SECTION A: MULTIPLE CHOICE
USE THE ANSWER SHEET PROVIDED

1. Element X has the following ionisation energies: 577.5 kJ mol^{-1} (first), 1816.7 kJ mol^{-1} (second), 2744.8 kJ mol^{-1} (third), 11577 kJ mol^{-1} (fourth), 14842 kJ mol^{-1} (fifth). Which of the following is most likely to be element X?

   (a) magnesium
   (b) sodium
   (c) nitrogen
   (d) phosphorus
   (e) aluminium

2. Which of the following molecules is the most polar?

   (a) O_2
   (b) CF_4
   (c) CO_2
   (d) NH_3
   (e) BF_3

3. Which of the following molecules XY_n has the largest Y−X−Y bond angle?

   (a) H_2O
   (b) NH_3
   (c) CO_2
   (d) CF_4
   (e) BF_3

4. Which separating technique would be most appropriate to separate two miscible liquids with boiling points of 73 °C and 76 °C?

   (a) filtration
   (b) decantation
   (c) separatory funnel
   (d) fractional distillation
   (e) thin-layer chromatography

5. Which of the following substances has the highest boiling point?

   (a) water
   (b) heptane
   (c) ethanol
   (d) sulfur dioxide
   (e) sodium chloride

6. When E10 fuel is combusted, it involves the combustion of organic compounds ethanol and octane, as shown in the following chemical equations:

$$C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$$
$$2C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$$

When 1.00 g of ethanol and 1.00 g of octane are combusted in excess oxygen, what is the total volume of CO_2 produced from the combustion, measured at 25 °C and 100 kPa?

(a) 1.08 L
(b) 2.58 L
(c) 2.81 L
(d) 3.68 L
(e) 4.55 L

7. When the complex ion $Cr(OH)_6^{3-}$ is heated with hydrogen peroxide solution under alkaline conditions, it is oxidised to CrO_4^{2-} through a redox reaction. The relevant half equations are:

$$H_2O_2 + 2\ e^- \rightarrow 2\ OH^-$$
$$Cr(OH)_6^{3-} + 2\ OH^- \rightarrow CrO_4^{2-} + 4\ H_2O + 3\ e^-$$

If 100 mL of 2 M $Cr(OH)_6^{3-}$ solution is heated with excess hydrogen peroxide solution under alkaline conditions, what is the net chemical amount (in mol) of hydroxide ions produced?

(a) 0.1 mol
(b) 0.2 mol
(c) 0.6 mol
(d) 1.0 mol
(e) 2.0 mol

8. Five beakers (labelled 1 to 5) each contain 0.5 moles of silver nitrate, dissolved in water. Into each of these beakers is added a certain amount of a metal chloride, also dissolved in water, as shown in the table below. Silver chloride precipitates from solution in all five beakers.

1	2	3	4	5
0.15 mol $CaCl_2$	0.20 mol $AlCl_3$	0.25 mol $CaCl_2$	0.30 mol NaCl	0.40 mol NaCl

Which two beakers contain the maximum mass of silver chloride precipitate?

(a) 1 and 4
(b) 2 and 3
(c) 2 and 4
(d) 3 and 5
(e) 4 and 5

9. When solid zinc is added to a solution containing silver nitrate, solid silver precipitates from solution, according to the following chemical equation:

$$2\ AgNO_3(aq) + Zn(s) \rightarrow Zn(NO_3)_2(aq) + 2\ Ag(s)$$

Which of the following shows the relative changes in concentration of each species over time?

	$[Ag^+]$	$[NO_3^-]$
(a)	decreases	no change
(b)	decreases	decreases
(c)	no change	no change
(d)	increases	increases
(e)	increases	decreases

10. Elements W and X react to form an ionic compound. W and X have 2 and 6 valence electrons respectively. What is the formula of this compound formed from the reaction between W and X?

(a) W_2X_6
(b) WX_3
(c) WX
(d) W_3X
(e) W_6X_2

11. Which of the following elements has an electronegativity closest to that of Sr?

(a) In
(b) Sn
(c) Sb
(d) Te
(e) I

12. “Parts-per” notation is commonly used in chemistry to describe small values of dimensionless quantities. For example, a mass fraction of 1 part per million (ppm) is equivalent to a 1 g of solute per million grams of solution (i.e. solute + solvent), or 1 mg of solute per kg of solution.

A solution is made by dissolving 358.4 mg of iodine in 0.2500 L of ethanol (the density of ethanol is 0.7893 kg L^{-1}). What is the mass fraction of iodine in this solution, expressed in ppm?

(a) 1130 ppm
(b) 1132 ppm
(c) 1434 ppm
(d) 1813 ppm
(e) 1816 ppm

13. Isotopologues are molecules that differ only in their isotopic composition. The most abundant carbon dioxide isotopologue is $^{12}C^{16}O_2$, with a relative molecular mass of 44. Relative abundance of the most common isotopologue with a relative molecular mass of 47 ($^{13}C^{16}O^{18}O$) has been used to estimate the past temperature of the earth, but such data must be corrected to account for the presence of other isotopologues with the same relative molecular mass.

The natural abundance of the relevant carbon and oxygen isotopes is shown in the table below.

Isotope	Abundance	Isotope	Abundance
^{11}C	$< 10^{-18}$ %	^{16}O	99.8%
^{12}C	98.9%	^{17}O	0.04%
^{13}C	1.1%	^{18}O	0.16%
^{14}C	$<10^{-10}$ %		

Which of the following is the next most abundant carbon dioxide isotopologue having a relative molecular mass of 47?

(a) $^{11}C^{18}O^{18}O$
(b) $^{12}C^{16}O^{17}O$
(c) $^{12}C^{17}O^{18}O$
(d) $^{13}C^{17}O^{17}O$
(e) $^{14}C^{16}O^{17}O$

14. A chemist is trying to determine the mass percentage of sulfate ions in a fertiliser. They know that the fertiliser contains only three anions: nitrate, carbonate and sulfate.

The chemist decides to dissolve 4.000 g of fertiliser in water and add barium nitrate solution (this precipitates $BaCO_3$ and $BaSO_4$). They record that exactly 40.00 mL of 1.000 M barium nitrate solution was required for precipitation to be complete.

The chemist prepares a second aqueous solution containing 4.000 g of the fertiliser and adds hydrochloric acid to it (this reacts with the CO_3^{2-} ions to produce CO_2). They record the mass of CO_2 produced as 1.600 g.

What is the mass percentage of sulfate ions in the fertiliser?

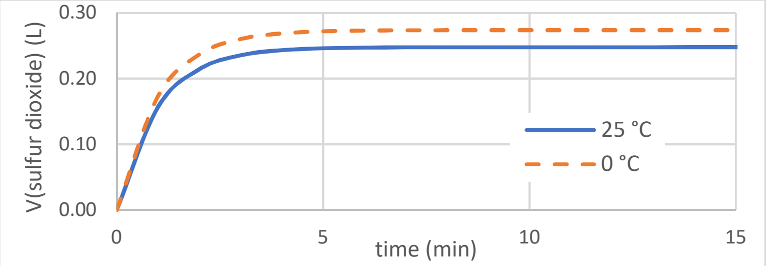
(a) 8.75%
(b) 23.43%
(c) 45.78%
(d) 59.89%
(e) 74.23%

15. Sodium thiosulfate ($Na_2S_2O_3$) reacts with hydrochloric acid according to the following chemical equation: $Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + S(s) + SO_2(g) + H_2O(l)$

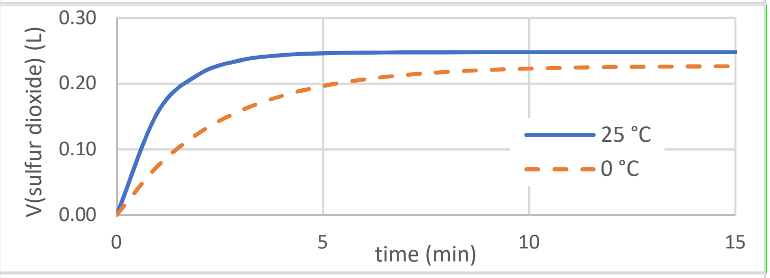
Solutions of sodium thiosulfate and hydrochloric acid were mixed and the volume of sulfur dioxide gas produced (at a pressure of 100 kPa) was recorded as a function of time. The experiment was first performed at 25 °C and then repeated at temperature of 0 °C.

Which of the following graphs show the results of these two experiments?

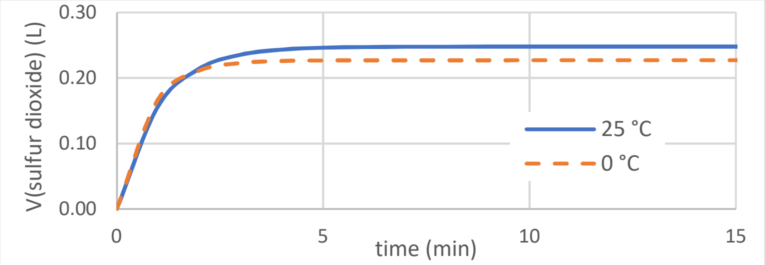
(a)



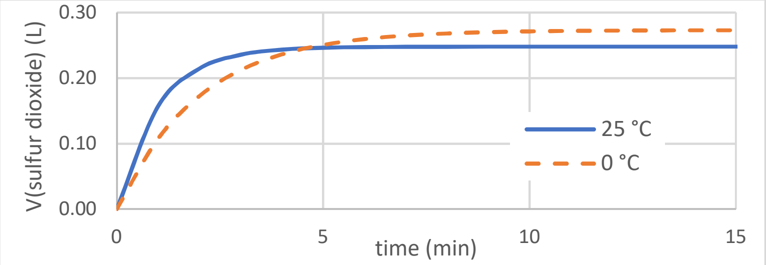
(b)



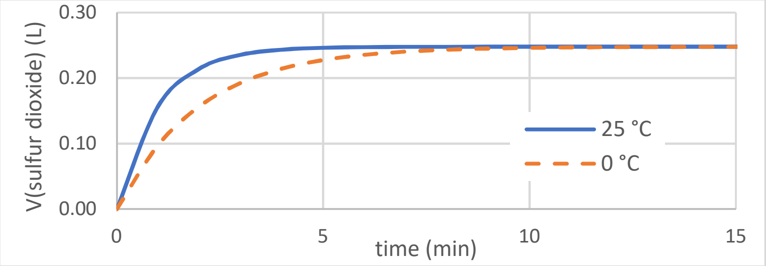
(c)



(d)



(e)



END OF SECTION A
SECTION B COMMENCES OVERLEAF

SECTION B

ANSWER IN THE SPACES PROVIDED

Question 16

There are a wide range of low melting alloys used for soldering, usually containing a mixture of heavy metals including bismuth, lead, tin, indium and cadmium. In this question, we will examine an alloy primarily consisting of bismuth, lead, cadmium and tin, using an alloy sample of mass **1.790 g**. This will be referred to throughout this question as the "**solid** alloy sample".

Initially the alloy is digested in nitric acid (HNO_3) to form $Bi^{3+}_{(aq)}$, $Pb^{2+}_{(aq)}$, $Cd^{2+}_{(aq)}$ and $SnO_{2(s)}$. The precipitated SnO_2 is collected via vacuum filtration and dried, and its mass is found be **0.3890 g**. The filtrate is collected and diluted to **100.0 mL**. This will be referred to throughout this question as the "alloy **solution**".

(a) Determine the mass of **Sn** in the **solid** alloy sample.

MM(SnO_2) = 150.71 g/mol
n(SnO_2) = 2.581×10^{-3} mol = n(Sn)
m(SnO_2) = 0.3064 g

The concentration of Bi^{3+}, Cd^{2+} and Pb^{2+} ions in the alloy **solution** can be determined by reaction with EDTA, which forms a 1:1 complex with most metals:

$Bi^{3+} + H_4EDTA \rightarrow [Bi(EDTA)]^{-} + 4\ H^{+}$
$Pb^{2+} + H_4EDTA \rightarrow [Pb(EDTA)]^{2-} + 4\ H^{+}$
$Cd^{2+} + H_4EDTA \rightarrow [Cd(EDTA)]^{2-} + 4\ H^{+}$

pH is used to control the selectivity of these reactions. Initially a low pH is used, which prevents the Pb^{2+} and Cd^{2+} ions from reacting with EDTA; this enables determination of the concentration of Bi^{3+} ions alone. **0.04000 M** H_4EDTA solution is added to an aliquot of the alloy solution until all of the Bi^{3+} has reacted, then hexamine (a base) is added. Further H_4EDTA solution is then added until all of the Pb^{2+} and Cd^{2+} ions have reacted.

18.78 mL of **0.04000 M** H_4EDTA solution is required to react with all of the Bi^{3+} in a **20.00 mL** aliquot of the alloy **solution**.

(b) Find the mass of Bi in the **solid** alloy sample.

n(EDTA) = 7.512×10^{-4} mol = n(Bi) in aliquot
n(Bi) in solid = 3.576×10^{-3} mol OR m(Bi) from aliquot = 0.1570 g
m(Bi) = 0.7849 g

21.83 mL of **0.04000 M** H_4EDTA solution is required to react with all of the Pb^{2+} and Cd^{2+} ions in the **20.00 mL** aliquot of the alloy **solution**.

(c) Find the combined concentration of Pb^{2+} and Cd^{2+} ions in the alloy **solution**.

n(EDTA) = 8.732×10^{-4} mol = n(Pb + Cd) in aliquot
[Pb + Cd] = 0.04366 M

(d) What happens to the determination of the combined concentration of Pb^{2+} and Cd^{2+} ions if too much of the H_4EDTA solution is added when determining the Bi^{3+} concentration?

The apparent concentration of Pb and Cd will be lower than the actual value

Since Pb^{2+} and Cd^{2+} ions react under the same conditions with EDTA, we cannot find their individual concentrations using this method. In order to do so, we can find the concentration or chemical amount (in mol) of one of the metals, and then find the other by difference.

Next **20.00 mL** of **0.05000 M** potassium chromate is added to a **20.00 mL** aliquot of the alloy solution. The chromate ions react with the only the Pb^{2+} ions to form the highly insoluble compound lead(II) chromate:

$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$

The analyst filters out the precipitate and adds **0.09000 M** Fe^{2+} solution to the filtrate. Fe^{2+} ions react with the excess chromate ions in the following redox reaction.

$3\ Fe^{2+}(aq) + CrO_4^{2-}(aq) + 8\ H^+(aq) \rightarrow 3\ Fe^{3+}(aq) + Cr^{3+}(aq) + 4\ H_2O(l)$

20.59 mL of **0.09000 M** Fe^{2+} solution is required for complete reaction with the excess chromate ions.

(e) What is the mass of Pb in the **solid** alloy sample?

$n(CrO_4^{2-})$ total = 1.000×10^{-3} mol
$n(Fe^{2+})$ reacted = 1.853×10^{-3} mol
$n(CrO_4^{2-})$ excess = $\{n(Fe^{2+})\ \text{reacted}\}/3 = 6.177 \times 10^{-4}$ mol
$n(CrO_4^{2-})$ reacted = $n(Pb^{2+})$ in aliquot = 3.823×10^{-4} mol
$n(Pb^{2+})$ total = 1.912×10^{-3} mol
$m(Pb^{2+}) = 0.3961$

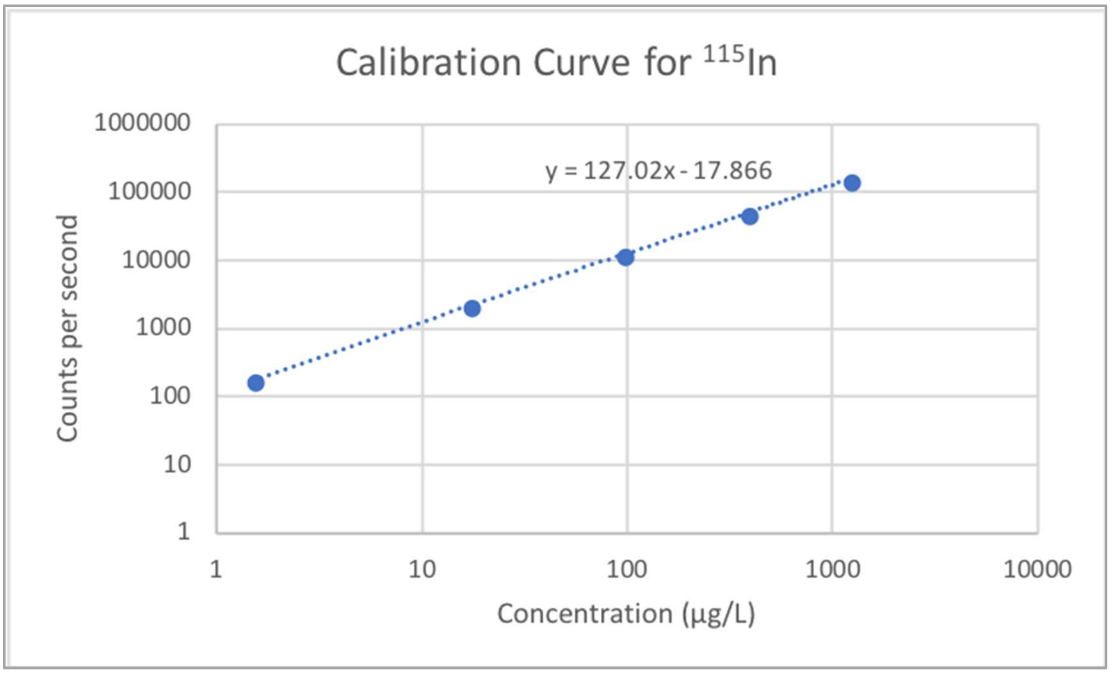
(f) Hence, find the mass of Cd in the **solid** alloy sample.

n(Pb + Cd) = 8.732 x 10^{-4} mol (if using aliquot) OR 4.366 x 10^{-3} mol (if using full sample)
n(Pb) = 3.823 x 10^{-4} mol OR 1.912 x 10^{-3} mol
n(Cd) = 4.909 x 10^{-4} mol OR 2.456 x 10^{-3} mol
m(Cd) = 0.2759 g

Determination of the minor constituents of the alloy requires other methods, such as inductively coupled plasma-mass spectrometry or ICP-MS. In ICP-MS, a solution is vapourised and ionised to form a plasma. The ions in this plasma are separated out by their mass-to-charge ratio or m/z, which is simply the relative mass of the ion divided by the charge on the ion. For example, $^{1}H^{+}$ has a m/z of 1, $^{115}In^{+}$ has a m/z of 115 and $^{32}S^{2+}$ has a m/z of 16. For our purposes, we will assume that ICP-MS only generates ions with a 1+ charge.

One advantage of ICP-MS is that it can determine the relative abundance of each isotope of an element in a sample, as different isotopes have different m/z ratios. A related disadvantage is that ions of different elements with the same mass and charge are observed at the same m/z ratio.

Indium is used as an internal standard to calibrate the instrument. ^{115}In is used, because there are no stable isotopes of other elements with the same mass.



(g) Using the equation on the graph, determine how many counts per second (cps) are observed at m/z = 115 for a solution containing 200 μg of ^{115}In per L.

2.539×10^4 cps

Indium is not the only element that can be analysed with ICP-MS, indeed most elements on the periodic table can be analysed to considerable accuracy, however different elements have different sensitivities. We can determine a Relative Sensitivity Factor, which is the ratio of counts per second for a particular element to the counts per second for ^{115}In at the same concentration.

For ^{121}Sb, at a concentration of 200 μg/L of ^{121}Sb, 1.172×10^4 counts per second are observed.

(h) What is the Relative Sensitivity Factor for Sb?

RSF = 0.4617

As different isotopes of an element have such similar chemical properties, we can use the same calibration for different isotopes of the same element. Practically, In has two abundant isotopes: ^{115}In has an abundance of 95.71% and ^{113}In, which has an abundance of 4.29%.

(i) If a solution with 200 μg/L of total In is analysed, how many counts per second will be observed at m/z = 113 and m/z = 115?

m/z = 113 – 1089 cps
m/z = 115 – 2.430×10^4 cps

As mass spectrometers can only separate ions by m/z ratio, isotopes of different elements with the same mass can be observed at the same m/z. In this situation, ^{142}Ce and ^{142}Nd have the same mass and charge. ^{140}Ce has an isotopic abundance of 88.5%, ^{142}Ce has an isotopic abundance of 11.1% and ^{142}Nd has an isotopic abundance of 27.2%. The Relative Sensitivity Factor for Ce is 0.692 and for Nd is 0.769.

The alloy solution is again analysed by ICP-MS at m/z = 140 and 142. At m/z = **140**, a measurement of **6620** counts per second was recorded and at m/z = **142**, a measurement of **1962** counts per second was recorded.

(j) What is the concentration (in μg L^{-1}) of Ce and Nd in the alloy solution?

For m/z = 140, cps(Ce-140) = 6620 cps

Scaled cps {cps(Ce)/RSF = cps(In)} = 9566 cps

[Ce-140] {from graph equation} = 75.5 μg/L

[Ce] total = 85.3 μg/L

[Ce-142] = 9.46 μg/L

scaled cps(Ce-142) = 1184 cps

cps(Ce-142) {scaled cps x RSF}= 819 cps

cps(Nd-142) = 1143 cps

scaled cps(Nd-142) = 1486 cps

[Nd-142] = 11.8 μg/L

[Nd] total = 43.5 μg/L

Question 17

Spectroscopy is an analytical method used to determine the structure of unknown molecules by measuring the absorbance of different wavelengths of electromagnetic radiation. One important type is infrared (IR) spectroscopy, which shines infrared light into a sample and measures how much light is absorbed by the molecule at each wavelength.

A common unit in spectroscopy is the wavenumber. It is the reciprocal of the wavelength expressed in centimetres, and therefore has units of cm^{-1}. The range of wavenumbers collected in an IR spectrum is usually from 4000 to 400 cm^{-1}.

(a) Calculate the wavelength corresponding to a wavenumber of 4000 cm^{-1}. Express your answer in **metres**, using scientific notation.

$$\frac{1}{4000\ cm^{-1}} \times 0.01\ m\ cm^{-1} = 2.500 \times 10^{-6}\ m$$

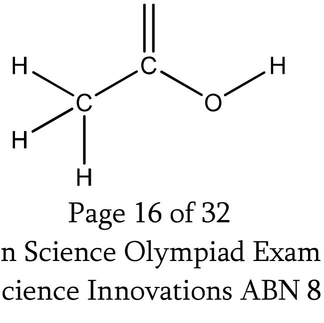
In a typical spectrum there are a series of peaks at different wavelengths at which the molecule absorbs IR radiation most strongly. Each of these peaks corresponds to one structural component of the molecule known as a *chromophore*. The reference table below shows the range of wavenumbers that correspond to specific chromophores. Note that some of the ranges overlap with each other, which can complicate the identification of which chromophores are in the molecule.

Chromophore	**Absorbance Wavenumber (cm^{-1})**
O – H	3650 – 3200
N – H	3500 – 3300
C ≡ N	2260 – 2220
C ≡ C	2260 – 2100
C = O	1780 – 1650
C = C	1680 – 1600
C = N	1650 – 1550

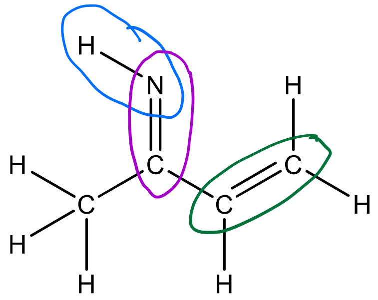
Table 1: Absorbances of some common chromophores (this table is reproduced throughout this question for your convenience)

Note that C – H and C – C stretches are common in almost all organic molecules so do not provide much insight into the structure of each compound. These chromophores have been omitted from Table 1 and will not be considered for the remainder of the question.

For example, the IR spectrum of acetic acid (CH_3COOH) contains a peak in the range 3650-3200 cm^{-1} (O–H bond) and another peak in the range 1780-1650 cm^{-1} (C=O bond).



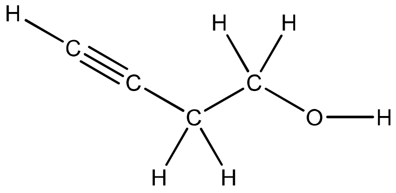
(b) Based on Table 1 and the information above, circle all chromophores in the molecule below that would absorb infrared light in the range 3650-1550 cm^{-1}.

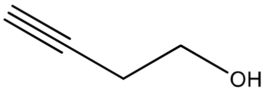


(c) How many peaks would you expect to see in the IR spectrum in that range?

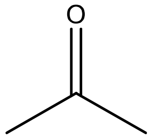
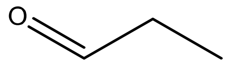
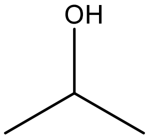
3

The structural formula of organic (carbon-based) molecules can be represented by skeletal formula notation. In this notation, bonds are represented by lines, with carbon atoms located at the end of each line segment or meeting point of line segments. Hydrogen atoms connected to carbon atoms are implied rather than explicitly shown. For example, the two drawings below represent the same molecule. Skeletal formula notation will be used for the remainder of this question.





(d) Consider the following three molecules: **A**, **B** and **C**.

		
A	**B**	**C**

Which of those compounds **A**, **B** and **C** would have similar IR spectra , based on Table 1?

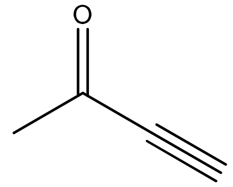
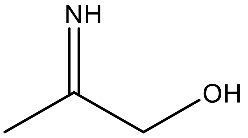
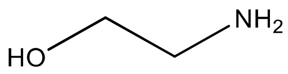
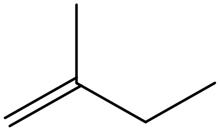
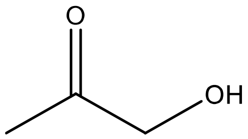
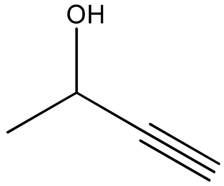
A and B

The IR spectra of five molecules are acquired and the peaks observed in their spectra are recorded in the table below. These five molecules correspond to five of the six molecules **D** to **I** below.

(e) Using the reference ranges in Table 1, assign each set of peaks to one of the six molecules **D** to **I**. Note that one of compounds **D** to **I** did not have its IR spectrum acquired.

	Peaks observed in the IR spectra (cm^{-1})	**Assigned molecule (D-I)**
1	1650	H
2	1720, 3410	F
3	2120, 3450	I
4	3200, 3350	E
5	1630, 3350, 3400	G

1780-1650
2260-2100

D		**G**	
E		**H**	
F		**I**	

3650-3200
3500-3300

1780-1650
3650-3200

3650-3200
3500-3300
1650-1550

1680-1600

3650-3200
2260-2100

Chromophore	**Absorbance Wavenumber (cm^{-1})**
O – H	3650 – 3200
N – H	3500 – 3300
C ≡ N	2260 – 2220
C ≡ C	2260 – 2100
C = O	1780 – 1650
C = C	1680 – 1600
C = N	1650 – 1550

Table 1: Absorbances of some common chromophores.

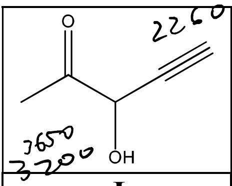
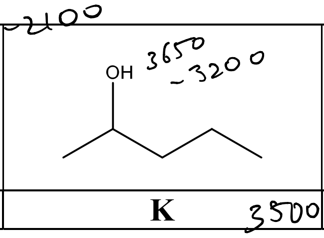
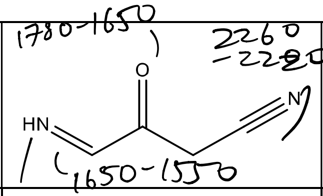
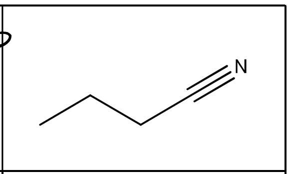
3650-3200

(f) Four compounds **J**, **K**, **L** and **M** (shown below) were dissolved in ethanol (CH_3CH_2OH). A chemist removes three compounds from the mixture sequentially, in such a way that she observes the disappearance of exactly one characteristic peak from the mixture's IR spectrum as each compound is removed. Each of the disappearing peaks unambiguously comes from the molecule being removed. The last compound is left dissolved in the ethanol solvent.

Complete the table below, identifying the 1st, 2nd and 3rd compounds removed from the mixture, and the wavenumber range of the peak lost from the spectrum.

1780-1650

2260-2220

 2260-2100 3650-3200	 3650-3200	 1780-1650 2260-2220 1650-1550	
J	**K**	3500-3300 **L**	**M**

Order	Compound removed	Wavenumber range of lost peak (cm^{-1})
1st	L	1650-1550
2nd	J	1780-1650
3rd	M	2260-2220

K if ethanol solvent not acknowledged.

Chromophore	Absorbance Wavenumber (cm^{-1})
O – H	3650 – 3200
N – H	3500 – 3300
C ≡ N	2260 – 2220
C ≡ C	2260 – 2100
C = O	1780 – 1650
C = C	1680 – 1600
C = N	1650 – 1550

Table 1: Absorbances of some common chromophores.

The reason that chromophores absorb light in the IR range is due to vibrational transitions within the molecule. For example, a molecule containing a C=O bond will absorb light that has the exact same energy as the energy required for it to undergo a vibrational transition.

The energy of the vibrational transition can be modelled by $\Delta E = \frac{h}{2\pi}\sqrt{\frac{k}{m_r}}$, where h is Planck's constant, equal to 6.626×10^{-34} J s; k is the bond force constant between the vibrating atoms (in **N m^{-1}**), and m_r is the reduced mass of the vibrating atoms (in **kg**).

The energy of a photon of light is related to its wavelength by the equation $E = \frac{hc}{\lambda}$, where h is Planck's constant, equal to 6.626×10^{-34} J s; c is the speed of light, equal to 2.998×10^{8} m s^{-1} and λ is the wavelength (in **m**).

(g) Does a peak at 2500 cm^{-1} correspond to radiation with higher or lower energy than a peak at 2000 cm^{-1}?

higher

$$\frac{1}{2500} < \frac{1}{2000} \qquad \therefore E_{2500} > E_{2000}$$

$$\lambda_{2500} < \lambda_{2000}$$

(h) The reduced mass of a diatomic molecule may be calculated using the formula: $m_r = \frac{m_1 m_2}{m_1 + m_2}$, where m_1 and m_2 are the masses of the atoms in the molecule, in kg. The average mass of a nitrogen atom is 2.326×10^{-26} kg.

i. Calculate the average mass (in kg) of an oxygen atom.

$$M_{O,\text{atom}} = \frac{16.00}{6.022 \times 10^{23}} \times 10^{-3}$$

$$= 2.657 \times 10^{-26} \text{ kg}$$

ii. Calculate the reduced mass of a nitrogen monoxide (NO) molecule.

$$m_r = \frac{m_N m_O}{m_N + m_O}$$

$$= \frac{2.326 \times 10^{-26} \times 2.657 \times 10^{-26}}{2.326 \times 10^{-26} + 2.657 \times 10^{-26}}$$

$$= 1.240 \times 10^{-26} \text{ kg}$$

Recall that the wavenumber is the reciprocal of the wavelength expressed in centimetres.

iii. Given that the bond force constant (k) of nitrogen monoxide (NO) is 1530 N m^{-1}, calculate the wavenumber of the vibrational transition of NO (in cm^{-1}).

$$\Delta E = \frac{h}{2\pi}\sqrt{\frac{k}{m_r}},$$

$$\Delta E = \frac{6.626\times10^{-34}}{2\pi}\sqrt{\frac{1530}{1.240\times10^{-26}}}$$

$$= 3.704\times10^{-20}\ \text{J}$$

$$E = \frac{hc}{\lambda},$$

$$\lambda = \frac{hc}{E}$$

$$= \frac{6.626\times10^{-34}\times2.998\times10^{8}}{3.704\times10^{-20}}$$

$$= 5.363\times10^{-6}\ \text{m}$$

$$\text{Wavenumber} = \frac{1}{\lambda_{cm}}$$

$$= \frac{1}{5.363\times10^{-6}\times10^{2}}$$

$$= 1865\ \text{cm}^{-1}$$

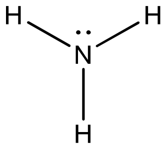
(i) The bond force constant (k) for the C=O bond in carbon dioxide is 1530 N m^{-1} and is 1900 N m^{-1} for the C≡O bond in carbon monoxide. Which compound will have an IR absorption at the higher wavenumber?

$$\Delta E = \frac{h}{2\pi}\sqrt{\frac{k}{m_r}}, \propto \sqrt{k}$$

$$E = \frac{hc}{\lambda}, \propto \frac{1}{\lambda}$$

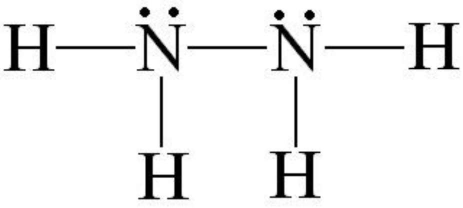
Carbon monoxide ($C\equiv O$) absorbs at higher wavenumber.

An example of a Lewis structure is shown below for ammonia (NH_3).

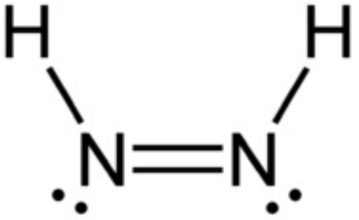


(j) *i.* Draw Lewis structures for hydrazine (N_2H_4), diazene (N_2H_2) and nitrogen gas.

N_2H_4



N_2H_2



N_2

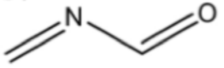
ii. In the answer box below, rank the nitrogen-nitrogen bonds in hydrazine, diazene and nitrogen gas in order of their IR absorbance wavenumbers, from lowest wavenumber (1) to highest wavenumber (3).

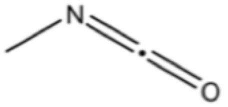
hydrazine	diazene	nitrogen
1	2	3

A student has three different compounds, **N**, **O** and **P**, each with the same molecular formula C_2H_3NO. A mixture of **N** and **O** is analysed, and it is determined that the mixture contains both C=O and C=N chromophores. A mixture of **O** and **P** is subsequently analysed and contains C=O, C=N, and N–H chromophores. Any chromophores listed in Table 1 can be detected by the analysis.

(k) *i.* Draw one possible structure for each of **N** and **O**.

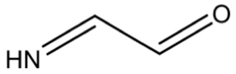
N and **O**:

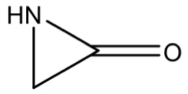




ii. Draw two possible structures for compound **P**.

P:





Question 18

Jean Servais Stas carried out many experiments that produced evidence for the laws that describe the manner in which elements combine. One of these is the Law of Conservation of Mass.

Stas synthesised silver iodide by mixing a solution of ammonium iodide (containing a known mass of iodine) with an acidic solution of silver sulfate (containing a known mass of silver). The iodide was present in slight excess, so extra silver sulfate was added until no more silver iodide was precipitated. Stas obtained the following data in one experiment (denoted experiment **1**):

Experiment	m(iodine) (g)	m(silver) (g)	m(extra silver) (g)	m(silver iodide) (g)
1	32.4665	27.6092	0.0131	60.0860

(a) Calculate the total mass of iodine and silver present in the reactants in experiment **1**.

m(reactants) = 32.4665 + 27.6092 + 0.0131 = 60.0888 g

(b) Calculate the difference between total mass of iodine and silver present in the reactants and the mass of silver iodide isolated.

Difference in mass = 60.0888 – 60.0860 = 0.0028 g

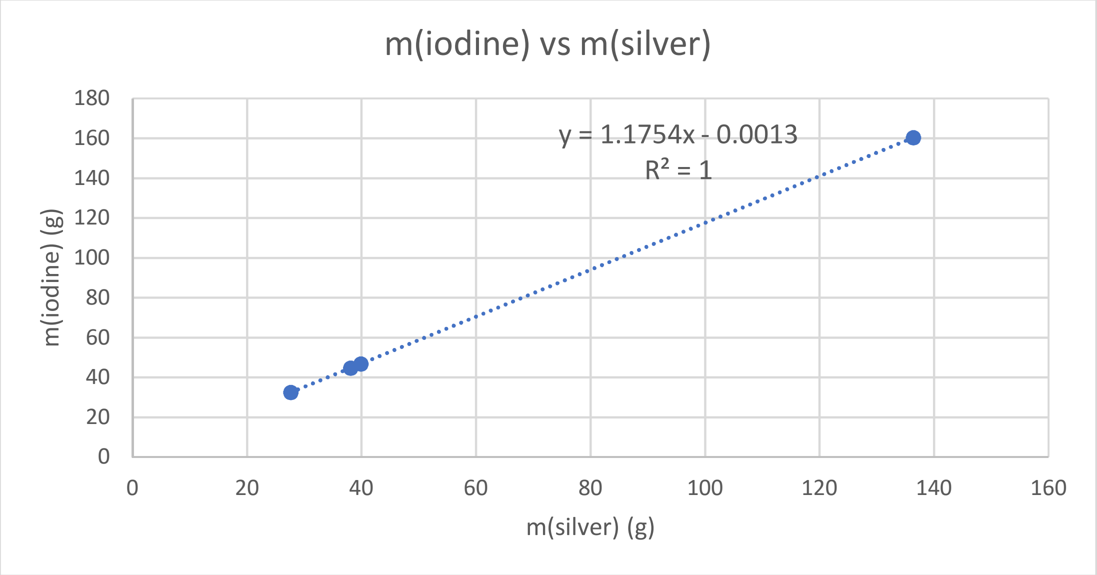
(c) From this data, calculate the mass of iodine that would combine with 100.000 g of silver.

$m(I_2) = (32.4665)/(27.6092 + 0.0131) \times 100 = 117.537$ g

Stas performed subsequent analogous experiments and obtained the following data, which is evidence for the Law of Definite Proportions, i.e. that chemical compounds contain their component elements in a fixed ratio (by mass).

Experiment	m(iodine) (g)	m(silver, total) (g)
1	32.4665	27.6223
2	46.8282	39.8405
3	44.7599	38.0795
4	160.2752	136.3547

This data is graphed below. The gradient of the line-of-best-fit is 1.1754.



(d) Using modern-day data (from the periodic table on page 3), calculate what the gradient of this line should be, in theory.

AgI → 1:1 stoichiometry

$m(I_2)/m(Ag) = RAM(I)/RAM(Ag) = 126.9/107.9 = 1.176$

Stas then synthesised silver iodide by direct reaction of the elements, using an excess of iodine, which was sublimed away at the conclusion of the reaction, leaving only silver iodide. If this is consistent with the data from experiments **1** to **4**, this is evidence that the composition of a compound is independent of the method used to prepare it, called the Law of Constant Composition.

Experiment	m(silver) (g)	m(silver iodide) (g)
5	13.5542	29.4858

(e) Show, using calculations, that this result is consistent with the data from experiments **1** to **4**.

m(I) = 29.4858 – 13.5542 = 15.9316 g

m(I)/m(Ag) = 15.9316/13.5542 = 1.1754

This is the same as the above gradient, so the result is consistent (other approaches are possible).

In 1858, Stanislao Cannizzaro championed the idea that molecular weights can be calculated from the densities of gases, stating that the molecular weight of any gas (relative to hydrogen = 2) is equal to 28.87 times the relative density of that gas (relative to air = 1). In 1858, Ludwig estimated the relative density of chlorine gas to be 2.450.

(f) Calculate the molecular weight of chlorine gas from this data.

$MW(Cl_2) = 28.87 \times 2.450 = 70.73$

In 1888, Lothar Meyer compiled the following list of chlorides from similar gas density data:

compound	molecular weight	weight of chlorine
hydrogen chloride	36.37	35.37
corrosive sublimate	270.5	70.74
liquid chloride of phosphorus	137	106.1
silicon chloride	169.5	141.5

Meyer reasoned that because the weight of chlorine in these compounds (and indeed many others) is an integer multiple of about 35.37, that “the atomic weight of chlorine is therefore limited to 35.37 or to the half, third, quarter or fifth of this number”. Obviously this is close, but slightly off the relative atomic mass of chlorine that we know today.

“Corrosive sublimate” is a compound of one element and chlorine only.

(g) Calculate two possible atomic weights for the element (other than chlorine) that is present in corrosive sublimate.

$XCl_2 \rightarrow 270.5 - 70.74 = 199.76$

$X_2Cl_2 \rightarrow 199.76/2 = 99.88$

(h) State the formula of the compound(s) that could correspond to “corrosive sublimate”.

$XCl_2 \rightarrow 199.76 \rightarrow HgCl_2$

$X_2Cl_2 \rightarrow 99.88 \rightarrow Ru_2Cl_2$

(i) Assuming that the atomic weight of chlorine is indeed 35.37, calculate the molecular formula of "liquid chloride of phosphorus".

n(Cl) = 106.1/35.37 = 3.000 → 3 mol Cl

n(P) = (127−106.1)/30.97 = 0.998 → 1 mol P

Formula is PCl_3

2.38 g of phosphorus reacts, via multiple steps, with 5.43 g of chlorine to form 7.81 g of a liquid. When this liquid is vapourised, the density of the gas is 7.049 (relative to air = 1).

(j) Calculate the molecular formula of this liquid.

Empirical formula:

n(P) = 2.38/30.97 = 0.0768 mol

n(Cl) = 5.43/35.37 = 0.1535 mol

n(P) : n(Cl) = 0.0768:0.1535 = 1:2 → PCl_2

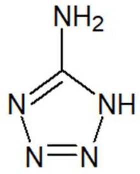
Molecular formula:

MM(liquid) = 7.049 × 28.87 = 203.5

MW(PCl_2) = 30.97 + 2(35.37) = 101.7

203.5/101.7 = 2 → P_2Cl_4

Green energetic materials are a group of compounds designed to reduce or eliminate the toxicity and environmental hazards of current energetic materials. The synthesis of one such promising family of compounds starts with 1*H*-tetrazol-5-amine, whose structure is shown below.



1*H*-tetrazol-5-amine

When 1*H*-tetrazol-5-amine (CH_3N_5) is treated with aqueous sulfuric acid, followed by copper(II) sulfate ($CuSO_4$) and sodium nitrite ($NaNO_2$), the highly sensitive compound **S** is produced.

Treatment of compound **S** with different metal hydroxides produces a variety of analogous salts, amongst them compounds **T** and **U**. Compound **T** is a product of the reaction between compound **S** and potassium hydroxide.

Compounds **T** and **U** are both comprised of atoms of four elements and have molar masses between 150 and 250 g mol^{-1}. Compound **T** contains 25.5289% potassium by mass. **U** has the lowest percentage by mass of nitrogen (28.3649%) and oxygen (12.9576%) of compounds **S**, **T** and **U**.

(k) Deduce the empirical formula of compounds **T** and **U**, showing all working and logic.

Molar mass of **T**:

Maximum K: 0.255289×250 g mol^{-1} = 63.8 g mol^{-1} → 63.8/39.10 = 1.63
Minimum K: 0.255289×150 g mol^{-1} = 38.3 g mol^{-1} → 38.3/39.10 = 0.98
T must have 1 K per formula unit
MM(**T**) = 39.10/0.255289 = 153.16 g mol^{-1}

Molar mass of **U**:

Maximum N: 0.283649×250 g mol^{-1} = 70.91 g mol^{-1} → 70.91/14.01 = 5.06
Minimum N: 0.283649×250 g mol^{-1} = 43.40 g mol^{-1} → 43.40/14.01 = 3.10
U must have 4 or 5 × N per formula unit

Maximum O: 0.129576×250 g mol^{-1} = 32.39 g mol^{-1} → 32.39/16.00 = 2.02
Minimum O: 0.129576×150 g mol^{-1} = 19.82 g mol^{-1} → 19.82/16.00 = 1.24
U must have 2 × O per formula unit

MM(**U**) = 2(16.00)/0.129576 = 246.96 g mol^{-1}

Answer continues over page.

Formula of anion:
Actual N: 0.283649 × 246.96 g mol^{-1} = 70.05 g mol^{-1} → 70.05/14.01 = 5

M(anion) = 153.16 – 39.10 = 114.06 g mol^{-1}

Anion contains 2 × O and 5 × N. Remainder of mass:
114.06 – 2(16.00) – 5(14.01) = 12.01 → 1 C

Hence, the anion has formula $CN_5O_2^-$

Identity of the cation in **U**:
MM(**U**) – MM($CN_5O_2^-$) = 246.96 – 114.06 = 132.9 → Cs

Hence: **T** is KCN_5O_2, **U** is $CsCN_5O_2$

As stated previously, when 1*H*-tetrazol-5-amine is treated with aqueous sulfuric acid, followed by copper(II) sulfate ($CuSO_4$) and sodium nitrite ($NaNO_2$), the highly sensitive compound **S** is produced. Compound **T** is a product of the reaction between compound **S** and potassium hydroxide; copper(II) hydroxide is also a product of this reaction.

0.1482 g of $Cu(OH)_2$ and 0.6980 g of compound **T** can be produced by the addition of excess potassium hydroxide to 0.6179 g of compound **S**, which contains 15.624% copper by mass.

(l) Deduce the empirical formula of compound **S**, showing all working and logic.

$n(Cu(OH)_2) = 0.1482/97.556 = 0.001519$ mol

$n(\mathbf{T}) = 0.6980/153.2 = 0.004557$ mol

$n(\mathbf{T})/n(Cu) = 0.004557/0.001518 = 3$
Hence, ratio of $Cu:(CN_5O_2) = 1:3$

Assuming 1 Cu per formula unit:

$MM(\mathbf{S}) = 63.55/0.15624 = 406.74\ g\ mol^{-1}$

$$\begin{aligned} MM(\text{remaining}) &= MM(\mathbf{S}) - MM(Cu) - 3 \times MM(CN_5O_2) \\ &= 406.74 - 63.55 - 3(114.06) = 1.018 \rightarrow H \end{aligned}$$

T is $CuH(CN_5O_2)_3$