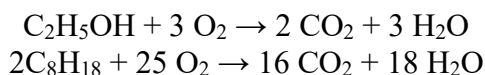


## SECTION A: MULTIPLE CHOICE USE THE ANSWER SHEET PROVIDED

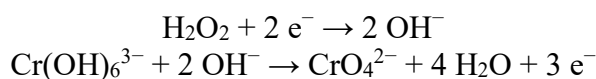
- Element X has the following ionisation energies:  $577.5 \text{ kJ mol}^{-1}$  (first),  $1816.7 \text{ kJ mol}^{-1}$  (second),  $2744.8 \text{ kJ mol}^{-1}$  (third),  $11577 \text{ kJ mol}^{-1}$  (fourth),  $14842 \text{ kJ mol}^{-1}$  (fifth). Which of the following is most likely to be element X?
  - magnesium
  - sodium
  - nitrogen
  - phosphorus
  - aluminium
- Which of the following molecules is the most polar?
  - $\text{O}_2$
  - $\text{CF}_4$
  - $\text{CO}_2$
  - $\text{NH}_3$
  - $\text{BF}_3$
- Which of the following molecules  $\text{XY}_n$  has the largest  $\text{Y-X-Y}$  bond angle?
  - $\text{H}_2\text{O}$
  - $\text{NH}_3$
  - $\text{CO}_2$
  - $\text{CF}_4$
  - $\text{BF}_3$
- Which separating technique would be most appropriate to separate two miscible liquids with boiling points of  $73 \text{ }^\circ\text{C}$  and  $76 \text{ }^\circ\text{C}$ ?
  - filtration
  - decantation
  - separatory funnel
  - fractional distillation
  - thin-layer chromatography
- Which of the following substances has the highest boiling point?
  - water
  - heptane
  - ethanol
  - sulfur dioxide
  - 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:



When 1.00 g of ethanol and 1.00 g of octane are combusted in excess oxygen, what is the total volume of  $\text{CO}_2$  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  $\text{Cr}(\text{OH})_6^{3-}$  is heated with hydrogen peroxide solution under alkaline conditions, it is oxidised to  $\text{CrO}_4^{2-}$  through a redox reaction. The relevant half equations are:



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

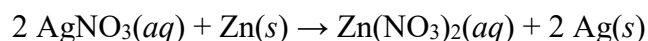
- (a) 0.1 mol  
**(b) 0.2 mol**  
 (c) 0.6 mol  
 (d) 1.0 mol  
 (e) 2.0 mol
8. Five beakers (labelled 1 to 5) each contain 0.5 moles of silver nitrate, dissolved in water. Into each of these beakers is added a certain amount of a metal chloride, also dissolved in water, as shown in the table below. Silver chloride precipitates from solution in all five beakers.

1	2	3	4	5
0.15 mol $\text{CaCl}_2$	0.20 mol $\text{AlCl}_3$	0.25 mol $\text{CaCl}_2$	0.30 mol $\text{NaCl}$	0.40 mol $\text{NaCl}$

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:



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

- |     | [Ag <sup>+</sup> ] | [NO <sub>3</sub> <sup>-</sup> ] |
|-----|--------------------|---------------------------------|
| (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<sub>2</sub>X<sub>6</sub>  
 (b) WX<sub>3</sub>  
 (c) WX  
 (d) W<sub>3</sub>X  
 (e) W<sub>6</sub>X<sub>2</sub>

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<sup>-1</sup>). 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  $^{12}\text{C}^{16}\text{O}_2$ , with a relative molecular mass of 44. Relative abundance of the most common isotopologue with a relative molecular mass of 47 ( $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ ) 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
$^{11}\text{C}$	$< 10^{-18} \%$	$^{16}\text{O}$	99.8%
$^{12}\text{C}$	98.9%	$^{17}\text{O}$	0.04%
$^{13}\text{C}$	1.1%	$^{18}\text{O}$	0.16%
$^{14}\text{C}$	$< 10^{-10} \%$		

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

- (a)  $^{11}\text{C}^{18}\text{O}^{18}\text{O}$
  - (b)  $^{12}\text{C}^{16}\text{O}^{17}\text{O}$
  - (c)  $^{12}\text{C}^{17}\text{O}^{18}\text{O}$
  - (d)  $^{13}\text{C}^{17}\text{O}^{17}\text{O}$
  - (e)  $^{14}\text{C}^{16}\text{O}^{17}\text{O}$
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  $\text{BaCO}_3$  and  $\text{BaSO}_4$ ). 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  $\text{CO}_3^{2-}$  ions to produce  $\text{CO}_2$ ). They record the mass of  $\text{CO}_2$  produced as 1.600 g.

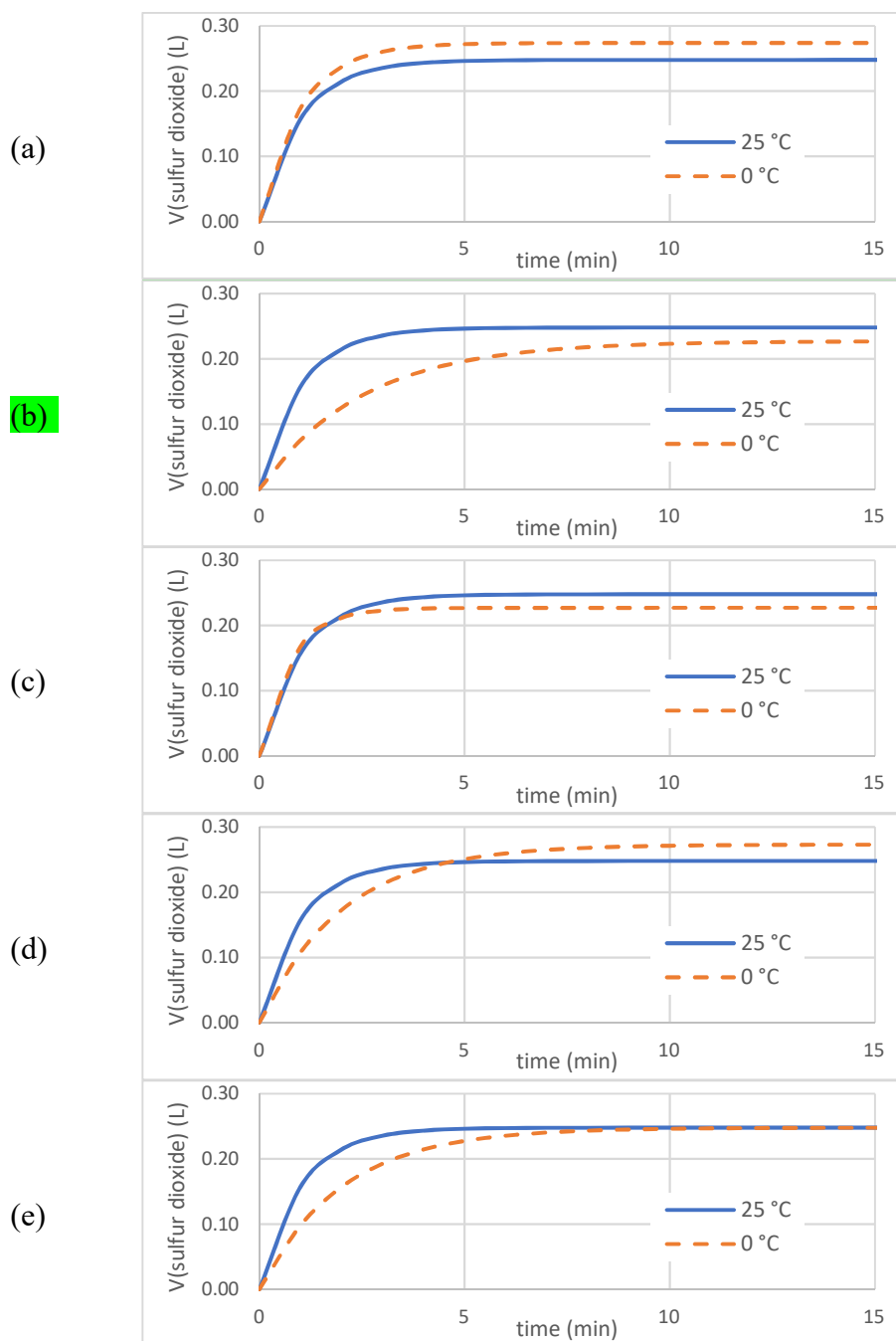
What is the mass percentage of sulfate ions in the fertiliser?

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

15. Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) reacts with hydrochloric acid according to the following chemical equation:  $\text{Na}_2\text{S}_2\text{O}_3(\text{aq}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{S}(\text{s}) + \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

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?



**END OF SECTION A**  
**SECTION B COMMENCES OVERLEAF**

**SECTION B****ANSWER IN THE SPACES PROVIDED****Question 16**

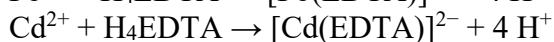
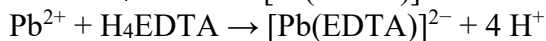
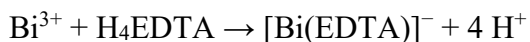
There are a wide range of low melting alloys used for soldering, usually containing a mixture of heavy metals including bismuth, lead, tin, indium and cadmium. In this question, we will examine an alloy primarily consisting of bismuth, lead, cadmium and tin, using an alloy sample of mass **1.790 g**.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

Initially the alloy is digested in nitric acid ( $\text{HNO}_3$ ) to form  $\text{Bi}^{3+}_{(\text{aq})}$ ,  $\text{Pb}^{2+}_{(\text{aq})}$ ,  $\text{Cd}^{2+}_{(\text{aq})}$  and  $\text{SnO}_{2(\text{s})}$ . The precipitated  $\text{SnO}_2$  is collected via vacuum filtration and dried, and its mass is found to 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**.

$$\begin{aligned} \text{MM}(\text{SnO}_2) &= 150.71 \text{ g/mol} \\ n(\text{SnO}_2) &= 2.581 \times 10^{-3} \text{ mol} = n(\text{Sn}) \\ m(\text{SnO}_2) &= 0.3064 \text{ g} \end{aligned}$$

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



pH is used to control the selectivity of these reactions. Initially a low pH is used, which prevents the  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ions from reacting with EDTA; this enables determination of the concentration of  $\text{Bi}^{3+}$  ions alone. **0.04000 M**  $\text{H}_4\text{EDTA}$  solution is added to an aliquot of the alloy solution until all of the  $\text{Bi}^{3+}$  has reacted, then hexamine (a base) is added. Further  $\text{H}_4\text{EDTA}$  solution is then added until all of the  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ions have reacted.

**18.78 mL** of **0.04000 M** H<sub>4</sub>EDTA solution is required to react with all of the Bi<sup>3+</sup> in a **20.00 mL** aliquot of the alloy **solution**.

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

$$\begin{aligned}n(\text{EDTA}) &= 7.512 \times 10^{-4} \text{ mol} = n(\text{Bi}) \text{ in aliquot} \\n(\text{Bi}) \text{ in solid} &= 3.576 \times 10^{-3} \text{ mol OR } m(\text{Bi}) \text{ from aliquot} = 0.1570 \text{ g} \\m(\text{Bi}) &= 0.7849 \text{ g}\end{aligned}$$

**21.83 mL** of **0.04000 M** H<sub>4</sub>EDTA solution is required to react with all of the Pb<sup>2+</sup> and Cd<sup>2+</sup> ions in the **20.00 mL** aliquot of the alloy **solution**.

(c) Find the combined concentration of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions in the alloy **solution**.

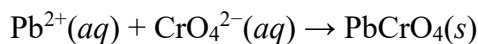
$$\begin{aligned}n(\text{EDTA}) &= 8.732 \times 10^{-4} \text{ mol} = n(\text{Pb} + \text{Cd}) \text{ in aliquot} \\[\text{Pb} + \text{Cd}] &= 0.04366 \text{ M}\end{aligned}$$

(d) What happens to the determination of the combined concentration of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions if too much of the H<sub>4</sub>EDTA solution is added when determining the Bi<sup>3+</sup> concentration?

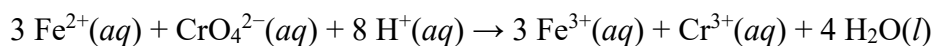
The apparent concentration of Pb and Cd will be lower than the actual value

Since  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  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  $\text{Pb}^{2+}$  ions to form the highly insoluble compound lead(II) chromate:



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



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

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

$$\begin{aligned} n(\text{CrO}_4^{2-}) \text{ total} &= 1.000 \times 10^{-3} \text{ mol} \\ n(\text{Fe}^{2+}) \text{ reacted} &= 1.853 \times 10^{-3} \text{ mol} \\ n(\text{CrO}_4^{2-}) \text{ excess} &= \{n(\text{Fe}^{2+}) \text{ reacted}\} / 3 = 6.177 \times 10^{-4} \text{ mol} \\ n(\text{CrO}_4^{2-}) \text{ reacted} &= n(\text{Pb}^{2+}) \text{ in aliquot} = 3.823 \times 10^{-4} \text{ mol} \\ n(\text{Pb}^{2+}) \text{ total} &= 1.912 \times 10^{-3} \text{ mol} \\ m(\text{Pb}^{2+}) &= 0.3961 \end{aligned}$$



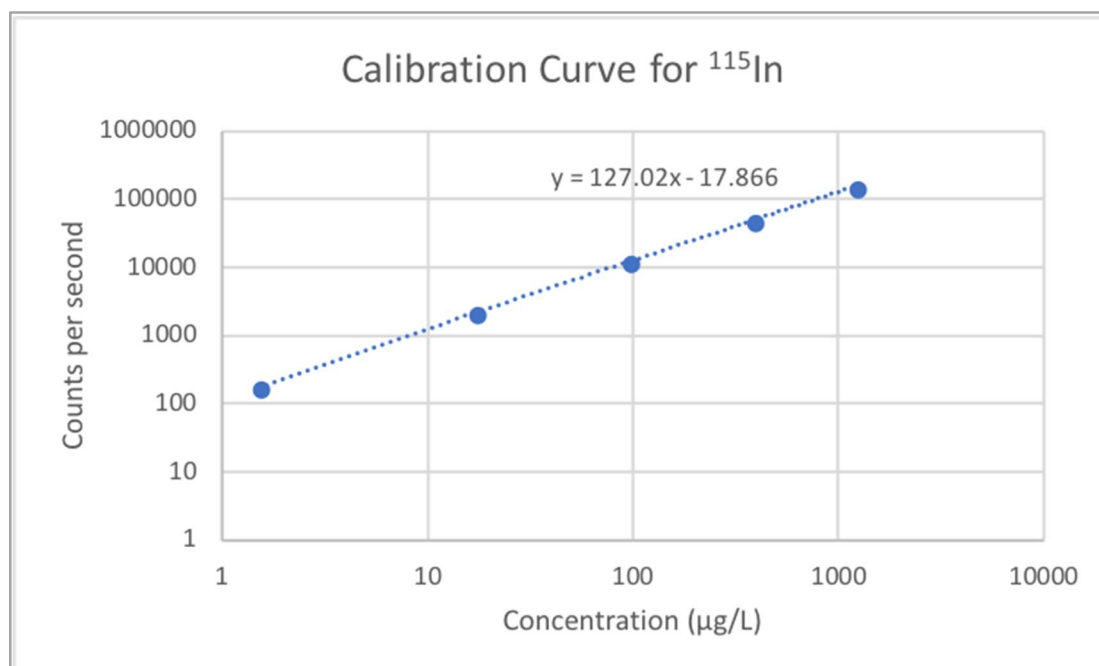
(f) Hence, find the mass of Cd in the **solid** alloy sample.

$$\begin{aligned}
 n(\text{Pb} + \text{Cd}) &= 8.732 \times 10^{-4} \text{ mol (if using aliquot) OR } 4.366 \times 10^{-3} \text{ mol (if using full sample)} \\
 n(\text{Pb}) &= 3.823 \times 10^{-4} \text{ mol OR } 1.912 \times 10^{-3} \text{ mol} \\
 n(\text{Cd}) &= 4.909 \times 10^{-4} \text{ mol OR } 2.456 \times 10^{-3} \text{ mol} \\
 m(\text{Cd}) &= 0.2759 \text{ g}
 \end{aligned}$$

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,  $^1\text{H}^+$  has a  $m/z$  of 1,  $^{115}\text{In}^+$  has a  $m/z$  of 115 and  $^{32}\text{S}^{2+}$  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.  $^{115}\text{In}$  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  $200 \mu\text{g}$  of  $^{115}\text{In}$  per L.

$2.539 \times 10^4 \text{ cps}$

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  $^{115}\text{In}$  at the same concentration.

For  $^{121}\text{Sb}$ , at a concentration of  $200 \mu\text{g/L}$  of  $^{121}\text{Sb}$ ,  $1.172 \times 10^4$  counts per second are observed.

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

$\text{RSF} = 0.4617$

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:  $^{115}\text{In}$  has an abundance of 95.71% and  $^{113}\text{In}$ , which has an abundance of 4.29%.

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

$$m/z = 113 - 1089 \text{ cps}$$

$$m/z = 115 - 2.430 \times 10^4 \text{ cps}$$

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,  $^{142}\text{Ce}$  and  $^{142}\text{Nd}$  have the same mass and charge.  $^{140}\text{Ce}$  has an isotopic abundance of 88.5%,  $^{142}\text{Ce}$  has an isotopic abundance of 11.1% and  $^{142}\text{Nd}$  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  $\mu\text{g L}^{-1}$ ) of Ce and Nd in the alloy solution?

$$\text{For } m/z = 140, \text{cps}(\text{Ce-140}) = 6620 \text{ cps}$$

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

$$[\text{Ce-140}] \{\text{from graph equation}\} = 75.5 \mu\text{g/L}$$

$$[\text{Ce}] \text{ total} = 85.3 \mu\text{g/L}$$

$$[\text{Ce-142}] = 9.46 \mu\text{g/L}$$

$$\text{scaled cps}(\text{Ce-142}) = 1184 \text{ cps}$$

$$\text{cps}(\text{Ce-142}) \{\text{scaled cps} \times \text{RSF}\} = 819 \text{ cps}$$

$$\text{cps}(\text{Nd-142}) = 1143 \text{ cps}$$

$$\text{scaled cps}(\text{Nd-142}) = 1486 \text{ cps}$$

$$[\text{Nd-142}] = 11.8 \mu\text{g/L}$$

$$[\text{Nd}] \text{ total} = 43.5 \mu\text{g/L}$$

## 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  $\text{cm}^{-1}$ . The range of wavenumbers collected in an IR spectrum is usually from  $4000$  to  $400 \text{ cm}^{-1}$ .

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

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

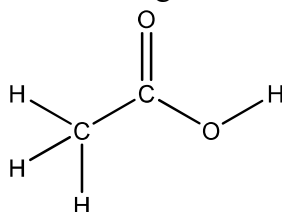
In a typical spectrum there are a series of peaks at different wavelengths at which the molecule absorbs IR radiation most strongly. Each of these peaks corresponds to one structural component of the molecule known as a *chromophore*. The reference table below shows the range of wavenumbers that correspond 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 ( $\text{cm}^{-1}$ )
O – H	3650 – 3200
N – H	3500 – 3300
$\text{C} \equiv \text{N}$	2260 – 2220
$\text{C} \equiv \text{C}$	2260 – 2100
$\text{C} = \text{O}$	1780 – 1650
$\text{C} = \text{C}$	1680 – 1600
$\text{C} = \text{N}$	1650 – 1550

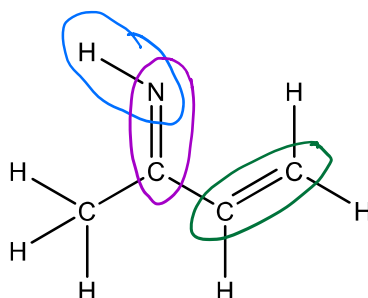
**Table 1:** Absorbances of some common chromophores (this table is reproduced throughout this question for your convenience)

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 ( $\text{CH}_3\text{COOH}$ ) contains a peak in the range  $3650$ - $3200 \text{ cm}^{-1}$  (O–H bond) and another peak in the range  $1780$ - $1650 \text{ cm}^{-1}$  (C=O bond).



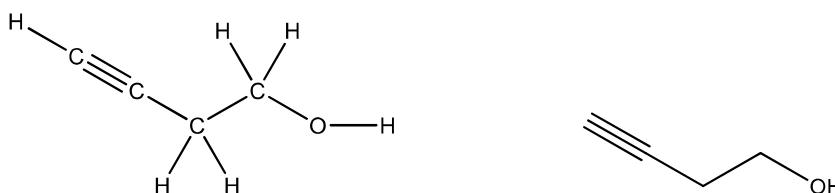
(b) Based on Table 1 and the information above, circle all chromophores in the molecule below that would absorb infrared light in the range  $3650\text{-}1550\text{ cm}^{-1}$ .



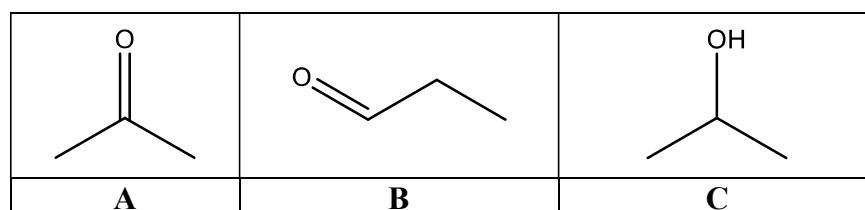
(c) How many peaks would you expect to see in the IR spectrum in that range?

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**.



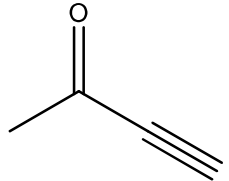
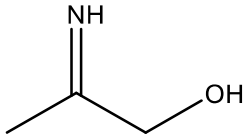
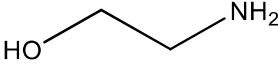
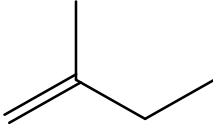
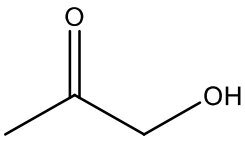
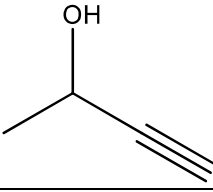
Which of those compounds **A**, **B** and **C** would have similar IR spectra, based on Table 1?

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 <sup>-1</sup> )	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	<b>D</b> 	<b>G</b> 	3650-3200 3500-3300 1650-1550
3650-3200 3500-3300	<b>E</b> 	<b>H</b> 	1680-1600
1780-1650 3650-3200	<b>F</b> 	<b>I</b> 	3650-3200 2260-2100

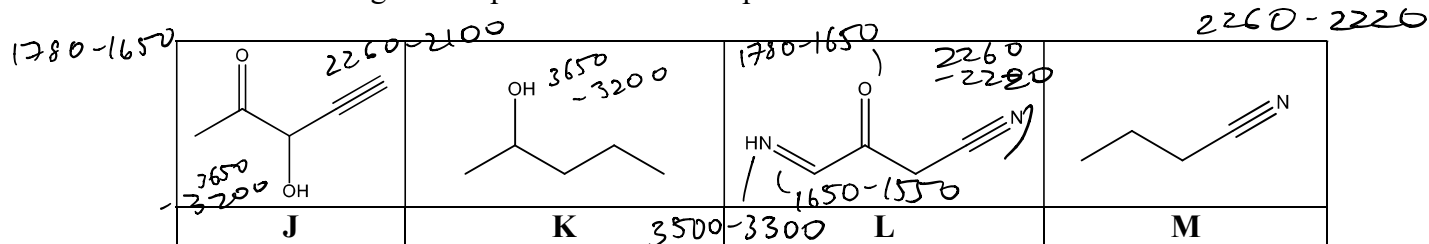
Chromophore	Absorbance Wavenumber (cm <sup>-1</sup> )
O-H	3650-3200
N-H	3500-3300
C≡N	2260-2220
C≡C	2260-2100
C=O	1780-1650
C=C	1680-1600
C=N	1650-1550

**Table 1:** Absorbances of some common chromophores.

3650-3200

(f) Four compounds **J**, **K**, **L** and **M** (shown below) were dissolved in ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ). 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 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> compounds removed from the mixture, and the wavenumber range of the peak lost from the spectrum.



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

K if ethanol solvent not acknowledged.

Chromophore	Absorbance Wavenumber ( $\text{cm}^{-1}$ )
O-H	3650-3200
N-H	3500-3300
$\text{C}\equiv\text{N}$	2260-2220
$\text{C}\equiv\text{C}$	2260-2100
$\text{C}=\text{O}$	1780-1650
$\text{C}=\text{C}$	1680-1600
$\text{C}=\text{N}$	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  $6.626 \times 10^{-34}$  J s;  $k$  is the bond force constant between the vibrating atoms (in  $\text{N m}^{-1}$ ), 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  $6.626 \times 10^{-34}$  J s;  $c$  is the speed of light, equal to  $2.998 \times 10^8$  m s<sup>-1</sup> and  $\lambda$  is the wavelength (in m).

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

higher

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

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

(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  $2.326 \times 10^{-26}$  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  $1530 \text{ N m}^{-1}$ , calculate the wavenumber of the vibrational transition of NO (in  $\text{cm}^{-1}$ ).

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

$$\Delta E = \frac{6.626 \times 10^{-34}}{2\pi} \sqrt{\frac{1530}{1.240 \times 10^{-26}}}$$

$$= 3.704 \times 10^{-20} \text{ J}$$

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

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

$$= \frac{6.626 \times 10^{-34} \times 2.998 \times 10^8}{3.704 \times 10^{-20}}$$

$$= 5.363 \times 10^{-6} \text{ m}$$

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

$$= \frac{1}{5.363 \times 10^{-6} \times 10^2}$$

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

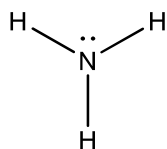
(i) The bond force constant ( $k$ ) for the C=O bond in carbon dioxide is  $1530 \text{ N m}^{-1}$  and is  $1900 \text{ N m}^{-1}$  for the C≡O bond in carbon monoxide. Which compound will have an IR absorption at the higher wavenumber?

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

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

Carbon monoxide (C≡O) absorbs at higher wavenumber.

An example of a Lewis structure is shown below for ammonia (NH<sub>3</sub>).



(j) i. Draw Lewis structures for hydrazine (N<sub>2</sub>H<sub>4</sub>), diazene (N<sub>2</sub>H<sub>2</sub>) and nitrogen gas.

N<sub>2</sub>H<sub>4</sub>

$$\begin{array}{c} \text{H} & - & \text{N} & - & \text{N} & - & \text{H} \\ & & | & & | & & \\ & & \text{H} & & \text{H} & & \end{array}$$

N<sub>2</sub>H<sub>2</sub>

$$\begin{array}{c} \text{H} & & & & \text{H} \\ & \diagdown & & / & \\ & \text{N} & = & \text{N} & \\ & \cdot & & & \cdot \end{array}$$

N<sub>2</sub>

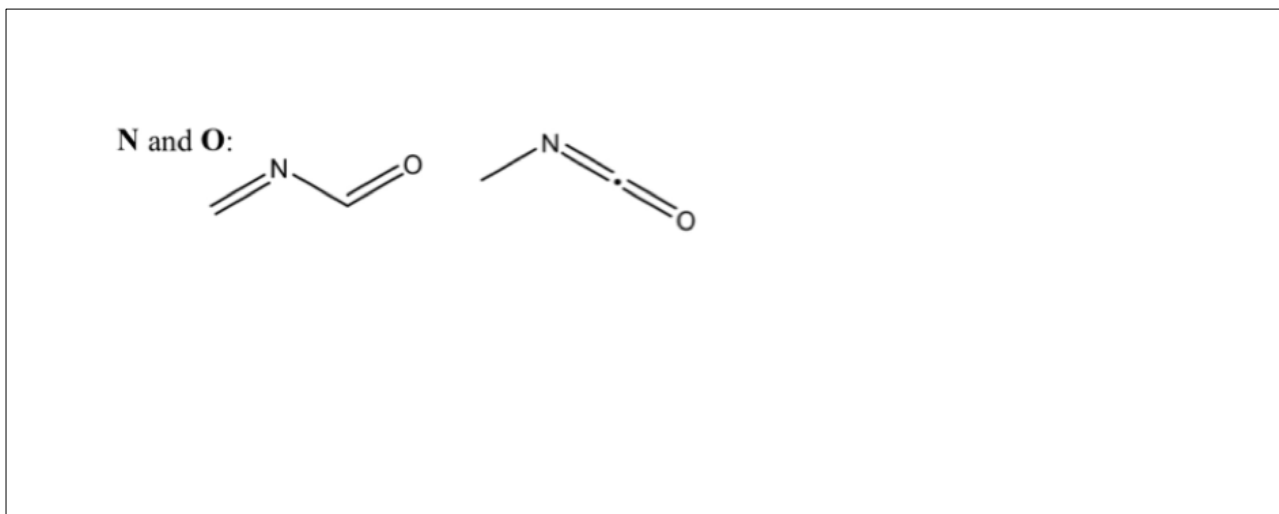
$$:\text{N} \equiv \text{N}:$$

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).

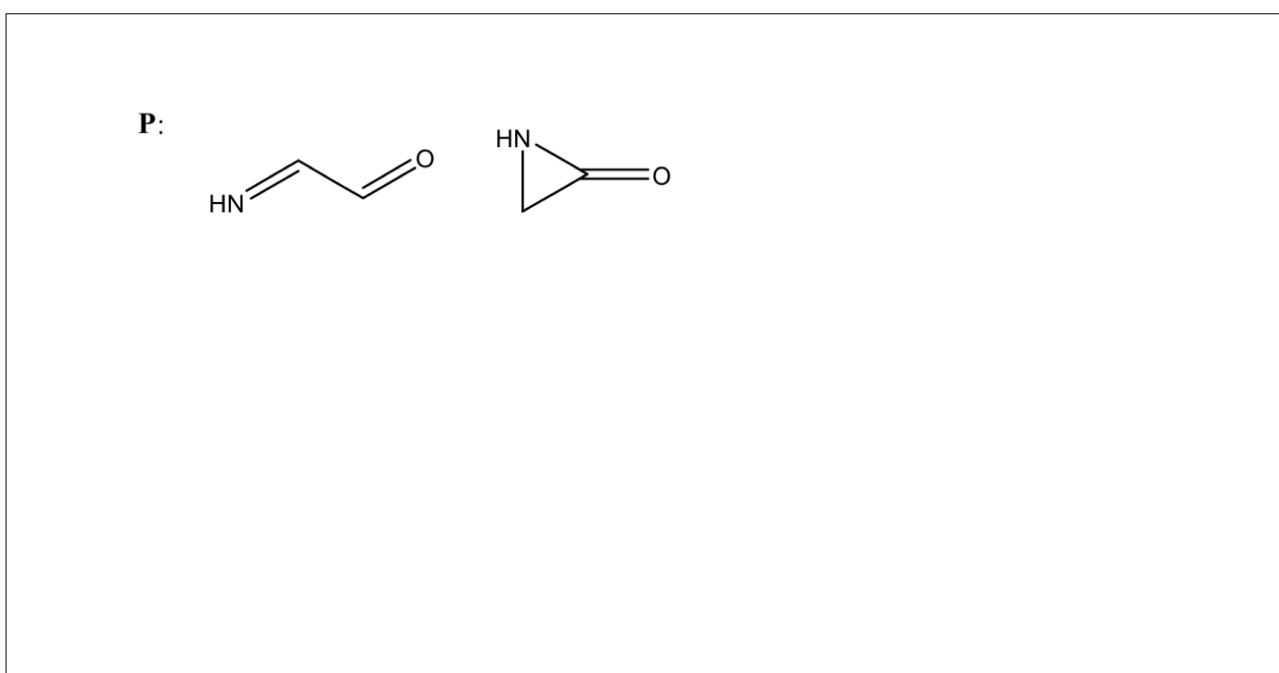
hydrazine	diazene	nitrogen
1	2	3

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**.



*ii.* Draw two possible structures for compound **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)
<b>1</b>	32.4665	27.6092	0.0131	60.0860

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

$$m(\text{reactants}) = 32.4665 + 27.6092 + 0.0131 = 60.0888 \text{ g}$$

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

$$\text{Difference in mass} = 60.0888 - 60.0860 = 0.0028 \text{ g}$$

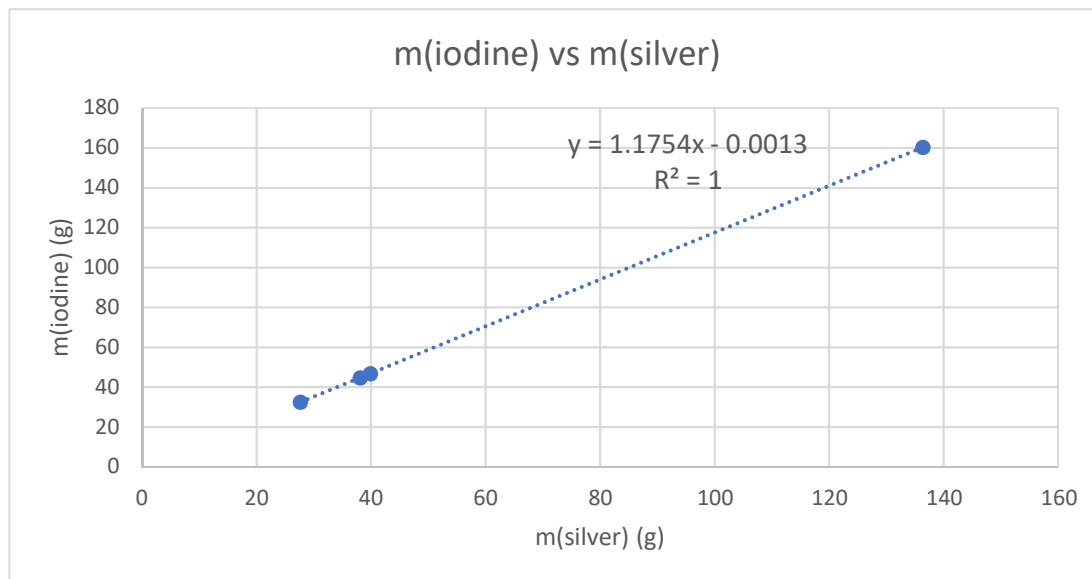
(c) From this data, calculate the mass of iodine that would combine with 100.000 g of silver.

$$m(\text{I}_2) = (32.4665)/(27.6092 + 0.0131) \times 100 = 117.537 \text{ g}$$

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.

$\text{AgI} \rightarrow 1:1$  stoichiometry

$$m(\text{I}_2)/m(\text{Ag}) = \text{RAM}(\text{I})/\text{RAM}(\text{Ag}) = 126.9/107.9 = 1.176$$

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)
<b>5</b>	13.5542	29.4858

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

$$m(\text{I}) = 29.4858 - 13.5542 = 15.9316 \text{ g}$$

$$m(\text{I})/m(\text{Ag}) = 15.9316/13.5542 = 1.1754$$

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.

$$\text{MW}(\text{Cl}_2) = 28.87 \times 2.450 = 70.73$$

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.

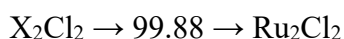
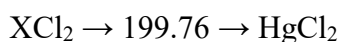
“Corrosive sublimate” is a compound of one element and chlorine only.

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

$$\text{XCl}_2 \rightarrow 270.5 - 70.74 = 199.76$$

$$\text{X}_2\text{Cl}_2 \rightarrow 199.76/2 = 99.88$$

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



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

$$n(\text{Cl}) = 106.1/35.37 = 3.000 \rightarrow 3 \text{ mol Cl}$$

$$n(\text{P}) = (127-106.1)/30.97 = 0.998 \rightarrow 1 \text{ mol P}$$

Formula is  $\text{PCl}_3$

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:

$$n(\text{P}) = 2.38/30.97 = 0.0768 \text{ mol}$$

$$n(\text{Cl}) = 5.43/35.37 = 0.1535 \text{ mol}$$

$$n(\text{P}) : n(\text{Cl}) = 0.0768:0.1535 = 1:2 \rightarrow \text{PCl}_2$$

Molecular formula:

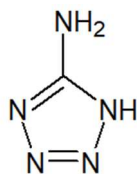
$$\text{MM}(\text{liquid}) = 7.049 \times 28.87 = 203.5$$

$$\text{MW}(\text{PCl}_2) = 30.97 + 2(35.37) = 101.7$$

$$203.5/101.7 = 2 \rightarrow \text{P}_2\text{Cl}_4$$



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 ( $\text{CH}_3\text{N}_5$ ) is treated with aqueous sulfuric acid, followed by copper(II) sulfate ( $\text{CuSO}_4$ ) and sodium nitrite ( $\text{NaNO}_2$ ), 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  $250 \text{ g mol}^{-1}$ . 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**:

$$\text{Maximum K: } 0.255289 \times 250 \text{ g mol}^{-1} = 63.8 \text{ g mol}^{-1} \rightarrow 63.8/39.10 = 1.63$$

$$\text{Minimum K: } 0.255289 \times 150 \text{ g mol}^{-1} = 38.3 \text{ g mol}^{-1} \rightarrow 38.3/39.10 = 0.98$$

**T** must have 1 K per formula unit

$$\text{MM}(\text{T}) = 39.10/0.255289 = 153.16 \text{ g mol}^{-1}$$

Molar mass of **U**:

$$\text{Maximum N: } 0.283649 \times 250 \text{ g mol}^{-1} = 70.91 \text{ g mol}^{-1} \rightarrow 70.91/14.01 = 5.06$$

$$\text{Minimum N: } 0.283649 \times 150 \text{ g mol}^{-1} = 43.40 \text{ g mol}^{-1} \rightarrow 43.40/14.01 = 3.10$$

**U** must have 4 or  $5 \times \text{N}$  per formula unit

$$\text{Maximum O: } 0.129576 \times 250 \text{ g mol}^{-1} = 32.39 \text{ g mol}^{-1} \rightarrow 32.39/16.00 = 2.02$$

$$\text{Minimum O: } 0.129576 \times 150 \text{ g mol}^{-1} = 19.82 \text{ g mol}^{-1} \rightarrow 19.82/16.00 = 1.24$$

**U** must have  $2 \times \text{O}$  per formula unit

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

Answer continues over page.

Formula of anion:

$$\text{Actual N: } 0.283649 \times 246.96 \text{ g mol}^{-1} = 70.05 \text{ g mol}^{-1} \rightarrow 70.05/14.01 = 5$$

$$M(\text{anion}) = 153.16 - 39.10 = 114.06 \text{ g mol}^{-1}$$

Anion contains  $2 \times \text{O}$  and  $5 \times \text{N}$ . Remainder of mass:

$$114.06 - 2(16.00) - 5(14.01) = 12.01 \rightarrow 1 \text{ C}$$

Hence, the anion has formula  $\text{CN}_5\text{O}_2^-$

Identity of the cation in **U**:

$$MM(\text{U}) - MM(\text{CN}_5\text{O}_2^-) = 246.96 - 114.06 = 132.9 \rightarrow \text{Cs}$$

Hence: **T** is  $\text{KCN}_5\text{O}_2$ , **U** is  $\text{CsCN}_5\text{O}_2$

As stated previously, when 1*H*-tetrazol-5-amine is treated with aqueous sulfuric acid, followed by copper(II) sulfate (CuSO<sub>4</sub>) and sodium nitrite (NaNO<sub>2</sub>), 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)<sub>2</sub> 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.

$$n(\text{Cu}(\text{OH})_2) = 0.1482/97.556 = 0.001519 \text{ mol}$$

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

$$n(\mathbf{T})/n(\text{Cu}) = 0.004557/0.001518 = 3$$

Hence, ratio of Cu:(CN<sub>5</sub>O<sub>2</sub>) = 1:3

Assuming 1 Cu per formula unit:

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

$$\begin{aligned} \text{MM}(\text{remaining}) &= \text{MM}(\mathbf{S}) - \text{MM}(\text{Cu}) - 3 \times \text{MM}(\text{CN}_5\text{O}_2) \\ &= 406.74 - 63.55 - 3(114.06) = 1.018 \rightarrow \text{H} \end{aligned}$$

**T** is CuH(CN<sub>5</sub>O<sub>2</sub>)<sub>3</sub>