| Class | Reg Number |
|---|---|
| | |

**Candidate Name** ______________________________

# Meridian Junior College
# 2009 JC 2 Preliminary Examination Answers
# H2 Chemistry 9746

## Paper 2
## STRUCTURED QUESTIONS

**Additional Materials**
*Data Booklet*

### INSTRUCTION TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.
Write in dark blue or black ink.
You may use a soft pencil for any diagrams or graphs.
You are reminded on the need for good English and clear presentation of your answers.

### INFORMATION FOR CANDIDATES

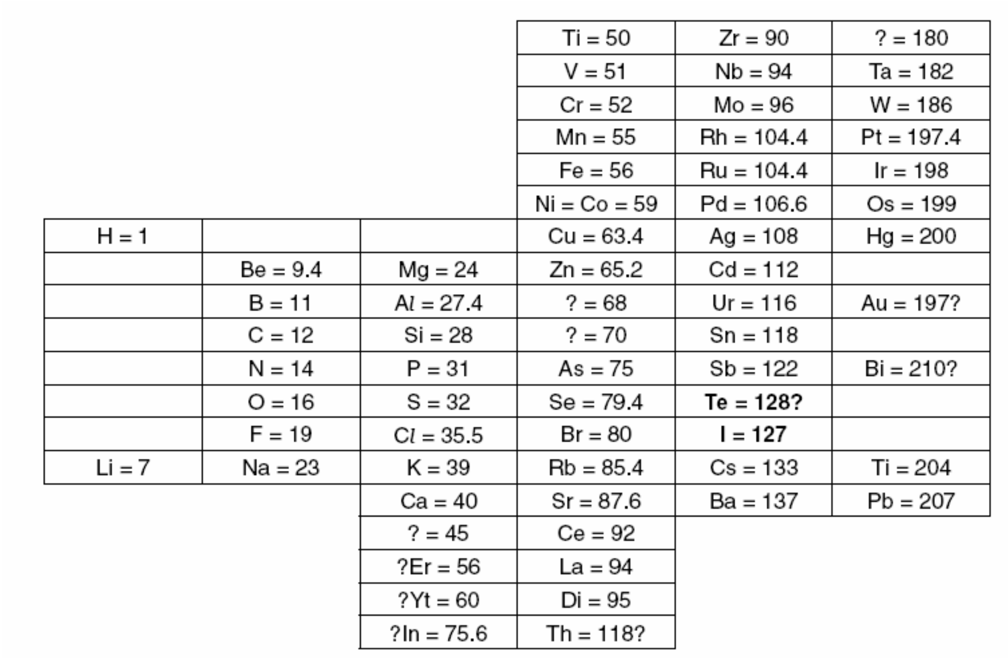
The number of marks is given in brackets [ ] at the end of each question or part of question.

| FOR EXAMINER'S USE | |
|---|---|
| Q1 | / 8 |
| Q2 | / 8 |
| Q3 | / 11 |
| Q4 | / 11 |
| Q5 | / 12 |
| Q6 | / 10 |
| Total | / 60 |

**This question paper consists of 17 printed pages**

***Answer all the questions in the space provided***

**1** Early Periodic Tables, such as that devised by Mendeleev, listed the then known elements in order of their relative atomic mass.



| | | | | | |
|---|---|---|---|---|---|
| | | | Ti = 50 | Zr = 90 | ? = 180 |
| | | | V = 51 | Nb = 94 | Ta = 182 |
| | | | Cr = 52 | Mo = 96 | W = 186 |
| | | | Mn = 55 | Rh = 104.4 | Pt = 197.4 |
| | | | Fe = 56 | Ru = 104.4 | Ir = 198 |
| | | | Ni = Co = 59 | Pd = 106.6 | Os = 199 |
| H = 1 | | | Cu = 63.4 | Ag = 108 | Hg = 200 |
| | Be = 9.4 | Mg = 24 | Zn = 65.2 | Cd = 112 | |
| | B = 11 | Al = 27.4 | ? = 68 | Ur = 116 | Au = 197? |
| | C = 12 | Si = 28 | ? = 70 | Sn = 118 | |
| | N = 14 | P = 31 | As = 75 | Sb = 122 | Bi = 210? |
| | O = 16 | S = 32 | Se = 79.4 | **Te = 128?** | |
| | F = 19 | Cl = 35.5 | Br = 80 | **I = 127** | |
| Li = 7 | Na = 23 | K = 39 | Rb = 85.4 | Cs = 133 | Ti = 204 |
| | | Ca = 40 | Sr = 87.6 | Ba = 137 | Pb = 207 |
| | | ? = 45 | Ce = 92 | | |
| | | ?Er = 56 | La = 94 | | |
| | | ?Yt = 60 | Di = 95 | | |
| | | ?In = 75.6 | Th = 118? | | |

**(a)** **(i)** When Mendeleev created the table, there were uncertainties regarding the relative atomic mass of tellurium. It is now known that there are eight isotopes of tellurium. Complete the following table and use it to calculate the relative atomic mass of tellurium.

| **isotope** | **percentage abundance** | **isotopic mass x percentage abundance** |
|---|---|---|
| tellurium-120 | 0.09 | 11 |
| tellurium-122 | 2.46 | 300 |
| tellurium-123 | 0.87 | 107 |
| tellurium-124 | 4.61 | 572 |
| tellurium-125 | 6.99 | 874 |
| tellurium-126 | 18.71 | 2357 |
| tellurium-128 | 31.79 | 4069.12 |
| tellurium-130 | 34.48 | 4482.40 |

Complete the above table and give your answers to **two** decimal places.

Hence, calculate the relative atomic mass of tellurium to **five** significant figures.

$$A_r \text{ of Te} = \frac{(11 + 300 + 107 + 572 + 874 + 2357 + 4069.12 + 4482.40)}{100} = \underline{\mathbf{127.73}}$$

**(ii)** $TeO_2$ resembles aluminium oxide in its acid-base properties. $TeO_2$, $SiO_2$ and $P_4O_{10}$ cannot be distinguished based on their physical appearance.

If a sample of one of the oxides was provided as a fine powder, describe the reactions you could carry out on the powder to determine which of the three oxides it was. Include all relevant equations in your answer.

Dissolve a portion of the sample in water. If the oxide is soluble in water, then the oxide is $P_4O_{10}$

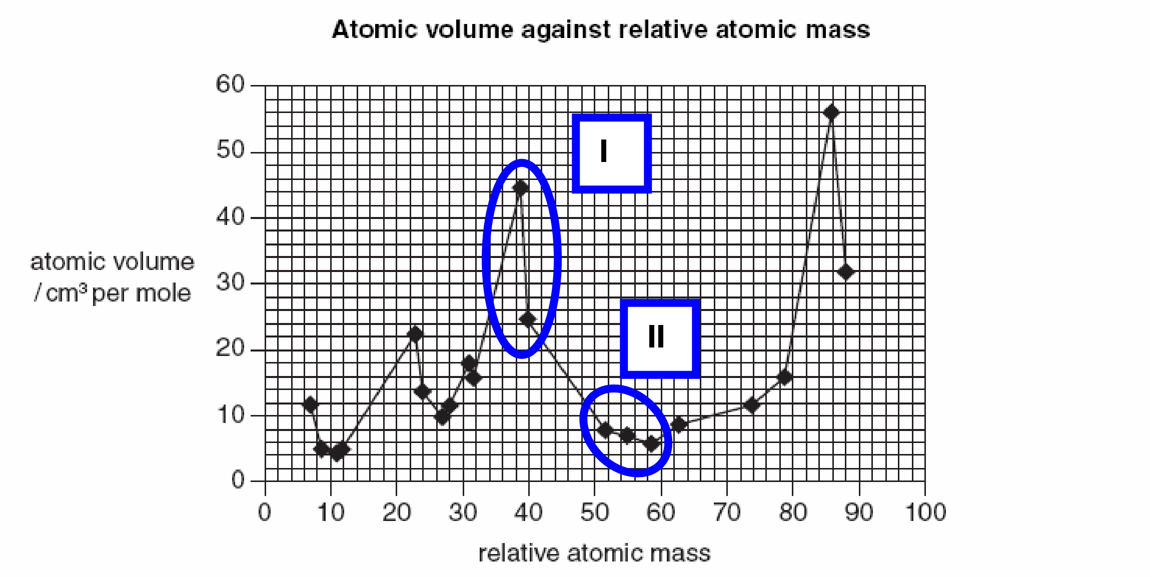
$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

Dissolve another sample of the oxide in HC*l*(aq). If the oxide is soluble in HC*l*, then the oxide is $TeO_2$ The oxide that is insoluble in HC*l* is then $SiO_2$

$$TeO_2 + 4\,HCl \rightarrow TeCl_4 + 2H_2O$$

**[5]**

**(b)** Another chemist looking for patterns in the properties of the elements around the time of Mendeleev was Julius Lothar Meyer. Lothar Meyer looked at how the atomic volume of an element varies with its relative atomic mass. A simplified version of the graph he plotted is shown below.



There are 2 circled regions on the graph. Explain why there is only a slight decrease in atomic volume between the elements in region **II** compared to region **I**.

Across the transition elements series,

–Inner 3d electrons provide effective shielding of the 4s electrons.

- Increase in shielding effect almosts cancels the increase in nuclear charge
- Effective nuclear charge increases slightly.
- Electrostatic forces of attraction between outer electrons and nucleus increases slightly hence atomic radius decreases slightly.

However, across the main group elements, increase in nuclear charge outweighs the negligible increase in screening effect.

- Effective nuclear charge increases drastically and atomic radius decreases drastically.

**[3]**

**[Total: 8]**

**2** 'Hard' water is water that has high mineral content such as calcium ions.

A common washing-up liquid contains sodium dodecylbenzenesulphonate, $C_{18}H_{29}SO_3Na$ [$M_r$ = 348]. In 'hard' water, it is ineffective as a detergent because it reacts with calcium ions to give a precipitate. The solubility product, $K_{sp}$, for $(C_{18}H_{29}SO_3)_2Ca$ (s) is $1.20 \times 10^{-17}$ mol$^3$ dm$^{-9}$.

The washing-up liquid contains 17.4% of sodium dodecylbenzenesulphonate by mass. In a factory production, 0.500 dm$^3$ of 0.102 g dm$^{-3}$ of the washing-up liquid was accidentally mixed with 0.200 dm$^3$ of 'hard' water.

A typical sample of 'hard' water has a concentration of calcium ions of $2.50 \times 10^{-4}$ mol dm$^{-3}$.

**(a)** Determine whether a precipitate is formed when the common washing-up liquid was accidentally mixed with 0.200 dm$^3$ of 'hard' water.

Ionic product of $(C_{18}H_{19}SO_3)_2Ca = (7.143 \times 10^{-5})\,(3.643 \times 10^{-5})^2$

$= \underline{\mathbf{9.48 \times 10^{-14}\ mol^3\ dm^{-9}}}$

Ionic product > $K_{sp}$ ⇒ precipitate of $(C_{18}H_{19}SO_3)_2Ca$ is formed.

**[2]**

**(b)** In order for the detergent to be used in 'hard' water, sodium tripolyphosphate, $Na_5P_3O_{10}$, is added as a water softening agent.

The sodium tripolyphosphate 'softens' water by complexing with calcium ions. The complexation reaction is as follows:

$$Ca^{2+}\,(aq) + P_3O_{10}^{5-}\,(aq) \rightleftharpoons CaP_3O_{10}^{3-}\,(aq)$$

For this reaction with calcium ions, the equilibrium constant is $7.7 \times 10^{8}$ mol$^{-1}$ dm$^{3}$.

**(i)** Write the $K_c$ expression for the reaction.

$$\boldsymbol{K_c} = \frac{[CaP_3O_{10}^{3-}]}{[Ca^{2+}][P_3O_{10}^{3-}]}$$

**(ii)** Hence, calculate the concentration of tripolyphosphate ions required to reduce the calcium ion concentration in a typical sample of "hard water" to $1.0 \times 10^{-6}$ mol dm$^{-3}$.

*Let x be the initial concentration of* $P_3O_{10}^{5-}$ *required*

At equilibrium,

$$7.7 \times 10^{8} = \frac{2.49 \times 10^{-4}}{(1.0x10^{-6})(x - 2.49 \times 10^{-4})}$$

**x = 2.493 ×10$^{-4}$ mol dm$^{-3}$**

**[3]**

**(c)** 'Hard' water also contains magnesium ions which can form a precipitate with the detergent. For example, magnesium ions form magnesium iodide, $MgI_2$, in the presence of aqueous potassium iodide.

**(i)** The lattice energy of $MgI_2$ is –2327 kJ mol$^{-1}$ while the values of the enthalpy changes of hydration are listed below:

| **Ions** | **$\Delta H_{hyd}$ / kJ mol$^{-1}$** |
|---|---|
| $Mg^{2+}$ | -1920 |
| $I^-$ | -295 |

Calculate the enthalpy change of solution of magnesium iodide.

Enthalpy change of solution of magnesium iodide

= -(-2327) + (-1920) + 2(-295)

= **-183 kJ mol$^{-1}$**

**(ii)** By using your answer from **(c)(i)**, and given the entropy change of solution of magnesium iodide is positive, predict whether magnesium iodide is soluble in water at room temperature and pressure. Give your reasoning.

At lower temperatures, $-T\Delta S^o$ and $\Delta H^o$ is both negative hence $\Delta G$ = is also negative . Therefore the dissolution process is feasible and hence $MgI_2$ is soluble in water.

**[3]**

**[Total: 8]**

**3** Cobalt is a bluish-white element that can form various cobalt compounds with the ligands ethylenediamine, $H_2NCH_2CH_2NH_2$, and ethanedioate, $C_2O_4^{2-}$. Ethylenediamine is commonly expressed with the short form "*en*".

**(a)** Passing air through an aqueous solution containing $CoCl_3$, *en* and $HCl$ produces a green complex cation, $[Co(en)_2Cl_2]^+$. Another complex, $[Co(C_2O_4)_3]^{3-}$ is obtained on passing air through an aqueous solution of $CoCl_3$ and $C_2O_4^{2-}$.

**(i)** State the coordination number of Co in $[Co(en)_2Cl_2]^+$.

Coordination number of Co = 6

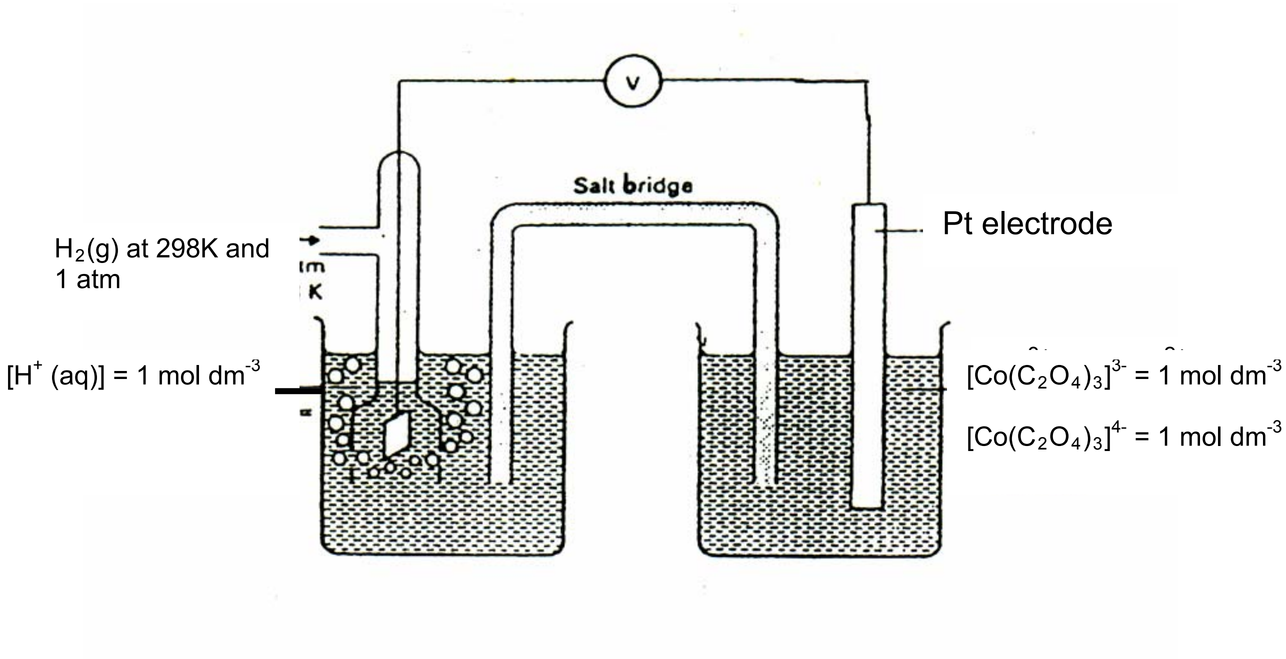
**(ii)** Explain why transition element complexes such as $[Co(en)_2Cl_2]^+$ are coloured.

In $Co^{2+}$ ions, the d orbitals are split into two groups due to the ability of the ligands to split them into the energy levels. d The d electrons undergoes d-d transition and is promoted to the higher d orbital. During the transition, the d electron absorbs a certain wavelength of light from the visible region of the electromagnetic spectrum and emits the remaining wavelength which appears as the colour of the complex observed.

**(iii)** The standard electrode potential of the $[Co(C_2O_4)_3]^{3-}$ / $[Co(C_2O_4)_3]^{4-}$ is given below.

$[Co(C_2O_4)_3]^{3-}(aq) + e^- \rightleftharpoons [Co(C_2O_4)_3]^{4-}(aq)$ $E^\ominus = +0.57$ V

Draw a fully labelled diagram to show how the standard electrode potential of the $[Co(C_2O_4)_3]^{3-}(aq)$ /$[Co(C_2O_4)_3]^{4-}(aq)$ system can be measured.



**(iv)** In general, the presence of ethanedioate ions, $C_2O_4^{2-}$, significantly decreases the oxidising ability of Co(III). Explain this effect by using the information in **(a)(iii)** and relevant data from the *Data Booklet*.

$[Co(H_2O)_6]^{3+} + e \rightleftharpoons [Co(H_2O)_6]^{2+}$ $E^\theta = +1.82$ V

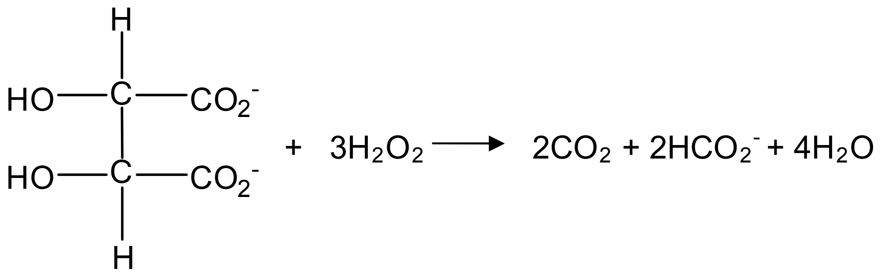
In water, the highly positive $E^\theta$ indicates that $Co^{3+}$ is unstable with respect to $Co^{2+}$ and should be spontaneously reduced to $Co^{2+}$

$[Co(C_2O_4)_3]^{3-}(aq) + e^- \rightleftharpoons [Co(C_2O_4)_3]^{4-}(aq)$ $E^\ominus = +0.57$ V

In the presence of $C_2O_4^{2-}$ ligands, the reduction potential decreases significantly to $E^\ominus$ $[Co(C_2O_4)_3]^{3-}$ / $[Co(C_2O_4)_3]^{4-}$=+0.57 meaning that $C_2O_4^{2-}$ ligand stabilises the +3 oxidation state of Co with respect to the +2 oxidation state

**[9]**

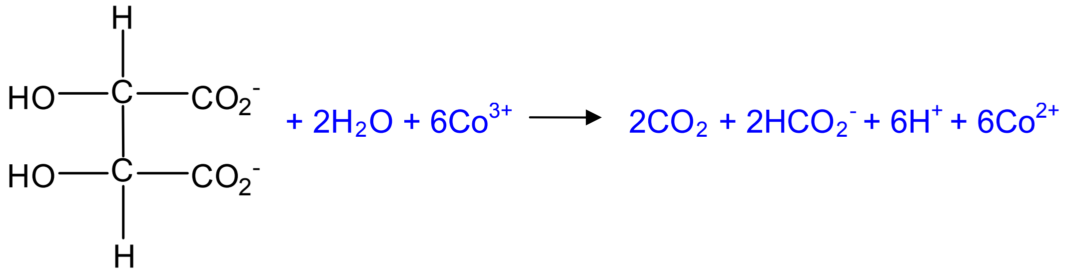
**(b)** Other than being used as silica gel, cobalt (II) chloride can also be used as a homogeneous catalyst for the reaction of 2,3-dihydroxybutanedioate ions and hydrogen peroxide to form carbon dioxide, methanoate ions and water.



$$HO{-}CH(CO_2^-){-}CH(CO_2^-){-}OH + 3H_2O_2 \longrightarrow 2CO_2 + 2HCO_2^- + 4H_2O$$

Suggest equations for a plausible mechanism for the catalysis of the above reaction using $Co^{2+}$ as the catalyst.

$2Co^{2+} + H_2O_2 + 2H^+ \rightarrow 2H_2O + 2Co^{3+}$



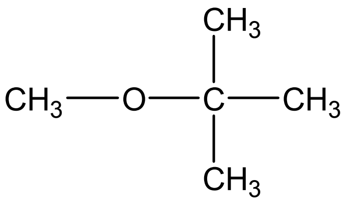
$$HO{-}CH(CO_2^-){-}CH(CO_2^-){-}OH + 2H_2O + 6Co^{3+} \longrightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6Co^{2+}$$

**[2]**

**[Total: 11]**

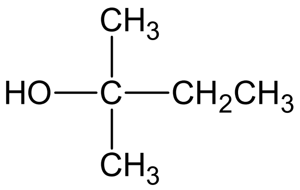
**4** *MTBE* as well as its isomer ***MTBE A*** is added to car petrol as oxygenates. There has been concern over the leakage of *MTBE* and ***MTBE A*** into water supplies, mainly because of the foul taste it gives to water supplies.

In the manufacture of fuel for industries, liquid ***MTBE A*** is added as a solvent to petroleum to reduce pollution.



$CH_3{-}O{-}C(CH_3)_3$

*MTBE*



$HO{-}C(CH_3)_2{-}CH_2CH_3$

*MTBE* **A**

**(a)** What is meant by the *standard enthalpy change of formation of MTBE **A***?

Standard enthalpy change of formation of *MTBE* ***A*** is the energy change when one mole of *MTBE A* is formed from its elements at standard conditions.

**[1]**

**(b)** Using relevant information from the *Data Booklet* and the data provided, obtain a value for the average bond energy for the O–H bond in *MTBE* ***A***, by means of an appropriate energy cycle.

Data provided: $\Delta H_{at}$ (C) = +715 kJ mol$^{-1}$,
$\Delta H_f$ (*MTBE* ***A***) = -380 kJ mol$^{-1}$
and $\Delta H_{vap}$ (*MTBE* ***A***) = +50.7 kJ mol$^{-1}$

$$\begin{tikzcd}
5\,C\,(s) + 6\,H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \arrow[rr, "\Delta H^{\theta}_{f\,(C_5H_{12}O)}"] \arrow[ddr] & & C_5H_{12}O\,(l) \arrow[d, "\Delta H_{vap}\,(MTBE\ \boldsymbol{A})"] \\
 & & C_5H_{12}O\,(g) \arrow[dl] \\
 & 5\,C\,(g) + 12\,H\,(g) + O\,(g) &
\end{tikzcd}$$

**Use Hess Law to solve**

$-380 = 5(715) + 6(436) + \tfrac{1}{2}(496) - [4(350) + 11(410) + 360 + BE(O\text{-}H)] - 50.7$

BE(O–H) = **+498 kJ mol$^{-1}$**

**[3]**

**(c)** Suggest a reason for the difference in the O–H bond energy obtained in **(b)** from the value given in the *Data Booklet*.

The bond energy values from the Data Booklet are average values

**[1]**

**(d)** In a combustion reaction of industrial fuel, *MTBE* is completely combusted in an engine cylinder at 175°C which had an internal volume of 1055 dm$^3$.

**(i)** Determine the pressure (in pascals) exerted by the carbon dioxide emitted by the combustion of 4 kg of *MTBE* fuel.

No. of moles of MTBE in 4 kg of fuel = $\dfrac{1000 \times 4}{88}$ = 45.45

$C_5H_{12}O \equiv 5\,CO_2$

Pressure of $CO_2$ $= \dfrac{227.27 \times 8.31 \times (175+273)}{1055 \times 10^{-3}}$

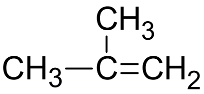
$= \underline{\mathbf{8.02 \times 10^{5}\ Pa}}$

**(ii)** In fact, the pressure inside the engine cylinder was found to be slightly lower than the value calculated in **d(i).** Explain this discrepancy in values observed.

$CO_2$ is not an ideal gas. There are significant intermolecular attractions between $CO_2$ molecules. Pressure observed is lower than the theoretical value.

**[4]**

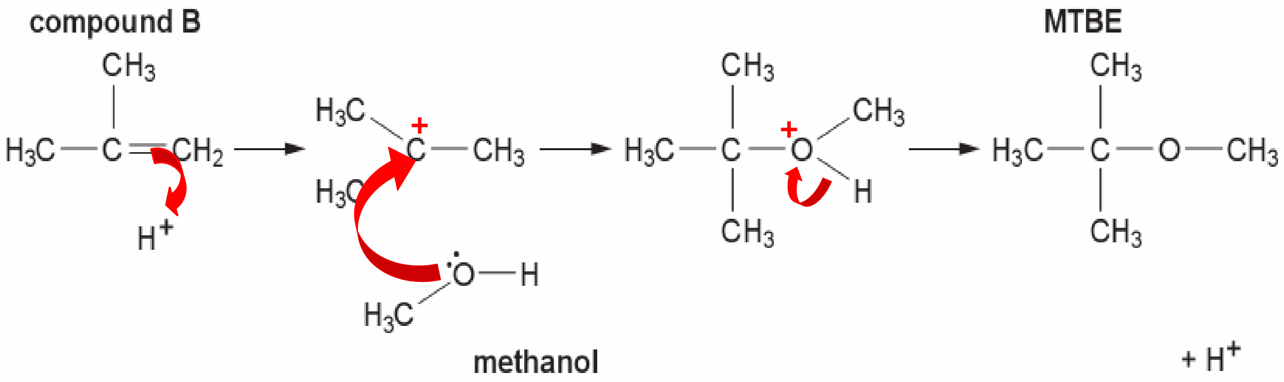
**(e)** *MTBE* can be made by reacting compound **B** with methanol in the presence of an acid catalyst.



$$CH_3-\overset{\overset{\large CH_3}{|}}{C}=CH_2$$

compound **B**

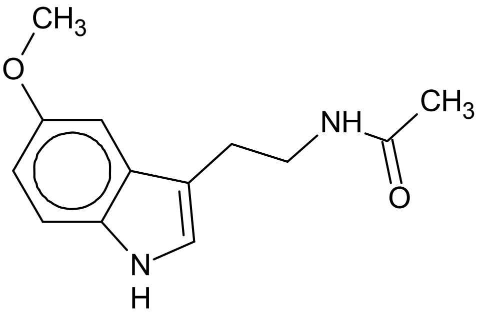
Complete the mechanism below by inserting "curly arrows" to show the movement of pairs of electrons and by inserting the appropriate charges.



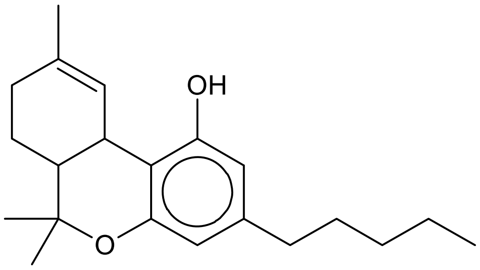
**[2]**

**[Total: 11]**

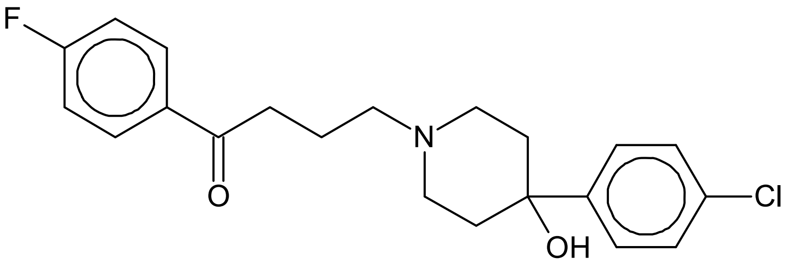
**5** *Melatonin* is a naturally occurring hormone found in animals, *THC* is a drug obtained from the cannabis plant, and *haloperiodol* is an antipsychotic drug.



*melatonin*



*THC*



*haloperiodol*

**(a)** Drug smugglers extract crude *THC* from cannabis leaves by using benzene as a solvent. Explain the rationale behind this extraction.

THC consists a large hydrophobic groups hence can form hydrophobic interactions with benzene molecules.

**[1]**

**(b)** All three organic molecules share similar reactions with some reagents only.

**(i)** State one reagent that will react with both *melatonin* and *haloperiodol* and **not** with *THC*.

Dilute $H_2SO_4$* *accept any other possible reagent*

**(ii)** State one reagent and the required condition that will react with both *melatonin* and *THC* but **not** with *haloperiodol*.

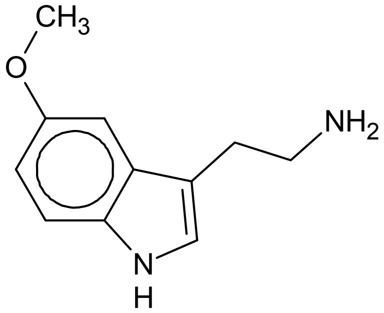
$Br_2$ in $CCl_4$ ,rtp * *accept any other possible reagent*

**(iii)** State one reagent, other than $MnO_4^-$ ions, and the conditions required that will react with all three compounds.

$H_2$ with Ni catalyst at high temperature and pressure **accept any other possible reagent*

**[3]**

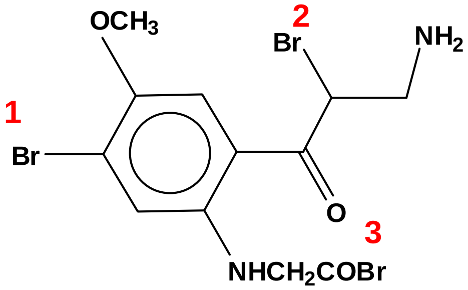
**(c)** *Melatonin* can be made through the reaction between two organic compounds in the laboratory. Suggest the structural formulae of these two compounds.



and $CH_3COCl$

**[1]**

**(d)** Melatonin can undergo a series of reactions to obtain compound **X**.



Compound **X**

Explain the different reactivities of the three bromine atoms in compound **X.**

It is easiest to hydrolyse the acyl bromide_as the electron deficient carbon atom/carbonyl carbon in –COBr is bonded to two electronegative atoms, O and Br. Hence, –COBr group is most susceptible to nucleophilic attack, thus it is most reactive. In Br (1) , the p-orbital of the bromine atom interacts with the π electron cloud of the benzene ring. bromide. Thus, rendering_nucleophile substitution difficult in aryl bromide. Hence, Br (1) is the least reactive.

**[3]**

**(e)** Describe a chemical test that would allow you to distinguish between the following pairs of compounds. The distinguishing may rely on a preliminary breaking-up of the compounds, and subsequent testing of the reaction products.

In each test, you must identify the **second** organic compound positively. State only the observations for the positive test.

**(i)** *THC* and *melatonin*

Test: Add dilute HC*l* **,** heat . Distill the products and add aqueous $Na_2CO_3$

Melatonin: Effervescence of $CO_2$ observed.

**(ii)** *THC* and *haloperiodol*

Test: Add 2,4-DNPH, heat

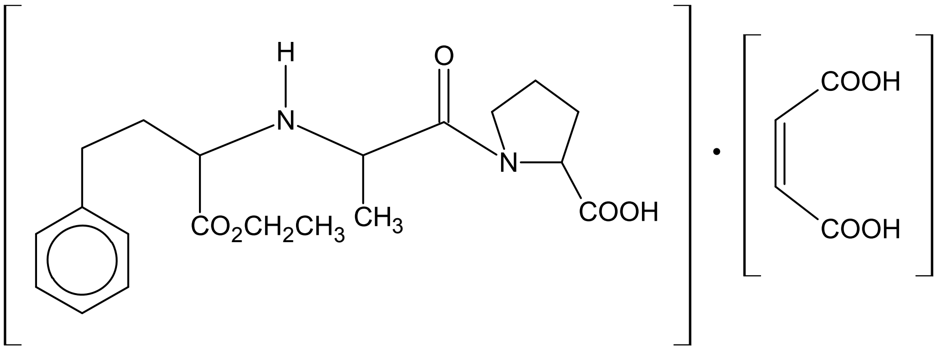
Haloperiodol: Orange ppt/crystals formed

**[4]**

**[Total: 12]**

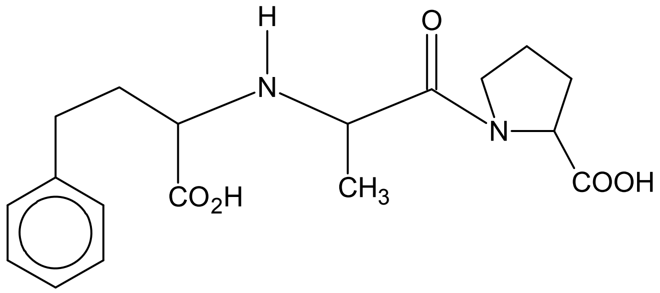
**6** *Enalapril maleate* is widely used in the treatment of hypertension and chronic heart diseases. When *Enalapril maleate* is consumed, the body hydrolyses the molecule into the active form, *Enalaprilate*, which suppresses the activity of enzymes that trigger high blood pressure.

*Enalapril maleate* is sold as tablets. Some additional information on *Enalapril maleate* and *Enalaprilate* are given below.



***Enalapril maleate***

Formula: $C_{24}H_{32}N_2O_9$
Relative molecular mass: 492
Route of administration: Oral
Dosage forms: 2.5 mg, 5.0 mg, 10.0 mg and 20.0 mg tablets



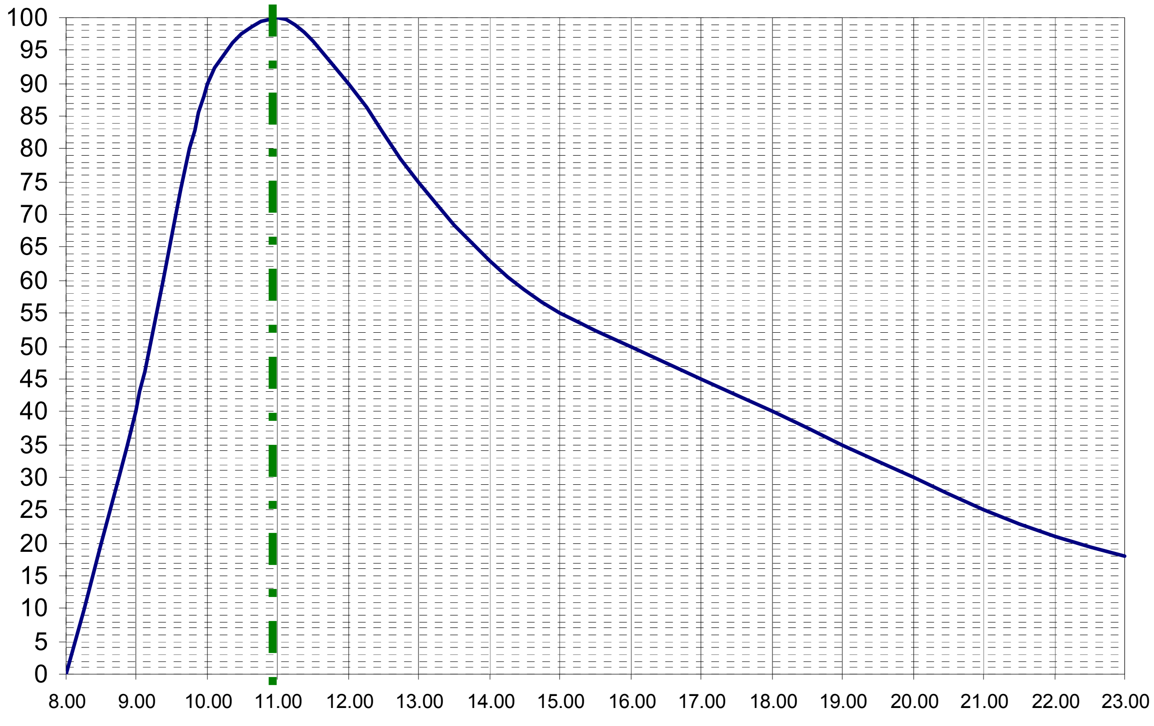
***Enalaprilate***
Formula: $C_{18}H_{24}N_2O_5$
Relative molecular mass: 348

**(a)** In a trial, a 55-kg patient took a 5.0 mg tablet of *Enalapril maleate* at 8 am in the morning. The body requires about 3 hours for *Enalapril maleate* to be hydrolysed to *Enalaprilate*.

Samples of the patient's blood were taken at fixed time intervals to measure the concentration of *Enalaprilate* in the plasma. The results are shown in the graph on the following page.

**% plasma concentration of *Enalaprilate***

**Concept : Start at 11 am since 3 hrs after 8 am**



**Time (hours)**

Deduce the order of reaction with respect to *Enalaprilate.* Hence, construct the rate equation for the breakdown of *Enaprilate* in the body.

There is a constant half-life hence the breakdown of *Enaprilate* follows first-order kinetics hence order is one.

Rate = k[Enaprilate]

**[2]**

**(b)** The toxicity level of *Enalapril maleate* is estimated to be approximately 71 µg per kg for human patients. Concentrations above this level would lead to harmful side effects.

Calculate the maximum number of 5.0 mg tablets that can be consumed by a 55-kg patient without any side effects, assuming that the body absorbs 60% of the administered dose and each tablet contains 50% by mass of *Enalapril maleate.*
[1 µg = $1 \times 10^{-6}$ g]

Maximum mass of *Enalapril maleate* for 55 kg patient

$= 71 \times 10^{-6} \times 55 = 3.905 \times 10^{-3}$ g

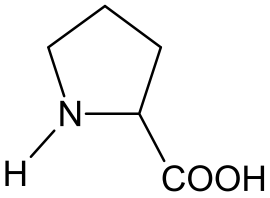
Mass of *Enalapril maleate* to be taken by patient $= \frac{60}{100} \times \frac{50}{100} \times 5 \times 10^{-3}$

$= 1.5 \times 10^{-3}$ g

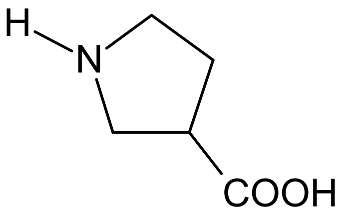
Max no. of tablets $= \frac{3.905 \times 10^{-3}}{1.5 \times 10^{-3}} = 2.6 \approx \underline{2}$

**[2]**

**(c)** Prolonged hydrolysis of *Enalapril maleate* in the laboratory produces compound **A**. State, with reasoning, how you would expect the volatility of **A** to compare with its isomer, compound **B**.



Compound **A**



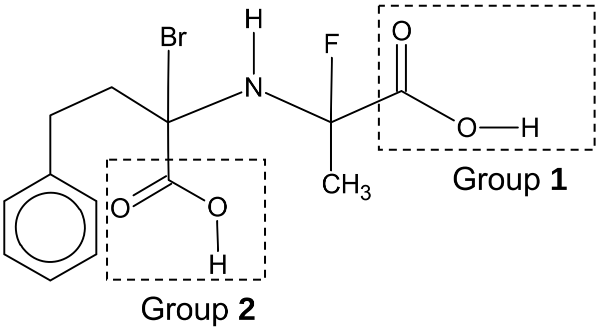
Compound **B**

Volatility of A > B.

| **A** | **B** |
|---|---|
| • Intramolecular hydrogen bonding occurs hence intermolecular hydrogen bonding is less feasible/extensive<br>. | • Boiling involves overcoming the stronger and more extensive hydrogen bonds between molecules.<br>• Larger amount of energy is required hence boiling point is higher |

**[3]**

**(d)** Compound **C** is derived from *Enalaprilate*.



Compound **C**

**C** possesses two carboxylic acid functional groups **1** and **2**. When **C** reacts with a base, predict which group would donate its proton first.
Explain your answer

Group **1**.

Electronegativity of F > Br hence electron-withdrawing effect on carboxylate ion for: F > Br . Extent of stabilisation of the conjugate base relative to the acid for : Group 1 > Group 2

**[3]**

**[Total: 10]**

**END OF PAPER**