

2023 AUSTRALIAN SCIENCE OLYMPIAD EXAM
CHEMISTRY

TO BE COMPLETED BY THE STUDENT. USE CAPITAL LETTERS.

Student Name:

Home Address:

..... **Post Code:**

Telephone: (.....) **Mobile:**

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

Male Female Unspecified **Year 10** **Year 11** **Other:**

Name of School: **State:**

Examiners Use Only:

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2023 AUSTRALIAN SCIENCE OLYMPIAD EXAM
CHEMISTRY

Time Allowed

Reading Time: 10 minutes
Examination Time: 120 minutes

INSTRUCTIONS

- *Attempt all questions in ALL sections of this paper.*
- Permitted materials: non-programmable, non-graphical calculator, pens, pencils, erasers and a ruler.
- Marks will not be deducted for incorrect answers.

MARKS

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

Integrity of Competition

If there is evidence of collusion or other academic dishonesty, students will be disqualified. Markers' decisions are final.

DATA

Avogadro constant (N) = $6.022 \times 10^{23} \text{ mol}^{-1}$	Velocity of light (c) = $2.998 \times 10^8 \text{ m s}^{-1}$
1 Faraday = 96 485 coulombs	Density of water at 25 °C = 0.9971 g cm^{-3}
1 A = 1 C s^{-1}	Acceleration due to gravity = 9.81 m s^{-2}
Universal gas constant (R) $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$	1 newton (N) = 1 kg m s^{-2}
Planck's constant (h) = $6.626 \times 10^{-34} \text{ J s}$	1 pascal (Pa) = 1 N m^{-2}
Molar volume of ideal gas <ul style="list-style-type: none"> at 0 °C and 100 kPa = 22.71 L at 25 °C and 100 kPa = 24.79 L at 0 °C and 101.3 kPa = 22.41 L at 25 °C and 101.3 kPa = 24.47 L 	$\text{pH} = -\log_{10}[\text{H}^+]$ $\text{pH} + \text{pOH} = 14.00 \text{ at } 25^\circ\text{C}$ $K_a = \{[\text{H}^+][\text{A}^-]\} / [\text{HA}]$ $\text{pH} = \text{p}K_a + \log_{10}\{[\text{A}^-] / [\text{HA}]\}$ $\text{PV} = n\text{RT}$ $E = h\nu$
Surface area of sphere $A = 4\pi r^2$	$c = \nu\lambda$

Periodic Table of Elements

	1																		18																			
	<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="text-align: center;">1 H 1.008</td> <td style="text-align: center;">2 He 4.003</td> </tr> </table>	1 H 1.008	2 He 4.003																																			
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57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

SECTION A: MULTIPLE CHOICE
USE THE ANSWER SHEET PROVIDED

1. Which of the following elements has the highest 7th ionisation energy?
- A. Mg
 - B. Cl
 - C. P
 - D. S**
 - E. Al
2. Which of the following molecules contain **more than** 3 lone pairs of valence electrons?
Select all that apply.
- A. H₂
 - B. CH₄
 - C. Cl₂O**
 - D. CO₂**
 - E. HCl
3. Which of the following compounds contains both ionic and covalent bonds?
- A. CO₂
 - B. NaCl
 - C. Na₂O
 - D. H₂CO
 - E. Na₂CO₃**

4. The density of water at 4°C is 1.00 g mL⁻¹. The density of ice at 0°C is 0.917 g mL⁻¹.

An ice cube of mass 7.92 g, initially at 0°C, melted to form liquid water with a final temperature of 4°C. What happens to the volume of the water?

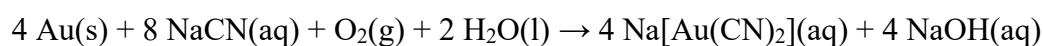
- A. The volume of water increases by 0.657 mL.
 - B. The volume of water decreases by 0.657 mL.
 - C. The volume of water increases by 0.717 mL.
 - D. The volume of water decreases by 0.717 mL.**
 - E. The volume of water does not change.
5. Which of the following lists elements in order of increasing first ionisation energy?
- A. Na, F, O, N
 - B. Na, N, O, F (half marks)**
 - C. Na, O, N, F**
 - D. N, O, F, Na
 - E. Na, O, F, N
6. 0.39 mol of magnesium chloride is dissolved in water to produce a solution with a volume of 1.5 L. What is the concentration, in mol L⁻¹, of chloride ions in this solution?
- A. 0.098 mol L⁻¹
 - B. 0.20 mol L⁻¹
 - C. 0.26 mol L⁻¹
 - D. 0.39 mol L⁻¹
 - E. 0.52 mol L⁻¹**

7. A substance does **not** conduct electricity well when solid but does when liquid.
Which of the following could this substance be? Select all that apply.
- A. neon
 - B. mercury
 - C. nitrogen monoxide
 - D. aluminium chloride**
 - E. calcium fluoride**
8. How many nitrogen atoms are there in 0.25 mol of ammonium nitrate?
- A. 1.5×10^{23}
 - B. 2.4×10^{23}
 - C. 3.0×10^{23}**
 - D. 6.0×10^{23}
 - E. 4.8×10^{24}
9. One mole of any gas, when measured at 310.0 K and 101.0 kPa, has a volume of 25.52 L.
Calculate the volume of 21.66 g of nitrogen gas under these conditions.
- A. 16.51 L
 - B. 19.73 L**
 - C. 25.52 L
 - D. 33.01 L
 - E. 39.45 L

10. Which of the following compounds contains 5.522% nitrogen by mass?

- A. NH_3
- B. NF_3
- C. NCl_3
- D. NBr_3**
- E. NI_3

11. Sodium cyanide (NaCN) is used in the extraction of gold from its ores, according to the following equation:



What volume (in L) of $0.0100 \text{ mol L}^{-1}$ sodium cyanide solution is required for complete reaction with 11.8 g of gold?

- A. 0.749 L
- B. 1.50 L
- C. 2.99 L
- D. 5.99 L
- E. 11.98 L**

12. Which of the following formulas is an empirical formula?

- A. C_2H_6
- B. C_3H_6O**
- C. $H_2C_2O_4$
- D. $C_3H_6O_2$
- E. $C_6H_{12}O_6$

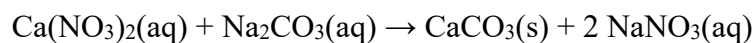
13. An element, Z, has 5 valence electrons. Which of the following species is likely to be the most stable?

- A. Z_3O
- B. ZH_3**
- C. Z^{3+}
- D. Z^{5+}
- E. Mg_2Z

14. Which of the following are molecules with tetrahedral electron pair geometry around the central atom? Select all that apply.

- A. CS_2
- B. BF_3
- C. NCl_3**
- D. H_2S**
- E. CH_4**

15. Solutions of calcium nitrate and sodium carbonate react to form a precipitate of calcium carbonate, as shown in the following equation:



Calculate the concentration of carbonate ions in the resulting solution when 75.0 mL of 1.065 mol L⁻¹ calcium nitrate solution is mixed with 125.0 mL of 1.445 mol L⁻¹ sodium carbonate solution, assuming that there is no change in volume.

- A. 0.190 mol L⁻¹
- B. 0.380 mol L⁻¹
- C. 0.504 mol L⁻¹**
- D. 0.723 mol L⁻¹
- E. 1.445 mol L⁻¹

Question 16

This question concerns analysis of substances for potassium ion content.

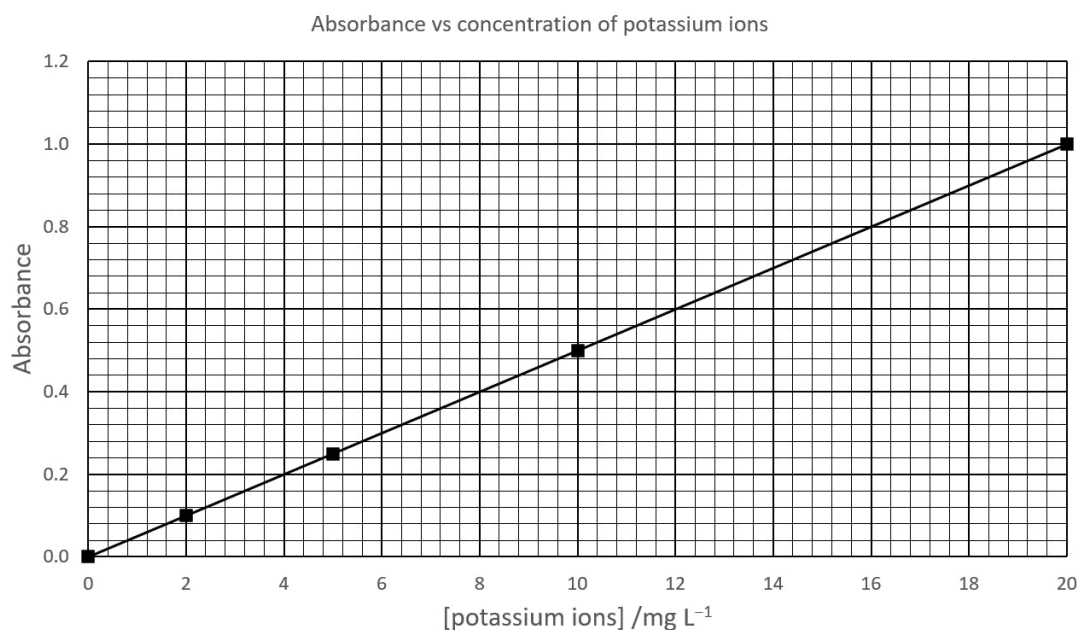
- (a) Calculate the molar mass of potassium chloride (in g mol^{-1}).

74.55 g mol^{-1} (1 mark)

- (b) Calculate the mass of potassium (in mg) present in 5.10 mg of potassium chloride. Give your answer to two decimal places.

$m(\text{K}) = 5.10 \text{ mg} \times 39.10 / 74.55 = 2.67 \text{ mg}$ (1 mark)

Atomic absorption spectroscopy can be used to determine the concentration of potassium ions in an unknown solution. A so-called "standard curve" is recorded by measuring the absorbance of a series of solutions containing known concentrations of potassium ions. This can be plotted on a graph, as shown.



- (c) Estimate the potassium ion concentration (in mg L^{-1}) of a solution with an absorbance of 0.68. Give your answer to 1 decimal place.

13.6 mg L^{-1} (1 mark)

(d) Estimate the absorbance of a solution with a potassium ion concentration of 15.4 mg L^{-1} .

0.77 (1 mark)

(e) Estimate the absorbance of a solution made by dissolving 4.5 mg of KCl in water and adjusting the solution volume to 0.500 L.

$$m(\text{K}) = 4.5 \text{ mg} \times 39.10 / 74.55 = 2.4 \text{ mg (1 mark)}$$

$$[\text{K}] = 2.4 \text{ mg} / 0.500 \text{ L} = 4.8 \text{ mg L}^{-1} \text{ (1 mark)}$$

$$A = 0.24 \text{ (1 mark)}$$

The tetraphenylborate ion, $\text{B}(\text{C}_6\text{H}_5)_4^-$, can be used to precipitate potassium ions from solution. Sodium tetraphenylborate ($\text{NaB}(\text{C}_6\text{H}_5)_4$), the compound usually employed for this purpose, can be prepared by the reaction of sodium tetrafluoroborate (NaBF_4) and phenylmagnesium bromide ($\text{C}_6\text{H}_5\text{MgBr}$), as shown below:



(f) Calculate the amount (in mol) of phenylmagnesium bromide ($\text{C}_6\text{H}_5\text{MgBr}$) required to produce 12.73 g of sodium tetraphenylborate (molar mass 342.2 g mol^{-1}).

$$n(\text{NaB}(\text{C}_6\text{H}_5)_4) = 12.73 \text{ g} / 342.2 \text{ g mol}^{-1} = 0.03720 \text{ mol (1 mark)}$$

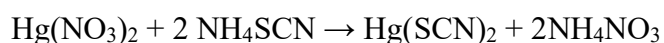
$$n(\text{C}_6\text{H}_5\text{MgBr}) = 4 \times n(\text{NaB}(\text{C}_6\text{H}_5)_4) = 0.1488 \text{ mol (1 mark)}$$

- (g) Calculate the mass of phenylmagnesium bromide ($\text{C}_6\text{H}_5\text{MgBr}$) required to produce 12.73 g of sodium tetraphenylborate (molar mass 342.2 g mol^{-1}).

$$\text{MM}(\text{C}_6\text{H}_5\text{MgBr}) = 12.01 \times 6 + 1.008 \times 5 + 24.31 + 79.90 = 181.31 \text{ g mol}^{-1} \text{ (1 mark)}$$

$$m(\text{C}_6\text{H}_5\text{MgBr}) = 0.1488 \text{ mol} \times 181.31 \text{ g mol}^{-1} = 26.98 \text{ g (1 mark)}$$

Analysis for potassium using tetraphenylborate is accomplished using an indirect method. Firstly, the concentration of a solution of mercury(II) nitrate is determined by reaction with an ammonium thiocyanate (NH_4SCN) solution of known concentration, as shown:



17.53 mL of $0.1511 \text{ mol L}^{-1}$ NH_4SCN are required for complete reaction with 25.00 mL of a $\text{Hg}(\text{NO}_3)_2$ solution.

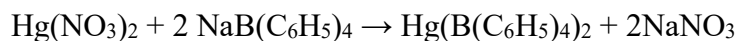
- (h) Calculate the concentration of the $\text{Hg}(\text{NO}_3)_2$ solution, in mol L^{-1} .

$$n(\text{NH}_4\text{SCN}) = 17.53 \text{ mL} \times 0.1511 \text{ mol L}^{-1} = 2.649 \text{ mmol (1 mark)}$$

$$n(\text{Hg}(\text{NO}_3)_2) = 2.649 \text{ mmol} / 2 = 1.324 \text{ mmol (1 mark)}$$

$$[\text{Hg}(\text{NO}_3)_2] = 1.324 \text{ mmol} / 25.00 \text{ mL} = 0.05298 \text{ mol L}^{-1} \text{ (1 mark)}$$

Once the concentration of the mercury(II) nitrate solution is known, it should be straightforward to calculate the concentration of a sodium tetraphenylborate solution, using the following reaction.



Unfortunately, this reaction is slightly non-stoichiometric, meaning that under constant conditions the two reactants combine in a consistent but non-integer mole ratio, rather than the expected 1:2 mole ratio.

20.00 mL of the mercury(II) nitrate solution from the previous question requires 17.97 mL of a sodium tetraphenylborate solution for complete reaction.

- (i) Calculate the volume of $\text{Hg}(\text{NO}_3)_2$ that reacts with 1 mL of $\text{NaB}(\text{C}_6\text{H}_5)_4$ under these conditions.

$$V(\text{Hg}(\text{NO}_3)_2) = 20.00 \text{ mL} / 17.97 \text{ mL} \times 1 \text{ mL} = 1.113 \text{ mL (1 mark)}$$

- (j) If the concentration of the $\text{NaB}(\text{C}_6\text{H}_5)_4$ solution is actually $0.1221 \text{ mol L}^{-1}$, calculate the chemical amount (in mol or mmol) of $\text{NaB}(\text{C}_6\text{H}_5)_4$ added.

$$n(\text{NaB}(\text{C}_6\text{H}_5)_4) = 0.1221 \text{ mol L}^{-1} \times 17.97 \text{ mL} = 2.194 \text{ mmol (1 mark)}$$

- (k) Calculate the amount (in mol) of $\text{NaB}(\text{C}_6\text{H}_5)_4$ that reacts with 1 mol of $\text{Hg}(\text{NO}_3)_2$ under these conditions.

$$n(\text{Hg}(\text{NO}_3)_2) = 20 \text{ mL} \times 0.052976 \text{ mmol mL}^{-1} = 1.060 \text{ mmol (1 mark)}$$

$$n(\text{NaB}(\text{C}_6\text{H}_5)_4) = 2.194 \text{ mmol} / 1.060 \text{ mmol} \times 1 \text{ mol} = 2.071 \text{ mol (2 marks)}$$

5.6311 g of a potassium salt is dissolved in water and the solution made up to 100.0 mL.

A 20.00 mL sample of this solution is taken and 50.00 mL of the same $0.1221 \text{ mol L}^{-1}$ $\text{NaB}(\text{C}_6\text{H}_5)_4$ as above is added. $\text{KB}(\text{C}_6\text{H}_5)_4$ precipitates and is filtered off, then the excess $\text{B}(\text{C}_6\text{H}_5)_4^-$ is titrated with the same $\text{Hg}(\text{NO}_3)_2$ solution as above, this time requiring 18.35 mL for complete reaction.

The equations for the two reactions are as follows:

- $\text{K}^+ + \text{NaB}(\text{C}_6\text{H}_5)_4 \rightarrow \text{KB}(\text{C}_6\text{H}_5)_4(\text{s}) + \text{Na}^+$
- $\text{Hg}(\text{NO}_3)_2 + 2 \text{NaB}(\text{C}_6\text{H}_5)_4 \rightarrow \text{Hg}(\text{B}(\text{C}_6\text{H}_5)_4)_2 + 2\text{NaNO}_3$ (but recall the non-stoichiometry of this reaction; the two reactants react in the ratio calculated above)

(l) Calculate the chemical amount (in mol or mmol) of $\text{Hg}(\text{NO}_3)_2$ added.

$$n(\text{Hg}(\text{NO}_3)_2) = 18.35 \text{ mL} \times 0.052976 \text{ mmol mL}^{-1} = 0.9721 \text{ mmol (1 mark)}$$

(m) Calculate the chemical amount (in mol or mmol) of $\text{KB}(\text{C}_6\text{H}_5)_4$ precipitated.

$$n(\text{NaB}(\text{C}_6\text{H}_5)_4, \text{ total}) = 0.1221 \times 50 = 6.105 \text{ mmol}$$

$$n(\text{NaB}(\text{C}_6\text{H}_5)_4, \text{ excess}) = 0.9721 \text{ mmol} \times 2.071 = 2.014 \text{ mmol (1 mark)}$$

$$n(\text{NaB}(\text{C}_6\text{H}_5)_4, \text{ reacting}) = 6.105 \text{ mmol} - 2.014 \text{ mmol} = 4.091 \text{ mmol (1 mark)}$$

(n) Calculate the chemical amount (in mol or mmol) of potassium in the original 5.6311 g of potassium salt.

$$n(\text{K}) = 100.0 \text{ mL} / 20.00 \text{ mL} \times 4.091 = 20.46 \text{ mmol (1 mark)}$$

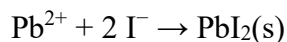
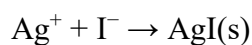
- (o) Calculate the molar mass of the original potassium salt, assuming that 1 mol of the salt contains 1 mol of potassium ions.

$$\text{MM} = 5.6311 \text{ g} / 0.02046 \text{ mol} = 275.3 \text{ g mol}^{-1} \text{ (1 mark)}$$

- (p) Calculate the percentage by mass of potassium in the original potassium salt.

$$\%(\text{K}) = 0.02046 \text{ mol} \times 39.1 \text{ g mol}^{-1} / 5.6311 \text{ g} = 14.20\% \text{ (1 mark)}$$

Aqueous mixtures containing both silver and lead ions can be analysed by adding potassium iodide until both silver iodide (molar mass 234.8 g mol^{-1}) and lead iodide (molar mass 461.0 g mol^{-1}) have precipitated completely from solution, according to the following equations:



The concentration of the potassium iodide solution can be determined by analysing it for potassium content, as previously described.

An aqueous mixture containing both silver and lead ions reacts completely with 15.01 mL of $0.2101 \text{ mol L}^{-1}$ potassium iodide solution. The total mass of precipitate produced is 0.7328 g .

(q) Calculate the amount (in mol or mmol) of potassium iodide added.

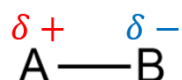
$$n(\text{KI}) = 15.01 \text{ mL} \times 0.2101 \text{ mol L}^{-1} = 3.154 \text{ mmol (1 mark)}$$

(r) Calculate the mass (in g) of lead(II) iodide produced.

$$0.4109 \text{ g (1 mark)}$$

Question 17

Molecules with polar bonds are drawn with the following notation:



where δ^+ and δ^- denote the partial positive and negative charges on the atoms respectively. Molecules with an asymmetric charge distribution are said to be polar, and have a net dipole moment.

(a) Identify the following statements are true or false. **(1 mark each)**

HF has a net dipole moment.	<input checked="" type="checkbox"/> True	<input type="checkbox"/> False
N ₂ has a net dipole moment.	<input type="checkbox"/> True	<input checked="" type="checkbox"/> False

Ionisation energy and electron affinity can be used to calculate the magnitude of partial charges. **(1 mark each)**

(b) Select the two statements from the list below that correspond to the best definitions for ionisation energy and electron affinity.

- the mean distance from the centre of the nucleus to the outermost electron
- the amount of energy released when an electron attaches to a neutral atom in the gaseous state
- the tendency for an atom to attract shared electrons when forming a chemical bond
- the minimum energy required to remove the most loosely bound electron of an isolated gaseous atom
- a measure of how readily a substance undergoes a chemical reaction
- the tendency of matter to acquire an electric dipole moment

To calculate the dipole moment of diatomic molecules, the magnitude of the partial charges need to be known. One way to approximate the partial charge starts with calculating Mulliken parameters, denoted a and b .

$$a_x = \frac{IE + EA}{2}$$

$$b_x = IE - EA$$

Where:

a_x is the "inherent electronegativity" of atom X

b_x is the "charge coefficient" of atom X

IE is the ionisation energy in electron volts (eV)

EA is the electron affinity in electron volts (eV)

In a bond between two atoms X and Y , a quantity known as the **equalised electronegativity**, a_{eq} , can be calculated according to the following equation:

$$a_{eq} = \frac{\frac{a_X}{b_X} + \frac{a_Y}{b_Y}}{\frac{1}{b_X} + \frac{1}{b_Y}}$$

A table of IE and EA values for carbon and oxygen is found below.

Element	IE (eV)	EA (eV)
C	11.26	1.26
O	13.62	1.46

- (c) For carbon monoxide (CO), calculate a and b for each atom, and calculate a_{eq} . **Give your answers to two decimal places.**

	a	b
Carbon	6.26	10.00
Oxygen	7.54	12.16

(1 mark each)

a_{eq} : 6.84 (2 marks)

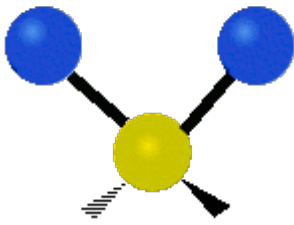
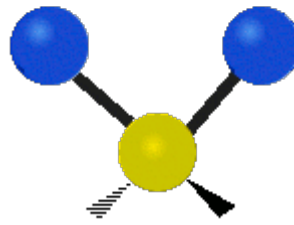
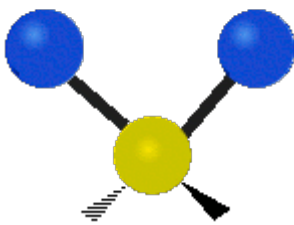
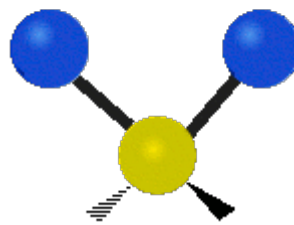
The partial charge on atom X can be calculated using the following formula:

$$\delta_X = \frac{a_{eq} - a_X}{b_X}$$

- (d) Calculate the magnitude of the partial positive charge δ^+ in CO. **Give your answer to five decimal places.**

$\delta^+ = 0.05776$ (1 mark)

Covalent bonds in molecules are able to move in periodic motions known as vibrational modes. Some of these vibration modes can be induced by absorbance of infrared (IR) light. The molecules that can absorb IR light are those that possess vibrational modes that cause a **change** to their dipole moment. These molecules can be classified as IR-active.

	
Symmetric stretching	Asymmetric stretching
	
Scissoring (in-plane bending)	Twisting (out-of-plane bending)

- (e) Classify the following molecules by circling the correct answer: **(0.5 mark each)**

	HF	N ₂	Ar	CO	CO ₂	CH ₄
Net dipole:	no response required	no response required	no response required	no response required	Yes / No	Yes / No
IR-active:	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No

Objects release energy through a process called blackbody radiation. A continuous spectrum of light is produced, but the wavelength of the peak intensity can be predicted using Wein's law:

$$\lambda = \frac{b}{T}$$

Where:

λ is the peak wavelength in metres (m)

b is a constant with a value of 2.90×10^{-3} m.K

T is the temperature in Kelvin (K)

The surface temperature of the Earth is 13.0 °C while the surface temperature of the Sun is 5500 to 5700 °C.

- (f) Calculate the wavelength (in μm) corresponding to the peak radiation emitted by the Earth. Give your answer to 1 decimal place.

n.b. 1 micron = $1 \mu\text{m} = 10^{-6}$ m.

$$T = 286 \text{ K}$$

$$\lambda = 2.90 \times 10^{-3} / 286 = 1.01 \times 10^{-5} \text{ m} = 10.1 \mu\text{m} \text{ (1 mark)}$$

- (g) Calculate the wavelength (in μm) corresponding to the peak radiation emitted by the sun, with surface temperature 5964 °C. Give your answer to 1 decimal place.

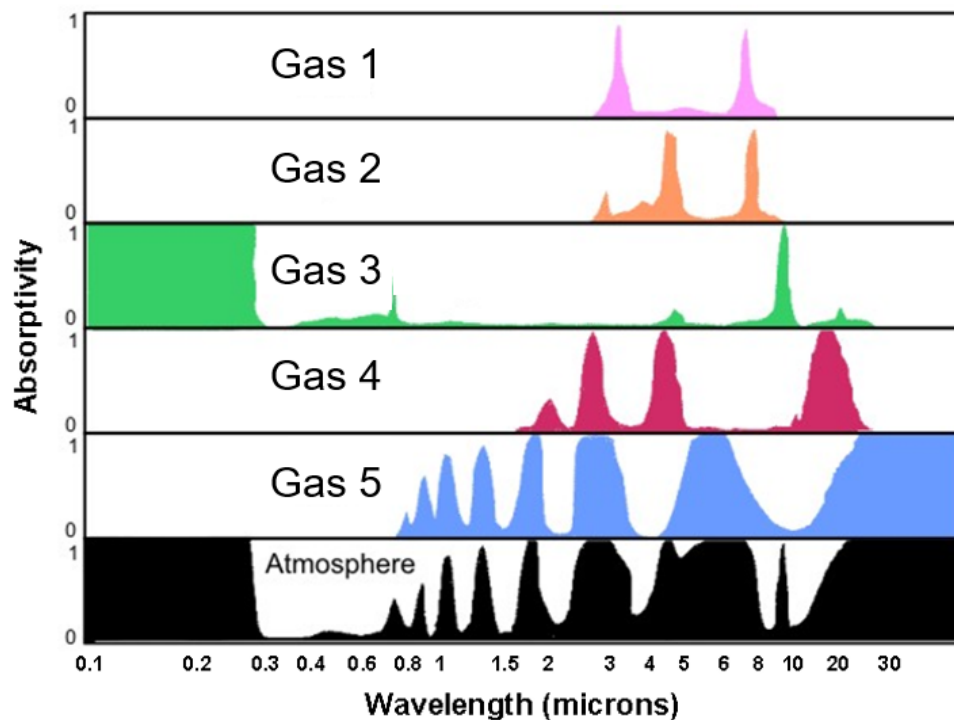
$$T = 6237 \text{ K}$$

$$\lambda = 2.90 \times 10^{-3} / 6237 = 4.6 \times 10^{-7} \text{ m} = 0.5 \mu\text{m} \text{ (1 mark)}$$

Absorption of the radiation emitted by the Earth by certain molecules in the atmosphere contributes to a phenomenon known as the greenhouse gas effect.

Additionally, ozone (O_3) can shield some of the radiation from the Sun from reaching the Earth.

The absorption spectra of some atmospheric gases have been provided:



(h) Select any gases that are likely to be a greenhouse gas. You may select more than one response. **(0.67 marks each)**

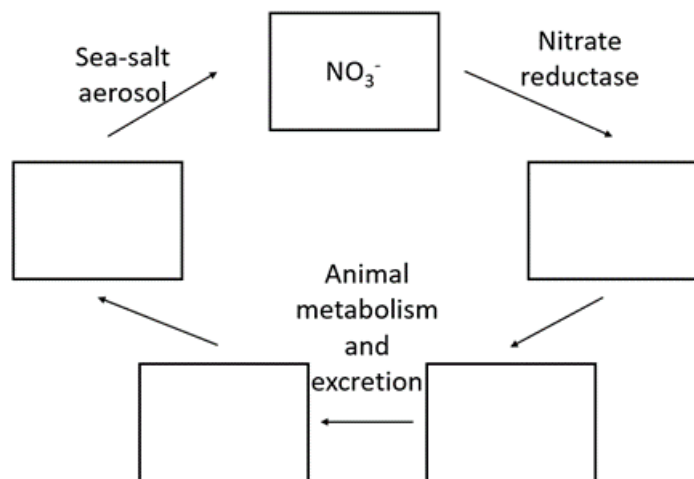
- Gas 1
- Gas 2
- Gas 3
- Gas 4
- Gas 5

(i) Select any gases that are likely to provide a protective effect from the sun's radiation. You may select more than one response. **(1 mark)**

- Gas 1
- Gas 2
- Gas 3
- Gas 4
- Gas 5

Below is a description and visual representation of the nitrogen cycle.

The product of reactions between sea salt and nitrogen oxides is deposited on dry land where it enters the soil. After uptake by plants, enzymatic reduction produces key molecules that are subsequently used in the biosynthesis of organic nitrogen compounds. A natural source of nitrogen oxides involves biological decay of animal waste by soil bacteria.



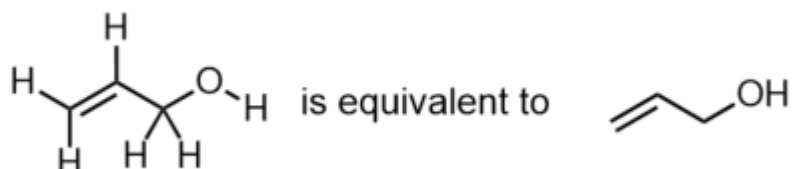
(m) Complete the following description of the nitrogen cycle by circling the correct answer to fill in the gaps. (0.5 marks each)

- NO_3^- is converted by nitrate reductase to
 - NO_2^- / amino acids / H_2NCONH_2 (urea) / NO_2 ,
- which is then converted by
 - plant biosynthesis / soil bacteria
- to give
 - NO_2^- / amino acids / H_2NCONH_2 (urea) / NO_2
- This is followed by animal metabolism and excretion to give
 - NO_2^- / amino acids / H_2NCONH_2 (urea) / NO_2 .
- Finally, this is converted to
 - NO_2^- / amino acids / H_2NCONH_2 (urea) / NO_2
- by plant biosynthesis / soil bacteria,
- before atmospheric sea-salt completes the cycle by producing NO_3^- .

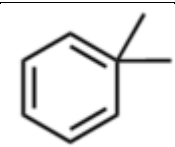
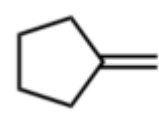
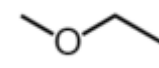
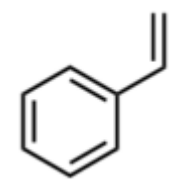
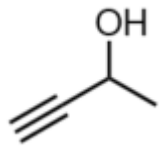
Question 18

To understand biology requires an understanding of organic chemistry. This question will examine some aspects of organic chemistry that underpins biological processes. 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.

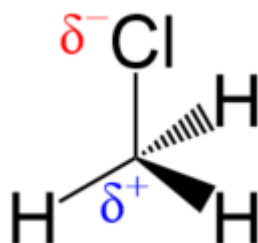
For example:



- (a) Which of the following structures is not a proper representation of skeletal structure. You may select more than one response. **(2 marks)**

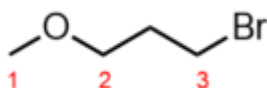
(i)	
(ii)	
(iii)	
(iv)	
(v)	

As discussed in question 17, in a molecule where two atoms with different electronegativity are covalently bonded together they form a dipole. This means that the more electronegative atom becomes partially negative, represented by δ^- , while the more electropositive atom becomes partially positive, represented by δ^+ . This is illustrated in the molecule below.



The trend for electronegativity of different elements is represented by the periodic table with electronegativity increasing to the right and to the top of the periodic table. Fluorine (F) is therefore the most electronegative atom.

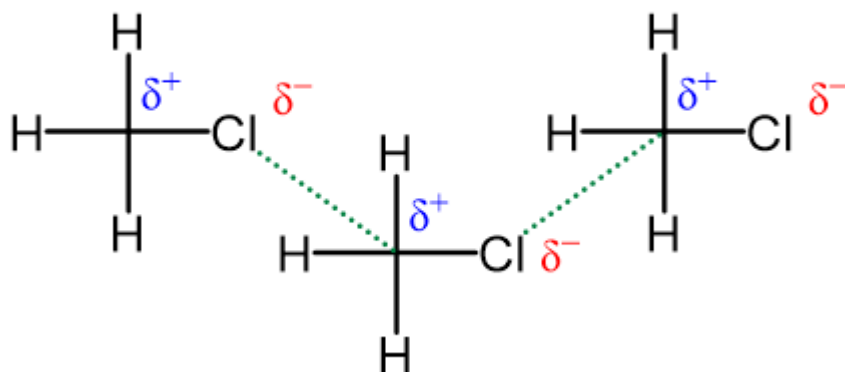
- (b) Select the correct partial charge on the following atoms in the molecule below: **(0.4 marks each)**



- carbon atom 1 would be: δ^+ / δ^- / **without partial charge**
- carbon atom 2 would be: δ^+ / δ^- / **without partial charge**
- carbon atom 3 would be: δ^+ / δ^- / **without partial charge**
- the oxygen atom would be: δ^+ / δ^- / **without partial charge**
- the bromine atom would be: δ^+ / δ^- / **without partial charge**

As well as the covalent bonds that make up individual molecules, other forces play a significant role in organic chemistry, and therefore biology. These forces exist between molecules and are weaker than covalent bonds.

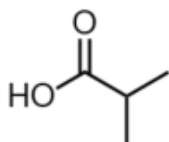
Some of the stronger forces form when a molecule possesses a dipole and the positive and negative parts of two separate molecules can interact. This is illustrated below with the non-covalent force shown in green.



The premise of dipoles is the underlying principle of many different types of forces of varying strength. These are listed below from strongest to weakest.

1. Ion-dipole – where a δ^+ atom interacts with a formal negative charge or a δ^- atom interacts with a formal positive charge.
2. Hydrogen bonding – where a hydrogen atom attached to a strongly electronegative atom such as F, O or N becomes strongly δ^+ and then interacts with a δ^- atom or lone pair.
3. Dipole-dipole – as illustrated above where a δ^+ atom interacts with a δ^- atom. This is also the term we use when a δ^+ atom interacts with a lone pair.
4. Dispersion forces – occur when no dipole exists within a molecule but close proximity between molecules causes a temporary dipole to form.

- (c) For the molecule below, which would be the strongest non-covalent force that would exist for this compound? **(1 mark)**



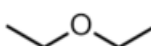
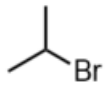

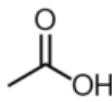
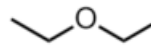
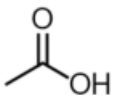
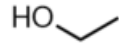
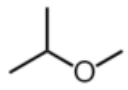


- (i) hydrogen bonding
- (ii) dipole-dipole
- (iii) dispersion forces
- (iv) ion-dipole
- (v) only covalent interactions are present
- (d) For the molecule below, which would be the strongest non-covalent force that would exist for this compound? **(1 mark)**



- (i) hydrogen bonding
- (ii) dipole-dipole
- (iii) dispersion forces
- (iv) ion-dipole
- (v) only covalent interactions are present

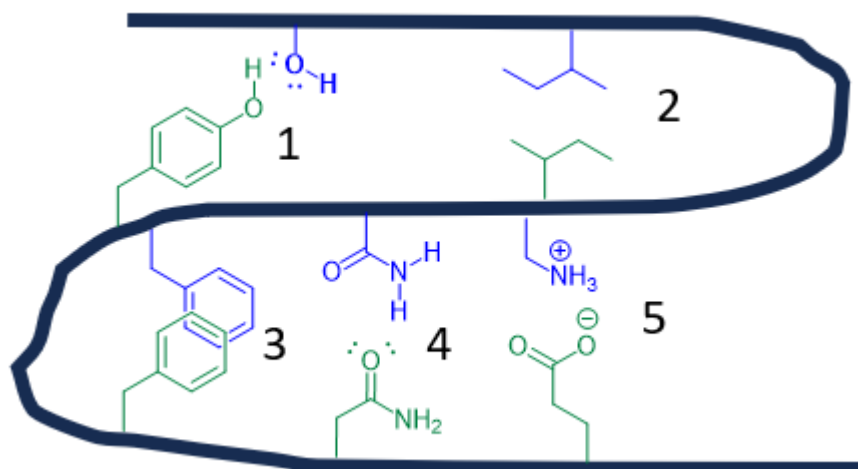
Non-covalent forces also occur between different types of molecules and can be used to explain solubility or insolubility of one substance in another. Different molecules with similar non-covalent forces are more likely to be able to mix.

Which of the following pairs of compounds would you expect to mix? You may select more than one answer. **(0.67 marks each)**

(i)	 and 
(ii)	 and 
(iii)	 and 
(iv)	 and 
(v)	 and 

When a molecule becomes big enough, such as in proteins, these same forces exist between different dipoles within the **same** molecule.

A protein is represented below with the covalent bonding backbone shown in black. Key forces between different parts of the molecule are shown in blue and green.


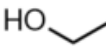


For the sentences below, pick the relevant interaction and location, represented by letters **A** to **F**. Write your answers in the answer box below.

For **A**, **C** and **E**, pick from the following:
dispersion forces, hydrogen bonding, ion-dipole interactions, dipole-dipole interactions

For **B** and **D**, pick from the following:
1 and 2, 1 and 3, 1 and 4, 1 and 5, 2 and 3, 2 and 4, 2 and 5, 3 and 4, 3 and 5, 4 and 5.

For **F**, pick from 1, 2, 3, 4 or 5.

- (e) If  was introduced to this protein, you would expect it to disrupt the **A** in the protein between the residues in environments **B**.
- (f) If  was introduced to this protein, you would expect it to disrupt the **C** in the protein between the residues in environments **D**.
- (g) If acid (H^+) was introduced to this protein, you would expect it to disrupt the **E** in the protein between the residues in environment **F**.

A: dispersion forces (0.5 marks)

B: 2 and 3 (1 mark)

C: hydrogen bonding (0.5 marks)

D: 1 and 4 (1 mark)

E: ion-dipole interactions (1 mark)

F: 5 (1 mark)

One critical function of proteins is to catalyse chemical reactions, these are given the name enzymes. An enzyme is considered a catalyst. This means it is not changed over the course of a reaction but lowers the activation energy of the process so it can more easily occur and occur faster. The simple enzymatic process can be represented by the following equation:



E = Enzyme, S = Substrate, ES = enzyme-substrate complex, P = Product

k_1 and k_{-1} are the forward and reverse rate constants for the formation of the enzyme-substrate (ES) complex. Rate constants are a measure of how quickly a reaction will proceed.

k_2 is the rate constant for the reaction of substrates into product and assumes this reaction is not reversible.

The ability for the ES complex to form depends largely on the intermolecular forces that exist between the substrate and the enzyme.

(h) If the intermolecular forces between enzyme and substrate are stronger will the value of k_1 to be larger or smaller than k_{-1} ?

Larger (1 mark)

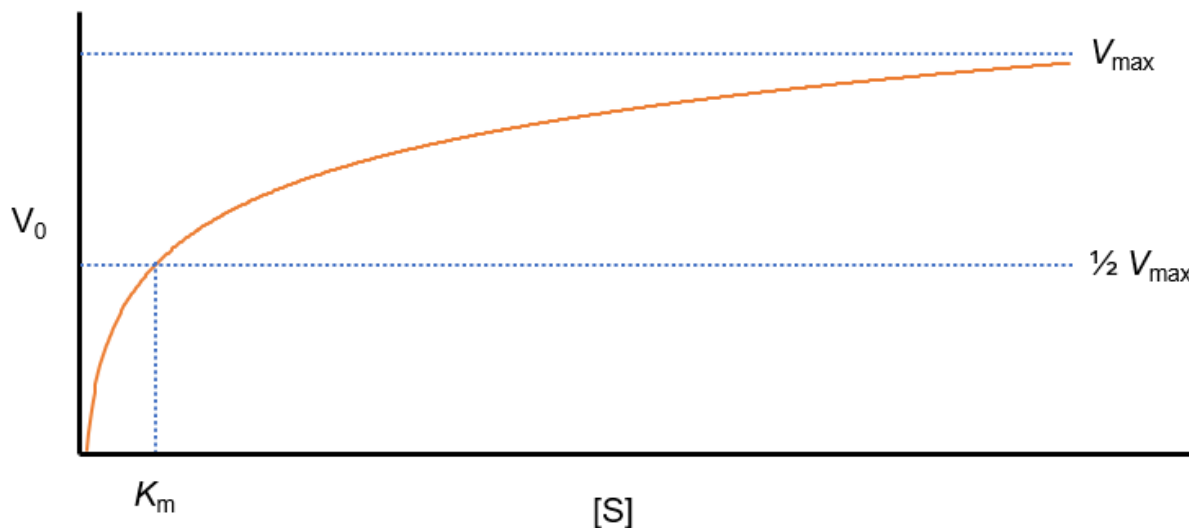
The overall reaction rate factoring in all values of k is represented by K_m . which is calculated by the following equation:

$$K_m = \frac{k_2 + k_{-1}}{k_1}$$

(i) If $k_2 = 0.003783 \text{ mM s}^{-1}$, $k_{-1} = 0.0006984 \text{ mM s}^{-1}$ and $k_1 = 0.0002556 \text{ mM s}^{-1}$, what is the value of K_m ?

$K_m = (0.003783 + 0.0006984) / 0.0002556 = 17.53 \text{ mM}$ (1 mark)

How quickly an enzyme catalysed reaction occurs will depend on the substrate concentration (denoted as [S]), so that the reaction rate (V_0) will increase as [S] increases. However, as there is normally much more substrate than enzyme, as [S] gets higher, the enzyme becomes saturated and no additional ES complex can form and the rate of reaction will reach its maximum, denoted as V_{\max} . This is represented in the following graph. Note that K_m can also be determined from this graph as the reaction rate measured at $\frac{1}{2} V_{\max}$.



This relationship can be represented by the Michaelis-Menten equation:

$$V_0 = \frac{V_{\max}[S]}{K_m + [S]}$$

An enzyme catalysed reaction with an initial substrate concentration of 0.022 mmol/L, had the initial velocity (V_0) measured as 0.0011 mmol/L.min, but when the substrate concentration was increased the velocity was shown to max out at 0.0046 mmol/L.min.

(j) Calculate the K_m value (in mmol L⁻¹) for this enzyme and substrate.

$$K_m = V_{\max}[S]/V_0 - [S] = (0.0046 \times 0.022 / 0.0011) - 0.022 = 0.070 \text{ mmol L}^{-1} \text{ (3 marks)}$$

Note that enzyme kinetics are dependent on both the particular enzyme and substrate and values will change accordingly.

The same enzyme used in the question above was then exposed to a different substrate of concentration 0.028 mmol/L and the initial velocity measured as 1.468 mmol/L.min and the K_m shown to be 0.062 mmol/L.

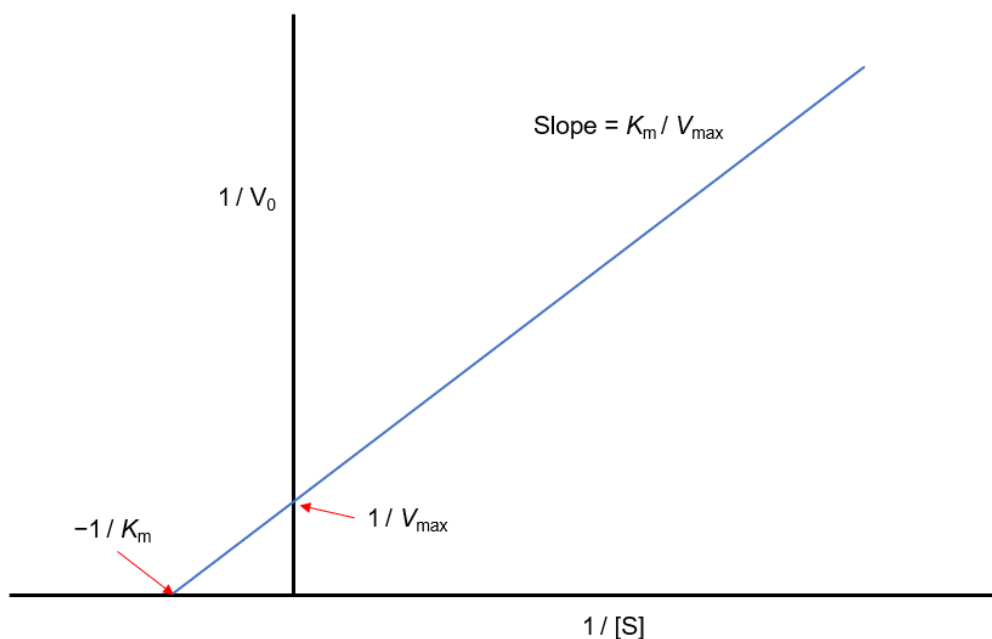
(k) Calculate the V_{\max} (in mmol/L.min) for the enzyme for this substrate.

$$V_{\max} = V_0(K_m + [S])/[S] = 1.468 \times (0.062 + 0.028) / 0.028 = 4.7 \text{ mmol/L.min (2 marks)}$$

One issue with the Michaelis-Menten equation is the requirement to know V_{\max} . As shown in the graph above, this is practically hard to reach and measure. Instead we can use the Lineweaver-Burk equation which is the inverse of Michaelis-Menten equation, and shown below.

$$\frac{1}{V_0} = \left(\frac{K_m}{V_{\max}} \right) \frac{1}{[S]} + \frac{1}{V_{\max}}$$

When this data is graphed, a linear plot is observed and allows the relevant data to be obtained from the axis intercepts and slope of the line as represented below.



For a particular enzyme/substrate reaction, the following equation was obtained for the line of best fit: $y = 595.65x + 25.346$.

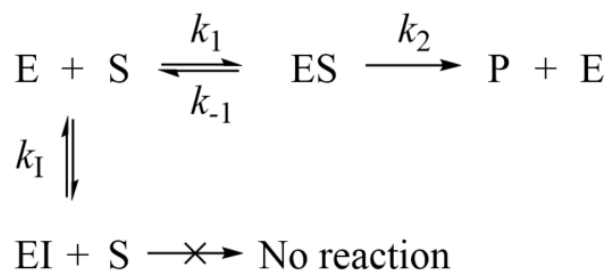
(l) Given this equation, determine the V_{\max} for this enzyme.

$$V_{\max} = 1 / 25.346 = 0.039454 \text{ (1 mark)}$$

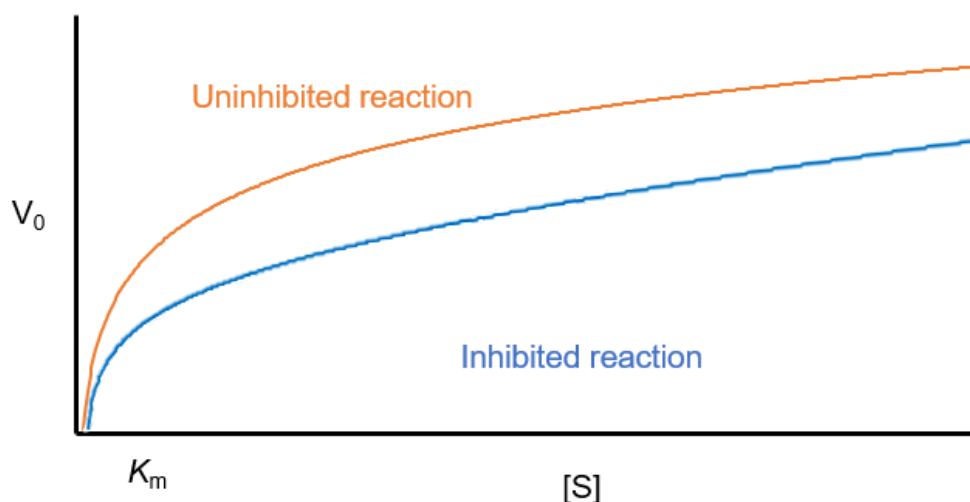
(m) Determine the K_m for this enzyme.

$$K_m = 595.65 \times 0.039454 = 23.500 \text{ (2 marks)}$$

Medications that are taken to treat illnesses often target enzymes to inhibit their function. An inhibitor (I) will form a complex with the enzyme but will not undergo further reaction. This is shown below.



The formation of the EI complex is also reversible and so will not stop the catalysed reaction completely but will slow it down. Graphing the Michaelis-Menten kinetics of an inhibited reaction compared to when no inhibitor is shown below.



- (n) Based on the information above, what changes, if any, would you expect to V_{\max} and K_m for an enzyme inhibited in this way? Select the correct response for each.

V_{\max} : increase / decrease / **stay the same** (1 mark)

K_m : **increase** / decrease / stay the same (1 mark)

- (o) Complete the sentence by selecting the relevant terms.

If an inhibitor has stronger non-covalent forces with the enzyme than the substrate, formation of the EI complex would be **favoured** / **disfavoured** over the ES complex and the formation of the product would be **slower** / **faster**.

Due to differences in non-covalent forces, a particular medicine might interact at a different location on the enzyme compared to the substrate. While it might not compete with the substrate for the same location on the enzyme it can still have an influence on enzyme activity. We call this a non-competitive inhibitor.

An enzyme catalysed reaction has a K_m and V_{max} of 0.0754 mmol/L and 0.0445 mmol/L.min. When the same reaction is repeated along with a non-competitive inhibitor a Lineweaver-Burke plot is produced and the equation for the linear line is $y = 2.629x + 34.878$.

(p) What is the V_{max} (in mmol/L.min) for this inhibited reaction?

$$V_{max} = 1 / 34.878 = 0.028671 \text{ mmol/L.min (1 mark)}$$

(q) What is the K_m (in mmol/L) for this inhibited reaction?

$$K_m = 2.629 \times 0.028671 = 0.07538 \text{ mmol/L (1 mark)}$$

- (r) Which of the following would you expect to represent the the V vs $[S]$ plot of the reaction with non-competitive inhibition and without? **(1 mark)**

(i)	
(ii)	
(iii)	
(iv)	The inhibited reaction would remain on the baseline.
(v)	No difference between the inhibited and uninhibited reaction for this graph type.

END OF EXAM