

CANDIDATE
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CHEMISTRY

Paper 3 Part B Written

9791/03

May/June 2014

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 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	
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Total	

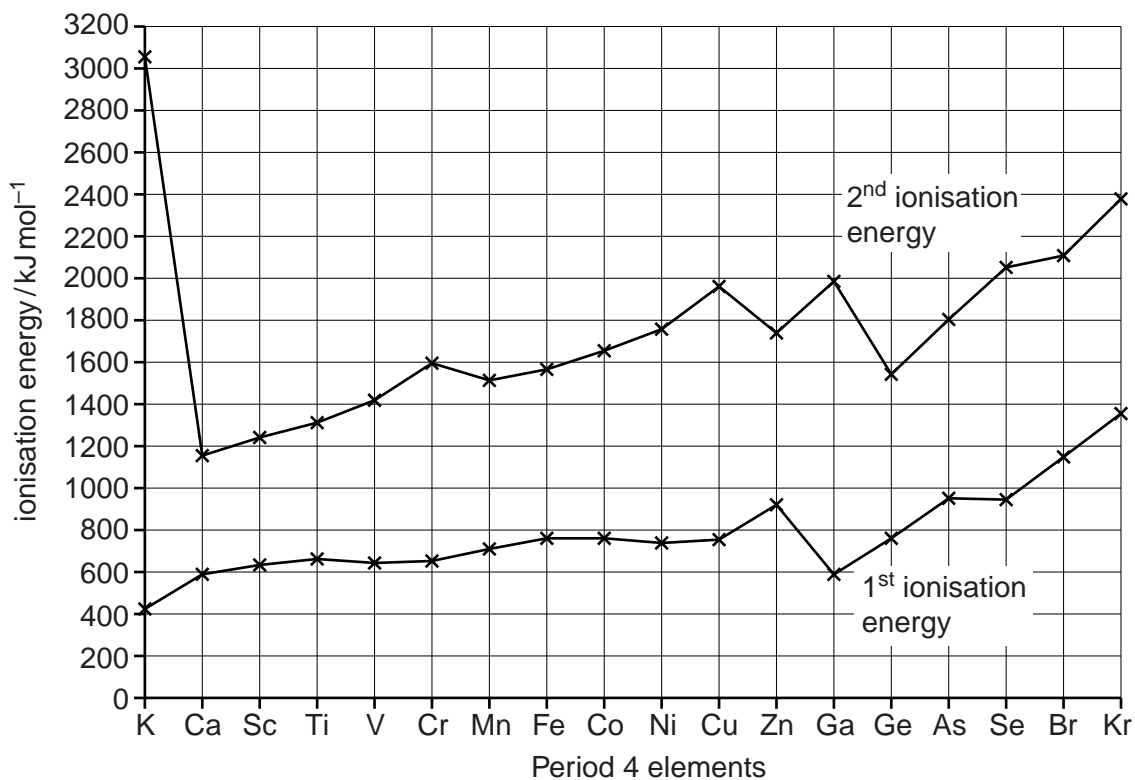
This document consists of **16** printed pages.

- 1 (a) Complete the full ground state electronic configurations for each of the following species.

Mn [Ar]

Fe²⁺ [Ar] [2]

- (b) The patterns of the first and second ionisation energies across Period 4 are shown.



- (i) Explain what is meant by the term *first ionisation energy*.

.....

 [3]

- (ii) Explain why the first ionisation energies of the elements Sc to Cu are relatively constant.

.....

 [3]

- (iii) Write the equation for the second ionisation energy of chromium.

..... [1]

- (iv) Explain why the **increase** between first and second ionisation energies for both Cr and Cu is bigger than for the rest of the transition elements shown.

.....
.....
.....
.....[3]

- (c) One of the key characteristics of transition elements is their ability to exhibit a range of different oxidation states.

- (i) Describe and explain the pattern of **maximum** oxidation states for the elements from Sc to Zn.

.....
.....
.....
.....
.....[3]

- (ii) Suggest the formula and charge of the ferrate(VI) oxy-anion.

.....[1]

- (d) Alfred Werner was awarded the Nobel Prize in 1913 for his work on complexes of cobalt with ammonia.

The compounds with the formula $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ exist in four isomeric forms, **W**, **X**, **Y** and **Z**.

W reacts with an aqueous solution of silver nitrate in a 1:3 mole ratio, forming a white precipitate.

X reacts with an aqueous solution of silver nitrate in a 1:2 mole ratio, forming a white precipitate.

Y and **Z** both react with aqueous silver nitrate in a 1:1 mole ratio, forming white precipitates in both cases.

- (i) Explain the conclusion that can be drawn from the different mole ratios of reaction with aqueous silver nitrate.

.....

[1]

- (ii) Give the formulae of the complex ions present in each of **W** and **X**.

W **X**[2]

- (iii) Name the type of isomerism shown by **W** and **X**.

.....[1]

- (iv) Name the type of isomerism shown by **Y** and **Z**.

.....[1]

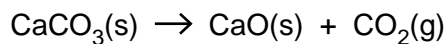
- (v) Draw three-dimensional diagrams of the structures of the complexes present in **Y** and **Z**.

[1]

[Total: 22]

Question 2 begins on page 6.

2 Quicklime is manufactured from limestone by the reaction shown.



Thermodynamic data for these compounds, at 298 K, is given in the table.

compound	standard entropy / $\text{JK}^{-1} \text{mol}^{-1}$	standard enthalpy change of formation / kJ mol^{-1}
$\text{CaCO}_3(\text{s})$	to be calculated in (a)(iii)	-1206.9
$\text{CaO}(\text{s})$	39.7	to be calculated in (b)(ii)
$\text{CO}_2(\text{g})$	213.6	-393.5

(a) (i) What type of reaction is involved in the conversion of limestone to quicklime?

.....[1]

(ii) Explain why the value for the standard entropy of CO_2 is greater than the value for CaO .

.....

.....

.....[1]

(iii) The standard entropy change of the system, $\Delta S^\ominus(298 \text{ K})$, for the conversion of limestone to quicklime is $+160.4 \text{ JK}^{-1} \text{ mol}^{-1}$.

Calculate the standard entropy of $\text{CaCO}_3(\text{s})$.
Give your answer to one decimal place.

$S^\ominus(298 \text{ K}) = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1}$ [2]

(b) (i) State Hess's law.

.....

.....

.....[2]

- (ii) The standard enthalpy change of reaction, $\Delta_r H^\ominus(298\text{ K})$, for the conversion of limestone to quicklime is $+178.3\text{ kJ mol}^{-1}$.

Calculate the standard enthalpy change of formation, $\Delta_f H^\ominus(298\text{ K})$, for CaO(s) . Give your answer to one decimal place and include a sign in your answer.

$$\Delta_f H^\ominus \text{CaO(s)}(298\text{ K}) = \dots\dots\dots \text{kJ mol}^{-1} \text{ [2]}$$

- (iii) Calculate the entropy change of the surroundings, at 298 K, during the conversion of limestone to quicklime and hence calculate the total entropy change of the reaction. Give your answers to one decimal place and include signs in your answers.

$$\Delta S_{\text{surroundings}}^\ominus(298\text{ K}) = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1}$$

$$\Delta S_{\text{total}}^\ominus(298\text{ K}) = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1} \text{ [3]}$$

- (iv) Calculate the temperature at which $\Delta S_{\text{total}}^\ominus$ is zero and explain the significance of this temperature. Assume that ΔH^\ominus and ΔS^\ominus are independent of temperature.

$$\text{temperature} = \dots\dots\dots \text{K}$$

explanation

.....

.....[3]

(c) A sample of calcium carbonate, CaCO_3 , was heated in a sealed container at 1200°C until no further change occurred.

(i) Give the expression for the equilibrium constant, K_p , for the reaction.

$$K_p =$$

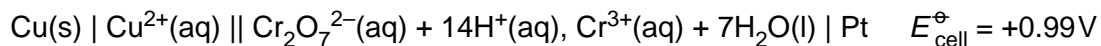
[1]

(ii) Using equations from the *Data Booklet*, and appropriate information from **(a)(iii)** and **(b)(ii)**, calculate the value of the equilibrium constant, K_p , for the reaction. Assume that $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ are independent of temperature and pressure.

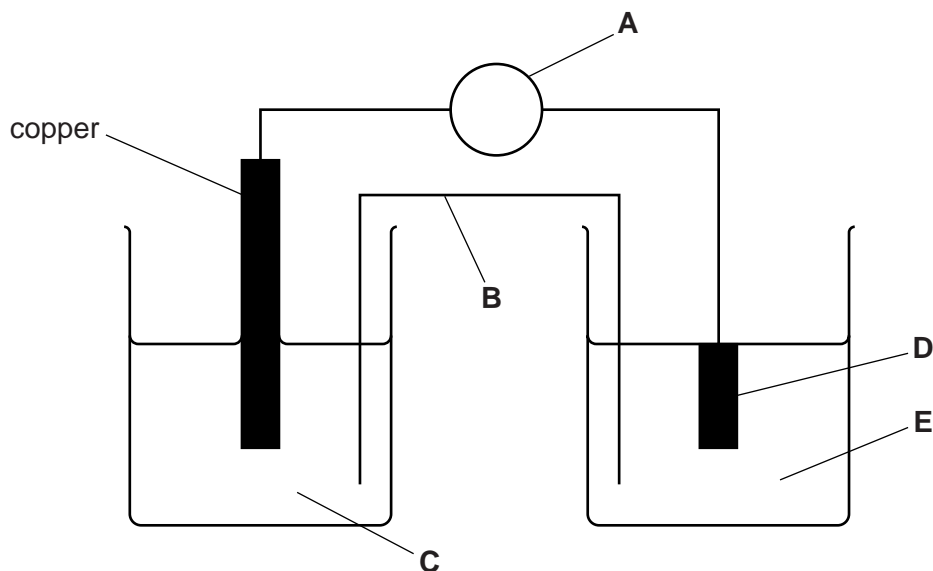
$$K_p = \dots\dots\dots [4]$$

[Total: 19]

- 3 An electrochemical cell was set up as illustrated by the cell diagram.



- (a) Some of the labels on a diagram of this electrochemical cell have been replaced with the letters **A – E**.



- (i) Name the parts of the cell labelled **A** to **E**.
Include any detail necessary to allow the cell to be used to measure the standard cell potential, $E_{\text{cell}}^{\ominus}$.

A

B

C

D

E

.....[6]

- (ii) Write the half-equations for the two half-cells that make up the cell.

.....

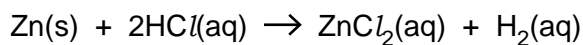
.....[2]

- (iii) Write the overall equation for the reaction that occurs in the cell when a current is allowed to flow.

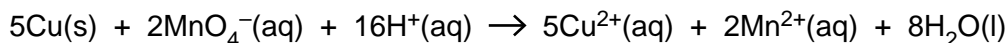
.....[1]

- (b) A sample of finely ground copper was contaminated with zinc powder.

Treatment of the sample with excess hydrochloric acid produced 126 cm^3 of hydrogen gas, measured at 303 K and 10^5 Pa , by the reaction shown.



The remaining copper was then reacted with acidified potassium manganate(VII).



It was found that $4.88 \times 10^{-3}\text{ mol}$ of potassium manganate(VII) was required for complete oxidation of the copper.

- (i) Calculate the mass of zinc present in the sample.
Give your answer to three significant figures.

mass of Zn = g [2]

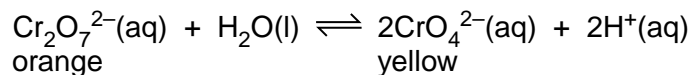
- (ii) Calculate the mass of copper present in the sample.

mass of Cu = g [2]

- (iii) Calculate the percentage by mass of copper in the original sample.

percentage by mass of Cu = % [1]

(c) In aqueous solution, dichromate(VI) ions exist in equilibrium with chromate(VI) ions.



- (i) Explain why the solution turns from orange to yellow on the addition of aqueous sodium hydroxide.

.....

[2]

- (ii) Following the addition of aqueous sodium hydroxide, the solution was cooled. This caused the colour of the solution to change from yellow back to orange.

Use Le Chatelier's principle to state and explain what you can conclude about the enthalpy change of the forward reaction.

.....

[1]

- (iii) Barium chromate(VI), BaCrO_4 , is sparingly soluble, while barium dichromate(VI), BaCr_2O_7 , is soluble.

State and explain the effect of adding barium nitrate solution, $\text{Ba}(\text{NO}_3)_2(\text{aq})$, to the original equilibrium mixture of dichromate(VI) ions and chromate(VI) ions.

Your answer should refer to the effect on equilibrium position, K_c and pH.

.....

[3]

[Total: 20]

- 4 The enantiomers of a compound with a chiral centre are normally described as having identical physical and chemical properties, apart from their effect on the plane of plane polarised light.

In many cases the enantiomers also have different odours. For example, (*R*)-(+)-2-methylbutan-1-ol has a fermented, fatty odour, while (*S*)-(-)-2-methylbutan-1-ol smells fresh.

- (a) Explain what is meant by each of the terms *enantiomers* and *chiral centre*.

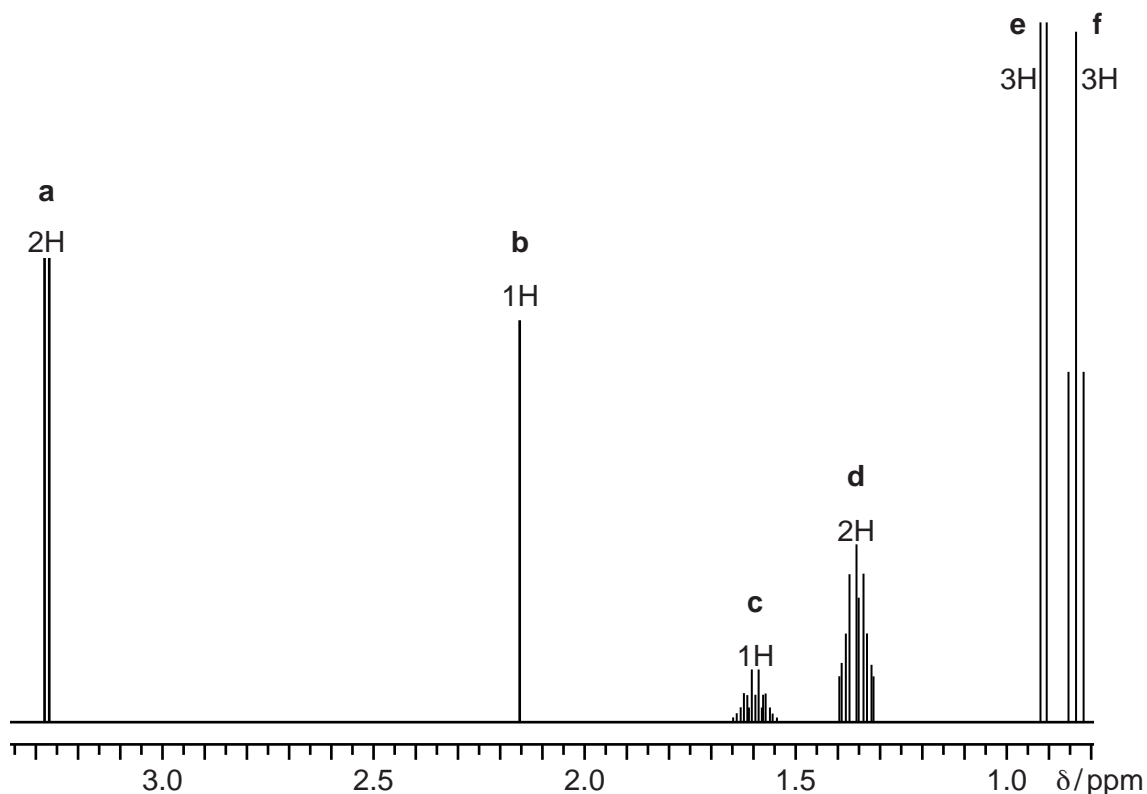
enantiomers

.....

chiral centre

.....[2]

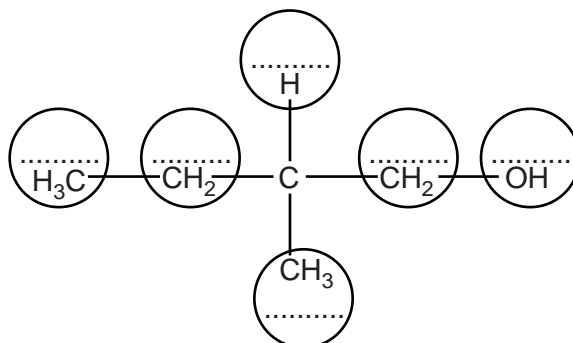
- (b) The diagram of the proton NMR spectrum of 2-methylbutan-1-ol has the signals labelled a–f for ease of reference, and the signal integrations are given.



- (i) Give the relative intensities of the peaks in signal f.

.....[1]

- (ii) Label the structure of 2-methylbutan-1-ol, with the letters **a–f**, to indicate which protons are responsible for each signal in the spectrum.



[3]

- (c) Oxidation of 2-methylbutan-1-ol, by acidified potassium dichromate(VI) with immediate distillation, produces a compound, **P**.

P turns acidified potassium dichromate(VI) from orange to green and produces **Q**.

Q effervesces on addition of sodium carbonate solution.

A pure enantiomer of **P**, when reacted with hydrogen cyanide, produces **R** as a mixture of optical isomers.

R forms **S**, with no change in functional group level, on reaction with dilute hydrochloric acid.

- (i) Give the **displayed** formula and name of **P**. Ignore stereochemistry.

name[2]

- (ii) State the type of reaction involved in the conversion of **P** to **Q**.

.....[1]

- (iii) Identify **Q** and write a balanced equation, using molecular formulae, for its reaction with sodium carbonate.

identity of **Q**

equation[2]

- (iv) Give the structural formula of **R**, name the mechanism by which it is formed from **P** and explain why it forms as a mixture of optical isomers.

structural formula

name of mechanism

explanation

.....[4]

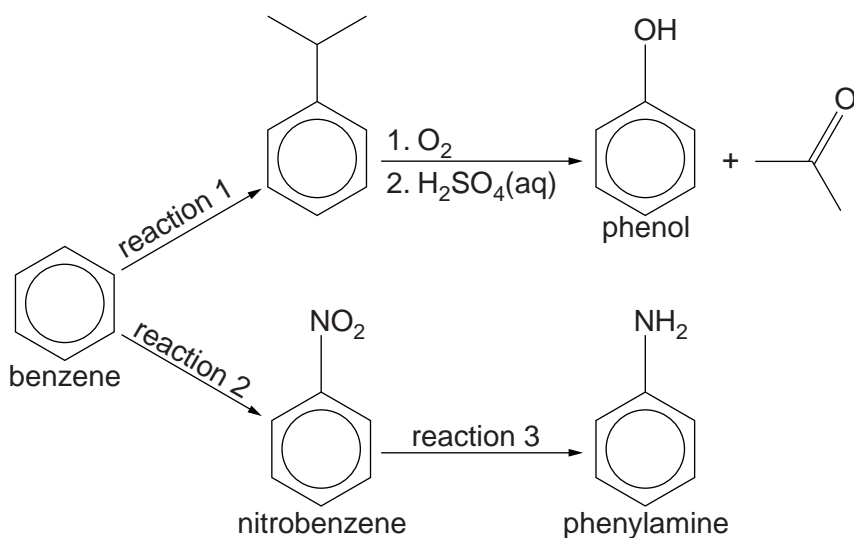
- (v) Identify **S** and state the type of reaction involved in its formation from **R**.

identity of **S**

type of reaction.....[2]

[Total: 17]

5 Some reactions starting from benzene, C_6H_6 , are shown.



(a) (i) Reactions 1 and 2 both proceed by electrophilic substitution.

Give the names of the reagent(s) needed, catalyst used and the identity of the electrophile in each case.

Reaction 1

reagent(s)

catalyst

electrophile

Reaction 2

reagent(s)

catalyst

electrophile[6]

(ii) For reaction 3, state the type of reaction undergone by nitrobenzene and the reagents needed.

reaction type

reagents[2]

(b) Phenol reacts readily with bromine water at room temperature, whereas nitrobenzene does not react with bromine water under these conditions.

(i) State what would be observed on addition of bromine water to phenol until in excess.

.....
 [2]

(ii) Give the equation for the reaction between excess bromine and phenol.

..... [2]

(iii) Explain why phenol is brominated under these conditions whereas nitrobenzene is not.

.....

 [4]

(c) The pK_a for phenol is about 10 while the value for ethanol is about 16.

Explain the relative magnitudes of these values.

.....

 [2]

(d) (i) Write an equation for the reaction of phenylamine with hydrochloric acid.

..... [1]

(ii) State and explain the relative basicities of ammonia, ethylamine and phenylamine.

.....

 [3]

[Total: 22]

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