Cambridge International AS & A Level

**Cambridge International Examinations**
Cambridge International Advanced Subsidiary and Advanced Level

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| CENTRE NUMBER | |
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*5794148263*

**CHEMISTRY** **9701/41**

Paper 4 A Level Structured Questions **October/November 2017**

**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 **17** printed pages and **3** blank pages.


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

**1** The compound nitrosyl bromide, NOBr, can be formed by the reaction shown.

$$2NO + Br_2 \rightleftharpoons 2NOBr$$

**(a)** Using oxidation numbers, explain why this reaction is a redox reaction.

.....

.....

..... [2]

**(b)** Nitrosyl bromide contains a trivalent nitrogen atom.

Draw the 'dot-and-cross' diagram for NOBr. Show outer electrons only.

[2]

**(c)** The rate of the reaction was measured at various concentrations of the two reactants, NO and $Br_2$, and the following results were obtained.

| experiment | $[NO]$ / mol dm$^{-3}$ | $[Br_2]$ / mol dm$^{-3}$ | initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | 0.03 | 0.02 | $3.4 \times 10^{-3}$ |
| 2 | 0.03 | 0.04 | $6.8 \times 10^{-3}$ |
| 3 | 0.09 | 0.04 | $6.1 \times 10^{-2}$ |
| 4 | 0.12 | 0.06 | to be calculated |

The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[NO]^a[Br_2]^b$$

**(i)** What is meant by the term *order of reaction* with respect to a particular reagent?

.....

..... [1]

**(ii)** Use the data in the table to deduce the values of *a* and *b* in the rate equation.
Show your reasoning.

.....

.....

.....

..... [2]

**(iii)** Use the data in the table to calculate the initial rate for experiment 4.

initial rate = ..... $mol\,dm^{-3}\,s^{-1}$ [1]

**(iv)** Use the results of experiment 1 to calculate the rate constant, *k*, for this reaction.
Include the units of *k*.

rate constant, *k* = ..... units ..... [2]

**(v)** By considering the rate equation, explain why the rate decreases with decreasing temperature.

.....

..... [1]

**(d)** The reaction between X and Y was studied.

$$2X + Y \rightarrow Z$$

The following sequence of steps is a proposed mechanism for the reaction.

step 1 $2X \rightarrow V$
step 2 $V + Y \rightarrow Z$

The general form of the rate equation for this reaction is as follows.

$$rate = k[X]^m[Y]^n$$

Step 1 is the slower step in the mechanism.

Deduce the values of *m* and *n* in the rate equation.

*m* = ..... *n* = .....
[1]

[Total: 12]

**2** **(a)** The table lists values of solubility products, $K_{sp}$, of some Group 2 carbonates.

| | solubility product in water at 298 K, $K_{sp}$ / mol$^2$ dm$^{-6}$ |
|---|---|
| $MgCO_3$ | $1.0 \times 10^{-5}$ |
| $CaCO_3$ | $5.0 \times 10^{-9}$ |
| $SrCO_3$ | $1.1 \times 10^{-10}$ |

Use the data in the table to describe the trend in the solubility of the Group 2 carbonates down the group.

.....

..... [1]

**(b)** **(i)** Write an equation to show the equilibrium for the solubility product for $MgCO_3$. Include state symbols.

$\rightleftharpoons$

..... [1]

**(ii)** With reference to your equation in **(i)**, suggest what is observed when a few cm$^3$ of concentrated $Na_2CO_3$(aq) are added to a saturated solution of $MgCO_3$. Explain your answer.

.....

.....

..... [2]

**(c)** Use the data in the table to calculate the solubility of $MgCO_3$ in water at 298 K, in g dm$^{-3}$.

solubility of $MgCO_3$ = ..... g dm$^{-3}$ [2]

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**(d) (i)** Magnesium nitrate decomposes at a **lower** temperature than barium nitrate.

Explain why.

.....

.....

..... [2]

**(ii)** A sample of barium nitrate was heated strongly until no further change occurred. A white solid was formed.

Write an equation for the action of heat on barium nitrate.

..... [1]

**(iii)** When water was added to the white solid produced in **(d)(ii)**, an alkaline solution was produced. Adding sulfuric acid to this solution produced a white precipitate.

Write equations to explain these observations.

.....

..... [2]

[Total: 11]

**3** **(a)** Define the term *standard cell potential*.

.....

.....

..... [2]

**(b)** **(i)** Draw a fully labelled diagram of the experimental set-up you could use to measure the standard electrode potential of the $Pb^{2+}(aq)/Pb(s)$ electrode. Include the necessary chemicals.

[4]

**(ii)** The $E^{\ominus}$ for a $Pb^{2+}(aq)/Pb(s)$ electrode is $-0.13\,V$.

Suggest how the $E$ for this electrode would differ from its $E^{\ominus}$ value if the concentration of $Pb^{2+}(aq)$ ions is reduced. Indicate this by placing a tick (✓) in the appropriate box in the table.

| more negative | no change | less negative |
|---|---|---|
| | | |

Explain your answer.

.....

.....

..... [2]

**(c)** Car batteries are made up of rechargeable lead-acid cells. Each cell consists of a negative electrode made of Pb metal and a positive electrode made of $PbO_2$. The electrolyte is $H_2SO_4(aq)$.

When a lead-acid cell is in use, $Pb^{2+}$ ions are precipitated out as $PbSO_4(s)$ at the negative electrode.

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

**(i)** Calculate the mass of Pb that is converted to $PbSO_4$ when a current of 0.40 A is delivered by the cell for 80 minutes.

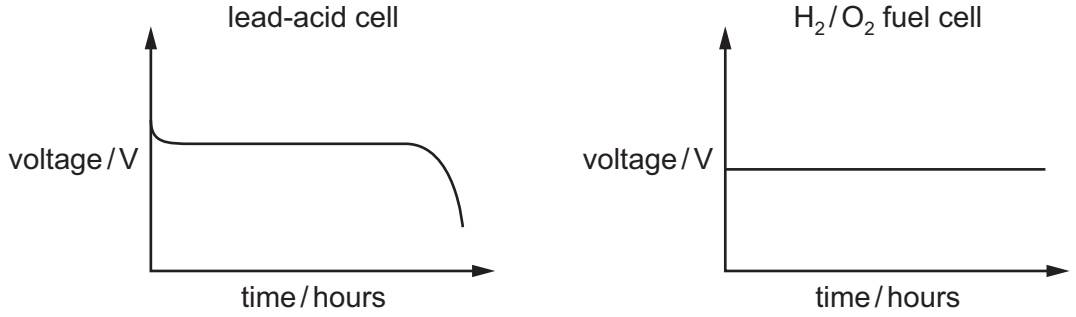
mass of Pb = ..... g [2]

**(ii)** Complete the half-equation for the reaction taking place at the positive electrode.

$$PbO_2(s) + SO_4^{2-}(aq) + ..... + ..... \rightarrow PbSO_4(s) + .....$$

[1]

**(d)** The diagrams show how the voltage across two different cells changes with time when each cell is used to provide an electric current.




Suggest a reason why

- the voltage of the lead-acid cell changes after several hours,

.....

.....

- the voltage of the fuel cell remains constant.

.....

.....

[2]

[Total: 13]

**4** **(a)** Describe and explain how the density and melting point of cobalt compare to those of calcium.

density of cobalt .....

explanation .....

.....

melting point of cobalt .....

explanation .....

.....

[3]

**(b)** Transition metals can form complexes.

What is meant by the term *transition metal complex*?

.....

..... [1]

**(c)** **(i)** Cobalt can form the compounds $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$.
These two compounds are structural isomers.

Define the term *structural isomer*.

.....

..... [1]

**(ii)** Draw a three-dimensional diagram to show the structure of the ion $[Co(NH_3)_5Br]^{2+}$.
Name its shape.

$[Co(NH_3)_5Br]^{2+}$

shape ..... [1]

**(iii)** State the type of bonding between the cobalt ion and $NH_3$ groups in the $[Co(NH_3)_5Br]^{2+}$ ion.

..... [1]

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**(iv)** State the oxidation number of cobalt in

- $[Co(NH_3)_5Br]^{2+}$ oxidation number of Co = .....
- $[Co(NH_3)_5SO_4]^{+}$ oxidation number of Co = .....

[1]

**(d)** Solutions of the compounds $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ can be distinguished from each other by simple chemical tests.
Assume that any species bonded to the cobalt ion does not react in these tests.

Complete the table with two **different** tests that could be used to positively identify each compound. Give the expected observation with each compound.

| test | observation with $[Co(NH_3)_5Br]SO_4(aq)$ | observation with $[Co(NH_3)_5SO_4]Br(aq)$ |
|---|---|---|
| | | |
| | | |

[2]

**(e)** The two compounds $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ are different colours.

Explain why the colours of the two compounds are different.

.....

.....

..... [2]

**(f)** Some transition metals and their compounds act as catalysts. The catalysis can be classified as heterogeneous or homogeneous.

Complete the table by placing **one** tick (✓) in each row to indicate the type of catalysis in each reaction.

| | heterogeneous | homogeneous |
|---|---|---|
| Fe in the Haber process | | |
| $Fe^{2+}$ in the $I^-/S_2O_8^{2-}$ reaction | | |
| $NO_2$ in the oxidation of $SO_2$ | | |
| $V_2O_5$ in the Contact process | | |

[2]

[Total: 14]

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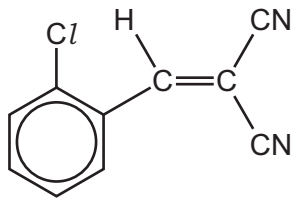
**[Turn over**

**5** Compound **P** contains several functional groups.




**P**

**(a)** Name the functional groups present in **P**.

.....

..... [2]

**(b)** Compound **P** can be polymerised.

Draw a section of the polymer of **P** showing **two** repeat units.
Name the type of polymerisation.

type of polymerisation .....
[2]

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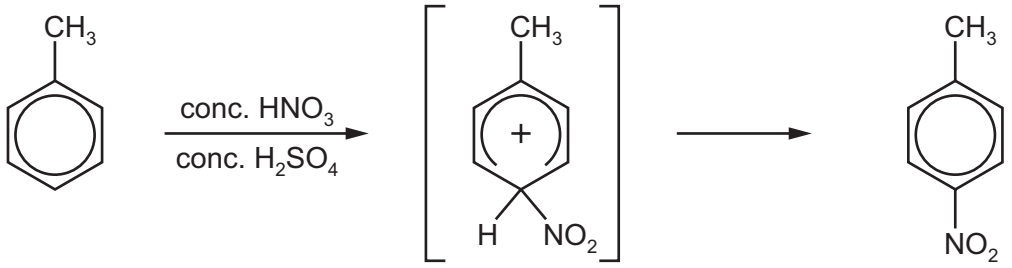
**(c)** Complete the following table to show the structures of the products formed and the *type of organic reaction* when **P** reacts with the four reagents.

| reagent | structure(s) of product(s) | | *type of organic reaction* |
|---|---|---|---|
| excess $Br_2(aq)$ | | | |
| excess hot, concentrated, acidified $MnO_4^-(aq)$ | | | |
| excess hot $HCl(aq)$ | | | |
| excess $H_2$ / Pt catalyst | | | |

[8]

[Total: 12]

**6** **(a)** 4-nitromethylbenzene can be prepared via an electrophilic substitution reaction as shown.




methylbenzene intermediate **T** 4-nitromethylbenzene

**(i)** This reaction also forms an isomer of 4-nitromethylbenzene as a by-product.

Draw the structure of this by-product.

[1]

**(ii)** Write an equation for the reaction between $HNO_3$ and $H_2SO_4$ that forms the electrophile for this reaction.

..... [1]

**(iii)** Describe how the **structure and bonding** of the six-membered ring in intermediate **T** differs from that in methylbenzene.

.....

.....

.....

..... [3]

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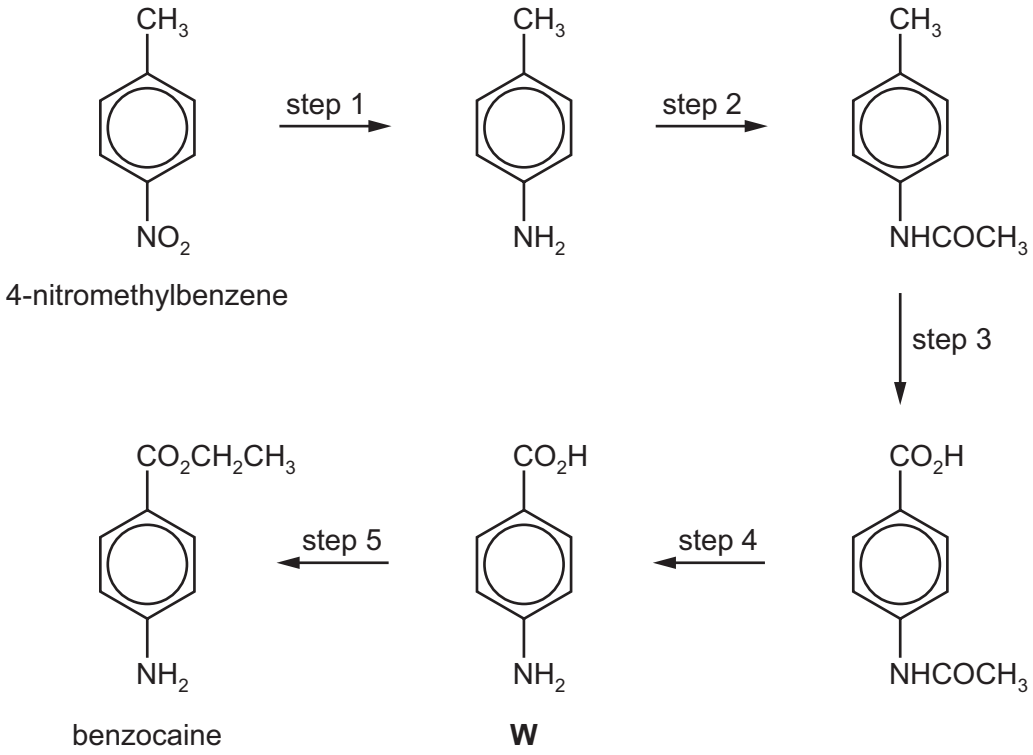
**(b)** Benzocaine is used as a local anaesthetic. It can be synthesised from 4-nitromethylbenzene by the route shown.




4-nitromethylbenzene

benzocaine

**W**

**(i)** Give the systematic name of compound **W**.

..... [1]

**(ii)** Suggest the reagents and conditions for steps 1–5.

step 1 .....

step 2 .....

step 3 .....

step 4 .....

step 5 .....

[6]

**(c)** Suggest how the basicity of benzocaine would compare to that of ethylamine.
Explain your answer.

.....

.....

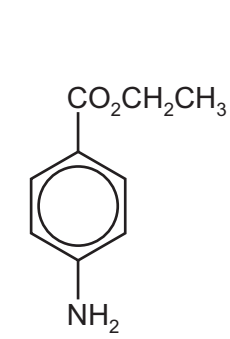
..... [2]

**(d)** A sample of benzocaine, shown below, was analysed by proton NMR and carbon-13 NMR spectroscopy.

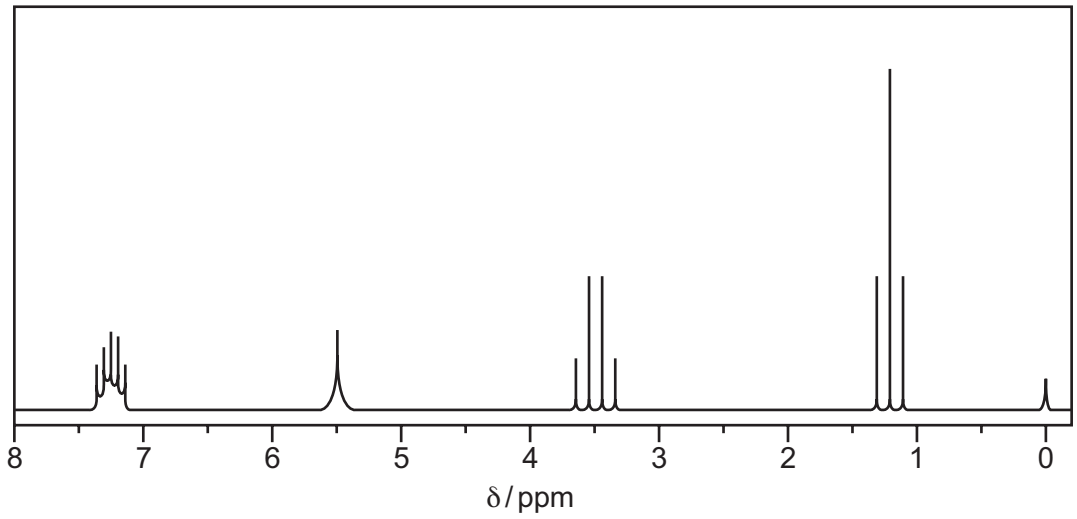
**(i)** Predict the number of peaks that would be seen in the carbon-13 NMR spectrum.

..... [1]

**(ii)** Benzocaine was dissolved in $CDCl_3$ and the proton NMR spectrum of this solution was recorded.




benzocaine




Suggest why $CDCl_3$ and not $CHCl_3$ is used as the solvent when obtaining a proton NMR spectrum.

.....

..... [1]

**(iii)** Use the *Data Booklet* and the spectrum in **(d)(ii)** to complete the table for the proton NMR spectrum of benzocaine. The actual chemical shifts, δ, for the four absorptions have been added.

| δ / ppm | group responsible for the peak | number of $^1H$ atoms responsible for the peak | splitting pattern |
|---|---|---|---|
| 1.2 | | | |
| 3.5 | | | |
| 5.5 | | | |
| 7.1–7.4 | | | multiplet |

[4]

**(iv)** Explain the splitting pattern for the absorption at δ1.2 ppm.

.....

..... [1]

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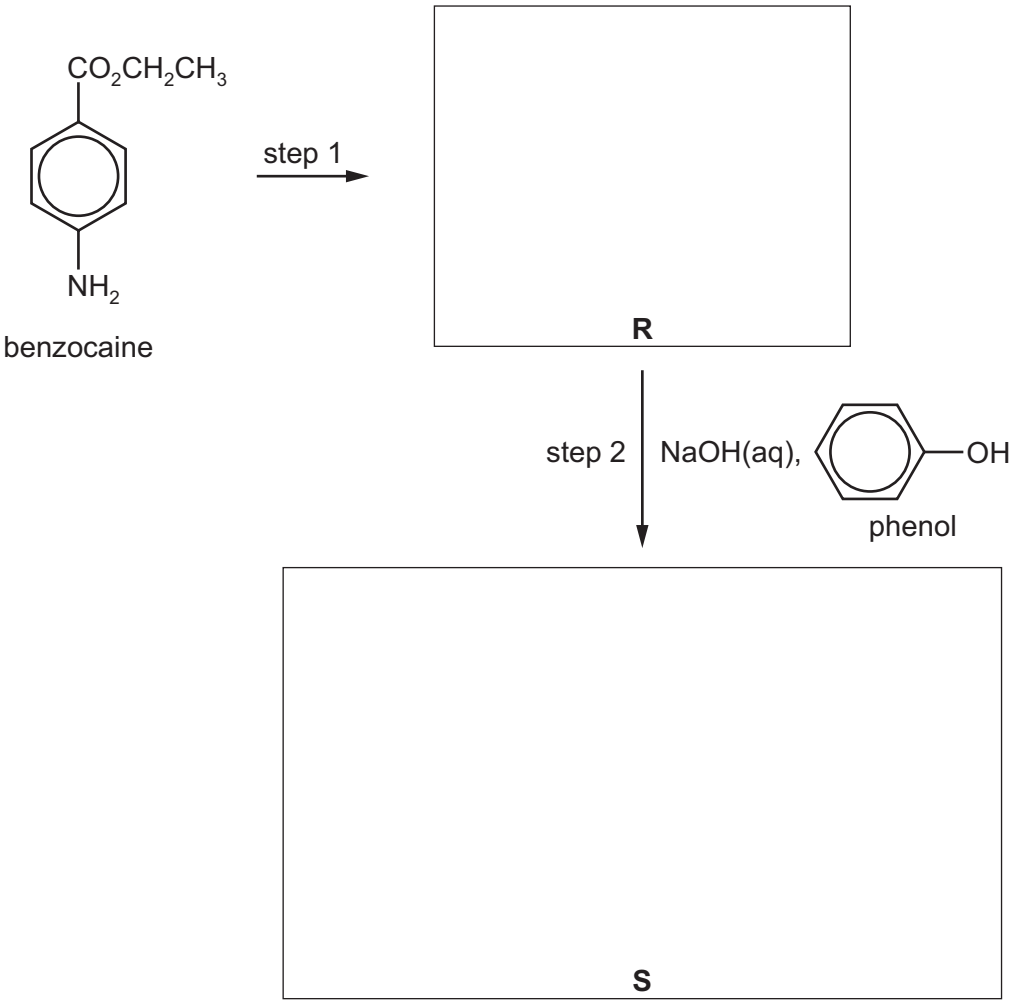
**(v)** The proton NMR spectrum of benzocaine dissolved in $D_2O$ was recorded.

Suggest how this spectrum would differ from the spectrum in **(d)(ii)**.
Explain your answer.

.....

..... [1]

**(e)** Benzocaine can also be used to synthesise the dyestuff **S** by the following route.




benzocaine

phenol

**(i)** Suggest the reagents used for step 1.

..... [1]

**(ii)** Suggest structures for compounds **R** and **S** and draw them in the boxes. [2]

[Total: 25]

**7** **(a)** Complete the following electronic structures.

- the iron atom, Fe $1s^2 2s^2 2p^6$ .....
- the iron(III) ion, $Fe^{3+}$ $1s^2 2s^2 2p^6$ .....

[1]

**(b)** Solutions of iron(III) salts are acidic due to the equilibrium shown.

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq) \qquad K_a = 8.9 \times 10^{-4}\,\text{mol dm}^{-3}$$

Calculate the pH of a $0.25\,\text{mol dm}^{-3}$ $FeCl_3$ solution.

pH = ..... [2]

**(c)** The table shows numerical values of the stability constants for the following equilibrium where M can be one of the metal ions listed and L one of the ligands which replaces **one** $H_2O$ molecule.

$$[M(H_2O)_6]^{n+}(aq) + L^-(aq) \rightleftharpoons [M(H_2O)_5L]^{(n-1)+}(aq) + H_2O(l)$$

| metal ion, M | ligand, L | stability constant, $K_{stab}$ |
|---|---|---|
| $Fe^{3+}$ | $F^-$ | $1.0 \times 10^6$ |
| $Fe^{3+}$ | $Cl^-$ | $2.5 \times 10^1$ |
| $Fe^{3+}$ | $SCN^-$ | $9.0 \times 10^2$ |
| $Hg^{2+}$ | $Cl^-$ | $5.0 \times 10^6$ |

**(i)** What is meant by the term *stability constant,* $K_{stab}$?

.....

..... [1]

**(ii)** Use the data in the table to predict the formula of the complex formed in the greatest amount when

- a solution containing equal concentrations of both $F^-$ and $SCN^-$ ions is added to $Fe^{3+}(aq)$,

.....

- a solution containing equal concentrations of both $Fe^{3+}$ and $Hg^{2+}$ ions is added to $Cl^-(aq)$.

.....

[1]

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Ethanedioate ions, $^{-}O_2CCO_2^{-}$, are bidentate ligands. The abbreviation $ed^{2-}$ can be used to represent ethanedioate ions.

**(d)** The complex $[Fe(ed)_2Cl_2]^{3-}$ can be formed according to the equation shown.

$$[Fe(H_2O)_4Cl_2]^{+}(aq) + 2ed^{2-}(aq) \rightleftharpoons [Fe(ed)_2Cl_2]^{3-}(aq) + 4H_2O(l)$$

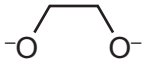
Write the expression for the equilibrium constant, $K_{stab}$, and state its units.

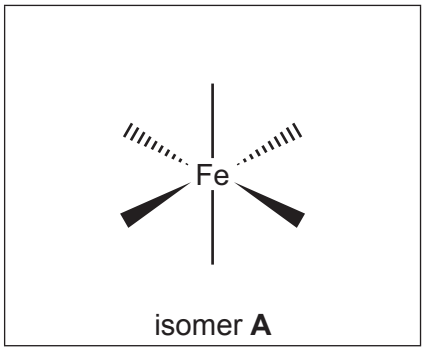
$K_{stab}$ =

units .....
[2]

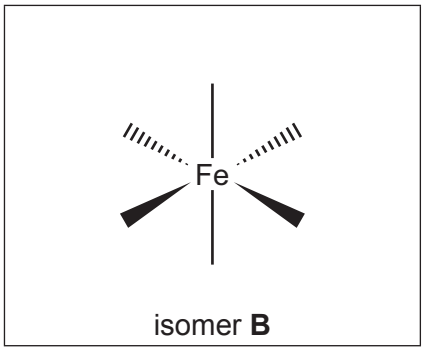
**(e)** $[Fe(ed)_2Cl_2]^{3-}$ shows geometrical and optical isomerism.

**(i)** Complete the three-dimensional diagrams to show the three stereoisomers of $[Fe(ed)_2Cl_2]^{3-}$.

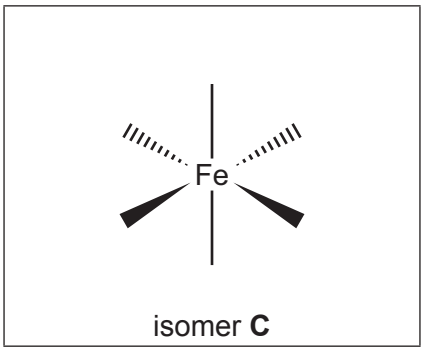
You may use  to represent $ed^{2-}$.




isomer **A**




isomer **B**




isomer **C**

[3]

**(ii)** Give the letters of two isomers of $[Fe(ed)_2Cl_2]^{3-}$ which are geometrical isomers of each other.

..... [1]

**(iii)** Give the letters of the two isomers of $[Fe(ed)_2Cl_2]^{3-}$ which show optical isomerism.

..... [1]

**(iv)** Give the letter of the isomer which has **no** dipole moment.

..... [1]

[Total: 13]

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