

# CHEMISTRY

## 2017 Australian Science Olympiad Exam

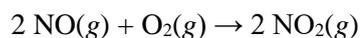
### Multiple choice answers

Correct answer marked in **yellow**

1. Which of the following will produce a gas when reacted with hydrochloric acid?

- (a) **NaHCO<sub>3</sub>**
- (b) NaOH
- (c) NaNO<sub>3</sub>
- (d) Na<sub>2</sub>SO<sub>4</sub>
- (e) NaH<sub>2</sub>PO<sub>4</sub>

2. Nitric oxide (NO) reacts completely with oxygen to form nitrogen dioxide according to the following balanced chemical equation:



If 2 L of NO and 1 L of O<sub>2</sub> are reacted in a balloon, what will be the final volume of the balloon after the reaction is complete, assuming that the temperature and pressure are unchanged?

- (a) 1.0 L
- (b) **2.0 L**
- (c) 2.5 L
- (d) 3.0 L
- (e) 5.0 L

3. Calcium hydroxide (Ca(OH)<sub>2</sub>) is sparingly soluble in water, with a solubility of 1.73 g/L at 20 °C. If 0.400 g of calcium hydroxide is placed in 200 mL of water at 20°C, what mass of calcium hydroxide will remain **undissolved**?

- (a) 0.027 g
- (b) **0.054 g**
- (c) 0.173 g
- (d) 0.346 g
- (e) 0.400 g

4. Prussian blue is a deep blue pigment containing Fe<sup>2+</sup>, Fe<sup>3+</sup> and CN<sup>-</sup> ions. It has the formula Fe<sub>7</sub>(CN)<sub>18</sub>. How many Fe<sup>2+</sup> and Fe<sup>3+</sup> ions are there per formula unit?

- (a) 0 Fe<sup>2+</sup> and 6 Fe<sup>3+</sup>

- (b) 3 Fe<sup>2+</sup> and 4 Fe<sup>3+</sup>
- (c) 4 Fe<sup>2+</sup> and 3 Fe<sup>3+</sup>
- (d) 5 Fe<sup>2+</sup> and 2 Fe<sup>3+</sup>
- (e) 9 Fe<sup>2+</sup> and 0 Fe<sup>3+</sup>

5. Element X forms compounds with two common ions: X<sup>+</sup> and X<sup>3+</sup>. Which group is element X likely to be in?

- (a) 1
- (b) 2
- (c) 13
- (d) 15
- (e) 17

6. Why does a catalyst increase the rate of reaction?

- (a) Decreases activation energy of the reaction
- (b) Increases the temperature of the reactants
- (c) Increases the concentration of the reactants
- (d) Decreases the pressure of the system
- (e) Decreases the surface area of the reactants

7. Acid number is a commonly used metric in the paint industry. It is defined as the mass (in mg) of potassium hydroxide required to completely neutralise the acid in 1 g of paint.

A paint has an acid number of 185. What volume of 0.100 M KOH is required to completely neutralise 0.5 g of that paint?

- (a) 1.65 mL
- (b) 3.30 mL
- (c) 16.5 mL
- (d) 18.5 mL
- (e) 33.0 mL

8. Phosphoric acid is a triprotic acid. What mass of Ca(OH)<sub>2</sub> would be required to neutralise 100 mL of a 1 mol L<sup>-1</sup> solution of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>)?

- (a) 3.7 g
- (b) 4.9 g
- (c) 7.4 g
- (d) 11.1 g
- (e) 22.2 g

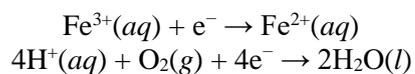
9. Consider four elements: calcium, oxygen, potassium and sulfur. What would be the correct order if they were arranged according to increasing electronegativity?

- (a) Calcium < oxygen < potassium < sulfur
- (b) Calcium < potassium < sulfur < oxygen
- (c) Oxygen < sulfur < potassium < calcium
- (d) Potassium < calcium < oxygen < sulfur
- (e) Potassium < calcium < sulfur < oxygen

10. A diene (di-alkene) is a hydrocarbon containing two double bonds. For example, 1,3-butadiene has a double bond between the first and second carbon atoms, and another double between the third and fourth carbon atoms. If the formula for 1,3-butadiene is  $C_4H_6$ , what is the formula for 2,4-hexadiene?

- (a)  $C_6H_8$
- (b)  $C_6H_9$
- (c)  $C_6H_{10}$
- (d)  $C_6H_{12}$
- (e)  $C_6H_{14}$

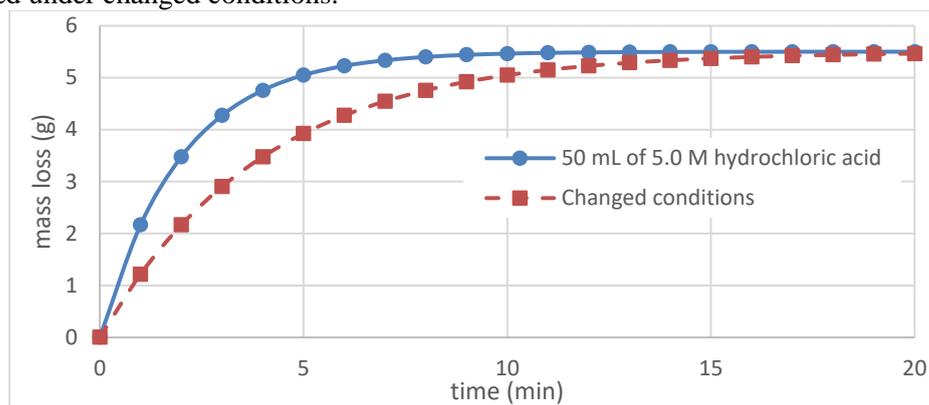
11. Aqueous  $Fe^{2+}$  ions are readily oxidised to  $Fe^{3+}$  ions by oxygen gas in acidic solutions. Consider the following relevant reduction half equations:



What chemical amount (in mol) of  $H_2O$  would be produced from the reaction of 2 mol of  $Fe^{2+}$  with excess oxygen under acidic conditions?

- (a) 1 mol
- (b) 2 mol
- (c) 4 mol
- (d) 8 mol
- (e) 16 mol

12. Excess calcium carbonate was treated with 50 mL of 5.0 M hydrochloric acid and the mass lost over 20 min recorded and plotted on the graph below. The experiment was then repeated under changed conditions.



Which of the following could be the changed conditions?

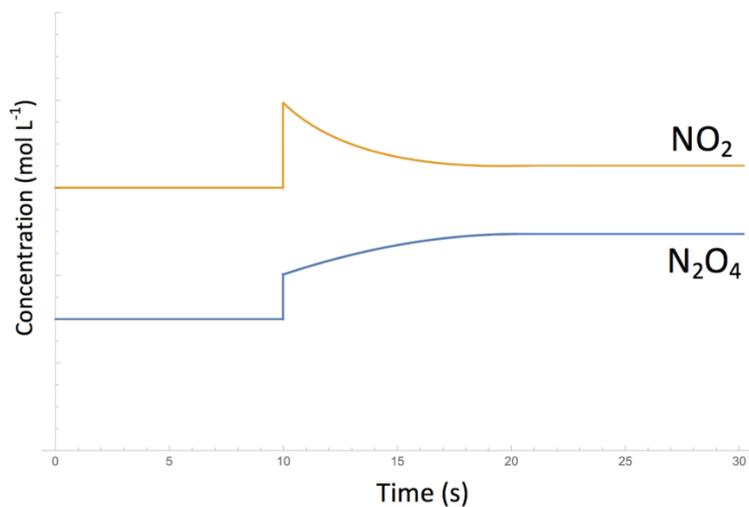
- (a) 25 mL of 5.0 M hydrochloric acid
  - (b) 25 mL of 10.0 M hydrochloric acid
  - (c) 50 mL of 2.5 M hydrochloric acid
  - (d) 50 mL of 10.0 M hydrochloric acid
  - (e) 100 mL of 2.5 M hydrochloric acid
13. Solid carbon dioxide, also known as dry ice, sublimates to form gaseous carbon dioxide. What type of bonding is significantly weakened because of this phase change?
- (a) Covalent bonding
  - (b) Hydrogen bonding
  - (c) Ionic bonding
  - (d) Intermolecular forces
  - (e) Metallic bonding
14. Which of the following elements is a solid at room temperature?

- (a) H<sub>2</sub>
- (b) F<sub>2</sub>
- (c) Cl<sub>2</sub>
- (d) Br<sub>2</sub>
- (e) I<sub>2</sub>

15. Nitrogen dioxide ( $\text{NO}_2$ ) dimerises to form  $\text{N}_2\text{O}_4$ , as represented by the equilibrium reaction:



The following graph depicts the concentration of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  gases in a closed reaction vessel.



At  $t = 10$  s, the equilibrium between the two species is disrupted, and a new equilibrium is reached at  $t = 20$ . Which one of the following disruptions at  $t = 10$  would be consistent with the graph?

- (a) Addition of only  $\text{N}_2\text{O}_4$  to the reaction vessel
- (b) Addition of only  $\text{NO}_2$  to the reaction vessel
- (c) Decrease in volume of the reaction vessel
- (d) Increase in temperature inside reaction vessel
- (e) Removal of only  $\text{NO}_2$  from the reaction vessel

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

**Question 16**

Our atmosphere is made up of 4 main gases: about 78% nitrogen gas, 21% oxygen gas, less than 1% argon, and around 0.04% carbon dioxide. Recently, a planet called TCAZ1HG was discovered. It looks similar to Earth and spectroscopic measurements revealed that its atmosphere consists of the same four gases in Earth's atmosphere.

(Throughout the question, air refers to the atmosphere of planet TCAZ1HG. All measurements have been performed at the same temperature and pressure.)

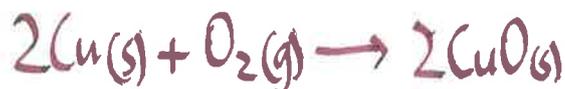
A 500.0 L container filled with air weighs 23.888 kg. When the container is completely evacuated of all air, it weighs 21.702 kg.

(a) Find the density of the air (in  $\text{g L}^{-1}$ ).

$$\begin{aligned} m(\text{air}) &= 23.888 - 21.702 = 2.186 \text{ kg} \\ &= 2186 \text{ g} \\ \rho(\text{air}) &= \frac{2186 \text{ g}}{500.0 \text{ L}} = 4.372 \text{ g L}^{-1} \end{aligned}$$

To determine the percentage by mass of oxygen gas in air, an excess of copper is added to a sealed 25.00 L container filled with air. This is heated and the oxygen reacts with the copper to form copper(II) oxide.

(b) Write a balanced chemical equation for this reaction.



(c) Calculate the mass of air in the container before the reaction occurred.

$$\begin{aligned} m(\text{air}) &= 25.00 \text{ L} \times 4.372 \text{ g L}^{-1} \\ &= 109.3 \text{ g} \end{aligned}$$

Upon complete reaction, the mass of the remaining gas is found to be 72.40 g.

(d) Calculate the mass of oxygen gas that reacted with the copper.

$$\begin{aligned}m(\text{O}_2) &= 109.3 \text{ g} - 72.40 \text{ g} \\ &= 36.9 \text{ g}\end{aligned}$$

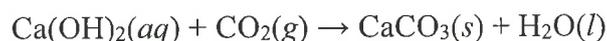
(e) Calculate the percentage by mass of oxygen in the air.

$$\%(\text{O}_2) = \frac{36.9 \text{ g}}{109.3 \text{ g}} \times \frac{100}{1} = 33.8 \%$$

(f) Calculate the mass of copper(II) oxide produced in this reaction.

$$\begin{aligned}n(\text{O}_2) &= \frac{36.9 \text{ g}}{32.00 \text{ g mol}^{-1}} = 1.15 \text{ mol} \\ n(\text{CuO}) &= 2 \times 1.15 \text{ mol} = 2.31 \text{ mol} \\ m(\text{CuO}) &= 2.31 \text{ mol} \times (63.55 + 16.00) \text{ g mol}^{-1} \\ &= 183 \text{ g}.\end{aligned}$$

To determine the percentage by mass of carbon dioxide in the air, a 10.00 L sample of air is continually bubbled through a solution of  $\text{Ca(OH)}_2$  or limewater, and a white precipitate of calcium carbonate forms, as described by the following balanced chemical equation:



Once the precipitation is complete, the solid is filtered, washed and dried, and has a mass of 11.05 g.

(g) Calculate the percentage by mass of  $\text{CO}_2$  in the air.

$$n(\text{CaCO}_3) = \frac{11.05 \text{ g}}{100.09 \text{ g mol}^{-1}} = 0.1104 \text{ mol}$$

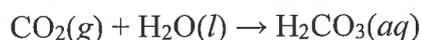
$$\therefore n(\text{CO}_2) = 0.1104 \text{ mol}$$

$$m(\text{CO}_2) = 0.1104 \text{ mol} \times 44.01 \text{ g mol}^{-1} = 4.859 \text{ g}$$

$$m(\text{air}) = 10.00 \text{ L} \times 4.372 \text{ g L}^{-1} = 43.72 \text{ g}$$

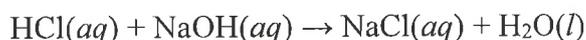
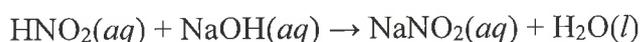
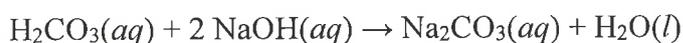
$$\%(\text{CO}_2) = \frac{4.859 \text{ g}}{43.72 \text{ g}} \times \frac{100}{1} = 11.11\%$$

To find the percentage by mass of  $\text{N}_2$  in the air, a 2.000 g sample of air is reacted with excess oxygen and water at high temperature. Under these conditions, the  $\text{CO}_2$  and  $\text{N}_2$  form acids according to the following equations:



The resulting acidic solution is quantitatively transferred to a 250.0 mL volumetric flask and made up to the mark. 50.00 mL of 0.1993 M NaOH is added to 20.00 mL samples of this mixture and reacts with the acids present. Neutralisation of the excess NaOH requires 18.36 mL of 0.2101 M HCl.

The following balanced chemical equations represent the reactions of aqueous  $\text{H}_2\text{CO}_3$ ,  $\text{HNO}_2$  and HCl with the solution of NaOH:



(h) Calculate the chemical amount (in mol or mmol) of HCl added.

$$\begin{aligned}n(\text{HCl}) &= 18.36 \text{ mL} \times 0.2101 \text{ M} \\ &= 3.857 \text{ mmol.}\end{aligned}$$

(i) Calculate the chemical amount (in mol or mmol) of NaOH that reacted with  $\text{H}_2\text{CO}_3$  and  $\text{HNO}_2$ .

$$\begin{aligned}n(\text{NaOH, total}) &= 50.00 \text{ mL} \times 0.1993 \text{ M} = 9.965 \text{ mmol} \\ n(\text{NaOH, reacted}) &= 9.965 \text{ mmol} - 3.857 \text{ mmol} \\ &= 6.108 \text{ mmol}\end{aligned}$$

(j) Calculate the chemical amount (in mol or mmol) of  $\text{H}_2\text{CO}_3$  that will be present in a 20.00 mL sample of the original acidic solution. (If you did not get an answer for part (g), you may assume that the percentage by mass of carbon dioxide in the air is 10%).

$$\begin{aligned}m(\text{CO}_2) &= 2.000 \text{ g} \times 0.1111 = 0.2222 \text{ g} \\ n(\text{CO}_2) &= \frac{0.2222 \text{ g}}{44.01 \text{ g mol}^{-1}} = 5.050 \text{ mmol} \\ \therefore n(\text{H}_2\text{CO}_3) &= 5.050 \text{ mmol} \\ \therefore n(\text{H}_2\text{CO}_3 \text{ in aliquot}) &= \frac{20.00 \text{ mL}}{250.0 \text{ mL}} \times 5.050 \text{ mmol} \\ &= 0.4040 \text{ mmol.}\end{aligned}$$

(k) Calculate the percentage by mass of  $N_2$  in the air.

$$n(\text{NaOH, reacts with H}_2\text{CO}_3) = 2 \times 0.4040 \text{ mmol} \\ = 0.8081 \text{ mmol}$$

$$n(\text{NaOH, reacts with HNO}_2) = 6.108 \text{ mmol} - 0.8081 \text{ mmol} \\ = 5.300 \text{ mmol.}$$

$$n(\text{N}) = \frac{250.0 \text{ mL}}{20.00 \text{ mL}} \times 5.300 \text{ mmol} = 66.24 \text{ mmol} \\ = 0.06624 \text{ mol}$$

$$m(\text{N}) = 14.01 \text{ g mol}^{-1} \times 0.06624 \text{ mol} \\ = 0.9281 \text{ g}$$

$$\%(\text{N}_2) = \frac{0.9281 \text{ g}}{2.000 \text{ g}} \times \frac{100}{1} = 46.40\%$$

The amount fraction (also known as mole fraction) is defined as the chemical amount of a substance in a mixture (in mol) divided by the total chemical amounts of all constituents of the mixture (in mol).

(l) Assuming that the remaining gas in the air is argon, calculate the amount fraction of argon in the air.

$$\% \text{ Ar} = 100 - 11.11 - 33.76 - 46.40 = 8.73\%$$

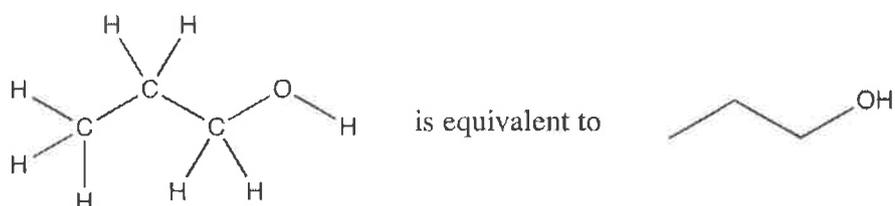
In 1 g air:	$\text{CO}_2$	$\text{O}_2$	$\text{N}_2$	Ar
mass (g)	0.1111	0.3376	0.4640	0.0873
amount (mmol)	2.525	10.55	16.56	2.18

$$\therefore \text{amount fraction (Ar)} = \frac{2.18}{2.525 + 10.55 + 16.56 + 2.18} = 0.0686$$

### Question 17

The field of organic chemistry (or carbon chemistry) involves the study of how to transform organic compounds into desired products. In organic chemistry, skeletal formula notation is often used to represent carbon backbones. 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:

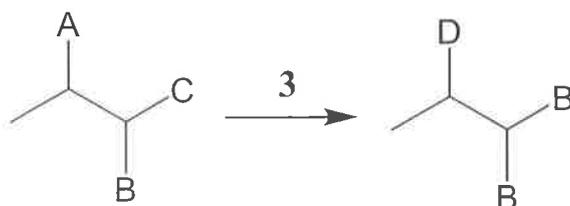


Specific reactions can be used to transform one functional group (such as the OH group in the structure above) into another. These reactions have been represented by numbers throughout this question, as shown in the table below. For the sake of simplicity, we have also represented various organic functional groups as letters of the alphabet from **A** to **F** (note that the letters **B**, **C** and **F** refer to functional groups, not the respective elements boron, carbon and fluorine which they usually denote). For your convenience, this table will be reproduced frequently in this question.

Reaction 1:	<b>A</b> → <b>C</b> <b>B</b> → <b>C</b>
Reaction 2:	<b>A</b> → <b>C</b>
Reaction 3:	<b>A</b> → <b>D</b> <b>C</b> → <b>B</b>
Reaction 4:	<b>D</b> → <b>A</b>
Reaction 5:	<b>C</b> → <b>E</b>
Reaction 6:	<b>E</b> → <b>C</b>

As an example, the functional group **A** can be converted to functional group **C** by either reaction **1** or **2**, or to functional group **D** by reaction **3**.

As a further example, the molecule shown on the left is converted into the molecule on the right by reaction **3**.



Reaction 1:	A → C B → C
Reaction 2:	A → C
Reaction 3:	A → D C → B
Reaction 4:	D → A
Reaction 5:	C → E
Reaction 6:	E → C

(a) Draw the product of the following reactions. Note that when two reactions are written on the same line they are applied sequentially from left to right, e.g. 1, 3 means do reaction 1, then apply reaction 3 to the products of the previous reaction. Blank skeletal structures for the products have been drawn for you.

(i)

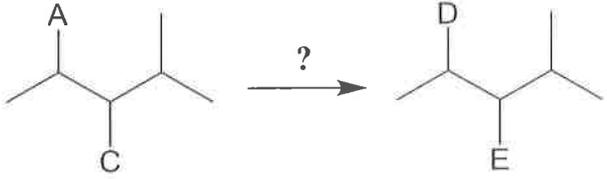
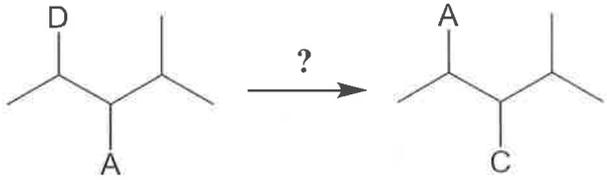
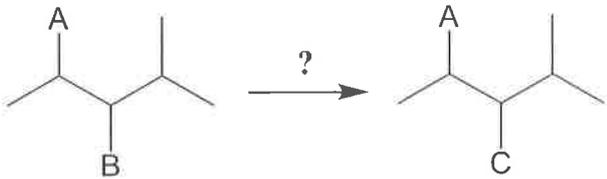
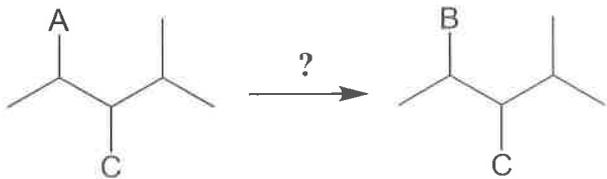
(ii)

(iii)

(iv)

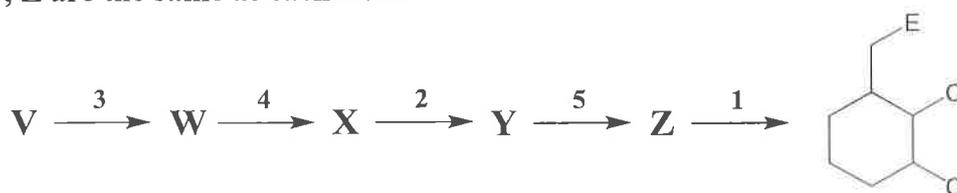
Reaction 1:	A → C
	B → C
Reaction 2:	A → C
Reaction 3:	A → D
	C → B
Reaction 4:	D → A
Reaction 5:	C → E
Reaction 6:	E → C

(b) Identify the reaction step(s) required to transform the reactant on the left to the product on the right. Note that this may require the sequential application of more than one reaction.

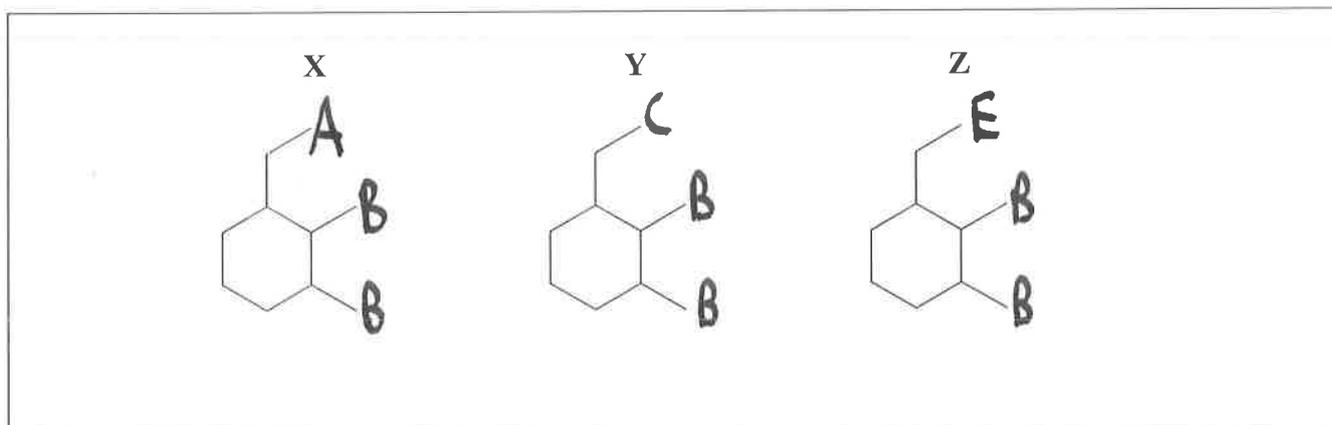
<p>(i)</p> 	<p>Reaction step(s):</p> <p>5,3</p>
<p>(ii)</p> 	<p>Reaction step(s):</p> <p>2,4</p>
<p>(iii)</p> 	<p>Reaction step(s):</p> <p>3,1,4</p>
<p>(iv)</p> 	<p>Reaction step(s):</p> <p>5,1,3,6</p>

Reaction 1:	A → C B → C
Reaction 2:	A → C
Reaction 3:	A → D C → B
Reaction 4:	D → A
Reaction 5:	C → E
Reaction 6:	E → C

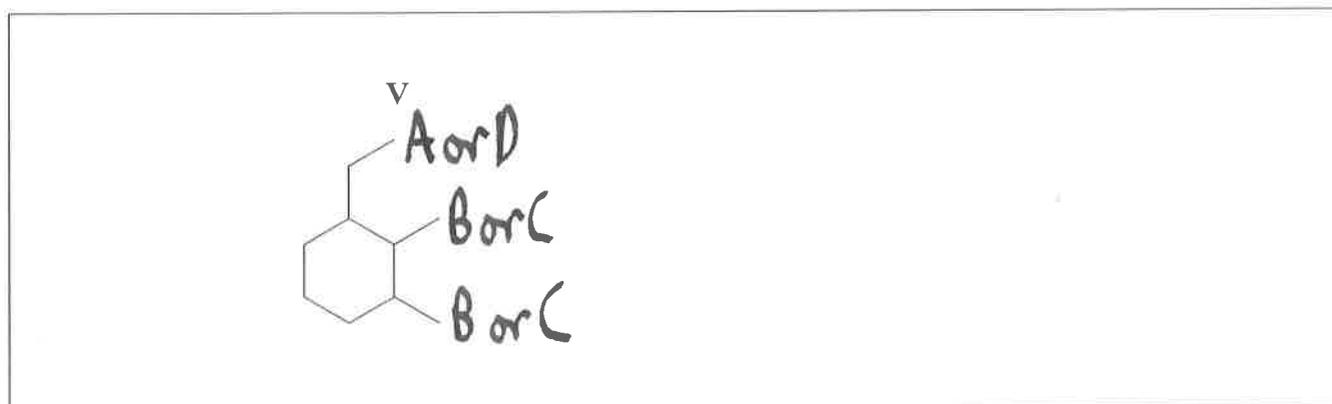
- (c) Consider the reaction scheme below, in which the product pictured on the right is synthesised from compound V via the reactions 3, 4, 2, 5 and then 1 respectively. **None of compounds V, W, X, Y, Z are the same as each other.**



- (i) Sketch the structures of X, Y and Z. Blank skeletal structures have been provided for you.



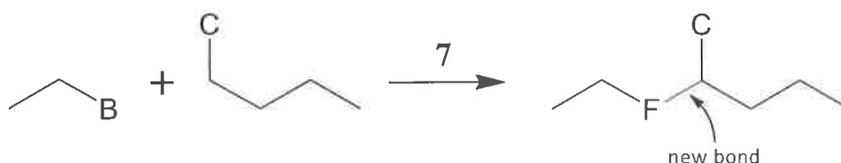
- (ii) Sketch one possible structure for V.



(iii) How many different possible compounds could **V** be?

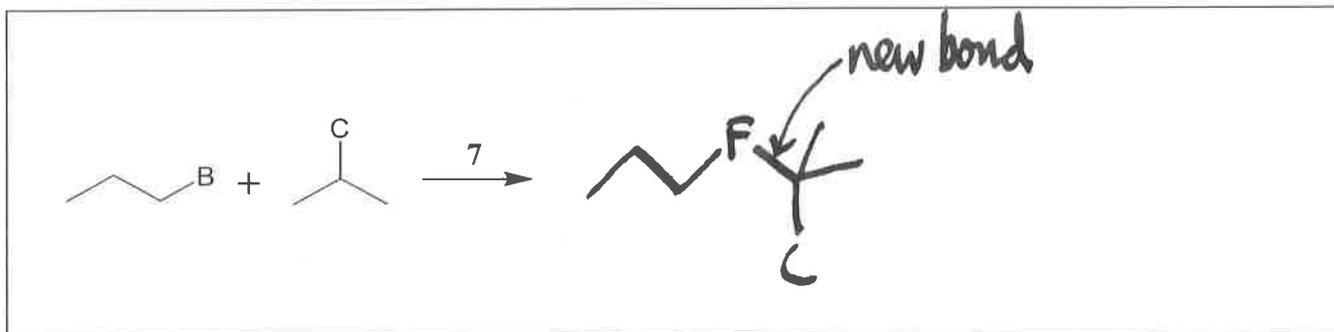
6.

(d) In reaction 7, the functional groups **B** and **C** react in the following way:



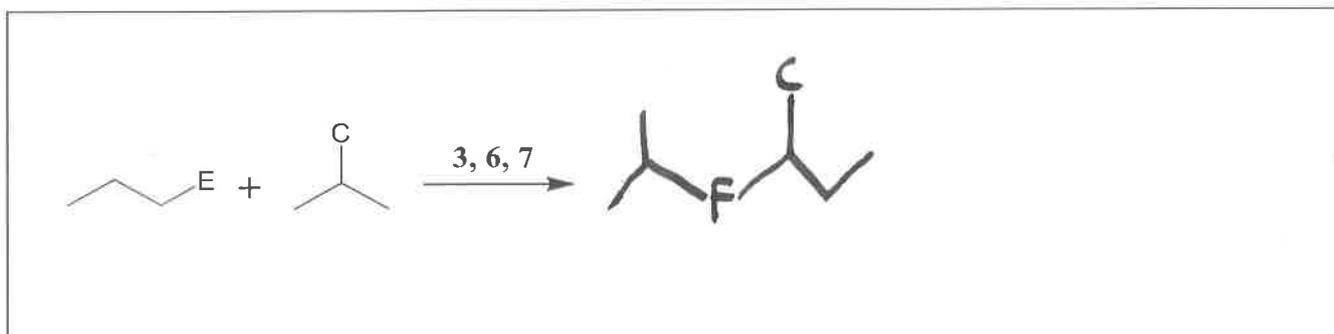
A new chemical bond is formed between the functional group **B** and the carbon *adjacent* to the functional group **C**, and **B** is turned into a new functional group **F** in the process.

(i) Draw the product of the following reaction, and label the new bond formed.

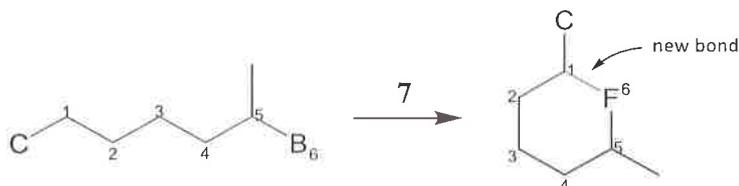


In the following reaction, the two starting materials are mixed and reactions 3, 6 and 7 are performed sequentially on this mixture.

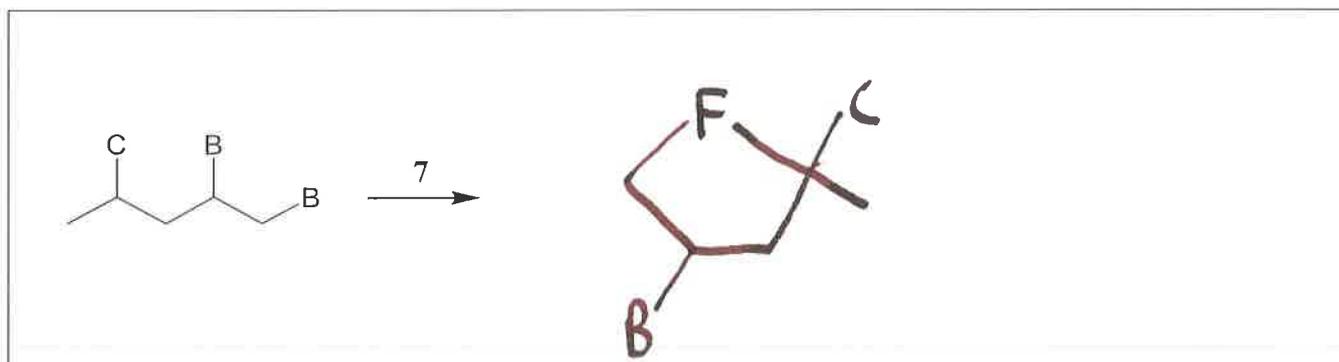
(ii) Draw the product of this series of reactions.



One complication to a reaction such as this is that *intramolecular* reactions can occur, i.e. a reaction between two functional groups on the same molecule, forming a ring. This will only occur if they form 5 or 6 membered rings. Shown below is an example of an intramolecular reaction that forms a 6 membered ring with reaction 7. The atoms labelled 1 to 6 in the compound on the left correspond to the atoms labelled 1 to 6 in the compound on the right.

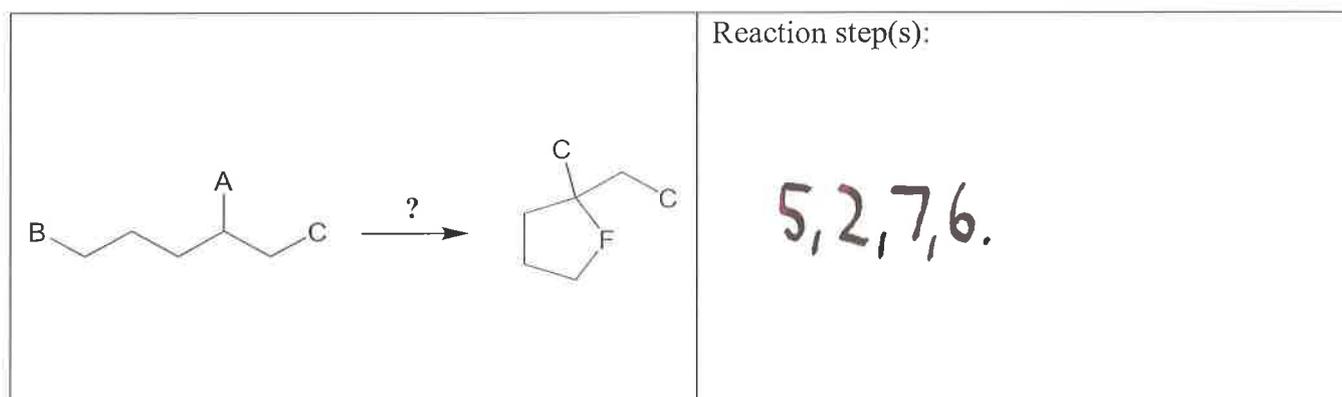


(iii) Draw the product of the following reaction:

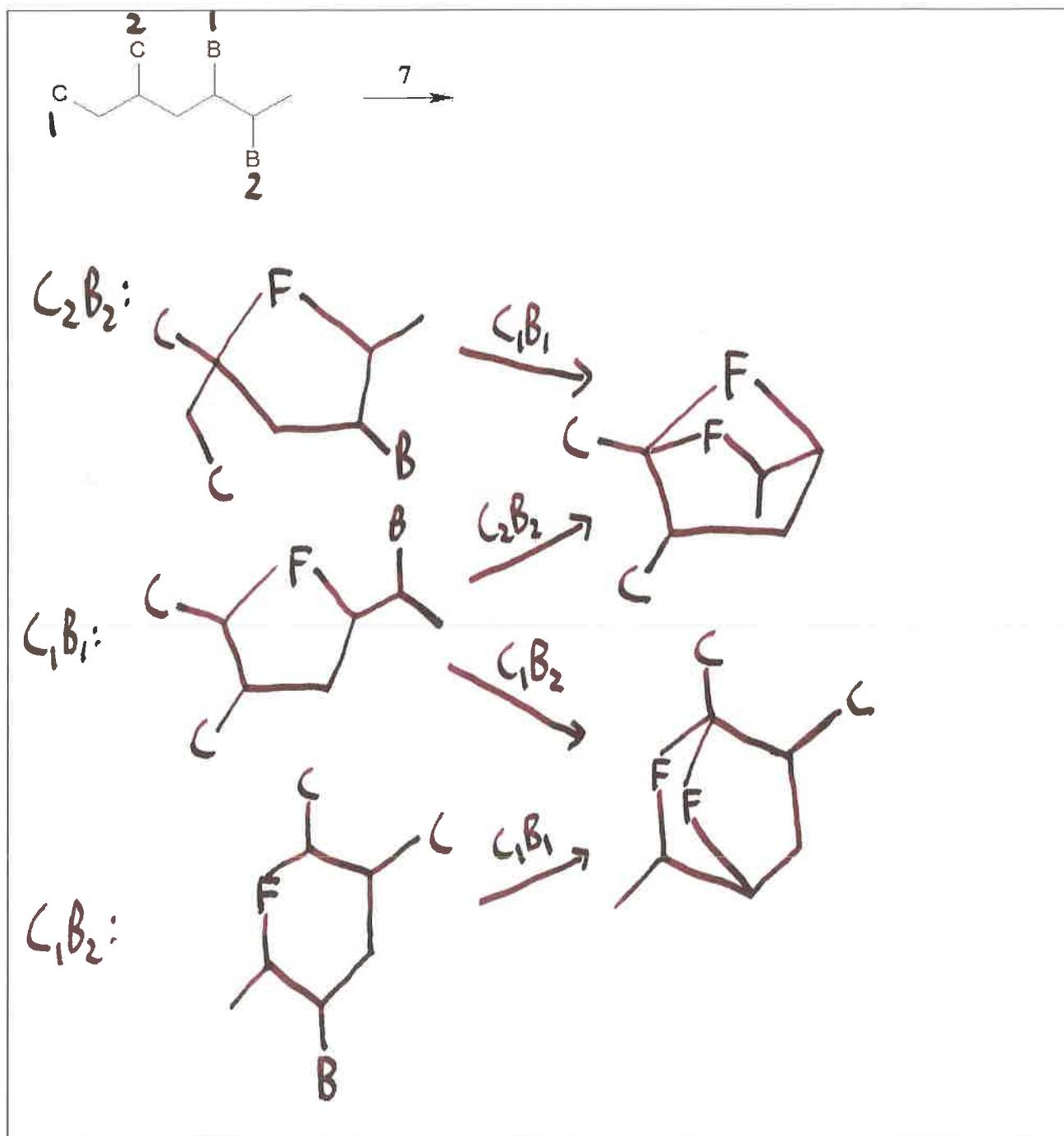


Reaction 1:	A → C B → C
Reaction 2:	A → C
Reaction 3:	A → D C → B
Reaction 4:	D → A
Reaction 5:	C → E
Reaction 6:	E → C

(iv) Suggest a series of reactions that would transform the reactant on the left **solely** into the product on the right.



(v) Draw all potential products of the following reaction:



### Question 18

An important property of metallic elements is their ability to bond to one or more molecules or ions to form *metal complexes*. Metal complexes may have an overall positive, negative or neutral charge depending on the charge on the metal and which molecules or ions are bound to it. Originally, many compounds now understood to contain metal complexes were thought of as “adducts” – compounds consisting of two chemically distinct species in a fixed ratio. For example,  $\text{CoCl}_3 \cdot 6\text{NH}_3$  was thought of as an adduct of  $\text{CoCl}_3$  and ammonia in a 1:6 ratio.

(a) What is the charge on the cobalt ion in  $\text{CoCl}_3$ ?

3+

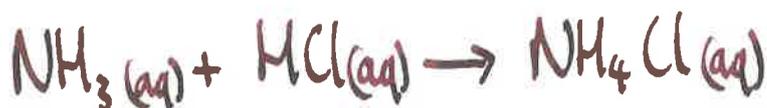
Despite appearing to consist of two pre-existing compounds in fixed ratios, these ‘adducts’ show different reactivity from their component parts. In the late 19th century, Sophus Mads Jørgensen investigated the reactivity of  $\text{CoCl}_3 \cdot 6\text{NH}_3$  with solutions of hydrochloric acid and silver nitrate.

(b) Write balanced chemical equations for the following reactions:

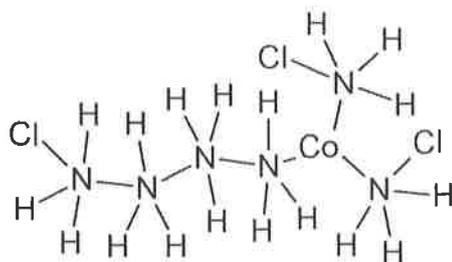
(i) Mixing aqueous solutions of  $\text{CoCl}_3$  and  $\text{AgNO}_3$  (a precipitate of  $\text{AgCl}$  is one of the products)



(ii) Mixing ammonia with hydrochloric acid.



It was discovered that one mole of  $\text{CoCl}_3 \cdot 6\text{NH}_3$  reacted with 3 moles of  $\text{AgNO}_3$ , however there was no reaction with hydrochloric acid. Jørgensen proposed that these observations suggested that the ammonia molecules were bonded in such a way as to be unreactive. He suggested the following structure, claiming that ammonia could form linear chains similar to  $-\text{CH}_2-$  units in hydrocarbon chains:



Jørgensen formulated this structure well before modern theories of valence and bonding like Lewis structures had been developed.

(iii) Draw a Lewis (or electron dot) structure for ammonia



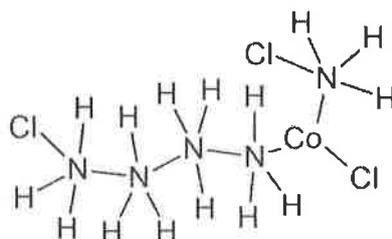
(iv) Suggest why the structure of  $\text{CoCl}_3 \cdot 6\text{NH}_3$  is unlikely to consist of these ammonia chains.

N usually forms 3 bonds with other atoms, or 4 if the lone pair is involved in dative (co-ordinate covalent) bonding. The N atoms in these chains would need to form 5 bonds, which would ordinarily be impossible due to the large energy involved.

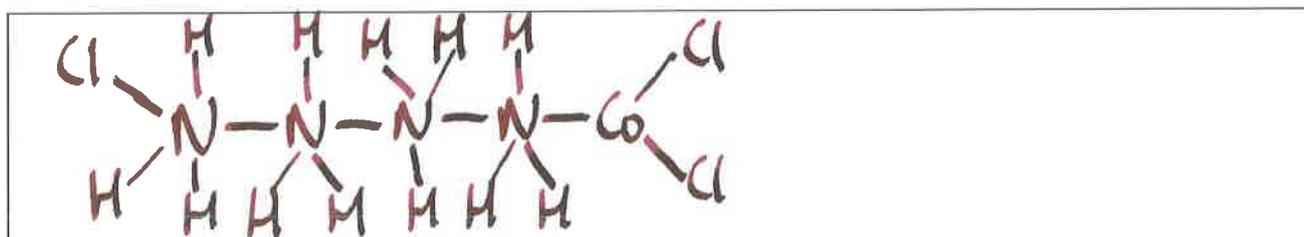
Nevertheless, Jørgensen's structure was consistent with the experimental evidence available at the time. Other adducts of the form  $\text{CoCl}_3 \cdot x\text{NH}_3$  were discovered, and their properties are summarised in the following table:

Composition	Colour	Amount of $\text{AgNO}_3$ (mol) required for complete reaction per mole of adduct
$\text{CoCl}_3 \cdot 6\text{NH}_3$	Orange	3
$\text{CoCl}_3 \cdot 5\text{NH}_3$	Pink	2
$\text{CoCl}_3 \cdot 4\text{NH}_3$	Green	1
$\text{CoCl}_3 \cdot 3\text{NH}_3$	Violet	0

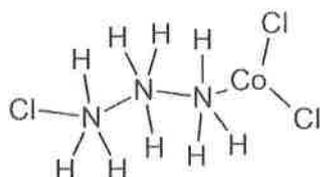
To explain the fact that one of the chlorine atoms in  $\text{CoCl}_3 \cdot 5\text{NH}_3$  did not react with silver nitrate, Jørgensen proposed the following structure, in which the "unreactive" or "masked" chlorine is bonded directly to the metal:



(c) Draw a structure for  $\text{CoCl}_3 \cdot 4\text{NH}_3$  that would, according to Jørgensen's theory, explain its observed reactivity with silver nitrate.



Unfortunately, Jørgensen's theory starts to break down when we consider  $\text{CoCl}_3 \cdot 3\text{NH}_3$ . Jørgensen proposed the following structure, in which the ammonia chain is shortened by one:



(d) Explain why Jørgensen's structure does not agree with the experimental results above.

There are two Cl atoms bound to Co and one bound to N. This should require 1 mol of  $\text{AgNO}_3$  per mol of adduct, rather than the observed 0 mol.

Alfred Werner conducted experiments with the same series of compounds, measuring their molar conductivities in solution (higher numbers mean greater conductivity per mole of compound dissolved). From this he reasoned that these compounds must dissociate into different numbers of ions in aqueous solution. Werner's data is shown in the table below:

Composition	Molar conductivity	Number of ions present per formula unit
$\text{CoCl}_3 \cdot 6\text{NH}_3$	431.6	4
$\text{CoCl}_3 \cdot 5\text{NH}_3$	296.4	3
$\text{CoCl}_3 \cdot 4\text{NH}_3$	98.35	2
$\text{CoCl}_3 \cdot 3\text{NH}_3$	?	?

(e) Explain the relationship between the conductivity of a solution and number of ions present.

Conductivity increases as the number of mobile charged particles increases, hence compounds that release more ions into solution will give higher conductivity.

(f) Notice that the data is missing for  $\text{CoCl}_3 \cdot 3\text{NH}_3$

(i) Predict the number of ions present in  $\text{CoCl}_3 \cdot 3\text{NH}_3$ .

0

(ii) Hence, predict the molar conductivity of  $\text{CoCl}_3 \cdot 3\text{NH}_3$ .

0

To rationalise both his conductivity data and Jørgensen's data, Werner proposed that 3 of the 4 ions in  $\text{CoCl}_3 \cdot 6\text{NH}_3$  correspond to  $\text{Cl}^-$  ions, which would therefore be able to react with silver nitrate. According to Werner's theory, the ammonia and the cobalt formed a single 'complex' ion:  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . Thus, it would be more appropriate to write the ionic formula for  $\text{CoCl}_3 \cdot 6\text{NH}_3$  as  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ .

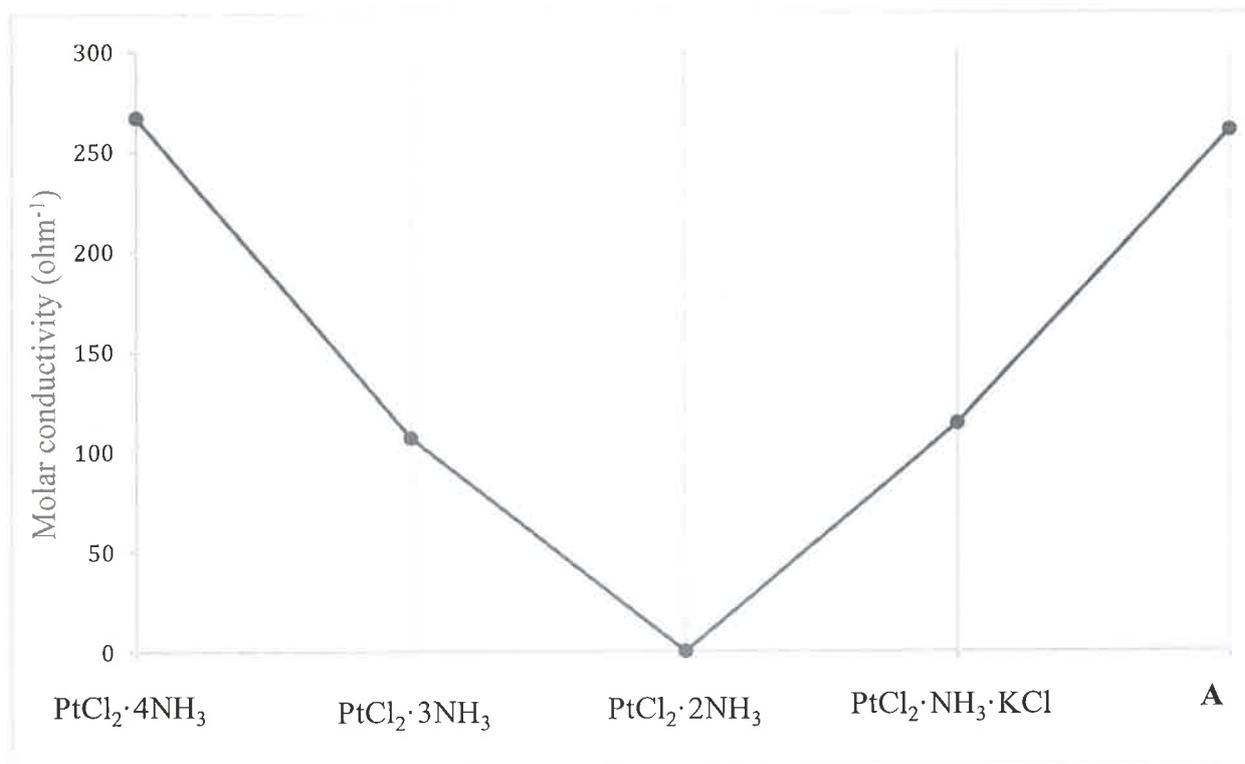
According to Werner's theory,  $\text{CoCl}_3 \cdot 5\text{NH}_3$  would consist of two  $\text{Cl}^-$  ions and the complex ion  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ . Werner suggested that this explained Jørgensen's observations, as only the two ionic chlorides could react with silver nitrate, while the chloride that is directly bonded to the cobalt would not react.

- (h) Write the formula of the complex ion in  $\text{CoCl}_3 \cdot 4\text{NH}_3$ . Does this formula agree with Jørgensen's silver nitrate observations and Werner's conductivity data? Explain your answer.

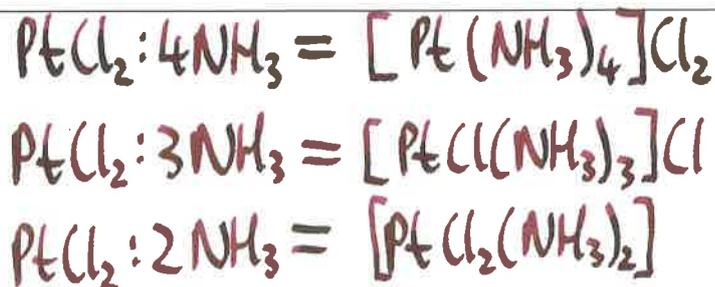
$[\text{CoCl}_2(\text{NH}_3)_4]^+\text{Cl}^-$ . This gives rise to two ions:  $[\text{CoCl}_2(\text{NH}_3)_4]^+$  and  $\text{Cl}^-$ , consistent with the conductivity data. The  $\text{Cl}^-$  ion produced will react with  $\text{AgNO}_3$  in a 1:1 mole ratio, in accordance with Jørgensen's observations.

Werner conducted further experiments with other adducts and found that he could use his model of metal complexes to explain their physical and chemical properties. The following table and graph summarise the conductivity and reactivity with  $\text{AgNO}_3$  of a series of adducts of the form  $\text{PtCl}_2 \cdot x\text{NH}_3$ . It is known that these compounds contain  $\text{Pt}^{2+}$ .

Composition	Amount of $\text{AgNO}_3$ (mol) required for complete reaction per mole of adduct
$\text{PtCl}_2 \cdot 4\text{NH}_3$	2
$\text{PtCl}_2 \cdot 3\text{NH}_3$	1
$\text{PtCl}_2 \cdot 2\text{NH}_3$	0
$\text{PtCl}_2 \cdot \text{NH}_3 \cdot \text{KCl}$	0
<b>A</b>	0



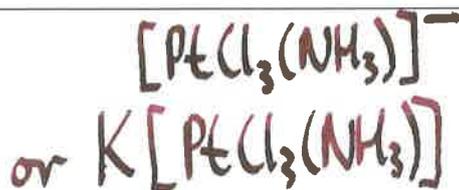
- (i) Use the data above to answer the following questions. You will need to use similar reasoning to that outlined in the earlier parts of the question.
- (i) Write formulae for  $\text{PtCl}_2 \cdot 4\text{NH}_3$ ,  $\text{PtCl}_2 \cdot 3\text{NH}_3$ , and  $\text{PtCl}_2 \cdot 2\text{NH}_3$  that reflect the fact that they contain complex ions.



- (ii) The concept of coordination number refers to the number of molecules or ions directly bonded to the metal centre. For example, the ion  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  has a coordination number of 6. What is the coordination number of this series of platinum complexes?

4

- (iii) Based on the trend in the first three compounds, and considering the experimental data predict the formula of the complex ion in  $\text{PtCl}_2 \cdot \text{NH}_3 \cdot \text{KCl}$ .



- (iv) Predict the formula for **A** given that it contains potassium, chlorine and a  $\text{Pt}^{2+}$  ion with the same coordination number as in part (ii), but contains no ammonia.



Boiling a solution of  $\text{PtCl}_2$  in ethanol followed by the addition of potassium chloride produces yellow crystals of a substance first isolated in the early 19th century. These yellow crystals react vigorously with both oxygen gas and hydrogen gas but not with silver nitrate. At the time of its discovery, elemental analysis was not possible for all elements but the following percentage composition by mass data was found: Pt 50.46%, Cl 27.51%, C 6.21%, O 4.14%, H 1.56%. Later studies showed that the  $\text{Pt}^{2+}$  ion also has the same coordination number as in part (ii).

(v) Predict the formula for these yellow crystals.

Pt	Cl	C	O	H
<u>50.46</u>	<u>27.51</u>	<u>6.21</u>	<u>4.14</u>	<u>1.56</u>
195.1	35.45	12.01	16.00	1.008
= 0.259	0.776	0.517	0.259	1.55
1	3	2	1	6

Mass missing :  $100 - (50.46 + 27.51 + 6.21 + 4.14 + 1.56) = 10.12$

Missing element = K

$n(\text{K}) = \frac{10.12}{39.10} = 0.259.$

$\therefore$  formula is  $\text{KPtCl}_3\text{C}_2\text{H}_6\text{O}.$

$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_5\text{OH})]$  explains the reaction with  $\text{O}_2$  but not  $\text{H}_2.$

$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$  explains the reaction with both  $\text{O}_2$  and  $\text{H}_2.$