NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

Paper 3 Free Response

9729/03

18 September 2018

2 hours

Additional Materials:	Writing Paper Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer all questions.

Section B
Answer one question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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 **14** printed pages and **0** blank page.

Section A

Answer **all** questions in this section.

1 Cobalt is a typical transition element which is commonly used as a catalyst and metal for electroplating. Cobalt also forms complex ions with ligands such as H_2O and NH_3 to give various coloured octahedral complexes such as $[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$ which are pink and yellow respectively.

(a) The ligand exchange in octahedral complexes is one of the most extensively studied reactions in transition metals.

An example of a ligand exchange reaction involving cobalt(II) ions is:

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

(i) Explain why cobalt forms coloured complexes. [3]

- The presence of ligands causes the energy level of the five 3d orbitals to be split into two different levels (crystal field splitting).
- The energy difference, ΔE, corresponds to wavelengths in the visible spectrum.
- When light energy is absorbed by the substance, an electron is promoted from a d orbital of lower to one of higher energy (d-d transition)
- Unabsorbed wavelengths are transmitted and the colour of the complex is complementary to the colour absorbed.

[3] for 4 marking points
[2] for 3 marking points
[1] for 2 marking points

(ii) Suggest why $[Co(NH_3)_6]^{2+}$ is of a different colour from $[Co(H_2O)_6]^{2+}$. [1]

- Different ligands give rise to a difference in the splitting of the *d*-orbitals, cause a different energy gap (Δ*E*).
- A different wavelengths of visible light is absorbed and thus a different wavelength of light is observed.

[1] for 2 marking points

(iii) A student wishes to investigate the kinetics of the ligand exchange reaction of $[Co(H_2O)_6]^{2+}$ to form $[Co(NH_3)_6]^{2+}$ by using a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a few cm^3 of the coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent.

The spectrometer is set to use the wavelength of light that is absorbed most strongly by the complex ion. The amount of light absorbed is expressed as an absorbance value. The more concentrated the solution, the higher the absorbance value. The temperature of the sample in the spectrometer can be thermostatically controlled for reaction rate analysis for which the sample has to be kept at a constant temperature.

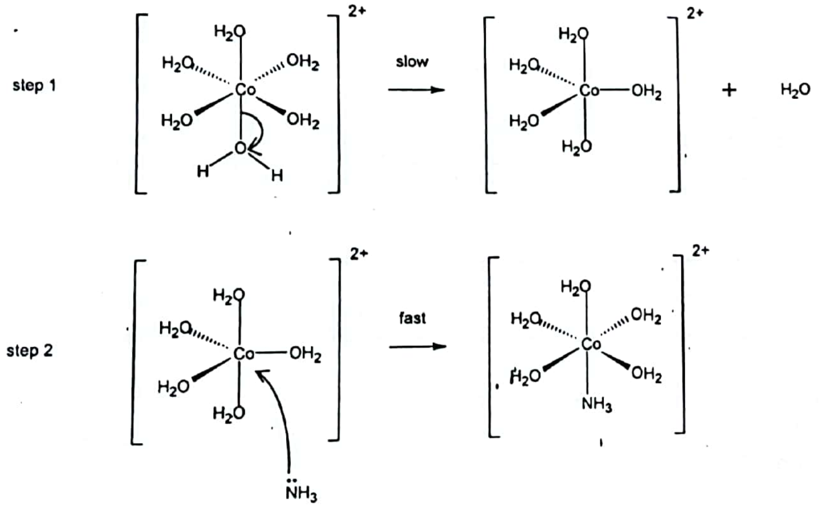
Outline the experimental procedure on how the student would accurately determine the initial rate of the ligand exchange reaction at 5 °C.

The details of the use of specific glassware for measurement are **not** required. [3]

- Spectrometer is set up to absorb the wavelength of violet (monitoring product) or green (monitoring reactant) and maintain the temperature of the sample at 5 °C.
- Separate solutions of $[Co(H_2O)_6]^{2+}$ and NH_3 are cooled to 5 °C in an ice-water bath.
- Stoichiometric amounts of $[Co(H_2O)_6]^{2+}$ and NH_3 (or excess NH_3) are mixed and swirled. A few cm^3 of the coloured solution is quickly placed into the spectrometer.
- A stop watch is started.
- The concentration of $[Co(H_2O)_6]^{2+}$ (or $[Co(NH_3)_6]^{2+}$) is then determined by measuring the absorbance of the reaction mixture at time = 0 minute and then at regular time intervals (e.g. every 5 minutes), to obtain at least 5 measurements.
- A graph of absorbance value against time is plotted.
- The initial rate is found by drawing a tangent at time = 0 minute.

7 marking points
[1] for 2 marking points

(iv) When $[Co(H_2O)_6]^{2+}$ is mixed with an excess of $NH_3(aq)$, each H_2O molecule is replaced by a NH_3 molecule one at a time. Given that the stepwise formation of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$ undergoes a dissociative mechanism which resembles a S_N1 mechanism in organic chemistry.
Suggest a possible mechanism for the formation of $[Co(H_2O)_5NH_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and show clearly how the shape of the complex ion changes.
In your mechanism, show appropriate curly arrows, lone pairs and dipoles. [3]



Square pyramidal intermediate is accepted as well.

[1] for correct shapes
[1] for arrows and lone pair on NH_3
[1] for intermediate and side product

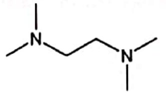
(v) State the rate equation for the above ligand exchange reaction. [1]

rate = k $[[Co(H_2O)_6]^{2+}]$ [1]

(vi) Hence, predict and explain the effect on the rate of reaction, if any, when the ammonia ligand is replaced with a fluoride ion. [1]

The rate of reaction remains constant as the rate is independent of the incoming ligand. [1]

(b) $[Co(H_2O)_6]^{2+}$ can also undergo ligand exchange reactions with TMEDA to form $[Co(TMEDA)_3]^{2+}$.



TMEDA

By considering the entropy and enthalpy changes during the formation of $[Co(TMEDA)_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and that of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$, suggest how the standard Gibbs free energy change of the two reactions will compare in sign and in magnitude.

Hence, predict which reaction will be more spontaneous. Explain your reasoning. [3]

$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$

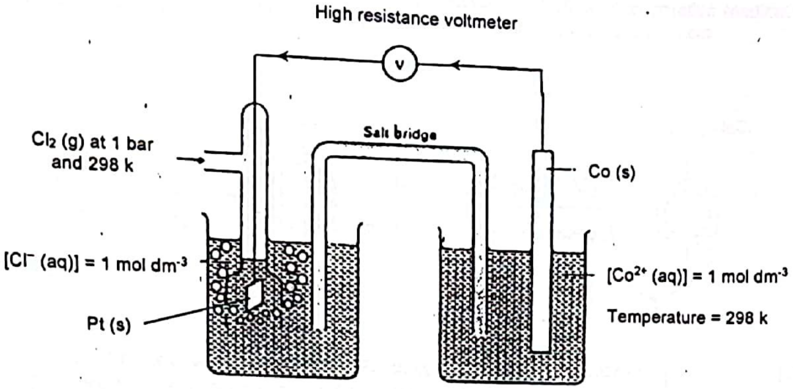
$[Co(H_2O)_6]^{2+} + 3TMEDA \rightleftharpoons [Co(TMEDA)_3]^{2+} + 6H_2O$

ΔH for formation of $[Co(NH_3)_6]^{2+}$ and $[Co(TMEDA)_3]^{2+}$ is similar in magnitude and sign due to the breaking of 6 similar Co—O bonds and forming of 6 similar Co—N bonds. [1]

ΔS for formation of $[Co(TMEDA)_3]^{2+}$ would be more positive than that of $[Co(NH_3)_6]^{2+}$ because there is an increase in number of aqueous particles when $[Co(TMEDA)_3]^{2+}$ is formed, allowing more ways of arranging the particles. [1]

Since ΔH for formation of $[Co(NH_3)_6]^{2+}$ and $[Co(TMEDA)_3]^{2+}$ are similar in magnitude and sign and ΔS for formation of $[Co(TMEDA)_3]^{2+}$ is more positive than that of $[Co(NH_3)_6]^{2+}$, ΔG for formation of $[Co(TMEDA)_3]^{2+}$ would be more negative than that of $[Co(NH_3)_6]^{2+}$ and hence more spontaneous. [1]

(c) **(i)** Draw a fully labelled diagram of an electrochemical cell composed of a standard $Cl_2|Cl^-$ electrode and a standard $Co^{2+}|Co$ electrode. Indicate the direction of the electron flow. [3]



[1] correct set-up
[1] concentration of ions, 298 and 1 bar
[1] electron flow

(ii) Calculate the $E^\ominus_{cell}$ of the electrochemical cell and write a balanced equation for the cell reaction. [2]

$E_{cell} = +1.36 - (-0.28) = +1.64$ V [1]

$Co + Cl_2 \rightarrow Co^{2+} + 2Cl^-$

(iii) Using your answer in **(ii)**, calculate ΔG for the cell reaction. [1]

Overall 2 mol of electrons are transferred.

$\Delta G = -nFE_{cell} = -2 \times 96500 \times 1.64 = -317\ 000$ J mol^{-1} = -317 kJ mol^{-1}

(iv) Use the *Data Booklet* to suggest the effect on the cell potential of this cell of adding excess aqueous ammonia to the Co^{2+}|Co half cell. Explain your answer. [1]

$Co^{2+} + 2e \rightleftharpoons Co$ $\quad E^\ominus = -0.28$ V
$[Co(NH_3)_6]^{2+} + 2e \rightleftharpoons Co + 6NH_3$ $\quad E^\ominus = -0.43$ V

In the presence of ammonia ligands, Co^{2+} undergoes ligand exchange to form a more stable complex ion of $[Co(NH_3)_6]^{2+}$. The $E^\ominus(Co^{2+}|Co)$ becomes more negative and the Ecell becomes more positive.

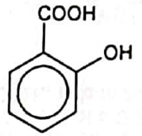
Or

The formation of $[Co(NH_3)_6]^{2+}$ decreases the concentration of Co^{2+}. This caused the position of equilibrium for $Co^{2+} + 2e \rightleftharpoons Co$ to shift left. The $E^\ominus(Co^{2+}|Co)$ becomes more negative and the Ecell becomes more positive.

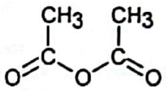
[Total: 22]

2(a) Aspirin is one of the most widely used drug in the world. It is a powerful analgesic (pain reliever), antipyretic (fever reducer) and anti-inflammatory drug.

It is synthesised using 2-hydroxybenzoic acid and ethanoic anhydride. 8 – 10 drops of 85% phosphoric acid which catalyses the reaction is added. The reaction mixture is then heated under reflux for around fifteen minutes. The other product of this reaction is ethanoic acid.



2-hydroxybenzoic acid

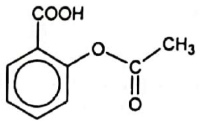


ethanoic anhydride

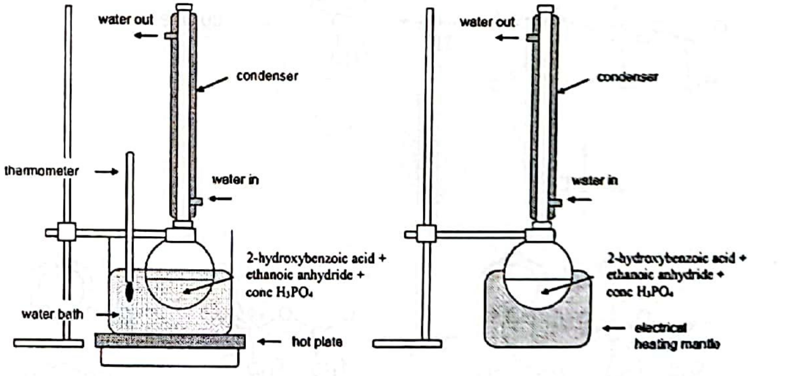
Ethanoyl chloride and phenol can undergo condensation reaction.

Ethanoic anhydride and 2-hydroxybenzoic acid can undergo a similar reaction to form aspirin.

(i) Draw the structure of aspirin. [1]

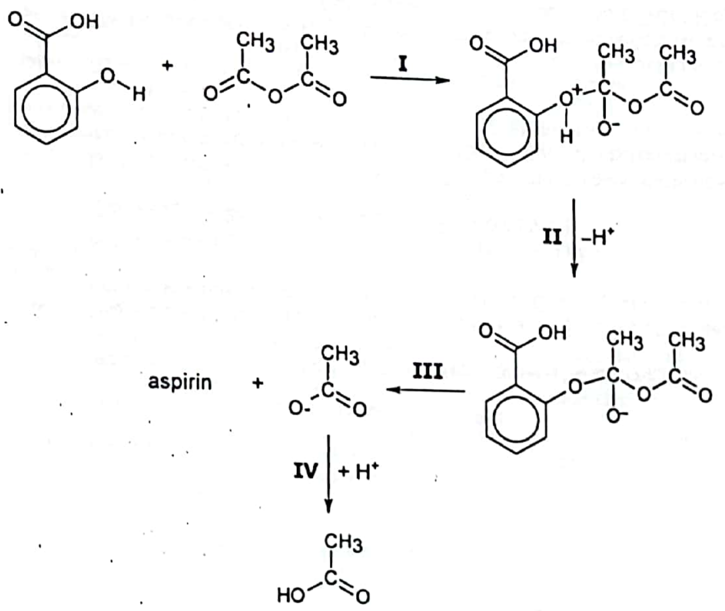


(ii) Draw a labelled diagram of the assembled apparatus for the synthesis of aspirin. [3]



[1] flask fitted with Liebig condenser
[1] clear label of water entering and leaving the condenser in a correct manner
[1] correct heat source (thermostated water bath if thermometer is not drawn)

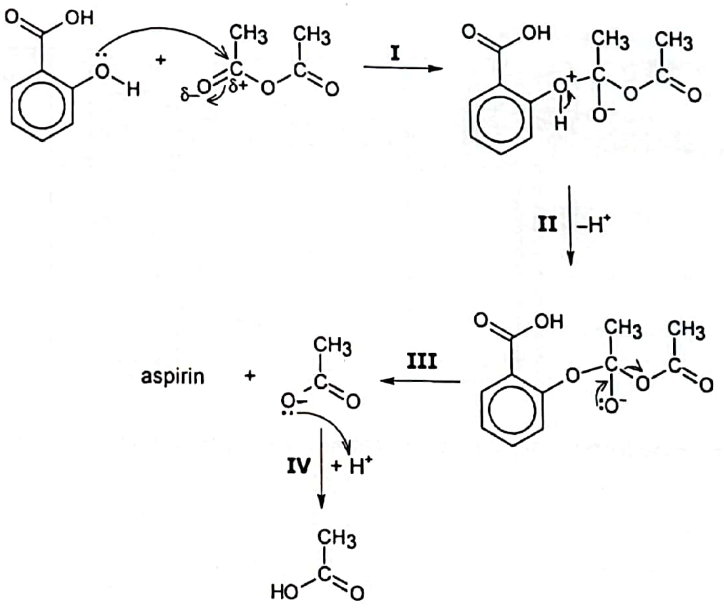
The mechanism for the reaction between 2-hydroxybenzoic acid and ethanoic anhydride involves four steps. It is proposed as below:



(iii) Using the information given above, state the type of mechanism in step **I**. [1]

Nucleophilic addition [1]

(iv) Copy and complete the whole mechanism above by showing any relevant charges, lone pairs of electrons and movement of electrons in your answer. [3]

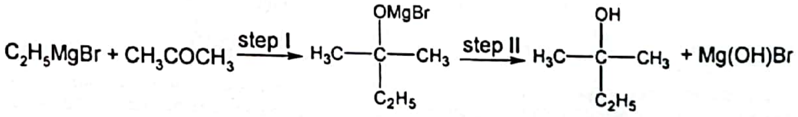


4 steps: 3 marks; 3 steps: 2 mark; 2 steps: 1 mark

(v) State a reason why ethanoic anhydride is used rather than ethanoyl chloride for the synthesis of aspirin. [1]

Safer because ethanoic anhydride is less corrosive as it does not produce corrosive and poisoning / toxic fumes of HCl [1] and less readily hydrolysed.

(b) In 1911, the French chemist F.A.V. Grignard reacted small pieces of magnesium with a warm solution of bromoethane in a dry, non-polar solvent and obtained a solution containing ethylmagnesium bromide, C_2H_5MgBr. Many Grignard reagents, with different alkyl or aryl groups, have now been prepared and are widely used in organic syntheses. A typical example of the use of a Grignard reagent is the two-step reaction of C_2H_5MgBr with propanone, CH_3COCH_3, to form 2-methylbutan-2-ol.

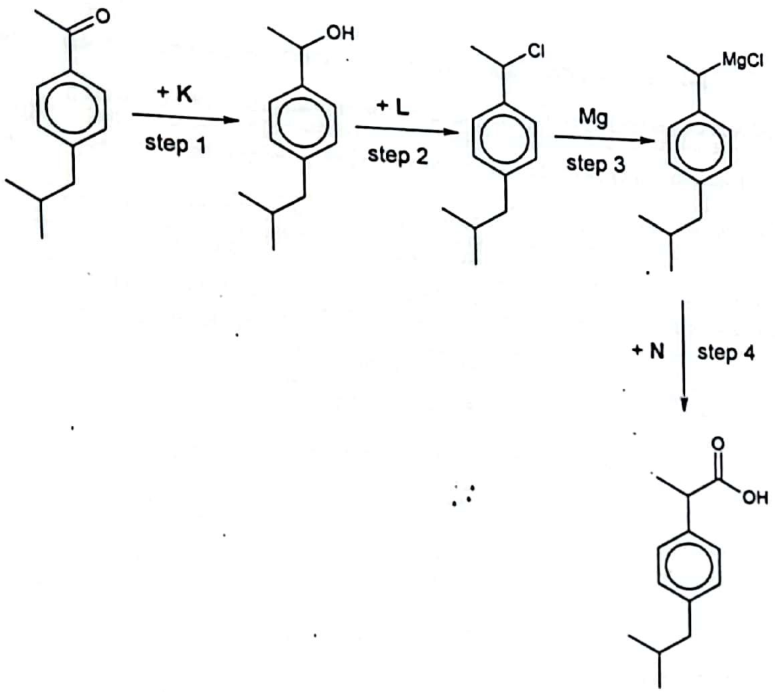


$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step I}} H_3C-C(OMgBr)(C_2H_5)-CH_3 \xrightarrow{\text{step II}} H_3C-C(OH)(C_2H_5)-CH_3 + Mg(OH)Br$$

Suggest the type of reaction which occurs in step II. [1]

Hydrolysis [1]

(c) The following scheme shows the synthesis of ibuprofen which is an alternative medication to aspirin. In step 4, the Grignard reagent readily converts into a carboxylic acid.



ibuprofen

(i) Suggest the identity of the reagent **K** in step 1. [1]

$NaBH_4$ [1]

(ii) Suggest the identity of the reagent **L** in step 2. [1]

PCl_5 or $SOCl_2$ [1]

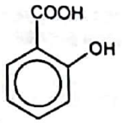
(iii) Suggest the identity of the reagent **N** in step 4. [1]

CO_2 [1]

(d) Suggest a simple chemical test that could be used to distinguish between aspirin and ibuprofen. You should state what you would observe for **each** compound. [3]

1. Add H_2SO_4(aq), heat [1] – test
2. Distill

Product obtained from aspirin: CH_3COOH,



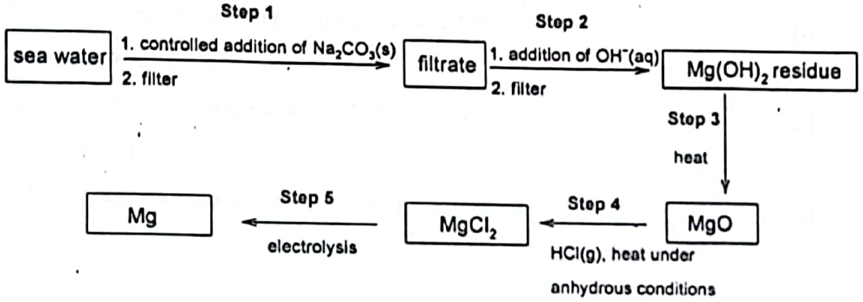
3. Add Br_2(aq).
Orange Br_2 decolourises with aspirin; Orange Br_2 remains for ibuprofen. [1]

[Total: 16]

3 Magnesium is present as dissolved magnesium ions in sea water and is the only metal directly extracted from sea water. There is enough magnesium dissolved in the Earth's oceans to supply all of our magnesium needs for the next 1000 years.

(a) Apart from magnesium ions, the two other most abundant cations found in sea water are sodium and calcium ions.

Magnesium can be extracted from sea water by the following steps:



Concentration of common ions in sea water:

ion	concentration / mol dm^{-3}
magnesium	0.056
calcium	0.010
sodium	0.457
chloride	0.535

The numerical values of solubility products are given below:

compound	value of solubility product
magnesium carbonate	1.00×10^{-5}
calcium carbonate	8.70×10^{-9}
magnesium hydroxide	5.61×10^{-12}
calcium hydroxide	5.50×10^{-6}

(i) Explain why the addition of sodium carbonate in **step 1** has to be controlled. [1]

If too much carbonate ions was added, both $MgCO_3$ and $CaCO_3$ will be precipitated.

(ii) Hence, state the cations present in the filtrate after **step 1** is carried out. [1]

Na^+ and Mg^{2+}

(iii) What is the maximum mass of solid sodium carbonate that can be added to 1 dm^3 of sea water in **step 1**? [2]

The $[CO_3^{2-}]$ must be controlled such that only calcium carbonate precipitates out, leaving $MgCO_3$ in the solution.

$$K_{sp} = [Mg^{2+}][CO_3^{2-}]$$

$$\text{maximum}[CO_3^{2-}] = \frac{K_{sp}}{[Mg^{2+}]} = \frac{1.0 \times 10^{-5}}{0.056} = 1.785 \times 10^{-4} \text{ [1]}$$

$$m_{CaCO_3} = 1.785 \times 10^{-4} \times 100.1 = 0.0179 \text{ g [1]}$$

(iv) Use the data provided to explain the following:

- Solid sodium carbonate was added to sea water (under controlled conditions) **before** the hydroxide ions.
- The reverse order (i.e. adding hydroxide ions before sodium carbonate) is **not** preferred over the extraction of magnesium.

[2]

Comparing the K_{sp} of the 2 carbonates, $CaCO_3$ is less soluble and will be precipitated out first, leaving the Mg^{2+} ions in solution, and can be further purified via other steps. [1]

If hydroxide ions was added before carbonate ions, $Mg(OH)_2$ having a smaller K_{sp} value than $Ca(OH)_2$ will be less soluble and precipitate out first, together with other solid impurities in sea water, leading to an impure product. [1]

(v) Calculate the minimum pH of the hydroxide solution required for precipitation of magnesium hydroxide in **step 2** if an equal volume of hydroxide ions was added to the filtrate. Give your answer to 2 decimal places. [2]

Assume $[Mg^{2+}] = 0.056$ mol dm^{-3} (from table)

After adding equal volume of hydroxide ions, $[Mg^{2+}]_{new} = \frac{0.056}{2} = 0.028$ mol dm^{-3}

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{5.61 \times 10^{-12}}{0.028}} = 1.415 \times 10^{-5} \text{ [1]}$$

$$[OH^-]\text{required} = 1.415 \times 10^{-5} \times 2$$

$$pOH = -\log(1.415 \times 10^{-5} \times 2) = 4.55$$

pH = 9.45 [1] 2dp ans

(b) **(i)** Write the equations that occur during the electrolysis of magnesium chloride in **step 5**. State clearly the reactions that occur at the cathode and the anode, and include state symbols. [2]

Cathode: $Mg^{2+}(l) + 2e \rightarrow Mg(l)$ [1]

Anode : $2Cl^-(l) \rightarrow Cl_2(g) + 2e$ [1]

(ii) In a factory, a current of 95 kA was passed through a suitable setup for 24 hours. Assuming that the procedure is 90% efficient, calculate the mass of Mg that can be produced. [2]

Q= It = nzF

$$\frac{95\times1000\times24\times60\times60}{100}\times90 = n\times2\times96500$$

$n = 38.28\times10^4$ [1]

$m = 38.28\times10^4\times24.3 = 930{,}000g = 930kg$ [1]

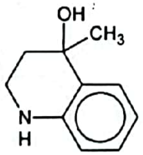
(iii) Give a reason why electrolysis of magnesium chloride is preferred to that of magnesium oxide in this industrial process. [1]

MgCl$_2$ has a lower melting point than MgO, hence the electrolysis can be carried out at a lower temperature, saving operation costs. [1]

(c) When 0.468 g of an organic compound **A** was evaporated in a syringe, the volume of the vapour produced after correction to s.t.p was 60 cm^3. On heating with aqueous sodium hydroxide, **A** gives a compound that dissolves in water.

A reacts with aluminium oxide to give two products **B** and **C**. Both **B** and **C** react with HBr to give the same product **D**. **D** exhibits enantiomerism and exists as a pair of enantiomers.

A gives **E** when reacted with lithium aluminium hydride in dry ether.



E

(i) Prove that the molar mass of **A** is 177 g mol^{-1}. [1]

From Data Booklet, at s.t.p, V_m = 22.7 dm^3 mol^{-1} at 10^5 Pa and 273 K

Either

$$10^5\times60\times10^{-6} = \frac{0.468}{M}\times8.31\times273$$

$M = 176.9 = 177$ g mol^{-1} [1]

Or

n(A) = 60 / 22700 = 2.643 × 10^{-7} mol

M_r(A) = 0.468 / 2.643 × 10^{-7} = 177.06 ≈ 177 g mol^{-1}

Comments

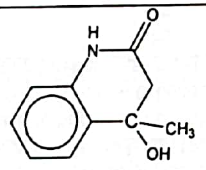
- Generally well-done.
- Common mistake include:
  Using incorrect V_m such as V_m = 24 dm^3 or V_m = 22.4 dm^3

- A small number of students did not use the numerical data of 0.468 g and 60 cm^3 to prove the molar mass of A. These students used the following approach, which is NOT acceptable for this question.

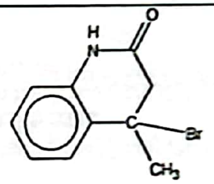
  1 mol of A undergoes reduction to give 1 mol of E.
  molar mass of E = 163.0 g mol^{-1}
  A has amide.
  molar mass of A = 163.0 – 2(1.0) + 16.0 = 177.0 g mol^{-1}

  Note that you are expected to use the numerical data of 0.468 g and 60 cm^3 to prove the molar mass of A.

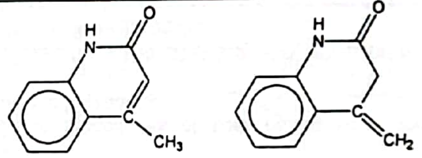
(ii) Hence, deduce the structural formulae of all the above structures, and explain the chemistry involved. [6]



A



D



B & C

1 mk for each structure [4]

1/2 mk for each point (max of 2 mks):

1) rom the molar mass of 177 g mol^{-1}, the molecular formula is likely to be $C_{10}H_{11}O_2N$.
2) A undergoes basic hydrolysis with NaOH (aq) to give –COO$^-$ (–COOH + NaOH) and –NH$_2$. –COO$^-$ is an ionic salt that dissolves in water by forming ion-dipole interactions with water. ⇒ A contains an amide group to give an amine and carboxylic salt when hydrolysed.

   Some students wrote that the compounds form from the hydrolysis of A dissolves in water to via formation of hydrogen bonds with water. It may seem correct, but note that A contains an amide in a cyclic structure, hence after hydrolysis, there will be only one single product
3) A undergoes elimination with Al$_2$O$_3$ to give alkenes B and C ⇒ A contains an alcohol group
4) The amide group in A undergoes reduction with LiAlH$_4$ to give an amine in E
5) Alkenes B and C undergo electrophilic addition with HBr to give halogenoalkane/alkyl halide/bromoalkane D.
6) D contains a chiral carbon and hence exists as a pair of enantiomers.

Comments

Out of the above 6 statements, the following key points are expected to gain credit.

- A undergoes (basic) hydrolysis with NaOH ⇒ A contains an amide group
- A undergoes elimination with Al$_2$O$_3$ to give alkenes B and C ⇒ A contains an alcohol group

- The amide group in A undergoes reduction with $LiAlH_4$ to give an amine in E
- Alkenes B and C undergo electrophilic addition with HBr to give halogenoalkane/alkyl halide/bromoalkane D.

OR

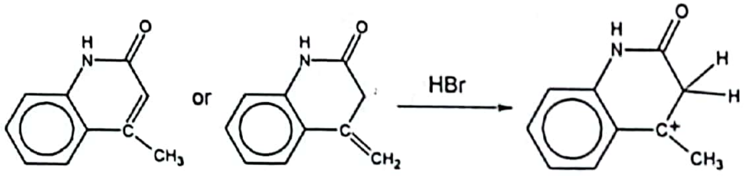
- D contains a chiral carbon and hence exists as a pair of enantiomers.

4 bullet pts correct – 2 marks
2 bullet pts correct (minimum) – 1 mark

(iii) State the type of isomerism exhibited by B and C. Explain why B and C both give the same product D when reacted with HBr. [2]

Constitutional isomerism. [1]

When alkenes B and C undergo electrophilic addition with HBr, both form the same carbocation. The carbocation will be attacked by Br^-, which leads to the formation of D.



B or **C** carbocation

[1] for explanation & structure of carbocation

[Total: 22]

Section B

Answer **one** question from this section.

4 Cycloalkanes are a homologous series of cyclic saturated hydrocarbons with the general formula C_nH_{2n} while n-alkanes are a homologous series of straight-chain saturated hydrocarbons with the general formula C_nH_{2n+2}.

n-alkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}	cycloalkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}
ethane	–89	–373.0	-	-	-
propane	–42	–530.4	cyclopropane	–33	–499.8
butane	–1	–687.8	cyclobutane	12	–656.0
pentane	36	–845.2	cyclopentane	49	–793.5
hexane	69	–1002.6	cyclohexane	81	–944.6
heptane	98	–1160.0	cycloheptane	119	–1108.3

(a) Explain the term "homologous series". [1]

Group of organic compounds with

- Same functional group
- Differ by a CH_2 group

(b) Explain the increase in magnitudes of both boiling point and enthalpy change of combustion from ethane to heptane. [3]

- Alkanes have simple molecular structure with weak instantaneous dipole-induced dipole (id-id) forces between molecules
- From ethane to heptane, the electron cloud gets bigger and more easily polarised, hence id-id forces become stronger.
- More energy needed to break the id-id forces, hence boiling point increases
- From ethane to heptane, the molecule increases by a CH_2 group
- This results in more C – C bonds and C – H bonds to break and more C=O and O – H bonds to form, hence more heat given off during combustion.

•✓•✓✓

(c) Suggest why combustion tends to be incomplete as the alkane increases in molecular mass. [1]

As the alkane increases in molecular mass, the alkane becomes liquid and liquid phase reactions are slower than gas phase reactions. Hence combustion tends to be incomplete.

Cyclopropane is a colourless gas with a "petroleum-like" odour. Unlike its straight-chain counterpart, it is considered to be highly strained and unstable. The instability of cyclic alkanes can be measured by calculating its "ring strain energy" using the formula below:

$$\text{Ring strain energy} = \begin{array}{c}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{array} \times \left(\left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in the}\\ \text{cyclic alkane, A}\end{array} \right| - \left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in an}\\ \text{unstrained n-alkane}\end{array} \right| \right)$$

(d) Given that the ΔH_f of CO_2 is −94.05 kcal mol^{-1} and ΔH_f of water is −68.3 kcal mol^{-1}, write an equation showing the formation of cyclopropane, and hence calculate the enthalpy change of formation of cyclopropane. [2]

$3C(s) + 3H_2(g) \rightarrow C_3H_6(g)$

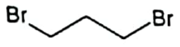
$\Delta H_f = [3(-94.05) + 3(-68.3)] - (-499.8) = +12.75$ kcal mol^{-1}

(e) Using the formula above, prove that the ring strain energy in cyclopropane is +27.6 kcal mol^{-1}. [2]

Enthalpy change of combustion of CH_2 group in unstrained molecule
= −530.4 − (−373.0) = −157.4 kcal mol^{-1} (can use other values to subtract)
Enthalpy change of combustion of CH_2 group in cyclopropane
= 1/3 (−499.8) = −166.6 kcal mol^{-1}
Strain energy of cyclopropane = 3 × (166.6 − 157.4) = +27.6 kcal mol^{-1}

(f) Due to the presence of ring strain, cyclopropane undergoes an addition reaction with bromine in the absence of ultraviolet radiation.

(i) Suggest the skeletal structure of the molecule formed after reaction with Br_2. [1]



(ii) Hence, using VSEPR theory, explain why the presence of ring strain causes cyclopropane to undergo addition reactions. [1]

Cyclopropane has a C – C – C angle of 60° which is smaller than the optimal angle of 109.5° in sp^3 carbons. As a result, bond pairs are much closer to each other and experience greater repulsion, hence weakening the C – C bonds, which breaks easily during addition.

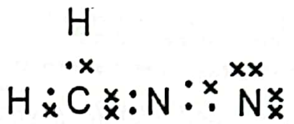
(g) Cyclopropane rings can be formed using a technique called "cyclopropanation".

One such cyclopropanation technique involves the 2 mechanistic steps stated below:

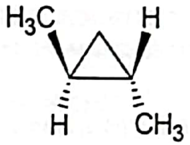
Step 1: Dissociation of diazomethane, CH_2N_2 to form methylene, CH_2, and N_2.

Step 2: Addition of methylene, CH_2, to trans-but-2-ene to form the cyclic ring. The reaction leaves the stereochemistry of the molecule unchanged.

(i) It is observed that the diazomethane molecule is trigonal planar in shape. By considering the shape, draw a dot-and-cross diagram of diazomethane, CH_2N_2, clearly showing the type of bonds formed within the molecule. [1]

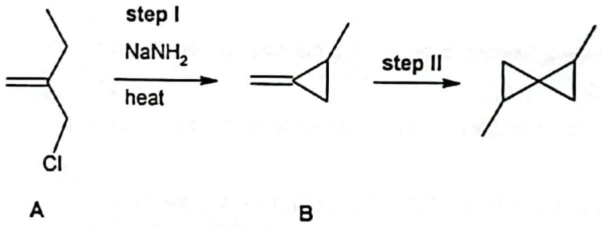


(ii) Draw the structure of the cyclic molecule formed in **step 2**, showing the stereochemical arrangement clearly. State and explain if the molecule can rotate plane-polarised light. [2]



Yes, the molecule contains two chiral centres and does not have an internal plane of symmetry.

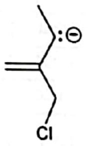
Cyclopropane rings are a precursor for many types of fatty acids. The following shows part of the synthetic route for fatty acids.



(iii) **Step I** involves the reaction of molecule **A** with $NaNH_2$ to form NH_3 and a negatively-charged organic intermediate which eventually formed molecule **B** upon heating.

State the type of reactions that took place in **step I** and draw the organic intermediate that was formed. [2]

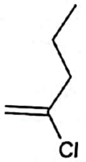
- Molecule A reacted with $NaNH_2$ in an acid base reaction



- (Intramolecular) nucleophilic substitution

•✓✓

(iv) By considering the reactivity of the Cl atom, explain why molecule **C** cannot be used to replace molecule **A** in the synthesis above. [1]



C

The chloro group is directly bonded to the double bond.

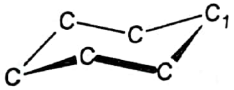
- The p orbital of Cl overlaps with the π orbital of the C=C bond,
- hence lone pair on Cl delocalises into the C=C bond,
- strengthening the C – Cl bond.

Hence, the Cl atom is resistant to nucleophilic substitution.

(v) Using the above information, suggest a suitable reagent for **step II**. [1]

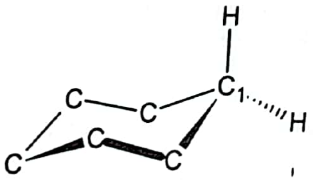
$CH(CH_3)N_2$

(h) Unlike the cyclic alkanes smaller than cyclohexane, cyclohexane does not experience ring strain due to the "chair shape" arrangement adopted by the six carbons as seen below:



chair shape arrangement of carbon atoms

By copying out the chair shape arrangement above and drawing the 3-D arrangement of hydrogen atoms bonded to C₁, explain why cyclohexane does not experience ring strain. [2]



- *Cyclohexane does not experience ring strain as cyclohexane bond angles are close to 109.5° due to the chair shape formation.*

[Total: 20]

5(a) The halogens and their compounds, show many similarities and trends in their properties. Some data are given for the elements fluorine, chlorine and iodine.

Element	Bond Energy / kJ mol^{-1}	Standard enthalpy change of atomisation / kJ mol^{-1}
Fluorine	158	79
Chlorine	242	121
Bromine	193	112
Iodine	151	107

(i) For fluorine and chlorine, their enthalpy changes of atomisation are half the value of their respective bond energies. For bromine and iodine, their enthalpy changes of atomisation are much more than half the value of their respective bond energies.

Explain in detail this difference. [1]

Fluorine and chlorine are gases but bromine is a liquid and iodine is a solid at room temperature. The enthalpy change of atomisation includes the energy required to change $Br_2(l) \rightarrow Br_2(g)$ and $I_2(s) \rightarrow I_2(g)$ [to vapourise bromine and iodine to the gaseous state].

(ii) The standard enthalpy change of formation of iodine monochloride, I–Cl, is −24.0 kJ mol^{-1}.

Use this information and the data from the table above to calculate the I–Cl bond energy. [1]

$\Delta H_r = \sum \text{Bonds broken} - \sum \text{Bonds formed}$

$-24.0 = \frac{1}{2}\text{BE(Cl–Cl)} + \frac{1}{2}\text{BE(I–I)} - \text{BE(I–Cl)}$

$\text{BE(I–Cl)} = +220.5$

$= +221 \text{ kJmol}^{-1}$

(iii) Explain why your answer in **(ii)** is larger in value compared to the average of the bond energies of I–I and Cl–Cl. [1]

I–Cl is polar while I–I and Cl–Cl are non-polar molecules. There is additional electrostatic attraction between $I^{\delta+}$ and $Cl^{\delta-}$. Hence, the actual bond energy of I–Cl is greater than the average bond energies of I–I and Cl–Cl.

(b) ICl reacts with pure water to form HCl and HI:

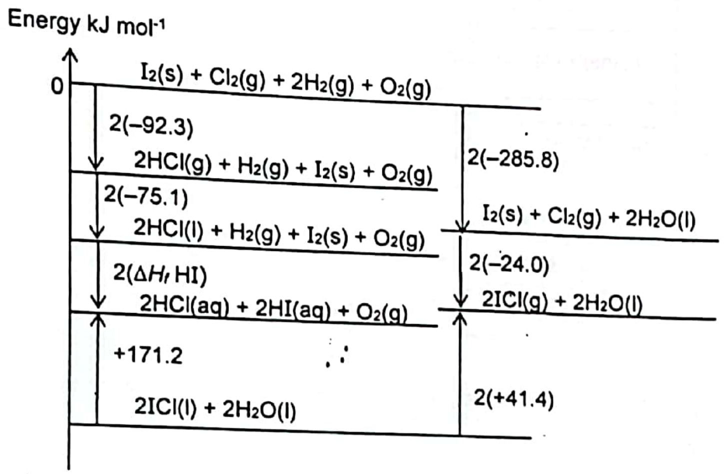
$2ICl(l) + 2H_2O(l) \rightarrow 2HCl(aq) + 2HI(aq) + O_2(g) \qquad \Delta H_r = +171.2 \text{ kJ mol}^{-1}$

Using ΔH_r, the following data, as well as relevant data from **a(ii)**, draw an energy level diagram to calculate the enthalpy change of formation of aqueous HI.

Label your diagram and draw arrows representing the energy terms involved. Use words or symbol to represent these energy terms.

	ΔH / kJ mol^{-1}
Standard enthalpy change of formation of H_2O	–285.8
Standard enthalpy change of formation of gaseous HCl	–92.3
Standard enthalpy change of reaction: $HCl(g) \rightarrow HCl(aq)$	–75.1
Standard enthalpy change of vaporisation of liquid ICl	+41.4

[4]



[1]x2 Balanced equations, State symbols and enthalpy for 3 reactions x 2

[1] Energy level diagram (energy axis, '0' at elements level, correct direction of arrows)

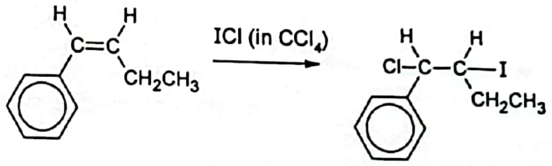
By Hess' Law:

$2(-24.0) + 2(-285.8) + (+171.2) = 2(41.4) + 2(-92.3) + 2(-75.1) + 2\Delta H_f(HI(aq))$

$2\Delta H_f(HI(aq)) = -2(-75.1) - 2(-92.3) + 2(-285.8) + 2(-24.0) - 2(41.4) + (+171.2)$

$\Delta H_f(HI(aq)) = -98.2$ kJ mol^{-1} [1]

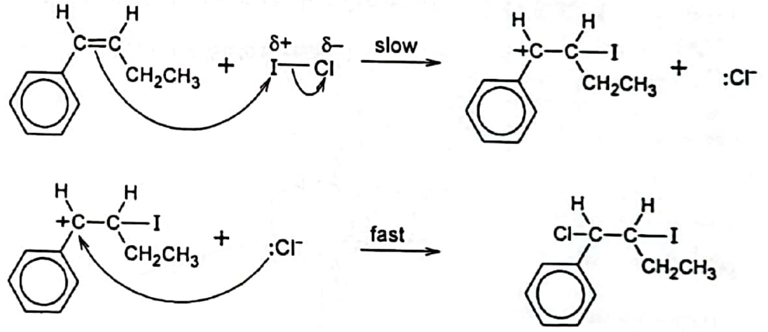
(c) ICl is a useful reagent in organic synthesis. It is used in the following reaction to form compound **E**.



E

(i) Describe the mechanism for the formation of **E**. [3]

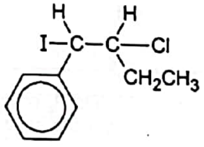
Electrophilic Addition



- Name of mechanism
- Correct arrows indicated
- Correct carbocation drawn
- Balanced equations
- Slow/ fast steps
- Charges on the atoms, lone pairs of electrons on Cl$^-$

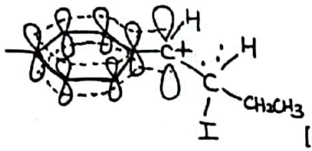
Every 2 points – 1 mark

(ii) With the aid of a diagram, explain why **E** is formed and not **F**. [2]



F

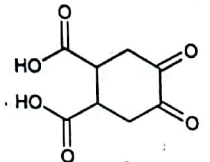
The carbocation and the C atoms in benzene ring are sp^2 hybridised. The (+) charge on carbocation is dispersed over the neighbouring benzene ring. Due to the effective overlap between the unhybridised p-orbitals of benzene and the empty p-orbital on the carbocation, the delocalised electrons makes the (+) charge on the carbocation less (+). [1]



[1]

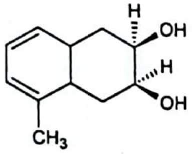
(d) Compound **J**, $C_{11}H_{16}O_2$, decolourises bromine water. 1 mole of **J** reacts with sodium metal to produce 22.7 dm^3 of hydrogen gas at s.t.p. On heating with acidified $KMnO_4$, **K**, $C_9H_{10}O_5$, is the only organic product formed.

K reacts with sodium carbonate and 2,4-DNPH. When **K** reacts with alkaline aqueous iodine, **L** is formed upon acidification.

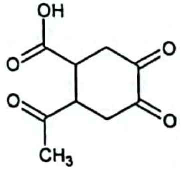


L

Suggest structures for **J** and **K** and explain the reactions described. [5]



J

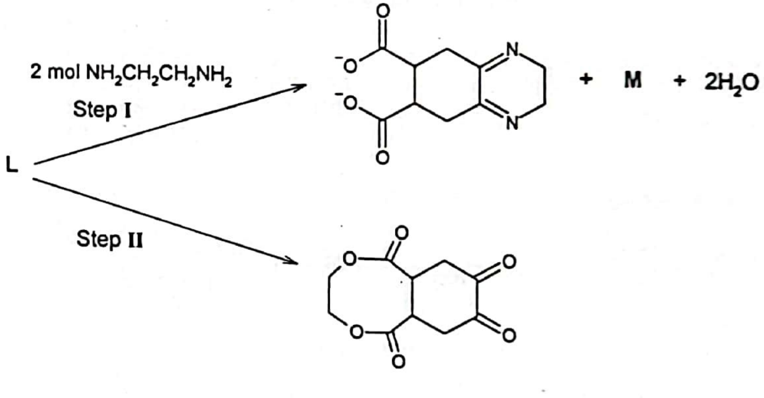


K

Observations	Deductions
J,$C_{11}H_{16}O_2$ decolourises bromine water	**J** could be alkene or phenol. An alkene undergoes electrophilic addition reaction with $Br_2(aq)$ to form halogenoalkane.
22.7 dm^3 of hydrogen is formed at s.t.p when **J** is reacted with sodium metal	$n(H_2) = \frac{22.7}{22.7}$ = 1 mol of H_2 is formed. $ROH + Na \rightarrow RO^-Na^+ + \frac{1}{2}H_2$ Since 1 FG produces ½ mole of H_2, there must be 2 –OH groups present. –COOH group is absent as it will only produce only ½ mole of H_2 and 2 –COOH groups or 1 –OH & 1 –COOH groups cannot be present as it will not correspond to the molecular formula of **J**.
On heating with acidified $KMnO_4$, **K**, $C_9H_{10}O_5$, is the only organic product formed	Secondary alcohol and the alkene in **J** undergoes oxidation with $KMnO_4$ to form ketones and carboxylic acid. There is a decrease in 2C atoms – which suggest that ethane-1,2-dioc acid was oxidised to form CO_2. From the given structure of **L**, it can be seen that **K** is unlikely a phenol and should not contain benzene as there will not be oxidation that leads to a reduction of 2 C atoms.
K reacts with sodium carbonate and 2,4 DNPH	**K** undergoes acid-base with Na_2CO_3 → –$COCH_3$ present. **K** undergoes condensation with 2,4 DNPH → –confirms presence of ketones.
K reacts with alkaline aqueous iodine to form **L**	**K** undergoes mild oxidation with alkaline $I_2(aq)$ → –$COCH_3$ present. **K** undergoes acid-base reaction with alkali to form salt → –COOH present.

1 mark for each correct structure
3 marks for explanation
5 points – 3 marks
3 to 4 points – 2 marks
2 points – 1 mark

(e) In the following reaction scheme, compounds **M** and **N** can be obtained from **L**.



N

(i) Draw the structure of **M**. State the type(s) of reaction in Step **I**. [2]

$^+NH_3CH_2CH_2NH_3^+$ [1] Types of reaction: Condensation, Acid – Base [1]

(ii) Suggest reagents and conditions to synthesise product **N** from **L**. [1]

$CH_2(OH)CH_2(OH)$, concentrated H_2SO_4 heat under reflux.

OR

1) PCl_5 at rtp 2) $CH_2(OH)CH_2(OH)$, rtp

[Total: 20]