [2]

(c) Write the rate equation for the reaction of Fe^{3+}(aq) and I$^-$(aq).

.... [1]

(d) **(i)** Use your rate equation and the initial rate you calculated in **(a)(i)** to calculate the rate constant.

k = ... [3]
value *units*

(ii) Deduce whether the reaction in part **(b)** was carried out at a higher or lower temperature than the original reaction. Explain your answer.

....

....

....

.... [2]

(e) One way of studying this reaction is by a 'clock' experiment. A fixed amount of aqueous sodium thiosulfate, $Na_2S_2O_3$, is added to the reaction mixture along with some starch indicator. Only when all the thiosulfate has reacted with the iodine to produce iodide ions, will the iodine persist in solution and turn the starch indicator blue-black. The time for this to happen can be used to calculate the rate of reaction.

(i) Give the equation, with state symbols, for the reaction of iodine and thiosulfate ions.

.... [2]

(ii) By assigning oxidation numbers, show that this is a redox reaction.

....

....

.... [2]

(f) **(i)** Rates of reaction determined by ‘clock’ experiments are usually lower than initial rates of reaction obtained by the method used in **(a)**.

Explain why this is the case.

....

....

.... [1]

(ii) Explain how the presence of thiosulfate ions in the ‘clock’ experiment in **(e)** minimises this difference.

....

....

.... [1]

[Total: 22]

2 Some crystal structures can be described as being close-packed.

(a) Name the two close-packed structures exhibited by metals.

Describe the arrangement of the close-packed layers in each structure.

name ....

arrangement of layers ....

name ....

arrangement of layers ....

[3]

(b) The structures of $NaCl$ and CaF_2 can be described using a cubic unit cell.

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

....

....

.... [2]

(ii) Describe the $NaCl$ structure and the CaF_2 structure in terms of the arrangement of the ions in the close-packed lattice and how the holes are occupied.

$NaCl$ ....

....

CaF_2 ....

....

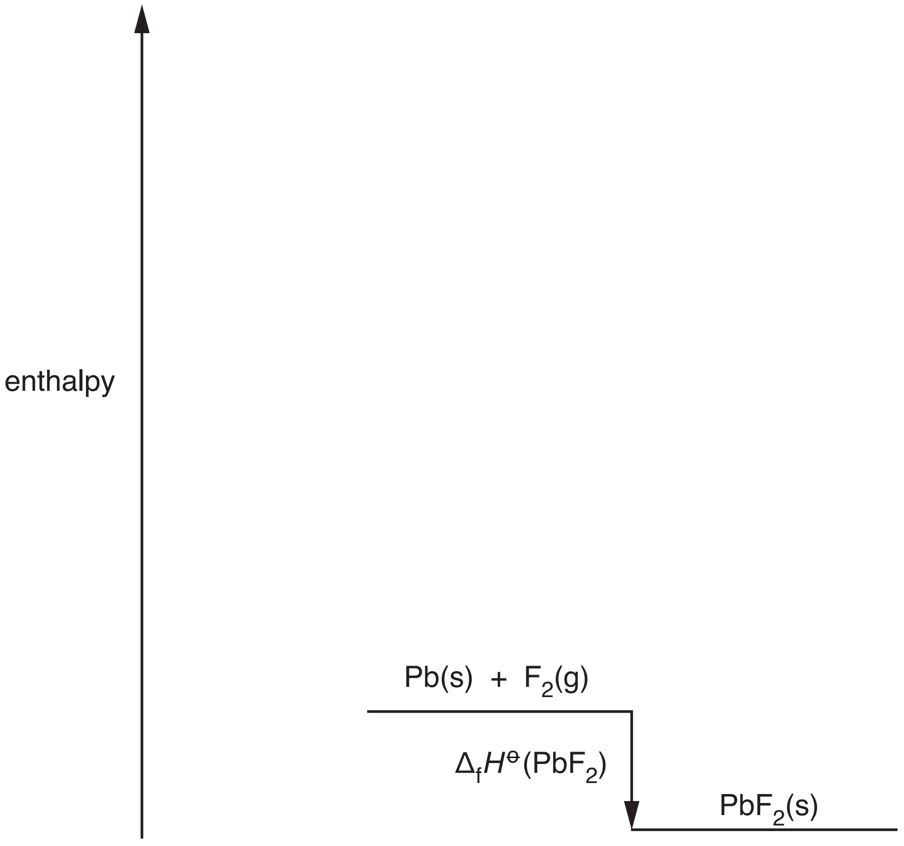
[3]

(c) Lead(II) fluoride, PbF_2, has the same structure as CaF_2.

The table shows data required to construct a Born-Haber cycle for PbF_2.

standard enthalpy change	enthalpy / kJ mol^{-1}
1st ionisation energy of Pb, $\Delta_{IE1}H^\ominus$ (Pb)	716
2nd ionisation energy of Pb, $\Delta_{IE2}H^\ominus$ (Pb)	1450
enthalpy of atomisation of Pb, $\Delta_{at}H^\ominus$ (Pb)	195
enthalpy of atomisation of F, $\Delta_{at}H^\ominus$ (F)	79
first electron affinity of F, $\Delta_{EA}H^\ominus$ (F) $X(g) + e^- \longrightarrow X^-(g)$	–328
enthalpy of formation of PbF_2, $\Delta_fH^\ominus$ (PbF_2)	–664

(i) Complete the Born-Haber cycle below to include the lattice enthalpy of PbF_2. Include state symbols. Identify each stage.



[6]

(ii) Calculate the lattice enthalpy of PbF_2.

lattice enthalpy of PbF_2 = ... kJ mol^{-1} [2]

(iii) The lattice energy for PbF_2 calculated by the Born-Haber cycle is 57 kJ mol^{-1} more exothermic than that calculated using the ionic model. In contrast, the value for PbI_2 is 240 kJ mol^{-1} more exothermic than the value given by the ionic model.

Explain this difference.

....

....

.... [2]

(d) $PbCl_4$ is a yellow oily liquid which undergoes thermal decomposition at 50 °C.

(i) Suggest the shape of $PbCl_4$ and state the bond angle.

shape ....

bond angle ....
[2]

(ii) Give the equation for the thermal decomposition of $PbCl_4$ at 50 °C.

.... [1]

(iii) PbF_4 is a yellow solid. Suggest why PbF_4 is a solid while $PbCl_4$ is a liquid at room temperature.

....

....

.... [3]

[Total: 24]

3 Iron can form complex ions and has a number of important biochemical applications.

(a) Describe the biological roles of ferritin and myoglobin.

ferritin ....

....

myoglobin ....

.... [2]

(b) Aqueous solutions of iron(III) compounds are acidic due to the equilibrium shown.

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$$

(i) State the coordination number of iron in the complex, $[Fe(H_2O)_5(OH)]^{2+}$.

....[1]

(ii) 14.46 g of iron(III) ammonium sulfate dodecahydrate, $(NH_4)Fe(SO_4)_2{\cdot}12H_2O$, is dissolved in distilled water to make up a solution of 400.0 cm^3.

The K_a for the equilibrium shown is 6.00×10^{-3}.

Calculate the pH. Ignore any effect on pH from the ammonium ion.

pH = ... [5]

(iii) The complex $[Fe(H_2O)_6]^{3+}$ is a very pale lilac. Suggest why aqueous solutions of Fe^{3+} appear pale yellow.

....

.... [1]

(iv) A solution of iron(II) containing $[Fe(H_2O)_6]^{2+}(aq)$ has the same concentration of iron ions as the solution in **(b)(ii)** but is less acidic.

Suggest why it is less acidic.

....

....

.... [1]

(c) The concentration of $Fe^{2+}(aq)$ ions can be determined by titration using acidified aqueous potassium manganate(VII).

(i) Give the two half-equations and hence construct the overall equation for this reaction.

....

....

....

.... [2]

(ii) When an alkaline solution of potassium manganate(VII) is used in the titration, a precipitate forms. Suggest the identity of this precipitate.

.... [1]

(d) A test for the presence of $Fe^{3+}(aq)$ ions is to add aqueous sodium thiocyanate, NaSCN.

(i) Complete the two possible dot-cross diagrams for the SCN^- ion.

In each case, ✱ represents the additional electron that is needed for the negative charge.

Show outer electrons only.

$$\left[\ {}^{*}\mathrm{S}\quad \mathrm{C}\quad \mathrm{N}\ \right]^{-}$$

$$\left[\ \mathrm{S}\quad \mathrm{C}\quad \mathrm{N}^{*}\ \right]^{-}$$

[2]

(ii) The thiocyanate ion can attach to a transition metal ion via either the S or the N atom.

Suggest how this can happen.

....

....

.... [2]

(iii) When $SCN^-(aq)$ is added to $Fe^{3+}(aq)$, the solution turns blood red due to the formation of a new complex. In this complex one water molecule is replaced by one SCN^- ion. Assume the thiocyanate ligand coordinates via the N atom.

Give the formula and draw a 3-dimensional representation of the new iron(III) complex.

formula ....

3-dimensional representation

[2]

[Total: 19]

4 **(a)** Butanone reacts with hydrogen cyanide to form 2-hydroxybutanonitrile. An intermediate is formed in this reaction.

(i) Give the name of the mechanism for this reaction.

.... [1]

(ii) Draw the mechanism for this reaction.

Include all relevant lone pairs of electrons, dipoles and curly arrows.

[4]

(iii) Explain why this reaction forms a racemic mixture.

....

....

.... [2]

(iv) The cyano group, CN, can be converted to a carboxylic acid, COOH. State the functional group level (FGL) of the carbon in each group. State the type of reaction and suggest the reagent(s) used for this conversion.

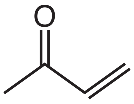
FGL in CN = ...

FGL in COOH = ...

type of reaction ....

reagent(s) .... [3]

(b) Butenone is shown.

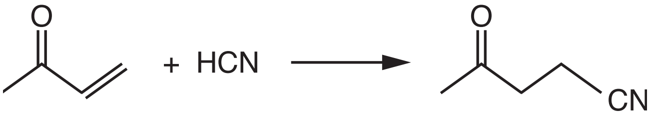


(i) By reference to the bonding suggest why the $H_2C=C–C=O$ part of the molecule is planar.

....

.... [1]

(ii) When butenone is reacted with HCN the C=C double bond can be attacked to give the product shown.



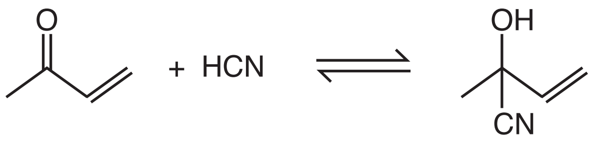
Assuming that the mechanism is an electrophilic addition, explain whether you would predict this as the product that is formed when HCN attacks the C=C double bond.

....

....

.... [1]

(c) Butenone also can react with HCN at the carbonyl group.



This reaction is reversible while the reaction in **(b)(ii)** is irreversible.

Which of the two products, the product in **(b)(ii)** or the product in **(c)**, would you expect to obtain after a long reaction time? Explain your answer.

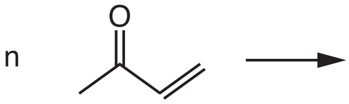
....

....

.... [1]

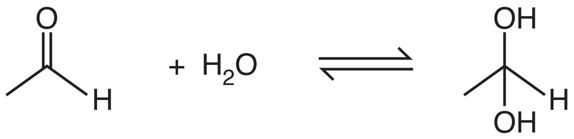
(d) Pure butenone polymerises spontaneously to form poly(butenone). In this process the carbonyl groups remain intact.

Complete the equation to show the formation of the polymer.



[2]

(e) The following equilibrium occurs when ethanal is dissolved in water.



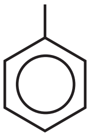
$\Delta G^{\ominus}$ for this reaction is $-0.282\,\text{kJ}\,\text{mol}^{-1}$.

Use the appropriate equation from the *Data Booklet* to calculate the equilibrium constant for the reaction.

K = ... [2]

[Total: 17]

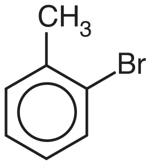
5 **(a)** Methylbenzene is shown.



Draw the mechanism by which methylbenzene can be prepared from benzene. Include the role of the catalyst.

[4]

(b) When methylbenzene reacts with bromine, the two major products are as shown.



A

B

(i) A student expected the ratio of **A**:**B** to be 2:1. Explain why this ratio might be expected.

....

.... [1]

(ii) Suggest why the actual ratio of **A**:**B** is less than 2:1.

....

.... [1]

(c) A method of forming benzoic acid starts from bromobenzene and involves the formation of a Grignard reagent.

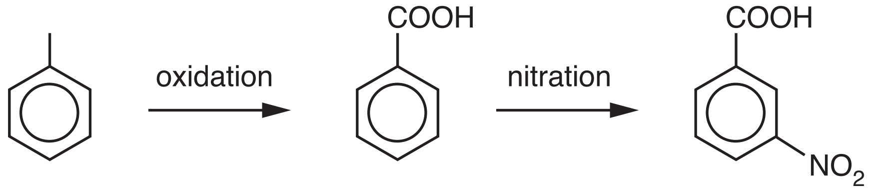
(i) Give the formula of the Grignard reagent.

.... [1]

(ii) What is reacted with the Grignard reagent to produce benzoic acid?

.... [1]

(d) Methylbenzene can be converted to 3-nitrobenzoic acid in two steps.



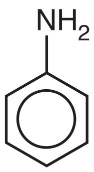
Explain why the oxidation is carried out before the nitration and not in the reverse order.

....

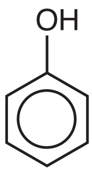
....

.... [2]

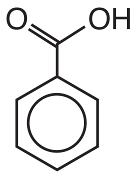
(e) A mixture contains the three compounds shown, dissolved in methylbenzene.



phenylamine



phenol



benzoic acid

- The solution is shaken with dilute hydrochloric acid and two layers form.
- One of the three compounds, **X**, reacts with the HC*l* and the product, **C**, is soluble in the aqueous layer.
- The aqueous layer is then separated. Base is added to this aqueous solution which causes **X** to be reformed. **X** is extracted by dissolving in fresh methylbenzene.

- The original methylbenzene solution now only contains the other two compounds, **Y** and **Z**.

- This methylbenzene solution is shaken with $NaHCO_3$(aq). Only one of the compounds, **Y**, reacts and the organic product, **D**, is soluble in the aqueous layer.
- This aqueous layer is then separated. Substance **T** is added which causes **Y** to be reformed. **Y** is extracted by dissolving in fresh methylbenzene.

- The original methylbenzene solution now only contains one of the compounds, **Z**.

Identify **X**, **Y** and **Z**.

Suggest the identity of **T**.

Draw the structures of **C** and **D**.

X = ...   **Y** = ...

Z = ...   **T** = ...

C	**D**

[5]

(f) The table shows the pK_a values for water, ethanol and phenol.

compound	pK_a
H_2O	14.0
C_2H_5OH	15.9
C_6H_5OH	10.0

(i) Explain the difference in acid strength of phenol and water.

....

....

.... [2]

(ii) Explain the difference in acid strength of ethanol and water.

....

.... [1]

[Total: 18]

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