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AUSTRALIAN SCIENCE INNOVATIONS

ASI School ID:

AUSTRALIAN SCIENCE OLYMPIADS

2012 AUSTRALIAN SCIENCE OLYMPIAD EXAM

CHEMISTRY – SECTIONS A & B

TO BE COMPLETED BY THE STUDENT. USE CAPITAL LETTERS

Student Name: ……

Home Address: ……

…… **Post Code:** ……

Telephone: (……) …… **Mobile:** ……

E-Mail: …… **Date of Birth:** ……/……/……

☐ **Male** ☐ **Female** **Year 10** ☐ **Year 11** ☐ **Other:** …….

Name of School: ……**State:** ……..

To be eligible for selection for the Australian Science Olympiad Summer School, students must be able to hold an Australian passport by the time of team selection (March 2013).

The Australian Olympiad teams in Biology, Chemistry and Physics will be selected from students participating in the Science Summer School.

Signature: …… Date: ……

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CHEMISTRY

2012 Australian Science Olympiad Exam

Time Allowed:

Reading Time: 10 minutes

Examination Time: 120 minutes

INSTRUCTIONS

- *Attempt ALL questions in ALL sections of this paper.*
- Permitted materials: Non-programmable non-graphical calculator, pens, pencils, erasers and a ruler.
- Answer SECTION A on the Multiple Choice Answer Sheet provided. **Use a pencil.**
- Answer SECTION B in the spaces provided in this paper. Write in pen and use a pencil only for graphs.
- Ensure that your diagrams are clear and labelled.
- All numerical answers must have correct units.
- Marks will not be deducted for incorrect answers.
- Rough working must be done only on pages 28 to 29 of this booklet.
- Relevant data that may be required for a question will be found on page 3.
- Do not staple the multiple choice answer sheet to this booklet.

MARKS

SECTION A	15 multiple choice questions	30 marks
SECTION B	3 short answer questions	90 marks
	Total marks for the paper	120 marks

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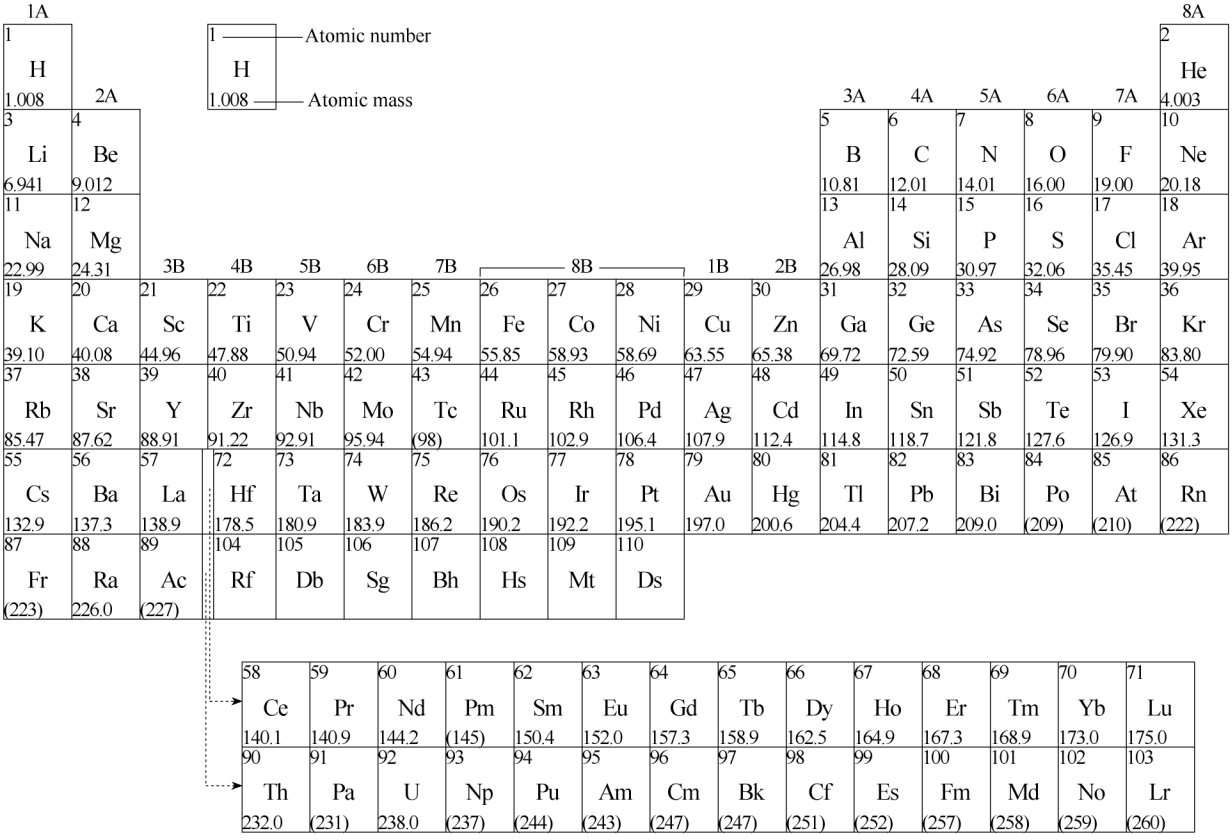
DATA

Avogadro constant (N)	6.02×10^{23} mol^{-1}	Velocity of light (c)	2.998×10^{8} m s^{-1}
1 faraday	96,486 coulombs	Density of water at 25°C	0.9971 g cm^{-3}
1 coulomb	1 A s^{-1}	Acceleration due to gravity	9.81 m s^{-2}
Universal gas constant (R) 8.314 J K^{-1} mol^{-1} 8.206×10^{-2} L atm K^{-1} mol^{-1}		1 newton (N)	1 kg m s^{-2}
Planck's constant (h)	6.626×10^{-34} J s	1 pascal (Pa)	1 N m^{-2}
Standard temperature and pressure (STP) 273 K and 100 kPa 0°C and 100 kPa 0°C and 1 bar 0°C and 750 mm Hg		$pH = -\log_{10}[H^+]$ $pH + pOH = 14.00$ at 25°C $K_a = \{[H^+][A^-]\} / [HA]$ $pH = pK_a + \log_{10}\{[A^-] / [HA]\}$ $PV = nRT$ $E = h\nu$	
Molar volume of ideal gas at STP	22.7 L	$c = \nu\lambda$	
1 bar = 100 kPa		Surface area of sphere $A = 4\pi r^2$	

Periodic table of the Elements



Atomic mass values given here are to four significant figures. A value given in parentheses denotes the mass of the longest-lived isotope.

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SECTION A: MULTIPLE CHOICE
USE THE ANSWER SHEET PROVIDED

1. Which one of the following compounds is the most acidic oxide?

   a. Na_2O
   b. MgO
   c. $A\ell_2O_3$
   d. SiO_2
   e. SO_2

2. Which one of the following elements has the highest electronegativity value?

   a. $C\ell$
   b. S
   c. P
   d. Si
   e. $A\ell$

3. A working galvanic cell is constructed using an iron electrode in an iron(II) nitrate solution and a silver electrode in a silver(I) nitrate solution. When the cell runs down, it can be charged up again. Which of the following scenarios will occur during the charging process? [$E^o(Ag^+_{(aq)}/Ag_{(s)} = +0.80$ V and $E^o(Fe^{2+}_{(aq)}/Fe_{(s)} = -0.41$ V]

   a. A minimum of 1.21 volts is applied to the cell and electrons move from the silver electrode to the iron electrode.
   b. A minimum of 1.21 volts is applied to the cell and electrons move from the iron electrode to the silver electrode.
   c. A minimum of 0.39 volts is applied to the cell and electrons move from the silver electrode to the iron electrode.
   d. A minimum of 0.39 volts is applied to the cell and electrons move from the iron electrode to the silver electrode.
   e. A minimum of 2.01 volts is applied to the cell and electrons move from the silver electrode to the iron electrode.

4. DNA consists of two strands that run in opposite directions to each other with one end being labelled 5' and the other 3'. Just like words on a page, DNA is read in one direction, from the 5' to the 3' end. A restriction enzyme, used to cut DNA, reads the DNA and recognises the sequence GAATTC and cuts the strands between G and A. If applied to the following helix of DNA how many pieces would result after denaturing the strand?

   5` A GTACGATATAACGAATTCTGACGTAGCGTTAGACTGAATTCATAG 3`
   3` T CATCCTATATTGCTTAAGACTGCATCGCAAGCTGACTTAAGTATC 5`

   a. 2
   b. 4
   c. 6
   d. 8
   e. 10

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5. Chlorine occurs naturally as a gas at room temperature, yet iodine is a solid. What is the **best** explanation for this behaviour?

a. The iodine molecule is heavier and hence has a lower vapour pressure.
b. The iodine molecule has more electrons and a larger nuclear charge, so it forms stronger bonds with its neighbours in solid form.
c. The chlorine molecule has a higher electronegativity and hence interacts more strongly with polar molecules in the atmosphere.
d. The iodine molecule has more electrons over a greater volume, so there are more dispersion forces due to induced dipoles.
e. The chlorine molecule is polar, and so is more easily displaced from solid or liquid phase by the molecules in air.

6. What is the p*H* of a 0.010 mol L^{-1} solution of a weak monoprotic acid that is 4.0% ionised?

a. 2.00
b. 2.40
c. 2.80
d. 3.40
e. 7.00

7. The salt $Na_2HAsO_4.nH_2O$ is an ionic salt containing n waters of crystallization. In warm air, this compound readily effloresces and loses these water molecules to its surroundings. If the mass lost during this process is 40.42% of the original, how many waters of crystallization were there originally?

a. 1
b. 3
c. 5
d. 6
e. 7

8. Which one of the following elements would be expected to form the largest ion with a noble gas electron configuration?

a. Aℓ
b. Cℓ
c. P
d. K
e. S

9. A certain buffer solution contains equal concentration of weak acid (HX) and its conjugate base (X^-). K_a for HX is 2.9×10^{-5}. What is the p*H* of the buffer?

a. 4.53
b. 5.53
c. 7.00
d. 8.47
e. 9.47

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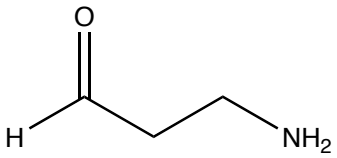
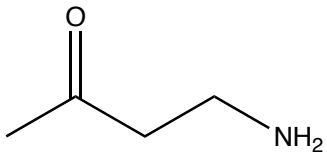
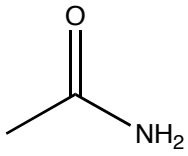
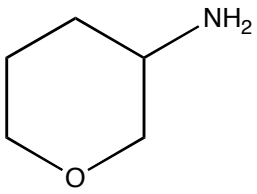
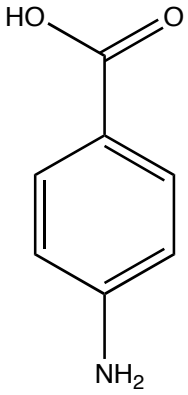
10. Which one of the following compounds is both an amine and a ketone?

a. 

b. 

c. 

d. 

e. 

11. The molecules listed below are of the general formula XY_n with n≥2. In which is the Y–X–Y bond angle the greatest?

a. BF_3
b. CH_4
c. H_2O
d. NH_3
e. $PC\ell_3$

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12. The enthalpy change of formation ($\Delta_f H^0$) for a species at 298 K is defined as the enthalpy change that accompanies the formation of one mole of a substance from its constituent elements in their standard states. Which of the following species has $\Delta_f H^0 = 0$ kJ mol^{-1}?

a. $H_2O_{(l)}$
b. $Na_{(g)}$
c. $Na_{(s)}$
d. $CO_{2(g)}$
e. $O_{3(g)}$

13. Doctor Who has a secret laboratory on Venus where atmospheric pressure is 92 times that of Earth and room temperature is 735 Kelvin. There, Doctor Who mixes 4.00 g of $CaCO_3$ with 40.00 mL of 1.00 mol L^{-1} HCℓ. What volume of carbon dioxide gas at VSTP (Venusian Standard Temperature and Pressure) is produced?

a. 1.81 mL
b. 13.1 mL
c. 26.2 mL
d. 52.4 mL
e. 111 mL

14. Use the standard reduction potential given below to calculate E^o for the following reaction:

$$Cr_2O_7^{2-}{}_{(aq)} + 14\ H^+{}_{(aq)} + 6\ Fe^{2+}{}_{(aq)} \rightarrow 2\ Cr^{2+}{}_{(aq)} + 7\ H_2O_{(\ell)} + 6\ Fe^{3+}{}_{(aq)}.$$

$$[E^o(Cr_2O_7^{2-}{}_{(aq)}/Cr^{3+}{}_{(aq)} = +1.33\ V \text{ and } E^o(Fe^{3+}{}_{(aq)}/Fe^{2+}{}_{(aq)} = +0.77\ V]$$

a. 0.56 V
b. 0.98 V
c. 1.00 V
d. 2.10 V
e. 3.29 V

15. One way to measure the concentration of a substance is through molality. A 1 molal solution is defined as 1 mol of substance per 1 kg of the solvent used to make up the solution. What is the molality of a solution made by dissolving 100 g of bromothymol blue ($C_{27}H_{28}Br_2O_5S$) in 1.00 L of ethanol on a winter's day at 10ºC? The density of ethanol at this temperature is 0.7979 kg L^{-1}.

a. 0.100 mol kg^{-1}
b. 0.128 mol kg^{-1}
c. 0.160 mol kg^{-1}
d. 0.201 mol kg^{-1}
e. 0.252 mol kg^{-1}

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SECTION B: 3 SHORT ANSWER QUESTIONS
ANSWER IN THE SPACES PROVIDED

Question 16

The final step in the industrial production of copper is electrolytic refinement. This process involves submerging two electrodes in a solution of copper(II) sulfate. One electrode is composed of unrefined (crude) copper and the second electrode is composed of refined copper. The electrodes are connected and a current is induced such that copper atoms of the crude electrode lose electrons to form Cu^{2+} ions that pass into solution. Simultaneously at the other electrode, copper ions in solution gain electrons and form solid (refined) copper.

(a) (i) Write the half-equation for the process occurring at the crude copper electrode.

(ii) Is the process occurring at the crude copper electrode oxidation or reduction?

The purpose of electrolytic refinement is to remove impurities present in the crude copper electrode. These impurities include Fe, Pb, Ni, Co, Ag, Au, Pt, Pd, Ru and Ir.

During electrolytic refinement some of these metals also form ions and pass into solution. Such metals include Fe, Ni and Co. Other metals do not react at all and form a solid mixture below the anode called the **'anode mud'**. Such metals include Ag, Au, Pt, Pd, Ru and Ir.

(b) Based on the information above, which **one** of the following would lead to a chemical reaction? Place your answer of A, B, C or D in the box.

A. $Ag_{(s)}$ is added to a copper(II) sulfate solution.
B. $Ir_{(s)}$ is added to a dilute sulfuric acid solution.
C. $Co_{(s)}$ is added to a ruthenium(III) chloride solution.
D. None of the above

Lead forms Pb^{2+} ions during electrolysis. Most lead impurity, however, is found in the anode mud and not in solution.

(c) Why is lead found in the anode mud?

Anode mud provides a raw material from which highly valuable metals may be extracted. After the removal of lead from the anode mud, the first step in the purification of such metals is treatment of the anode mud with *aqua regia* – a mixture of concentrated nitric and hydrochloric acids. In this first step $Au_{(s)}$, $Pt_{(s)}$ and $Pd_{(s)}$ pass into solution as $HAuC\ell_4$, $H_2PtC\ell_6$, and $H_2PdC\ell_4$ respectively, whereas Ru and Ir remain as solids and silver precipitates as $AgC\ell_{(s)}$.

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(d) What is the oxidation state of the indicated metal in each of the following compounds?

(i) Au in $HAuC\ell_4$	
(ii) Pt in $(NH_4)_2PtC\ell_6$	
(iii) Pd in $H_2PdC\ell_4$	
(iv) Ru in Sr_2RuO_4	

Next, iron(II) sulfate solution is added to the solution containing $HAuC\ell_4$, $H_2PtC\ell_6$, and $H_2PdC\ell_4$ in order to precipitate gold metal, Au. In this process the $AuC\ell_4^-$ ion is converted into $Au_{(s)}$ and $C\ell^-$ ions. Fe^{3+} ions are also formed.

(e) Write two balanced half-equations and the overall redox equation for the reaction that occurs when iron(II) sulfate solution is added.

Oxidation Half-Equation:

Reduction Half-Equation:

Redox Equation:

Anode mud is at most 2.50% gold by mass.

(f) (i) Calculate the maximum mass of gold that can be attained from 75.0 kg of anode mud.

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(ii) Calculate the minimum volume of a saturated (1.70 mol L^{-1}) $FeSO_4$ solution that is required to ensure complete precipitation of gold from 75.0 kg of anode mud.

During electrolytic refinement the concentrations of the soluble impurities – Fe, Ni and Co – build up in the copper(II) sulfate solution and must be removed before they reach levels that interfere with the refinement process.

In order to determine the amount of these impurities, the copper(II) sulfate solution obtained after the refinement of 100.0 kg of crude copper was analysed. The concentration of the copper(II) sulfate solution remained constant at 1.000 mol L^{-1} throughout electrolysis.

A 25.00 mL sample of the solution was diluted to 250.0 mL. 20.00 mL aliquots were titrated with a 0.1000 mol L^{-1} solution of EDTA with an average titre at endpoint of 21.37 mL. EDTA binds strongly to Cu^{2+}, Fe^{2+}, $Co^{2+}$and Ni^{2+} in the following way:

$$M^{2+} + EDTA \rightarrow M(EDTA)^{2+}.$$

(g) Calculate the total concentration of M^{2+} ions in solution following refinement.

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Triethanolamine was added to 50.00 mL samples of the **undiluted** solution. Triethanolamine binds to Fe^{2+}, Co^{2+} and Cu^{2+} **but not to Ni^{2+}**. Triethanolamine-bound metal ions are unable to react with EDTA. Titration of these aliquots with the 0.1000 mol L^{-1} EDTA solution gave an average titre of 8.79 mL.

(h) Calculate the concentration of Ni^{2+} ions in solution following refinement.

Excess ammonium sulfide solution – $(NH_4)_2S$ – is added to a 100.0 mL sample of the **undiluted** solution. Cu^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} ions all form insoluble sulfide salts of the formula $MS_{(s)}$. Filtration, drying and weighing of the resulting precipitate yielded 10.180 g.

(i) Given that Cu, Fe, Co and Ni are only present in the M^{2+} form, calculate the concentration of Fe^{2+} and Co^{2+}. [Remember the copper(II) sulfate concentration is constant at 1.000 mol L^{-1}.]

More working space can be found on the next page.

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$[Fe^{2+}]$:	$[Co^{2+}]$:

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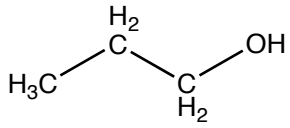
Question 17

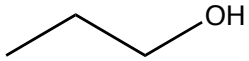
Analysis of compounds is essential in Chemistry in order to determine chemical structure. One valuable method of analysis is mass spectrometry which allows for the mass of a compound to be determined. Mass spectrometry can be so sensitive that compounds with different isotopes can be differentiated. Therefore, when determining mass, the exact mass of atoms must be used and not the average mass of naturally occurring isotopes. The exact masses of some common atoms, expressed in atomic mass units (amu, where 1 amu is 1/12 the mass of a ^{12}C atom), are:

$^{1}H = 1.0078$
$^{12}C = 12.0000$
$^{14}N = 14.0031$
$^{16}O = 15.9949$

When drawing organic compounds a simplified method of representing the structure is used to reduce complexity. Carbon atoms and the implicit hydrogen atoms on carbon atoms are not drawn, so that



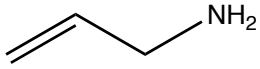
is identical to



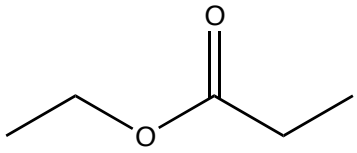
(a) Using exact masses, determine the mass in amu of each of the following compounds when they are composed of the isotopes listed above.

(i) CH_2O

(ii)



(iii)



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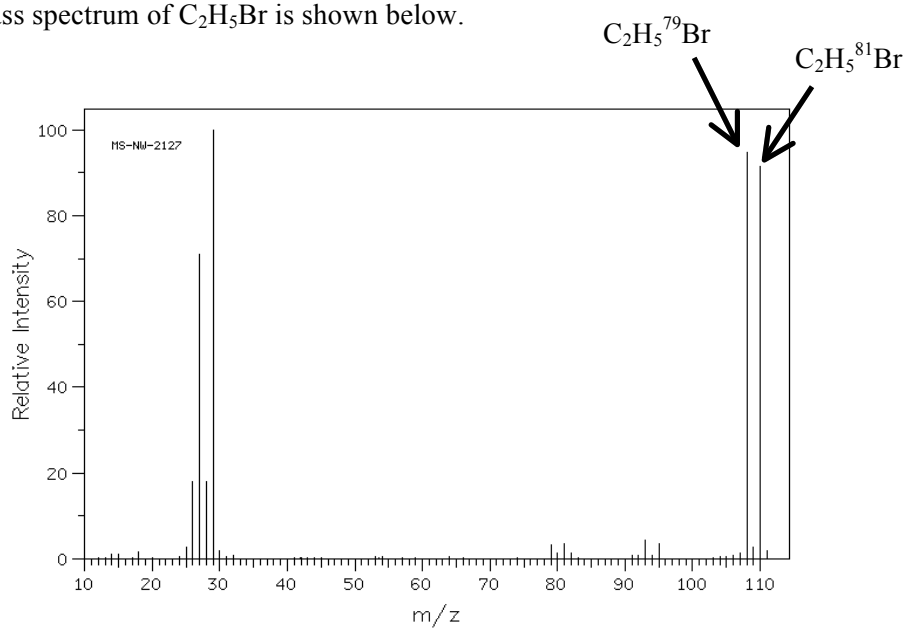
An example of a mass spectrum of C_2H_5Br is shown below.

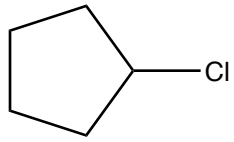


The peak corresponding to the mass of the compound is termed the **molecular peak** (indicated with an arrow on the above diagram). Some elements exist in nature as a mixture of more than one isotope of high natural abundance. For example, bromine appears as two abundant isotopes: ^{79}Br (49.3% abundance) and ^{81}Br (50.7% abundance). Molecules of a compound containing one bromine atom will give rise to two molecular peaks. One peak will result from molecules that contain ^{79}Br, and the other will result from molecules that contain ^{81}Br. The two peaks differ by two mass units. The relative intensities of these two peaks correspond to the natural abundance of the isotopes (49.3 : 50.7).

(b) Consider the following isotopic ratios for different elements.

Isotope	Exact mass (amu)	Natural Abundance
$^{35}C\ell$	34.9689	75.8
$^{37}C\ell$	36.9659	24.2

Molecules that differ from each other only in their isotopic composition are called isotopologues. Determine the exact mass of **each** chlorine isotopologue of the following compound and state the relative intensities of their corresponding peaks in the compound's mass spectrum.



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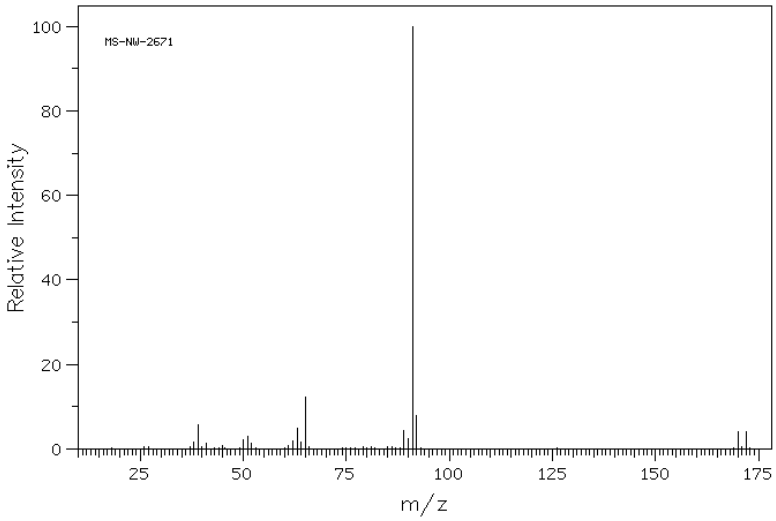
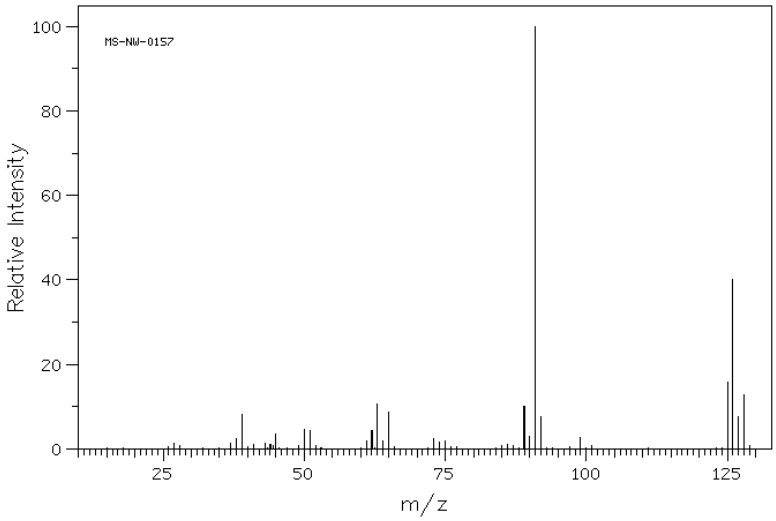
Electron impact mass spectrometry involves a stream of electrons fired at a molecule dislodging an electron and creating a radical or lone unpaired electron. These radical compounds are unstable and fragment or decompose into multiple smaller more stable fragments. The height of the peaks is a representation of the stability of each fragment with each peak having the isotope ratio discussed above. These fragmentation patterns are diagnostic for individual compounds but have similarities for compounds with the same functional groups.

(c)
(i) Examine the following four mass spectra and determine the molecular mass for **either** isotopologue of each of the compounds being analysed.

(A) Atoms present C, H and Br.



(B) Atoms present C, H and Cℓ.



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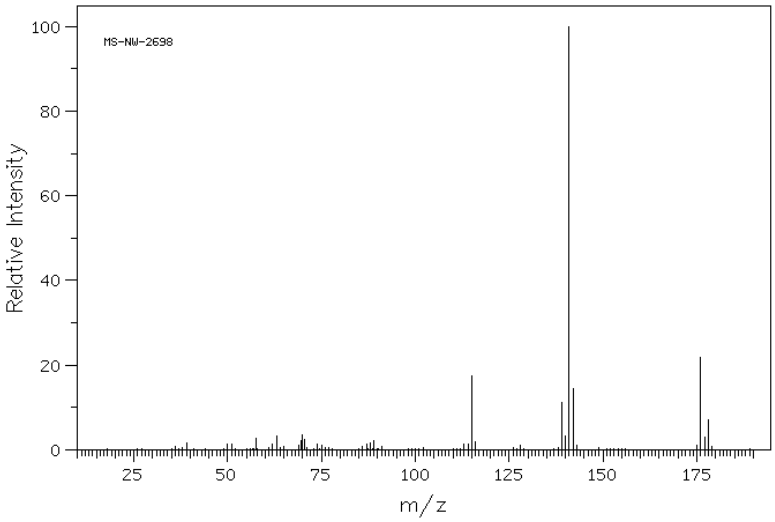
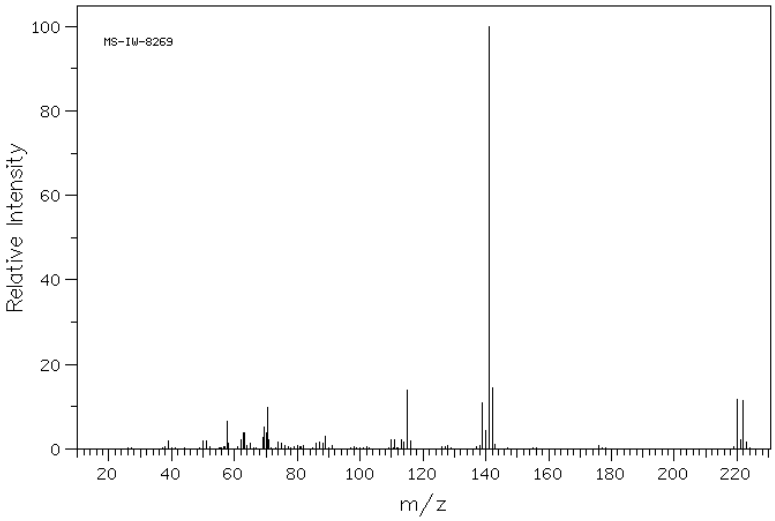
(C) Atoms present C, H and Cℓ.



(D) Atoms present C, H and Br .



(ii) On the basis of fragmentation, determine which pairs of spectra have related functionality and give an explanation as to how you reached this conclusion.

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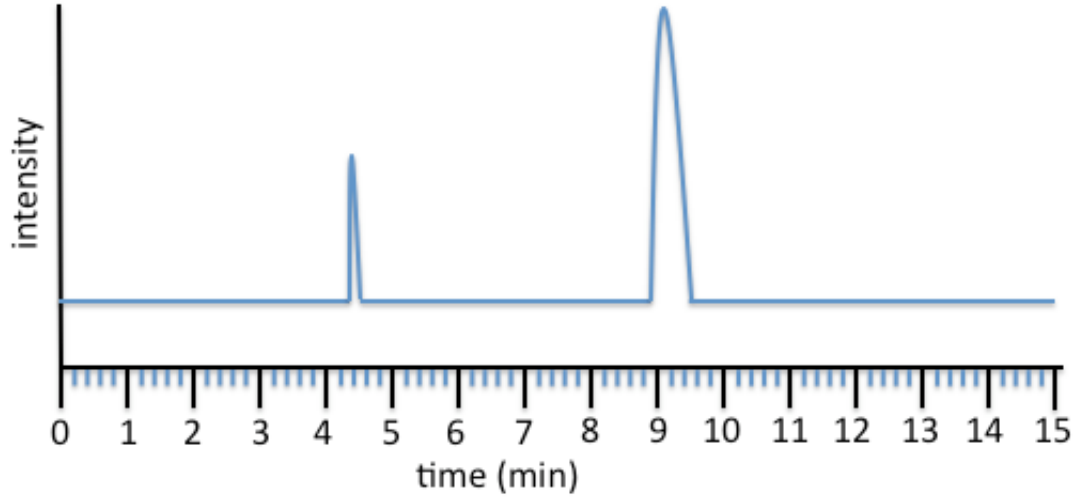
Before proper analysis can take place a sample must first be purified. One method of purification is known as gas chromatography. Gas chromatography involves a gas mobile phase that passes through a stationary phase, which is packed into a column. The phases are chosen such that components of the sample for purification have different affinities for each phase. A component which is strongly attracted to the stationary phase will take longer to travel through than a component which is not as strongly attracted to the stationary phase, especially if the latter has a strong affinity for the mobile phase. As a result of these differences, sample components will become separated from each other as they travel through the stationary phase. The time it takes for a compound to leave the stationary phase is called the **retention time**. At the end of the stationary phase compounds are detected giving rise to a chromatogram. A chromatogram has a flat line when no compounds are coming off the column and once a compound is detected this gives rise to a peak. Different types of compounds are likely to have different retention times measured at the maximum height of the peak.

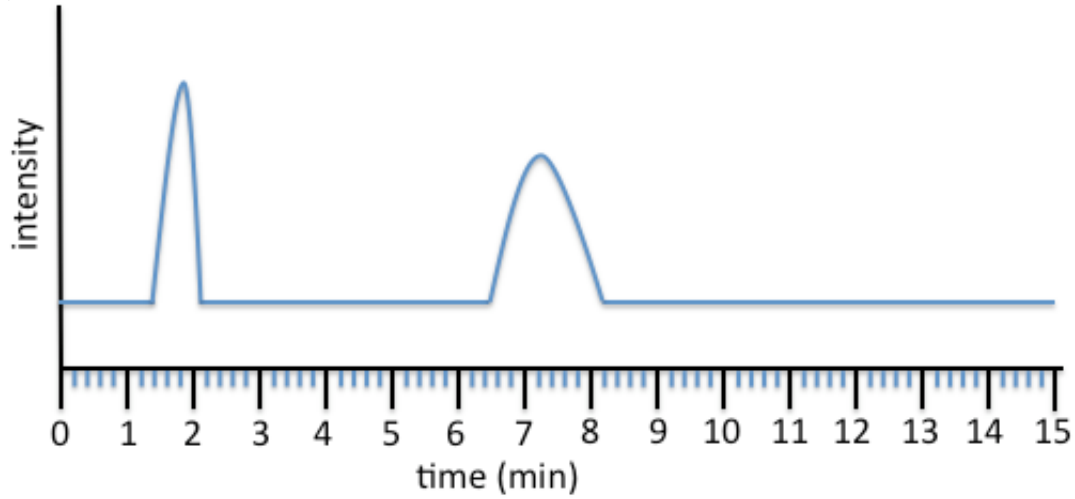
(d) Examine each of the following gas chromatograms and give a single retention time for each of the peaks.

(i)



Retention time for peak 1 (min):	Retention time for peak 2 (min):

(ii)



Retention time for peak 1 (min):	Retention time for peak 2 (min):

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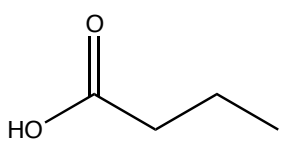
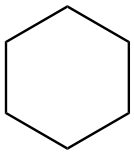
Compounds are generally separated on the basis of polarity. Normal stationary phase columns are polar which means more polar compounds adhere better to the stationary phase and have greater retention times.

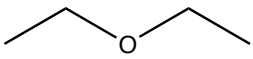
(e) Arrange each of the following compounds (using **A**, **B**, **C**, **D**) in order from lowest retention time to highest retention time for a normal stationary phase.



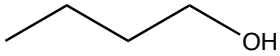
A



B



C

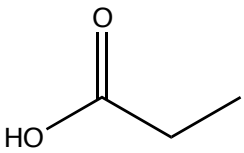


D

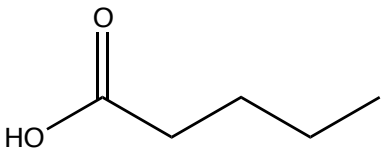
Lowest retention time			Highest retention time

A reverse stationary phase column is non-polar which means more polar compounds do not adhere as well to the stationary phase and have lower retention times.

(f) If a mixture of the following two compounds is purified with gas chromatography, one with a normal stationary phase and another with a reverse stationary phase the following two chromatograms are obtained.

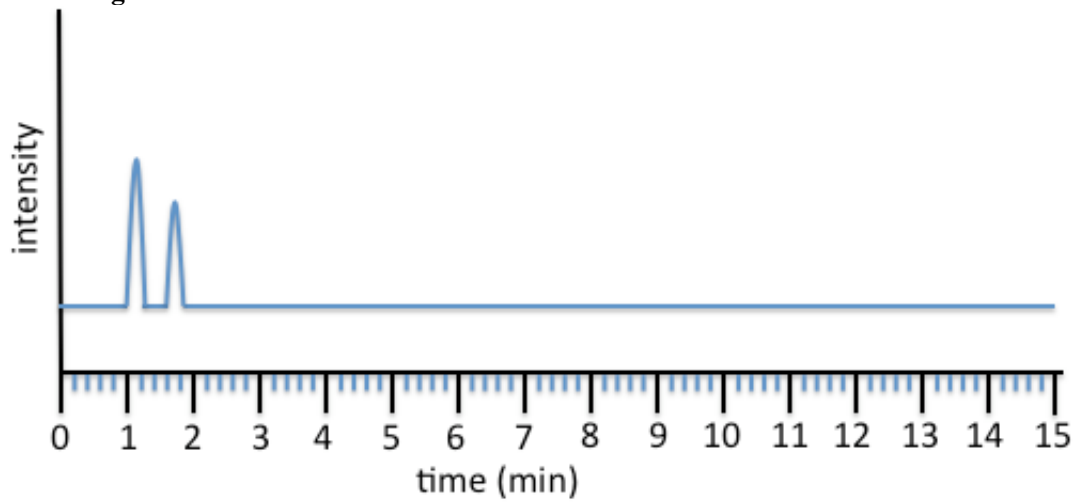


E



F

Chromatogram 1:



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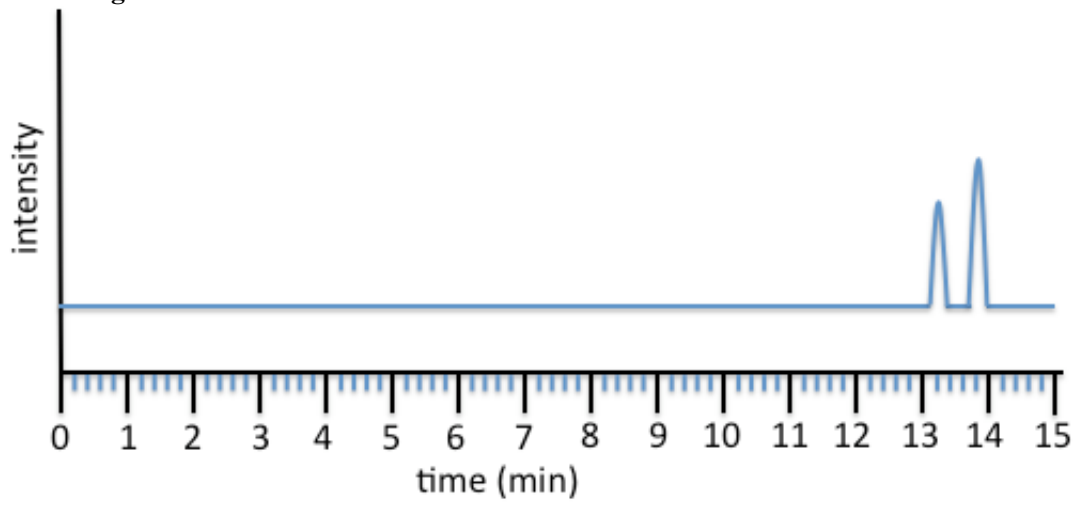
Chromatogram 2:



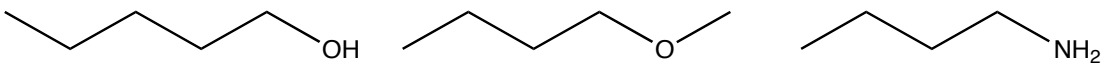
(i) Identify which chromatogram is obtained when using the normal stationary phase and which is obtained when using the reverse stationary phase.

normal stationary phase	reverse phase stationary phase

(ii) Label the peaks on **both spectra** identifying which peak corresponds to which compound **E** or **F**.

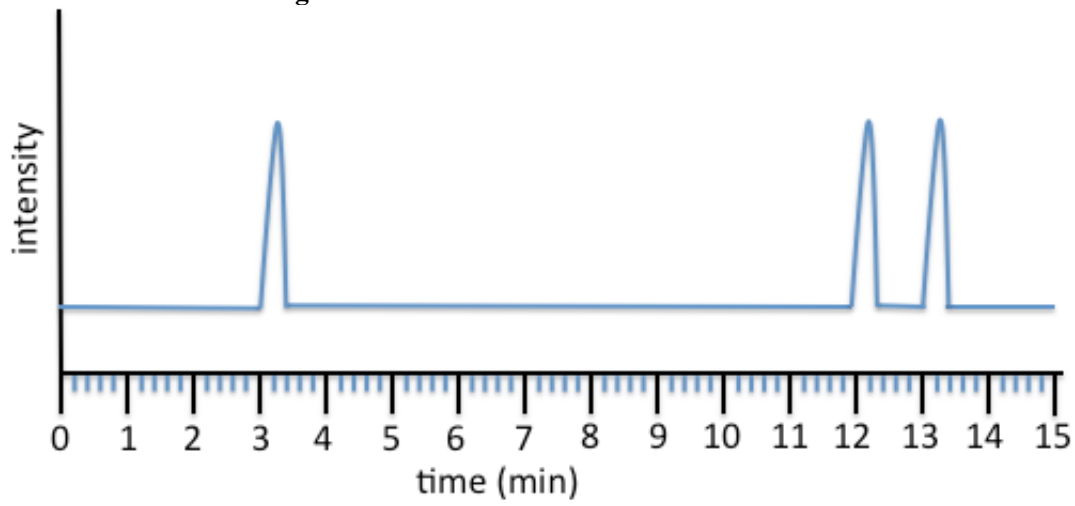
Gas chromatography and mass spectrometry can be combined into one technique known as gas chromatography mass spectrum (GCMS). This enables a mass spectrum to be obtained for each individual peak from the gas chromatograph.

(g) A mixture of the following compounds is subjected to GCMS, one with a normal stationary phase and another with a reverse stationary phase. Label each of the peaks (**G**, **H**, **I**) on **both chromatograms**.



G **H** **I**

Normal Phase Chromatogram



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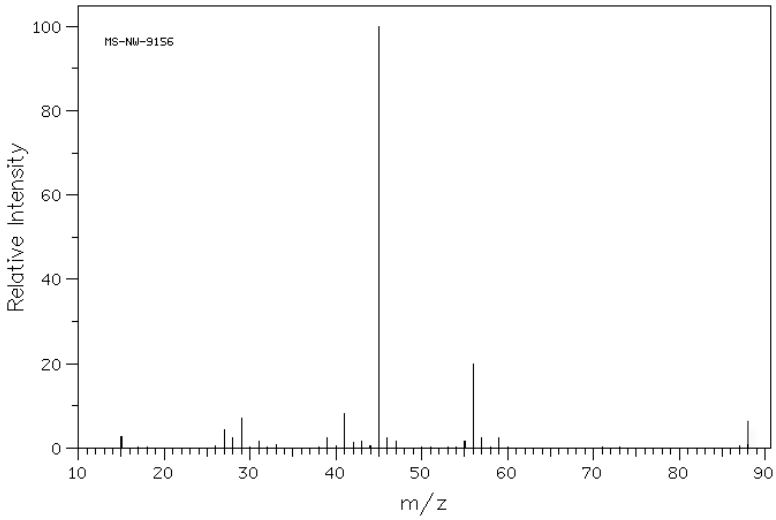
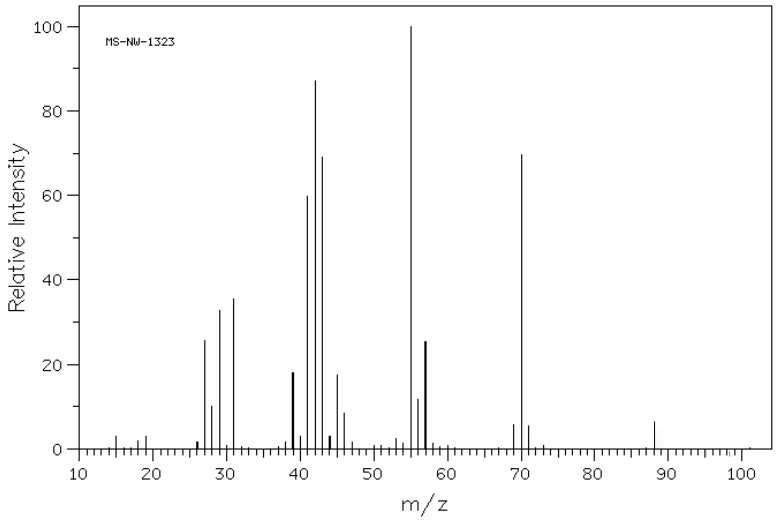
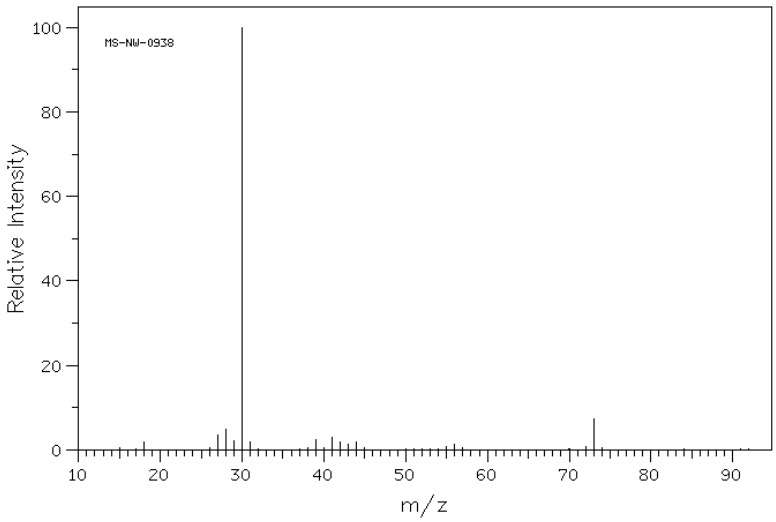
Spectrum 1: Retention time = 3.22 min



Spectrum 2: Retention time = 12.10 min



Spectrum 3: Retention time = 13.21 min



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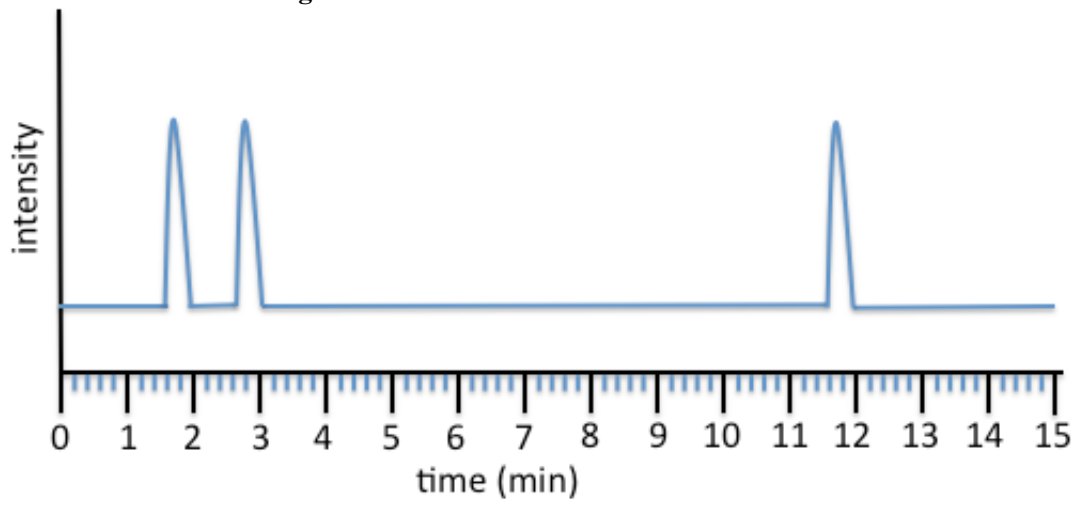
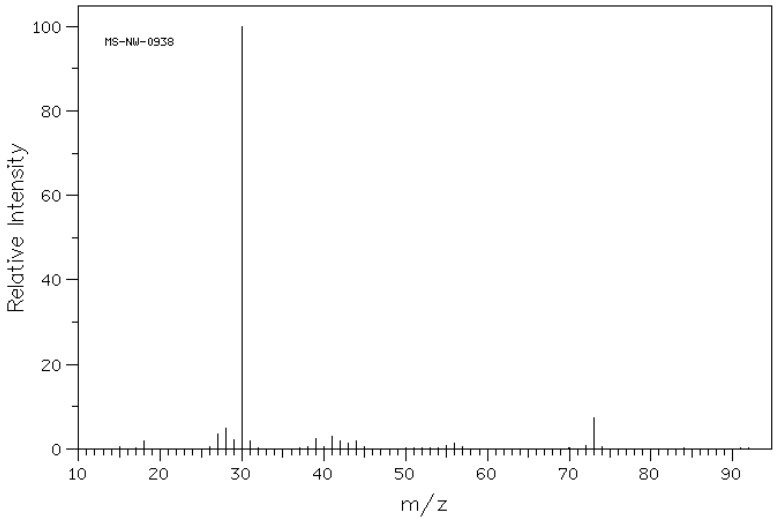
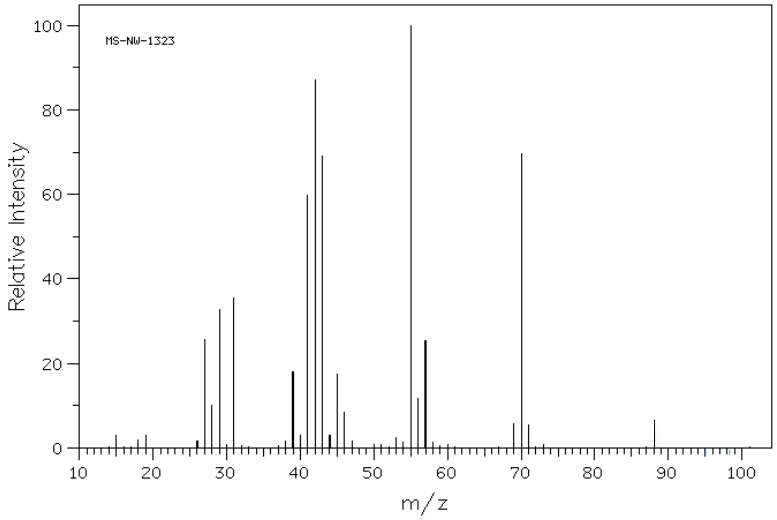
Reverse Phase Chromatogram



Spectrum 1: Retention time = 1.70 min



Spectrum 2: Retention time = 2.83 min



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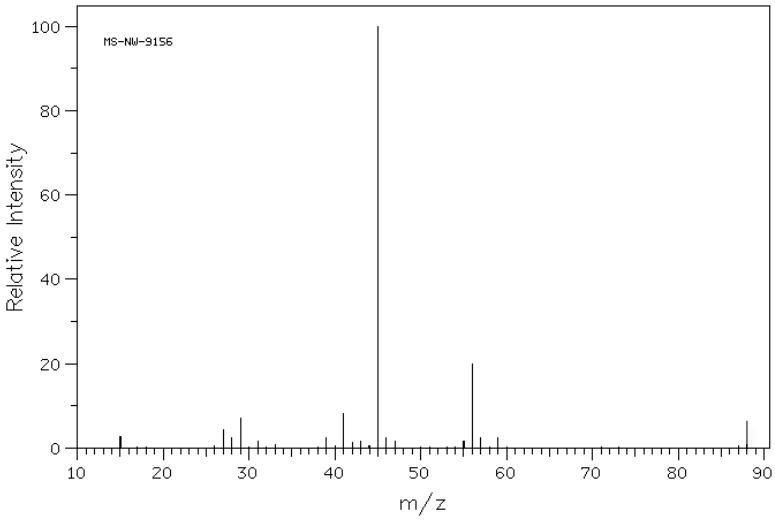
Spectrum 3: Retention time = 11.75 min



Mass spectra obtained from SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology)

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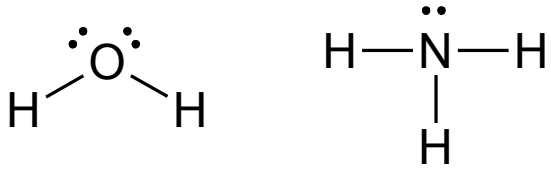
Question 18

Lewis structures provide a simple model of bonding and lone pairs of electrons and, to some extent, molecular shape. For example, Lewis structures for water and ammonia are shown below.



(a) Draw a Lewis structure for each of the following species:

(i) $C\ell_2O$

(ii) $PC\ell_3$

(iii) CS_2

The molecular geometry of simple molecules can be predicted by identifying the number of regions of electron density around the central atom. The AXE method involves counting the number of bonding regions, denoted 'X', (single and multiple bonds are treated identically) and the number of non-bonding regions, denoted 'E', around a central atom, 'A'.

Bonding (X)	Non-bonding (E)	AXE designation	Molecular geometry
2	0	AX_2	linear
2	1	AX_2E	bent
2	2	AX_2E_2	bent
3	0	AX_3	trigonal planar
3	1	AX_3E	trigonal pyramidal
3	2	AX_3E_2	T-shaped

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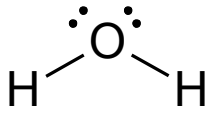
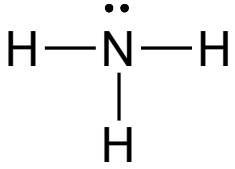
(b) What molecular geometry does each of the following molecules have?

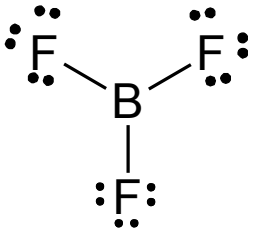
(i)



(ii)



(iii)



In any covalent bond between atoms of different electronegativity (a measure of the nucleus' attraction for electrons) there will be an asymmetric distribution of charge. Such bonds are said to have a bond dipole moment.

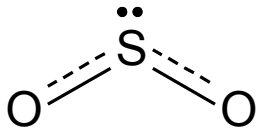
Similarly, if there is an asymmetric distribution of charge over a molecule, it is said to have a net dipole moment. The presence of individual bond dipole moments and the symmetry of the molecule determine whether a molecule has a net dipole moment. A molecule will **not** possess a net dipole moment if the symmetry of the molecule results in the individual bond dipole moments cancelling each other out.

Bonds or molecules with a net dipole moment are said to be polar.

(c) **Circle any polar bonds** in the molecules shown below.

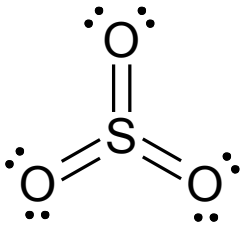
(d) **Tick the appropriate box** to indicate whether or not the molecule is polar.

(i)



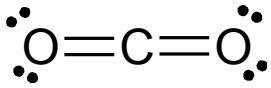
☐ polar ☐ non-polar

(ii)



☐ polar ☐ non-polar

(iii)



☐ polar ☐ non-polar

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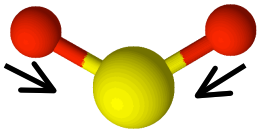
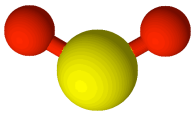
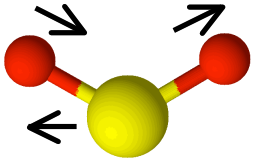
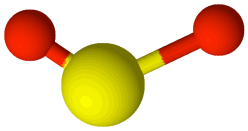
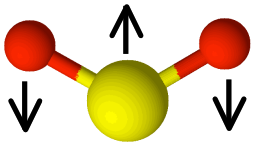
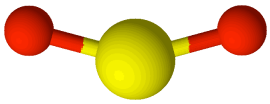
Vibrational modes are characteristic displacements of one or more atoms in a molecule. A linear molecule with N atoms will have 3N-5 vibrational modes and a non-linear molecule with N atoms will have 3N-6 vibrational modes.

(e) How many vibrational modes will $POC\ell_3$ have?

For a vibrational mode to absorb infrared (IR) radiation, the displacement of atoms involved must give rise to a change in the net dipole moment of the molecule. If this occurs, the vibrational mode is said to be "IR active" and will give rise to an absorption in the IR spectrum.

(f) The table below shows the 3 vibrational modes of SO_2 (arrows indicate displacement of the atoms involved). Indicate which of these will be IR active by filling out the right-hand column.

Vibration type	Equilibrium structure	Displaced structure	IR active? (Y/N)
symmetric stretch			
asymmetric stretch			
deformation			

(g) How many vibrational modes will water have, and how many of these will be IR-active?

Number of vibrational modes:	IR-active modes:

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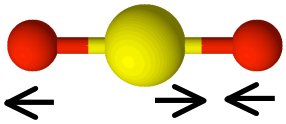
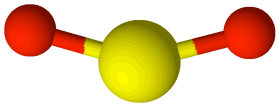
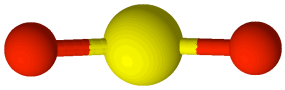
IR spectroscopy provides evidence for molecular shape. In the following example, we consider what the IR spectrum of SO_2 would look like if it were linear rather than bent.

(h) The table below shows the 4 vibrational modes of "linear SO_2" (again, arrows indicate displacement of the atoms involved; + and – symbols indicate displacement out of and into the plane of the page respectively). Complete the table by adding the following features:

(i) Vibration 1: Displaced structure and IR activity.

(ii) Vibration 2: Displaced structure and IR activity.

(iii) Vibration 3: Direction arrows on equilibrium structure to show movement of atoms.

Vibration	Equilibrium structure	Displaced structure	IR active? (Y/N)
1			
2			
3			Y
4			Y

We would expect "linear SO_2" to have four vibrational modes, as shown above, however in practice two of these vibrational modes are of equal energy. Such vibrational modes are called *degenerate* and give rise to a single absorption in the IR spectrum.

(i) Which of the four "linear SO_2" vibrational modes in the table above are degenerate (of equal energy)?

(j) How many absorptions in the IR spectrum would you expect for "linear SO_2"?

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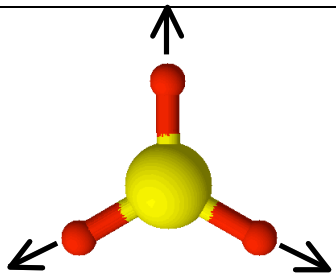
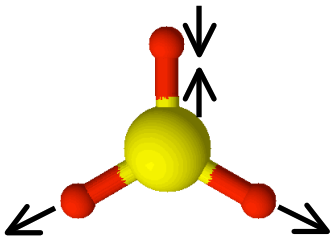
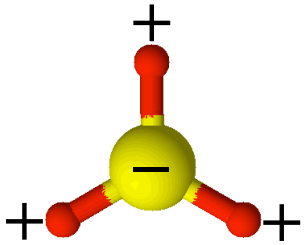
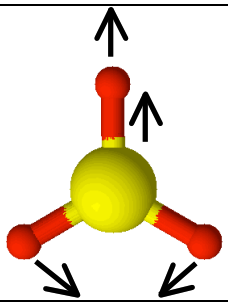
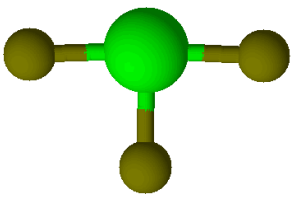
(k) The table below shows 4 vibrational modes of SO_3 (again, arrows indicate displacement of the atoms involved; + and – symbols indicate displacement out of and into the plane of the page respectively). Indicate which of these will be IR active by filling out the right-hand column.

Vibration type	Equilibrium structure	IR active? (Y/N)
symmetric stretch		
asymmetric stretch		
asymmetric deformation 1 (doubly degenerate)		
asymmetric deformation 2 (doubly degenerate)		

(l) Now consider $SOC\ell_2$. How many absorptions in the IR spectrum would you expect for $SOC\ell_2$?

(m) $C\ell F_3$ has the following T-shaped structure. It has six vibrational modes, none of which are degenerate. How many of these will be IR active?



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