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CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

May/June 2018

2 hours

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 use 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.

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

Answer **all** the questions in the spaces provided.

- 1 Silicon tetrachloride, SiCl_4 , is formed when silicon reacts with chlorine under suitable conditions. It is a colourless liquid with a low boiling point.

(a) Explain why SiCl_4 has a low boiling point.

.....

 [2]

(b) SiCl_4 reacts with water to produce an acidic solution.

(i) Write an equation for this reaction.

..... [1]

(ii) Describe **two** visual observations when silicon tetrachloride is added drop by drop to a small amount of water.

1

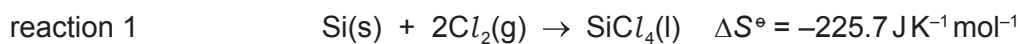
2 [2]

(iii) A sample of 0.8505 g of SiCl_4 is added to 800 cm³ of water. All of the soluble acidic product is dissolved in the water.

Calculate the pH of the solution obtained.

pH = [3]

- (c) (i) Silicon tetrachloride can be prepared according to reaction 1.



standard entropy of silicon, $S^\circ \text{ Si(s)}$	$18.7 \text{ JK}^{-1} \text{ mol}^{-1}$
standard entropy of silicon tetrachloride, $S^\circ \text{ SiCl}_4(\text{l})$	$239.0 \text{ JK}^{-1} \text{ mol}^{-1}$

Calculate the standard entropy of chlorine, $S^\circ \text{ Cl}_2(\text{g})$. Show all your working.

$$S^\circ \text{ Cl}_2(\text{g}) = \dots\dots\dots \text{ JK}^{-1} \text{ mol}^{-1} \quad [2]$$

- (ii) Explain why the entropy change for reaction 1 is negative.

.....
 [1]

- (d) The standard enthalpy change of formation of silicon tetrachloride, $\Delta H_f^\circ \text{ SiCl}_4(\text{l})$, is -640 kJ mol^{-1} .

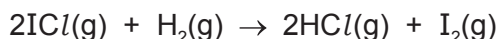
Reaction 1 is spontaneous at lower temperatures, but it is not spontaneous at very high temperatures.

Calculate the temperature above which reaction 1 is **not** spontaneous.

$$\text{temperature} = \dots\dots\dots \text{ K} \quad [2]$$

[Total: 13]

- 2 Iodine monochloride, ICl , is a yellow-brown gas. It reacts with hydrogen gas under certain conditions as shown.



Experiments are performed using different starting concentrations of ICl and H_2 . The initial rate of each reaction is measured. The following results are obtained.

experiment	$[\text{ICl}]/\text{mol dm}^{-3}$	$[\text{H}_2]/\text{mol dm}^{-3}$	relative rate of reaction
1	4.00×10^{-3}	4.00×10^{-3}	1.00
2	4.00×10^{-3}	7.00×10^{-3}	1.75
3	4.00×10^{-3}	1.00×10^{-2}	2.50
4	5.00×10^{-3}	8.00×10^{-3}	2.50
5	7.00×10^{-3}	8.00×10^{-3}	3.50

- (a) Identify a change, taking place in the reaction mixture, that would enable measurements of the rate of this reaction to be made.

..... [1]

- (b) Use the data in the table to show that the reaction is first order with respect to $\text{H}_2(\text{g})$.

.....

 [1]

- (c) Use the data in the table to show that the reaction is first order with respect to $\text{ICl}(\text{g})$.

.....

 [1]

- (d) Complete the rate equation for the reaction between $\text{ICl}(\text{g})$ and $\text{H}_2(\text{g})$.

rate = [1]

(e) Use experiment 3 to calculate a numerical value for the rate constant, k .

$k = \dots\dots\dots$ [1]

(f) The reaction $2\text{ICl}(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + \text{I}_2(\text{g})$ is first order with respect to $\text{ICl}(\text{g})$ and first order with respect to $\text{H}_2(\text{g})$.

Suggest a mechanism for this reaction. You should assume

- the mechanism has two steps,
- the first step is much slower than the second step.

first step $\dots\dots\dots \rightarrow \dots\dots\dots$

second step $\dots\dots\dots \rightarrow \dots\dots\dots$

[2]

(g) An alternative method is used to show that the reaction is first order with respect to $\text{H}_2(\text{g})$. This method uses a large excess of $\text{ICl}(\text{g})$ and measures how the concentration of $\text{H}_2(\text{g})$ varies with time.

(i) Describe two ways of using these results to show the reaction is first order with respect to $\text{H}_2(\text{g})$ concentration.

$\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$
 $\dots\dots\dots$ [3]

(ii) Explain the reason for using a large excess of $\text{ICl}(\text{g})$.

$\dots\dots\dots$
 $\dots\dots\dots$ [1]

(h) A chemical reaction may be speeded up by the presence of a catalyst.

Explain why a catalyst increases the rate of a chemical reaction.

$\dots\dots\dots$
 $\dots\dots\dots$ [1]

[Total: 12]

- 3 (a) Complete the table by predicting the identity of the substance liberated at each electrode during electrolysis with inert electrodes.

electrolyte	substance liberated at the anode	substance liberated at the cathode
NaOH(aq)		
dilute $\text{CuCl}_2(\text{aq})$		
concentrated $\text{MgCl}_2(\text{aq})$		

[3]

- (b) (i) The electrolysis of molten ZnBr_2 is a redox process.

Identify the ion that is oxidised and the ion that is reduced.

Use ionic half-equations to explain your answer.

.....

.....

.....

.....

.....

..... [3]

- (ii) Describe **one** visual observation that would be made during this electrolysis.

..... [1]

- (c) Dilute sulfuric acid is electrolysed for 50.0 minutes using inert electrodes and a current of 1.20A. A different gas is collected above each electrode. The volumes of the two gases are measured under room conditions.

Calculate the maximum volume of gas that could be collected at the **cathode**.

volume = cm^3 [3]

[Total: 10]

4 (a) (i) Write an equation, including state symbols, for the reaction that takes place when a sample of anhydrous calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is heated strongly in a test-tube.

..... [2]

(ii) Describe what will be seen during this reaction.

.....
.....
..... [2]

(b) Describe and explain how the solubility of the Group 2 sulfates varies down the group.

.....
.....
.....
.....
.....
.....
.....
..... [4]

[Total: 8]

- 5 Cobalt is a transition element with atomic number 27. Cobalt forms ions with charges of +2 and +3. Both these ions form complexes.

(a) Complete the electronic configurations of a Co atom and a Co^{2+} ion.

Co atom $1s^2 2s^2 2p^6$

Co^{2+} ion $1s^2 2s^2 2p^6$

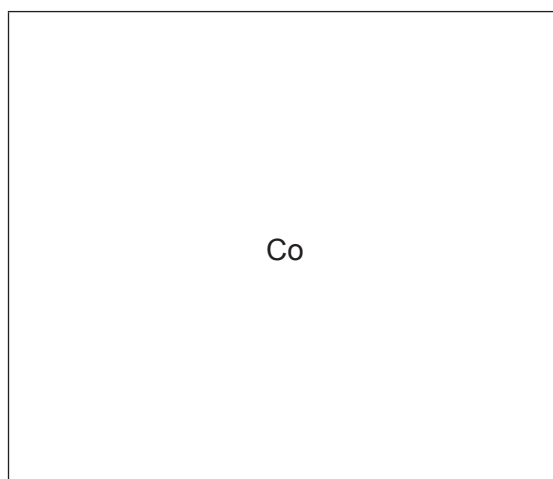
[2]

(b) One Co^{2+} ion can form a tetrahedral complex ion with four Cl^- ions. This complex is blue.

(i) What is meant by the term *complex ion*?

.....
 [1]

(ii) Draw the tetrahedral complex ion formed by one Co^{2+} ion with four Cl^- ions. Your drawing should clearly show three-dimensional shape, and should include the overall charge on the ion.



[2]

(iii) Explain why many transition metal complexes are coloured.

.....

 [3]

(iv) Using ideas from your answer to (iii) suggest why the colour of the complex formed by one Co^{2+} ion with four Cl^- ions is **blue**.

.....
 [1]

- (c) Describe the colour change that occurs when water is added to blue crystals of the cobalt(II)-chloride complex. Name the type of reaction responsible for this colour change.

colour change

type of reaction

[2]

- (d) $\text{Co}^{2+}(\text{aq})$ can be oxidised to $\text{Co}^{3+}(\text{aq})$.

- (i) Use the *Data Booklet* to suggest a suitable oxidising agent for this reaction.

..... [1]

- (ii) Calculate the $E_{\text{cell}}^{\ominus}$ of this reaction.

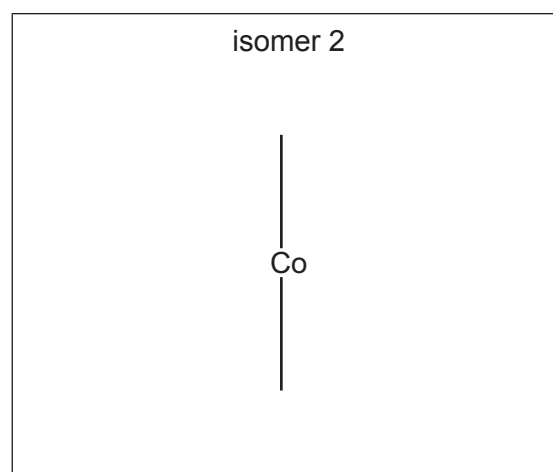
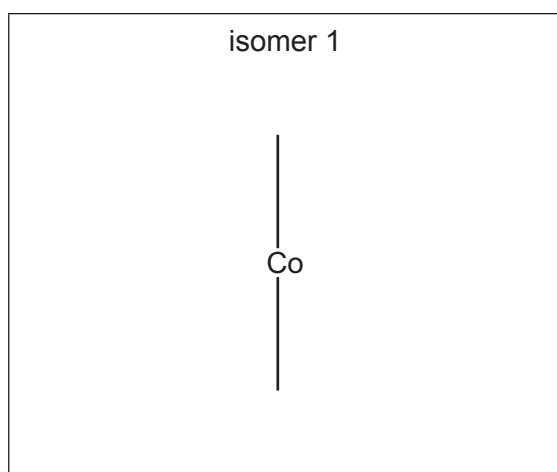
$$E_{\text{cell}}^{\ominus} = \dots\dots\dots \text{V} \quad [1]$$

- (iii) Write an equation for the reaction between Co^{2+} and the oxidising agent you chose in (d)(i).

..... [1]

- (e) Cobalt(III) forms two isomeric octahedral complexes with the formula $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$. The NO_2^- ion is monodentate.

Complete the diagrams to show the three-dimensional structures of the two isomers and suggest the type of isomerism shown here.



type of isomerism

[3]

[Total: 17]

6 Phenol is an important industrial chemical used in the manufacture of dyestuff and other substances.

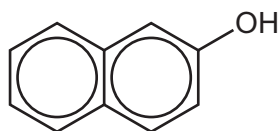
- (a) Suggest **two** different substances that react with phenol to produce potassium phenoxide, $C_6H_5O^-K^+$. Identify the second product formed in each case.

substance second product

substance second product

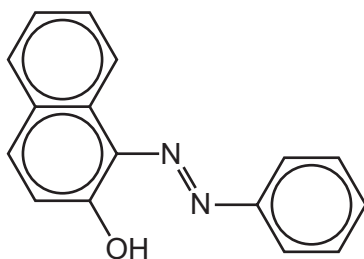
[3]

- (b)



2-naphthol

2-naphthol can show similar properties to phenol. It can be used to produce Sudan I, an orange coloured dyestuff.



Sudan I

- (i) On the diagram of Sudan I above **circle** the bond or bonds that make this substance a dyestuff. [1]
- (ii) Describe how Sudan I can be made using phenylamine and 2-naphthol as the organic starting materials.

.....

.....

.....

.....

.....

.....

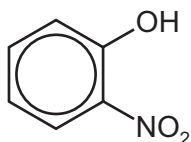
.....

.....

.....

..... [3]

(c) Phenol can be used to make 2-nitrophenol.



2-nitrophenol

The nitration reaction of phenol to form 2-nitrophenol shows that phenol is more reactive than benzene.

(i) Describe the conditions used for the nitration of phenol.

Explain how these conditions show phenol to be more reactive than benzene.

conditions

explanation

.....

.....

[2]

(ii) Suggest why phenol is more reactive than benzene.

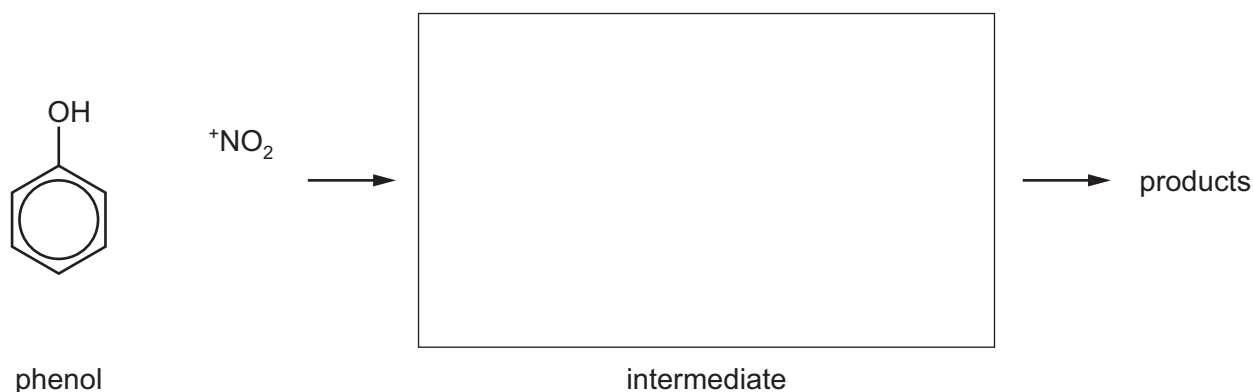
.....

.....

..... [1]

(iii) Complete the mechanism for the nitration of phenol to form 2-nitrophenol. You should assume that the mechanism is the same as that for the nitration of benzene.

- Include all relevant charges and curly arrows to show the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.



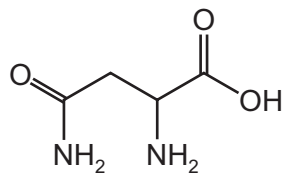
[3]

(iv) Name the isomer of 2-nitrophenol which is also a major product of this reaction.

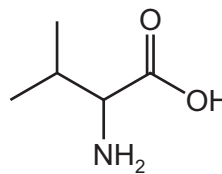
..... [1]

[Total: 14]

7 Asparagine and valine are two naturally occurring amino acids.



asparagine



valine

(a) Give the molecular formula of asparagine.

..... [1]

(b) Name **all** of the functional groups in an asparagine molecule.

..... [2]

(c) Draw the structure of the dipeptide formed by valine and asparagine.

The peptide bond should be shown displayed and should be clearly labelled.

[2]

(d) A solution of valine in water acts as a buffer solution.

(i) Explain what is meant by a *buffer solution*.

.....

 [2]

(ii) Write **two** equations to explain how valine can act as a buffer. Use the formula $\text{H}_2\text{NCH(R)CO}_2\text{H}$ for valine in your equations.

.....
 [2]

(e) Each valine molecule has one chiral carbon atom.

Draw three-dimensional diagrams to show the two optical isomers of valine.
The $(\text{CH}_3)_2\text{CH}$ group can be represented as R.

[2]

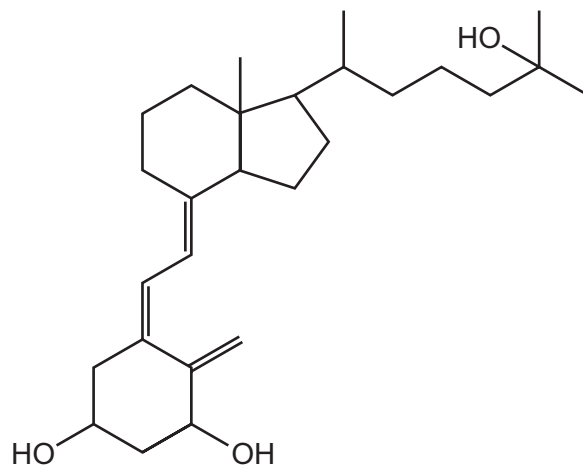
(f) Asparagine is hydrolysed when heated with aqueous sulfuric acid.

Write an equation for this reaction.

..... [2]

[Total: 13]

- 8 Calcitriol is a steroid hormone found in human blood.



calcitriol

- (a) Give the number of primary, secondary and tertiary alcohol groups in one molecule of calcitriol.

primary secondary tertiary [1]

- (b) Give the number of chiral carbon atoms in one molecule of calcitriol.

..... [1]

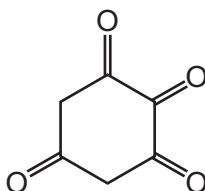
- (c) Calcitriol shows geometrical isomerism.

Give the number of geometrical isomers of calcitriol, including calcitriol.

..... [1]

- (d) A sample of calcitriol is treated with an excess of hot, concentrated, acidified potassium manganate(VII). There are three different carbon-containing products of this reaction.

One of these three products, **X**, is shown.



X

- (i) Predict the number of peaks in the carbon-13 NMR spectrum of **X**.

..... [1]

- (ii) For the carbon-13 NMR spectrum of **X**, state the expected chemical shift ranges (δ) of the peaks predicted in (i) and the number of peaks in each range.

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

- (iii) Predict the number of peaks this compound would show in its proton NMR spectrum.

..... [1]

- (iv) For each of the peaks in the proton NMR spectrum you have identified in (iii) give the expected splitting pattern. Explain your reasoning.

.....
.....
..... [2]

- (e) In addition to the product shown in (d), two other carbon-containing products are formed when a sample of calcitriol is treated with an excess of hot, concentrated, acidified potassium manganate(VII).

- (i) Of these two other carbon-containing products, identify the product with the **smaller** molecular mass. Explain how this product is formed.

.....
.....
.....
..... [2]

- (ii) Of these two other carbon-containing products, identify the product with the **larger** molecular mass by drawing its skeletal formula in the space below.

[1]

[Total: 13]

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