Cambridge Pre-U

Cambridge International Examinations
Cambridge Pre-U Certificate

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

CHEMISTRY (PRINCIPAL) **9791/03**

Paper 3 Part B Written **May/June 2018**

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	
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Total	

This syllabus is approved 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 (LEG/FC) 145237/5

CAMBRIDGE International Examinations

[Turn over

1 Benzene is more stable than ethene. It undergoes a range of different reactions.

(a) By describing the π bonding in benzene, explain why it is less reactive than ethene.

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.....

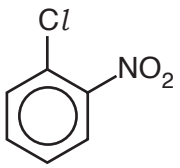
.....[4]

(b) Draw the mechanism for the reaction between chlorine and nitrobenzene, in the presence of $AlCl_3$, to form the monochlorinated product.

Include the equation for the formation of the electrophile.

[4]

(c) Nitration of chlorobenzene gives two major products, **A** and **B**.



A

B

(i) Suggest the reagents required for the nitration of chlorobenzene.

.....[1]

(ii) Explain why **A** and **B** are the two major products formed.

.....[1]

(iii) Suggest why **B** is formed in a greater proportion than **A**.

.....

.....[1]

(d) Cycloocta-1,3,5,7-tetraene, COT, has the molecular formula C_8H_8.

(i) Draw the skeletal formula of COT.

[1]

(ii) COT, unlike benzene, is not aromatic.

Comment on the relative lengths of bonds between carbon atoms in COT compared to those in benzene.

.....

.....

.....

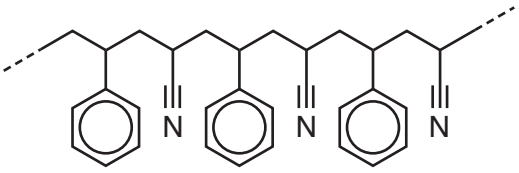
.....[2]

(iii) Draw the mechanism for the electrophilic addition of bromine to COT to form $C_8H_8Br_2$.

[4]

(e) Styrene acrylonitrile, SAN, is a copolymer formed by the addition polymerisation of two different alkenes.

Part of the SAN polymer is shown.



Draw the structures of the two monomers that react to form SAN.

[2]

[Total: 20]

2 When ethanoic acid, ethanol and ethyl ethanoate are mixed together in the presence of dilute hydrochloric acid, the following equilibrium is established.

$$\underset{\text{ethanoic acid}}{CH_3COOH} + \underset{\text{ethanol}}{C_2H_5OH} \rightleftharpoons \underset{\text{ethyl ethanoate}}{CH_3COOC_2H_5} + H_2O$$

(a) State K_c for this equilibrium.

$K_c =$

[1]

(b) Name the functional group in $CH_3COOC_2H_5$.

.....[1]

(c) What is the role of the hydrochloric acid in this reaction?

.....[1]

(d) The following volumes of each reagent are mixed together to give a total volume of 95.0 cm^3. The mixture is left for one week.

- 25.0 cm^3 of ethanoic acid
- 35.0 cm^3 of ethanol
- 20.0 cm^3 of ethyl ethanoate
- 15.0 cm^3 of hydrochloric acid with a concentration of 1.00 $mol\,dm^{-3}$

(i) The initial amounts, in moles, of three of the species in the mixture are given.

- initial amount of CH_3COOH = 0.438 mol
- initial amount of C_2H_5OH = 0.601 mol
- initial amount of H_2O = 0.833 mol

The density of $CH_3COOC_2H_5$ is 0.902 $g\,cm^{-3}$.

Calculate the initial mass of $CH_3COOC_2H_5$ and hence the initial amount, in moles, of $CH_3COOC_2H_5$.

initial amount of $CH_3COOC_2H_5$ = ... mol [2]

(ii) Calculate the amount, in moles, of HC*l* added to the initial mixture.

amount of HC*l* = ... mol [1]

(iii) The solution was left for one week.
Suggest why it was necessary for the solution to be left for one week.

.....

.....[1]

(iv) After the reaction mixture had been left for one week:

- A 1.00 cm^3 sample of the mixture was removed from the total volume of 95.0 cm^3.
- Distilled water was added to the sample until the volume was 25.0 cm^3.
- This 25.0 cm^3 solution was titrated using 0.250 mol dm^{-3} sodium hydroxide.
- The titre was 11.30 cm^3.

Calculate the amount, in moles, of sodium hydroxide needed to react with the acid present in the **total** volume of the equilibrium mixture.

amount of NaOH = ... mol [1]

(v) Calculate the amount, in moles, of CH_3COOH present at equilibrium.

amount of CH_3COOH = ... mol [1]

(vi) Use your expression from **(a)** to calculate the value of K_c.
[If you were unable to calculate an answer to **(v)**, assume that the amount, in moles, of CH_3COOH present at equilibrium is 0.238. This is not the correct answer.]

K_c = ...[4]

[Turn over

(vii) The enthalpy change for the reaction between ethanoic acid and ethanol is $-9.50\,kJ\,mol^{-1}$. A student carries out the same experiment but in a warmer laboratory.

State how you expect the titre value in **(iv)** to change. Explain your answer.

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.....

.....[2]

[Total: 15]

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[Turn over

3 The gas-phase reaction between carbon monoxide and nitrogen dioxide has been studied extensively.

$$CO + NO_2 \rightarrow CO_2 + NO$$

(a) The rate equation for the reaction is shown.

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

This rate equation is consistent with the possible mechanism shown.

step 1 $2NO_2 \rightarrow N_2O + O_3$

step 2 $N_2O + 2CO + O_3 \rightarrow 2NO + 2CO_2$

(i) What is meant by the term *rate-determining step*?

.....[1]

(ii) Deduce which of the two steps of the possible mechanism shown is the rate-determining step. Explain your answer.

.....

.....[1]

(b) **(i)** What is meant by the term *activation energy*?

.....

.....[1]

The value of the rate constant, k, at 298 K in the rate equation shown is 0.0421 $dm^3 mol^{-1} s^{-1}$.

$$rate = k [NO_2]^2$$

(ii) Using the Arrhenius equation from the *Data Booklet*, determine the activation energy for the reaction at 298 K in $kJ\,mol^{-1}$.
[$A = 5.52 \times 10^5\,dm^3\,mol^{-1}\,s^{-1}$]

activation energy = ... $kJ\,mol^{-1}$ [3]

(iii) Calculate the rate of reaction at 315 K if the initial concentration of NO_2 is 0.500 $mol\,dm^{-3}$.

Include the units in your answer.

[If you were unable to calculate the activation energy in **(ii)**, assume it has a value of 80.0 $kJ\,mol^{-1}$. This is not the correct value.]

rate of reaction = ...[4]

(iv) State **two** assumptions you have made in using the Arrhenius equation when calculating the rate of reaction in **(iii)**.

.....

.....

.....[2]

[Total: 12]

4 Cacodylic acid, $(CH_3)_2AsO_2H$, is a weak monoprotic acid. It can be used to prepare buffers to stabilise biological samples.

(a) State the expression for K_a for cacodylic acid, $(CH_3)_2AsO_2H$.

K_a =

[1]

(b) Explain what is meant by the term *buffer* and describe, in terms of the relevant equilibrium, how a buffer works. You may represent the acid as HA.

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.....[6]

(c) A buffer containing the weak acid, cacodylic acid, and the salt of the weak acid, sodium cacodylate, was prepared by the following steps.

- 4.87 g of sodium cacodylate, $(CH_3)_2AsO_2Na.3H_2O$, was dissolved in 100 cm^3 of distilled water.
- To this solution was added 75.0 cm^3 of hydrochloric acid with a concentration of 0.200 mol dm^{-3}.
- Distilled water was added until the total volume was 500 cm^3.

(i) Write an equation for the reaction of a solution of $(CH_3)_2AsO_2Na$ with hydrochloric acid.

.....[2]

(ii) The pK_a of cacodylic acid is 6.27. Calculate the pH of the buffer solution.

pH = ...[8]

[Total: 17]

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5 **(a)** The transition metal complex $[Co(en)_2Cl_2]Cl$ can be prepared by the reaction

$$4CoCl_2.6H_2O + O_2 + 4HCl + 8en \rightarrow 4[Co(en)_2Cl_2]Cl + 26H_2O$$

where en represents the bidentate ligand, $H_2NCH_2CH_2NH_2$.

(i) Define the term *ligand.*

.....

.....[1]

(ii) Explain how $H_2NCH_2CH_2NH_2$ can act as a bidentate ligand.

.....

.....

.....[2]

(b) $[Co(en)_2Cl_2]^+$ has three different stereoisomers.

(i) Draw a 3D diagram of each stereoisomer.

You should use N⌒N to represent the $H_2NCH_2CH_2NH_2$ ligand.

X

Y

Z

[4]

(ii) State which pairs of isomers are geometric isomers. Explain your choices.

.....

.....[2]

(iii) State which pair of isomers are optical isomers. Explain your choice.

.....

.....[2]

(c) In the first stage of the reaction to form $[Co(en)_2Cl_2]Cl$, $Co^{2+}(aq)$ ions are oxidised to $Co^{3+}(aq)$ by oxygen in the presence of the en ligand.

A student wanted to work out whether it was possible to oxidise Co^{2+} to Co^{3+} in the absence of the ligand.

The relevant standard electrode potentials are given.

$$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq) \qquad E^{\ominus} = +1.82\,V$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \qquad E^{\ominus} = +1.23\,V$$

(i) Construct the overall equation for the oxidation of $Co^{2+}(aq)$ to $Co^{3+}(aq)$ by oxygen. Include state symbols.

.....[2]

(ii) Use the standard electrode potentials and the relevant equation from the *Data Booklet* to calculate $\Delta G^{\ominus}$ for the reaction you have written in **(i)**. Include the units and a sign in your answer.

$\Delta G^{\ominus}$ = ...[4]

(iii) Is the reaction you have written in **(i)** feasible? Justify your answer with reference to your answer in **(ii)**.

.....[1]

(iv) In which way does the feasibility of this reaction change if the solution is made less acidic? Explain your answer.

.....

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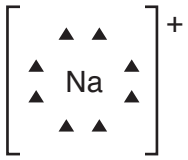
.....[2]

[Total: 20]

[Turn over

6 The salt sodium amide, $NaNH_2$, is used in a number of organic reactions.

(a) Complete the dot-cross diagram for $NaNH_2$.



[3]

(b) **(i)** Explain what is meant by the term *conjugate acid–base pair*.

.....

.....[1]

(ii) The reaction between NH_2^- and water produces ammonia.

Give the equation for this reaction and label the conjugate acid–base pairs.

.....[2]

(c) Solid sodium amide can be made in a redox reaction between molten sodium and gaseous ammonia.

Give the equation for this reaction and, by assigning oxidation numbers, state what is oxidised and what is reduced.

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.....[3]

(d) The organic compound allene, $H_2C=C=CH_2$, can be synthesised from 2,2-dichloropropane in an elimination reaction using sodium amide as a base.

(i) With the aid of a diagram, explain how the bonding in ethene, C_2H_4, makes it a planar molecule.

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.....[1]

(ii) Draw a 3D diagram of allene and suggest why the molecule has this shape.

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.....[2]

(e) The amide ion can act as a nucleophile. Benzoyl chloride, C_6H_5COCl, reacts with the amide ion to give benzamide, $C_6H_5CONH_2$.

(i) Suggest a mechanism for this reaction.

[3]

(ii) Suggest another reagent that could be used to convert benzoyl chloride to benzamide.

.....[1]

[Total: 16]