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

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

4763402847

CHEMISTRY **9791/03**

Paper 3 Part B Written **May/June 2013**

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.
Electronic calculators may be used.
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	
2	
3	
4	
5	
Total	

This document consists of **17** printed pages and **3** blank pages.

DC (RW/CGW) 57705/4

UNIVERSITY of CAMBRIDGE International Examinations

[Turn over

1 The elements scandium to zinc in the Periodic Table make up the first row of the d-block elements.

(a) Why are these elements referred to as *d-block* elements?

.... [1]

(b) (i) Give the full ground state electronic configuration of an atom of zinc.

.... [1]

(ii) Explain why zinc is **not** a transition element.

....

.... [1]

(c) The graph in Fig. 1.1 shows the pattern of first ionisation energies for the elements sodium to zinc.

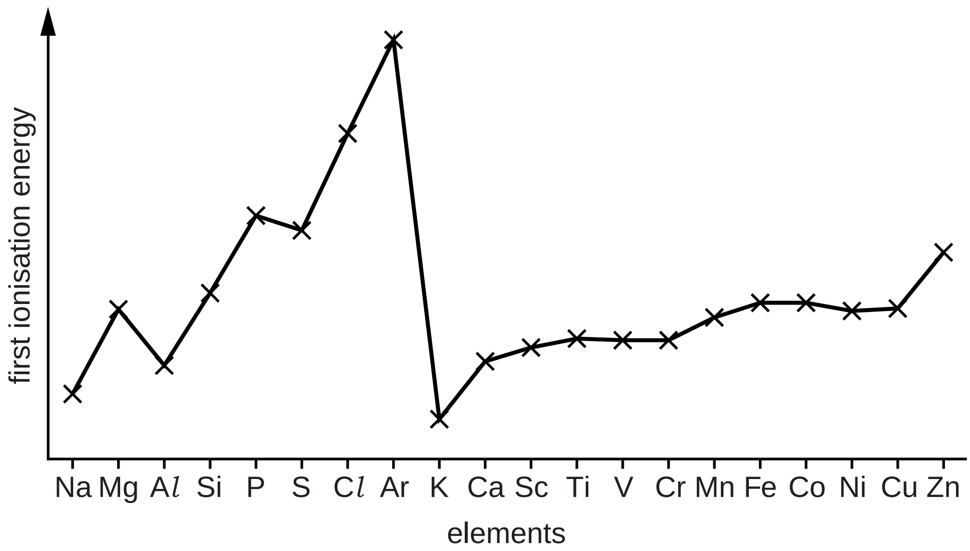


Fig. 1.1

(i) With reference to the graph in Fig. 1.1, explain the pattern of first ionisation energies across Period 3, Na to Ar.

....

....

....

....

....

.... [3]

For Examiner's Use

(ii) With reference to the graph in Fig. 1.1, explain why the first ionisation energies of the elements Sc to Cu are relatively constant with only a slight general increase.

....

....

....

.... [2]

(d) The crystal structures of the elements iron, copper and zinc are described, using the standard abbreviations, as BCC, CCP and HCP, respectively.

(i) What does the abbreviation CCP stand for?

.... [1]

(ii) In terms of layer structure representations, describe the HCP and CCP crystal structures.

HCP ....

CCP ....
[2]

(e) A chloride of a transition metal, *M*, has a unit cell consisting of a CCP framework of chloride anions, with the metal ions occupying half of the tetrahedral holes between the anions.

(i) What is meant by the term *unit cell*?

....

....

.... [2]

(ii) State, and explain in terms of the ratio of anions to tetrahedral holes, what the formula of this compound is.

formula ....

explanation ....

....

.... [2]

For Examiner's Use

(f) Cobalt(II) chloride exists in two forms, **A**, which is blue, and **B**, which is pink.

Addition of a small amount of either of these solids to water results in a pink solution in which the colour is due to the presence of a complex ion, **C**.

On addition of concentrated hydrochloric acid this solution turns blue as another complex ion, **D**, forms with a different shape to the complex ion **C**.

(i) Give the formulae of **A**, **B**, **C**, and **D**.

A ....

B ....

C ....

D .... [4]

(ii) Give the shape of, and bond angles in, the ion **C**.

shape ....

bond angle .... [2]

(iii) Write an equation to illustrate the ligand exchange reaction involved in the conversion of **C** to **D**.

.... [1]

(iv) State and explain why the ion **D** has a different shape to the ion **C**.

....

....

.... [1]

[Total: 23]

BLANK PAGE

2 *Aerozine 50* is a 50/50 mix of hydrazine, N_2H_4, and UDMH, $(CH_3)_2N_2H_2$. It is used as a rocket fuel, typically mixed with dinitrogen tetroxide, N_2O_4, as the oxidising agent.

For Examiner's Use

The equation for the reaction of the UDMH with dinitrogen tetroxide is given in equation 2.1 and relevant thermodynamic data is in Table 2.1.

equation 2.1 $(CH_3)_2N_2H_2(l) + 2N_2O_4(l) \longrightarrow 2CO_2(g) + 4H_2O(g) + 3N_2(g)$

Table 2.1

substance	$\Delta_f H^\ominus(298\,K) / kJ\,mol^{-1}$	$S^\ominus(298\,K) / J\,K^{-1}\,mol^{-1}$
$(CH_3)_2N_2H_2(l)$	83.3	304.7
$N_2O_4(l)$	9.1	304.4
$CO_2(g)$	–393.5	213.8
$H_2O(g)$	–241.8	188.8
$N_2(g)$	0.0	191.6

(a) Suggest an equation for the reaction between hydrazine, N_2H_4, and dinitrogen tetroxide, N_2O_4.

.... [1]

(b) Define the term *standard enthalpy change of formation*.

....

.... [2]

(c) (i) Calculate the enthalpy change, $\Delta_r H^\ominus(298\,K)$, for the reaction in equation 2.1, giving your answer to one decimal place.

$\Delta_r H^\ominus(298\,K)$ .... $kJ\,mol^{-1}$ [3]

(ii) The entropy change, $\Delta_r S^\ominus(298\,K)$, for the reaction in equation 2.1 is $+844.1\,J\,K^{-1}\,mol^{-1}$.

Explain, without calculation, why this entropy change has such a large, positive value.

....

....

.... [2]

For Examiner's Use

(iii) Calculate the free energy change, $\Delta_r G^{\ominus}(298\,K)$, for the reaction in equation 2.1, giving your answer to one decimal place.

$\Delta_r G^{\ominus}(298\,K)$ .... $kJ\,mol^{-1}$ [2]

(d) Pure UDMH, $(CH_3)_2N_2H_2$, can be used as an alternative to *Aerozine 50* in thruster rockets.

The total mass of propellant (UDMH and dinitrogen tetroxide, N_2O_4, together) used in the thruster rockets in the ascent stage of a lunar module was 244 kg.

Assume that the UDMH and dinitrogen tetroxide were mixed in the molar ratio 1:2.

(i) Calculate the mass of UDMH in the propellant mixture.

mass of UDMH = ... kg [1]

(ii) Calculate the total number of moles of gas produced from the complete reaction of this mass of UDMH with dinitrogen tetroxide, as in equation 2.1.

moles of gas = ... [2]

(iii) Calculate the total volume of product gases formed from the reaction of this mass of UDMH with dinitrogen tetroxide, as in equation 2.1, at a temperature of –10.0 °C and a pressure of 600 Pa.

Give your answer to three significant figures and **include the units**.

volume of gas = ... [3]

(e) Dinitrogen tetroxide, N_2O_4, exists in equilibrium with nitrogen dioxide, NO_2, which itself can be decomposed into nitrogen monoxide, NO, and oxygen, as shown in equation 2.2.

For Examiner's Use

equation 2.2 $$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

The rate equation for this thermal decomposition is as follows.

$$\text{rate} = k[NO_2]^2$$

The rate constant, *k*, for the thermal decomposition of nitrogen dioxide was measured at five different temperatures and the results were used to plot the graph in Fig. 2.1.

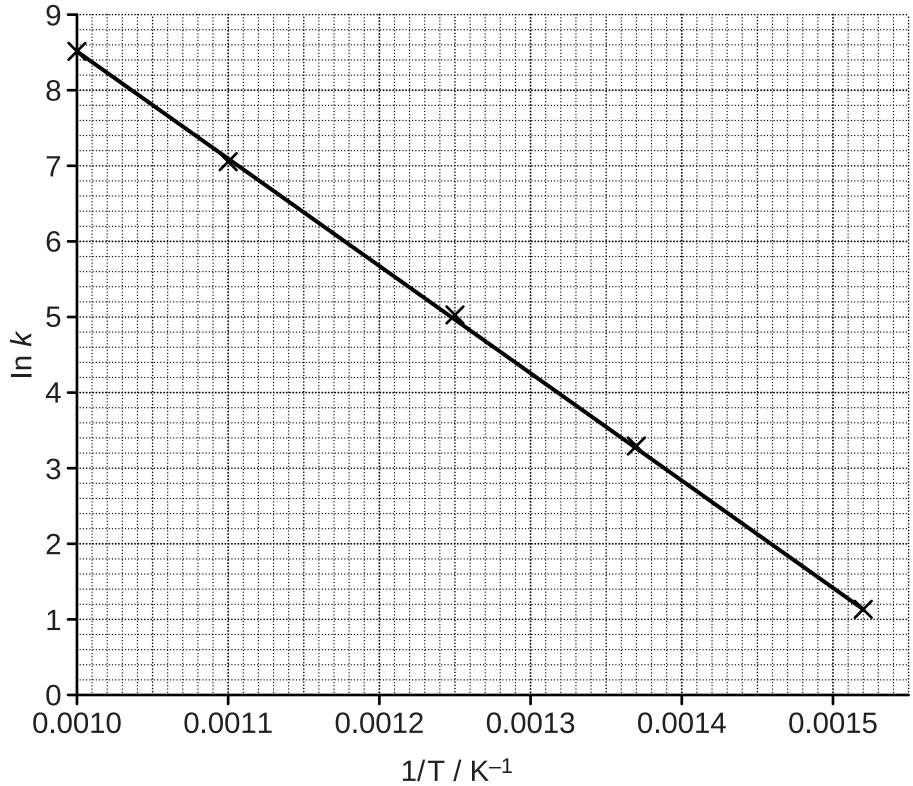


Fig. 2.1

(i) Equation 7 in the data booklet can be rewritten in the form $y = mx + c$, as follows.

$$\ln k = \frac{-E_a}{R}\frac{1}{T} + \ln A$$

Use the graph to calculate the activation energy, E_a, for the reaction in equation 2.2.

E_a = ... $kJ\,mol^{-1}$ [2]

For Examiner's Use

(ii) A vessel with a volume of 2.00 dm^3 is filled with 4.00 mol of NO_2 at a temperature of 650 K.

The rate constant, *k*, at this temperature is 3.16 $dm^3\,mol^{-1}\,s^{-1}$.

Calculate the initial rate of decomposition at this temperature for the reaction in equation 2.2 and **include the units**.

initial rate = ... [2]

(iii) A mechanism suggested for the thermal decomposition of nitrogen dioxide is shown.

step one $NO_2 + NO_2 \longrightarrow NO + NO_3$ *slow*

step two $NO_3 \longrightarrow NO + O_2$ *fast*

Explain whether or not this mechanism is consistent with the rate equation given.

....

....

.... [1]

[Total: 21]

For Examiner's Use

3 Halogenoalkanes react with sodium hydroxide in two different ways depending on the solvent, the temperature and the structure of the halogenoalkane.

(a) Under appropriate conditions (S)-(+)-2-bromobutane was reacted with sodium hydroxide to produce a mixture of three isomeric alkenes.

(i) State the type of reaction taking place.

.... [1]

(ii) State the conditions necessary to bring about this type of reaction.

....

.... [2]

(iii) Give the displayed formulae and names of the three alkenes formed.

[3]

(b) If (S)-(+)-2-bromobutane is hydrolysed with sodium hydroxide to form an alcohol then the reaction will proceed by a mixture of the S_N1 and S_N2 mechanisms.

(i) State the conditions necessary for the hydrolysis of (S)-(+)-2-bromobutane by sodium hydroxide.

....

.... [1]

(ii) Complete Fig. 3.1 to show the S_N1 mechanism of hydrolysis of (S)-(+)-2-bromobutane with sodium hydroxide. Include all necessary curly arrows, lone pairs and full or partial charges.

[4]

Fig. 3.1

(iii) Explain fully why one of the two mechanisms, S_N1 or S_N2, gives rise to an optically active product while the other mechanism gives an optically inactive product.

For Examiner's Use

....

....

....

....

....

....

....

....

.... [5]

(iv) Give the full name of the product formed by the S_N2 mechanism.

.... [1]

(c) A structural isomer of (S)-(+)-2-bromobutane undergoes hydrolysis almost exclusively by the S_N1 mechanism.

Identify this isomer and explain why the S_N1 mechanism is preferred over the S_N2 mechanism.

....

....

....

....

....

....

....

.... [3]

[Total: 20]

4 The use of methanol, CH_3OH, in fuel cells is the subject of considerable research. A commercial production of methanol involves a two step process.

For Examiner's Use

Step 1 production of hydrogen gas

equation 4.1 $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta_r H^{\ominus} = +206\,kJ\,mol^{-1}$

A temperature of 850 °C and pressure of 1500 kPa are used in this step.

Step 2 reaction of hydrogen and carbon monoxide to form methanol

equation 4.2 $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\Delta_r H^{\ominus} = -92\,kJ\,mol^{-1}$

A temperature of 300 °C and pressure of 7500 kPa are used in this step, with a catalyst of ZnO/CrO_3.

(a) **(i)** Write an expression for the equilibrium constant, K_p, for the reaction in equation **4.2**.

[1]

(ii) After the reaction shown in equation **4.2** had reached equilibrium, a mixture of gases was extracted. It contained 38.0 g of hydrogen, 462 g of carbon monoxide and 7200 g of methanol.

Calculate the mole fraction of each gas in the mixture.

mole fraction of hydrogen = ...

mole fraction of carbon monoxide = ...

mole fraction of methanol = ...
[2]

(iii) Use your values from **(a)(ii)** to calculate the value of the equilibrium constant, K_p, for the reaction shown in equation **4.2**.

K_p = ...[2]

(b) **(i)** Elevated temperatures are used in both steps, with the temperature used in step 1 being much higher than in step 2.

Explain why.

....

....

....

....

....

.... [3]

(ii) Pressures higher than atmospheric are used in both steps, with the pressure used in step 2 being much higher than in step 1.

Explain why.

....

....

....

....

....

.... [3]

For Examiner's Use

(c) In a direct methanol fuel cell, DMFC, methanol is oxidised at the anode.

For Examiner's Use

The protons produced migrate across the proton exchange membrane, PEM, to the cathode where oxygen is reduced to water.

The standard electrode potential of the oxygen cathode is +1.23 V.

(i) Write the half-equation for the reduction of oxygen to water in acidic conditions at the cathode.

.... [1]

(ii) The electrode potential for

$$6H^{+} + 6e^{-} + CO_2 \rightleftharpoons CH_3OH + H_2O$$

is +0.02 V.

Write the overall equation for the reaction taking place in the DMFC and calculate the standard cell potential.

equation ....

standard cell potential = ...V [2]

(d) One method for the construction of a DMFC involves electroplating a layer of platinum onto the surface of the proton exchange membrane, PEM. The electrolyte for this process consists of a solution of tetraammineplatinum(II) chloride, $Pt(NH_3)_4Cl_2$, and the PEM is the cathode in the electrolytic cell.

For Examiner's Use

(i) State the shape and bond angle of the tetraammineplatinum(II) ion, $[Pt(NH_3)_4]^{2+}$.

shape ....

bond angle ....[1]

(ii) Suggest the half-equation for the cathode reaction that deposits platinum on the PEM.

....[1]

(e) In one such preparation a PEM with a surface area of 25 cm^2 was immersed in an electrolyte bath and a current of 3.5×10^{-3} A cm^{-2} was passed for 95 minutes.

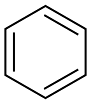
Calculate the mass of platinum deposited onto the surface of the PEM.

[3]

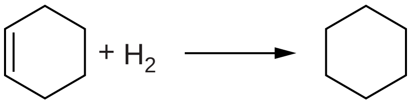
[Total: 19]

For Examiner's Use

5 Kekulé proposed the following structure for benzene.



(a) The enthalpy of hydrogenation of cyclohexene, as shown, is –121 kJ mol^{-1}.



Based on this value for cyclohexene it is possible to calculate that the enthalpy of hydrogenation of benzene, based on Kekulé's structure, should be –363 kJ mol^{-1}.

Explain the difference between this calculated value and the actual value for the enthalpy of hydrogenation of benzene of –209 kJ mol^{-1}.

....

....

....

....[2]

(b) Benzene undergoes electrophilic substitution reactions.

(i) What is meant by the term *electrophile*?

....

....[1]

(ii) Nitrobenzene, $C_6H_5NO_2$, can be formed from benzene. Give the reagents and conditions necessary for this process and identify the electrophile.

reagents ....

conditions ....

electrophile ....[3]

For Examiner's Use

(c) Fig. 5.1 shows a reaction sequence starting from nitrobenzene.

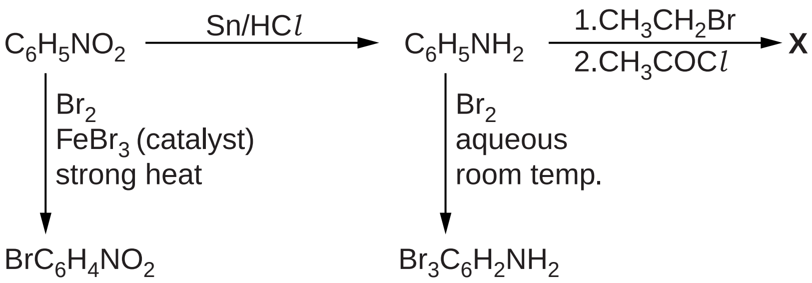


Fig. 5.1

(i) Explain why the bromination of phenylamine, $C_6H_5NH_2$, is possible with the mild conditions shown in Fig. 5.1.

....

....

....

....

....

.... [3]

(ii) Give the equation for the reaction between nitrobenzene and the reducing mixture, Sn/HC*l*. You should use [H] to represent the reducing agent in your equation.

.... [1]

(d) **(i)** Compound **X**, in Fig. 5.1, has the composition by mass:

carbon, 73.59%; hydrogen, 8.03%; nitrogen, 8.58%; oxygen, 9.80%.

It has a relative molecular mass of 163.

Calculate the molecular formula of **X**.

[3]

(ii) The [1]H NMR of **X** has a complex signal between 7.00 ppm and 7.55 ppm because of the five protons on its benzene ring, and three other signals as partly detailed in Table 5.1.

Table 5.1

δ / ppm	integration ratio	splitting pattern
1.12	3	
1.83		singlet
3.75	2	

Complete Table 5.1, give the structure of **X**, and explain the origin of the [1]H NMR signals.

....

....

....

....

....

....

....

....

....

.... [4]

[Total: 17]

BLANK PAGE

BLANK PAGE