2022 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:

2022 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 × 10^{23} mol^{-1}	Velocity of light (c) = 2.998 × 10^{8} 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 J K^{-1} mol^{-1} 8.206 × 10^{-2} L atm K^{-1} mol^{-1}	1 newton (N) = 1 kg m s^{-2}
Planck's constant (h) = 6.626 × 10^{-34} J s	1 pascal (Pa) = 1 N m^{-2}
Molar volume of ideal gas • 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	$pH = -\log_{10}[H^+]$ $pH + pOH = 14.00$ at 25°C $K_a = \{[H^+]\,[A^-]\} / [HA]$ $pH = pK_a + \log_{10}\{[A^-] / [HA]\}$ PV = nRT E = hν
Surface area of sphere A = $4\pi r^2$	c = νλ

Periodic Table of Elements

Key: atomic number / Symbol / atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

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. Sodium sulfite (Na_2SO_3) reacts with hydrochloric acid to produce sodium chloride, sulfur dioxide and water. What volume (in mL) of 10.1 mol L^{-1} hydrochloric acid is required for complete reaction with 32.6 g of sodium sulfite?

   A. 12.8 mL

   B. 17.1 mL

   C. 25.6 mL

   D. 51.2 mL

   E. 102.4 mL

2. Which of the following pairs lists elements in order of increasing electronegativity?

   A. Na, F, O, N

   B. Na, O, F, N

   C. Na, N, O, F

   D. N, O, F, Na

   E. Na, O, N, F

3. Which of the following contains molecules with linear molecular geometry in the solid state?

   A. CO_2

   B. KCl

   C. MgO

   D. GeO_2

   E. $MgCl_2$

4. A substance conducts electricity well when liquid but not when solid. Which of the following could this substance be? Select all that apply.

A. copper

B. sodium nitrate

C. argon

D. carbon tetrachloride

E. boron nitride

5. Calculate the concentration of chloride ions in the resulting solution when 50.0 mL of 2.68 mol L^{-1} calcium chloride solution is mixed with 150 mL of 1.13 mol L^{-1} silver nitrate solution.

A. 0.49 mol L^{-1}

B. 0.67 mol L^{-1}

C. 0.85 mol L^{-1}

D. 1.34 mol L^{-1}

E. 1.55 mol L^{-1}

6. What is the percentage by mass of fluorine in NF_3?

A. 31.13%

B. 57.56%

C. 73.06%

D. 80.27%

E. 87.15%

7. One step in the manufacture of aluminium is the production of aluminium hydroxide by the following process:

$$2\ NaAlO_2(aq) + 3\ H_2O(l) + CO_2(g) \rightarrow 2\ Al(OH)_3(s) + Na_2CO_3(aq)$$

What mass of aluminium hydroxide can be produced from a mixture of 40 g $NaAlO_2$, 15 g $H_2O(l)$ and 10 g $CO_2(g)$?

A. 17.7 g

B. 21.6 g

C. 35.4 g

D. 38.1 g

E. 43.3 g

8. How many hydrogen atoms are there in 0.2 mol of ammonium sulfate?

A. 6.0×10^{22}

B. 1.2×10^{23}

C. 2.4×10^{23}

D. 4.8×10^{23}

E. 9.6×10^{23}

9. Which of the following molecules has the highest boiling point?

A. CF_4

B. CCl_4

C. CBr_4

D. CI_4

E. CH_4

10. Which of the following has the largest atomic radius?

A. Rb

B. Xe

C. K

D. Kr

E. Sb

11. Element A has 3 valence electrons and element B has 6 valence electrons. Elements A and B are in the same period of the Periodic Table.

What is the likely formula of the compound that elements A and B form together?

A. AB

B. A_2B_3

C. AB_2

D. A_2B

E. A_3B_3

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

A. bromine

B. magnesium bromide

C. phosphorus tribromide

D. hydrogen bromide

E. hydrogen

13. Rubidium forms a number of oxides, one of which contains 78.08% rubidium by mass. What is the empirical formula of this oxide?

A. Rb_6O

B. RbO

C. RbO_2

D. Rb_2O

E. Rb_2O_3

14. Select all molecules that have the same molecular shape.

A. CO_2

B. BF_3

C. Cl_2O

D. H_2S

E. CH_4

15. 500 mL of a 0.10 mol L^{-1} sodium chloride solution is prepared. To this sodium chloride solution, 500 mL of 0.10 mol L^{-1} lithium chloride solution is added.

Which of the following describes the changes in concentration of sodium and chloride ions upon addition of the lithium chloride solution?

$[Na^+]$

A. Decreases

B. Stays the same

C. Increases

$[Cl^-]$

A. Decreases

B. Stays the same

C. Increases

Question 16

Basic carbonate minerals are found widely in nature and, as their name suggests, contain carbonate ions (CO_3^{2-}) together with other basic ions such as hydroxide (OH^-) or oxide (O^{2-}) and various metal cations.

Carbonate content can be determined by measuring the mass of carbon dioxide given off when the mineral is treated with excess nitric acid.

(a) Calculate the molar mass of the mineral with formula $Pb_{10}O_3(CO_3)_6(OH)_2$

MM = 207.2 × 10 + 16 × 3 + 60.01 × 6 + 17.008 × 2 = 2514.08 g mol^{-1}
(1 mark)

(b) Balance the chemical equation for the reaction of this mineral with excess nitric acid.

$Pb_{10}O_3(CO_3)_6(OH)_2 + 20\ HNO_3 \rightarrow 10\ Pb(NO_3)_2 + 6\ CO_2 + 11\ H_2O$
(1 mark total, 0.25 mark each non-mineral coefficient)

(c) Calculate the mass of carbon dioxide released when 10.00 g of this mineral reacts with excess nitric acid.

$m(CO_2)$ = 6 × 44.01 × 10 / (207.2 × 10 + 16 × 3 + 60.01 × 6 + 17.008 × 2)
= 1.050 g
(3 marks)

(d) Calculate the chemical amount (in mol) of nitric acid required to react with 10.00 g of this mineral.

$n(HNO_3)$ = 20 × 10 / (207.2 × 10 + 16 × 3 + 60.01 × 6 + 17.008 × 2) (1 mark)

Basic carbonate minerals undergo thermal decomposition, forming metal oxides and releasing carbon dioxide and water, whose total mass can be determined by weighing.

(e) Balance the chemical equation for thermal decomposition of this mineral.

$Pb_{10}O_3(CO_3)_6(OH)_2 \rightarrow 10\ PbO + 6\ CO_2 + H_2O$
(1 mark total, 0.25 mark each coefficient)

(f) Calculate the total mass lost when 10.00 g of this mineral is thermally decomposed.

mass = (1 × 18.016 + 6 × 44.01) × 10 / (207.2 × 10 + 16 × 3 + 60.01 × 6 + 17.008 × 2)
= 1.122 g
(2 marks)

A sample of a **different** mineral is analysed by the same methods. This mineral also contains only Pb^{2+}, CO_3^{2-}, OH^- and O^{2-} ions.

When a 5.000 g sample of this mineral is treated with 25.00 mL of 2.000 mol L^{-1} nitric acid (HNO_3), 0.5214 g of carbon dioxide is released, and 0.01051 mol of the acid remains.

When subjected to thermal decomposition, 5.000 g of this mineral loses 0.5926 g.

(g) Calculate the chemical amount (in mol or mmol) of nitric acid that reacts with the 5.000 g sample of this mineral.

n(HNO_3, total) = 25.00 / 1000 × 2.000 = 0.05000 mol
n(acid, reacted with mineral) = 0.05000 – 0.01051 = 0.03949 mol

(h) Calculate the chemical amounts (in mol or mmol) of carbon dioxide and water released in the thermal decomposition.

n(CO_2) = 0.5214 / 44.01 = 0.01185 mol
m(H_2O) = 0.5926 – 0.5214 = 0.0712 g
n(H_2O) = 0.0712 / 18.016 = 0.00395 mol

(i) Calculate the chemical amounts (in mol or mmol) of Pb^{2+}, CO_3^{2-}, OH^- present in the 5.000 g sample of this mineral.

n(CO_3^{2-}) = 0.01185 mol
n(OH^-) = 2 × 0.00395 = 0.00790 mol
n(Pb^{2+}) = 0.03949 / 2 = 0.01963 mol

(j) Calculate the empirical formula of this mineral.

n(O^{2-}) = 2 × n(Pb^{2+}) − 2 × n(CO_3^{2-}) − 1 × n(OH^-) = 0.003924 mol
(Can also do O^{2-} by mass balance)

For the simplest ratio, divide by n(O^{2-}): $Pb_5O(CO_3)_3(OH)_2$

A related series of water soluble minerals contain only Na^+, HCO_3^- and CO_3^{2-} ions. Such minerals can be analysed by reaction with hydrochloric acid under two different reaction conditions, which we will refer to as **A** and **B**.

Reaction A

CO_3^{2-} ions present react to form HCO_3^- ions only; HCO_3^- ions present do not react further.

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$

Reaction B

Both CO_3^{2-} ions and HCO_3^- ions present react completely to form CO_2 and H_2O.

$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$

$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$

A 6.000 g sample of a mineral containing only Na^+, HCO_3^- and CO_3^{2-} ions is dissolved in water to form 100 mL of "dissolved mineral solution".

20.00 mL of "dissolved mineral solution" requires 10.32 mL of 0.5012 mol L^{-1} HCl in Reaction **A**, and 36.12 mL of 0.5012 mol L^{-1} HCl in Reaction **B**.

(k) Calculate the chemical amount of HCl consumed in reaction **A**. (in mol or mmol)

n(HCl, A) = 10.32 / 1000 × 0.5012 = 0.005172 mol

(l) Calculate the chemical amount of CO_3^{2-} ions present in 20.00 mL of the "dissolved mineral solution".

n(CO_3^{2-}) = 10.32 / 1000 × 0.5012 = 0.005172 mol

(m) Calculate the chemical amount of HCO_3^- ions present in 20.00 mL of the "dissolved mineral solution".

n(HCl, B) = 36.12 / 1000 × 0.5012 = 0.01810 mol

n(HCl reacting with CO_3^{2-}) = 2 × 10.32 / 1000 × 0.5012 = 0.01034 mol

n(HCO_3^-) = 36.12 / 1000 × 0.5012 – 2 × 10.32 / 1000 × 0.5012 = 0.007759 mol

(n) Calculate the empirical formula of this mineral.

n(HCO_3^-)/ n(CO_3^{2-}) = 0.07759 mol / 0.005172 mol = 1.5

Simplest ratio is 3 HCO_3^- : 2 CO_3^{2-}

Charge balance then requires 7 Na^+.

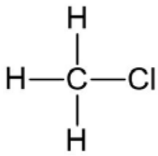
So the empirical formula is $Na_7(HCO_3)_3(CO_3)_2$.

Question 17

^{1}H Nuclear Magnetic Resonance (NMR) is an extremely useful analytical technique as it can convey detailed information about the structure of molecules.

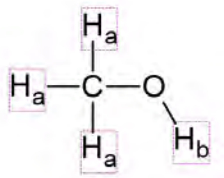
The number of signals in the ^{1}H NMR spectrum of a given molecule corresponds to the number of unique hydrogen atom environments in that molecule.

For example, chloromethane (CH_3Cl) has three hydrogen atoms in the same environment (i.e. attached to the same atom), so there is only one signal in its ^{1}H NMR spectrum.



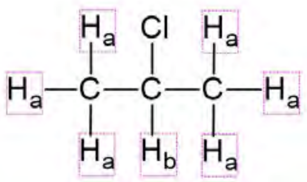
By contrast, methanol (CH_3OH) has two different hydrogen atom environments, labelled H_a and H_b in the diagram below.

- The H_a atoms are bonded to the carbon atom, whereas H_b is bonded to the oxygen atom.

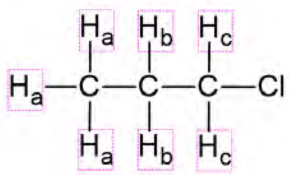


2-chloropropane also has two different hydrogen atom environments, labelled H_a and H_b in the diagram below.

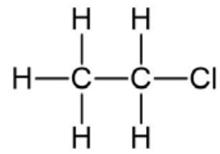
- the 6 H_a atoms are present in two equivalent CH_3 groups on either end of the molecule.
- The single H_b atom is bonded to the central carbon atom.



1-chloropropane has three different hydrogen atom environments, labelled H_a, H_b and H_c.

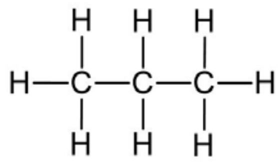


(a) How many signals would you expect in the ^{1}H NMR spectrum of the following molecule?



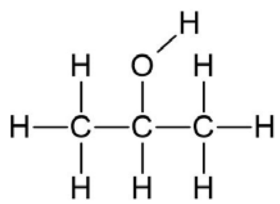
2

(b) How many signals would you expect in the ^{1}H NMR spectrum of the following molecule?



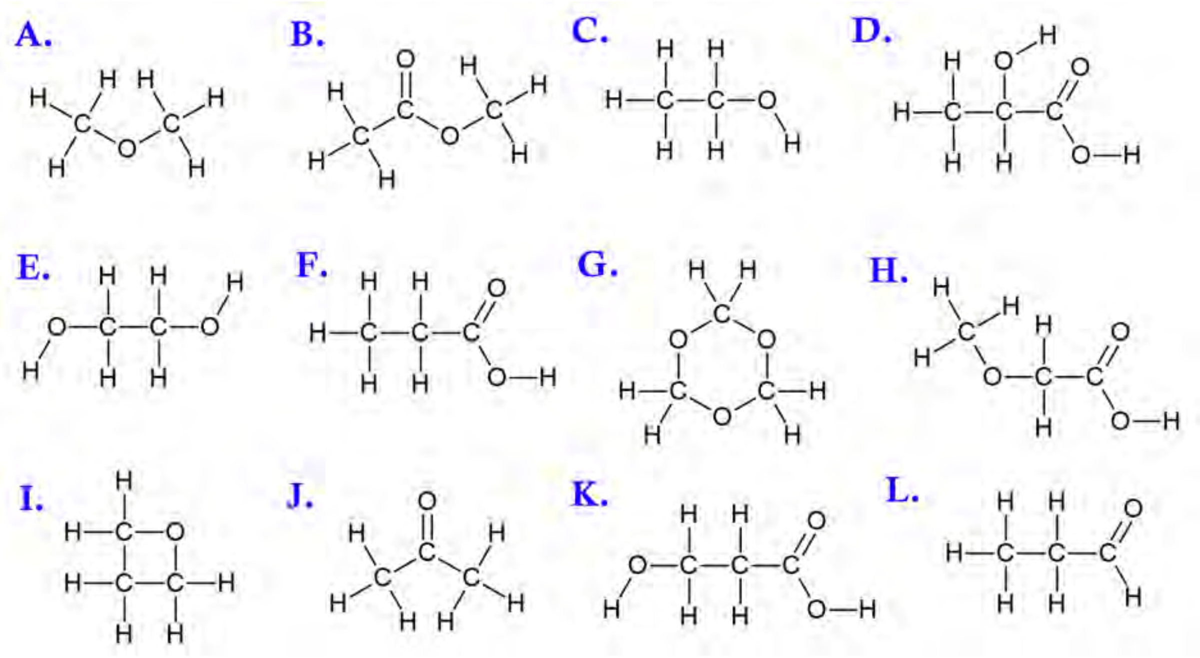
2

(c) How many signals would you expect in the ^{1}H NMR spectrum of the following molecule?



3

Use the following structures to answer the questions on this page.



(d) Using the identifying letters, which of the above molecules would you expect to have **one** signal in their ^{1}H NMR spectrum?

A, G, J

(e) Using the identifying letters, which of the above molecules would you expect to have **two** signals in their ^{1}H NMR spectrum?

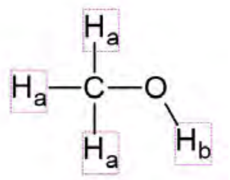
B, E, I

(f) Using the identifying letters, which of the above molecules would you expect to have **four** signals in their ^{1}H NMR spectrum?

D, K

If a molecule contains two or more different hydrogen atom environments, ^{1}H NMR can also provide information about the relative the number of hydrogen atoms in each environment.

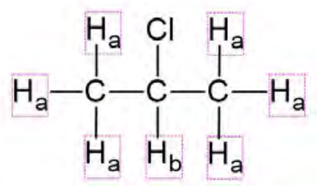
As we have seen before, methanol (CH_3OH) has two different hydrogen atom environments, labelled H_a and H_b in the diagram below.



There are 3 H_a atoms for every H_b atom. We can summarise this in table form:

Hydrogen atom environment	Relative number of hydrogen atoms
H_a	3
H_b	1

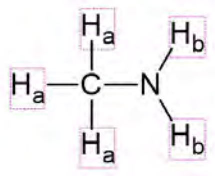
Similarly, 2-chloropropane has two different hydrogen atom environments, labelled H_a and H_b in the diagram below. There are 6 H_a atoms for every H_b atom.



Hydrogen atom environment	Relative number of hydrogen atoms
H_a	6
H_b	1

Normally the integral of the signal arising from the fewest protons is assigned an integral of 1, and all other integrals are expressed relative to that. This can give rise to non-integer integrals.

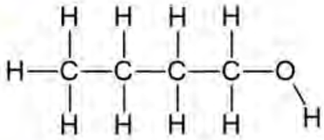
For example, methanamine has two different hydrogen atom environments: labelled H_a and H_b in the diagram below. The ratio hydrogen atoms is therefore 3:2, or more simply 1.5:1.



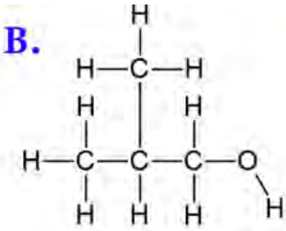
Hydrogen atom environment	Relative number of hydrogen atoms
H_a	1.5
H_b	1

Use the following structures to answer the questions on this page.

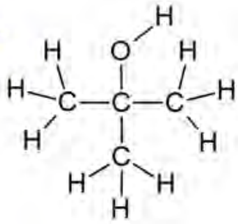
A.



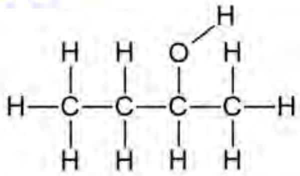
B.



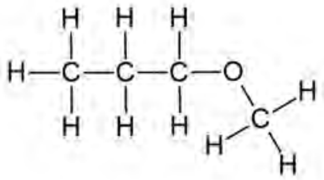
C.



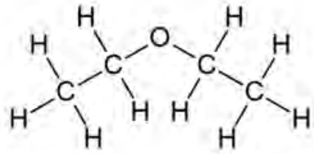
D.



E.



F.



(g) Using the identifying letters, which of the above molecules would you expect to give the following ^{1}H NMR data? Select all that apply.

Hydrogen atom environment	Relative number of hydrogen atoms
I	9
II	1

C.

(h) Using the identifying letters, which of the above molecules would you expect to give the following ^{1}H NMR data? Select all that apply.

Hydrogen atom environment	Relative number of hydrogen atoms
I	6
II	2
III	1
IV	1

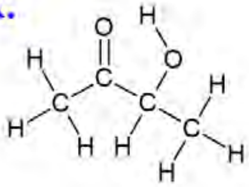
B.

(i) Using the identifying letters, which of the above molecules have at least one signal in their ^{1}H NMR spectrum with a relative number of hydrogen atoms of **1.5**? Select all that apply.

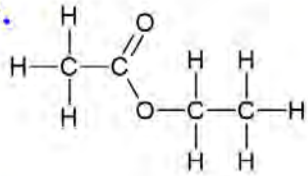
E, F.

Use the structures below to answer questions (j) to (m).

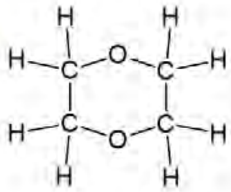
A.



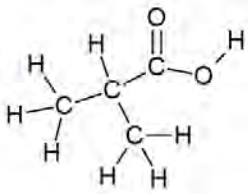
B.



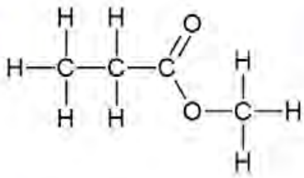
C.



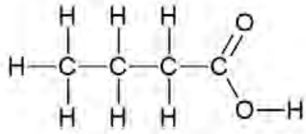
D.



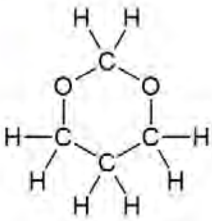
E.



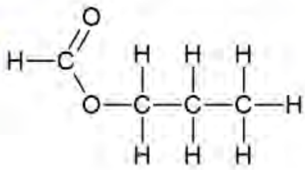
F.



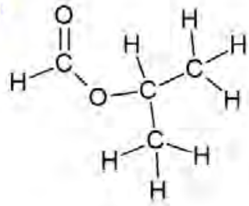
G.



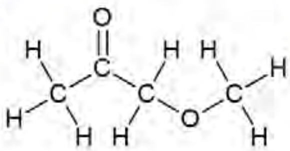
H.



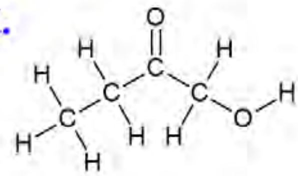
I.



J.



K.



(j) Using the identifying letters, which of the above molecules have one signal in their ^{1}H NMR spectrum with a relative number of hydrogen atoms of **6**? Select all that apply.

D, I.

(k) Using the identifying letters, which of the above molecules would you expect to give the following ^{1}H NMR data? Select all that apply.

Hydrogen atom environment	Relative number of hydrogen atoms
I	2
II	1
III	1

G.

(l) Using the identifying letters, which of the above molecules would you expect to give the following ^{1}H NMR data? Select all that apply.

Hydrogen atom environment	Relative number of hydrogen atoms
I	3
II	3
III	1
IV	1

A.

(m) Using the identifying letters, which of the above molecules would you expect to give the following ^{1}H NMR data? Select all that apply.

Hydrogen atom environment	Relative number of hydrogen atoms
I	3
II	3
III	2

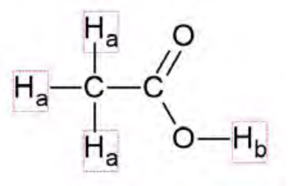
B, E, J.

Another useful aspect of ^{1}H NMR data is called chemical shift, a number usually between 0 and 12. Hydrogen atoms in specific chemical environments have characteristic chemical shifts, for example:

Hydrogen atom environment	Typical chemical shift range
C-C**H**$_x$	0.9 – 1.8
O=C–C**H**$_x$	2.0 – 2.7
O–C**H**$_x$	3.0 – 5.0
–COO**H**	10.5 – 12.0

(where *x* is 0, 1, 2 or 3)

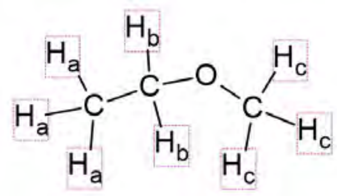
For example:



Hydrogen atom environment	Chemical shift
H_a	2.1
H_b	11.4

- The H_a atoms in the molecule above are adjacent to a C=O, so their chemical shift is between 2.0 – 2.7.
- The H_b atom is part of a –COOH group, so its chemical shift is between 10.5 – 12.0.

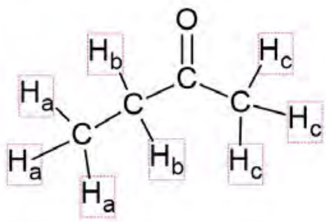
Similarly:



Hydrogen atom environment	Chemical shift
H_a	1.4
H_b	3.5
H_c	3.3

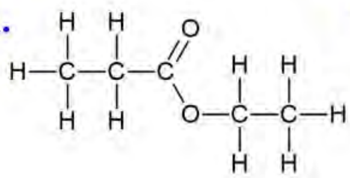
- The H_a atoms in the molecule above are part of a C-C**H**$_3$ group, so their chemical shift is between 0.9 – 1.8.
- The H_b and H_c atoms are part of O–C**H**$_2$ and O–C**H**$_3$ groups respectively, so their chemical shifts are between 3.0 – 5.0.

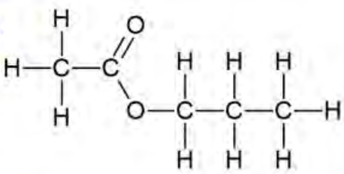
(n) Predict the chemical shift of each different hydrogen atom in the following molecule.

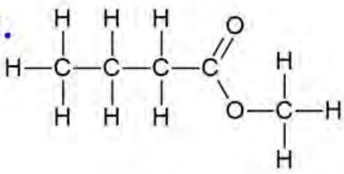


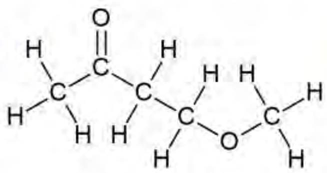
Hydrogen atom environment	Chemical shift
H_a	**0.9 – 1.8**
H_b	**2.0 – 2.7**
H_c	**2.0 – 2.7**

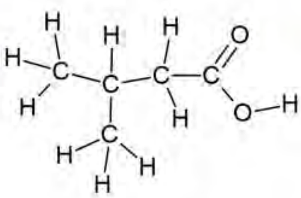
Use the structures below to answer questions (o) to (r).

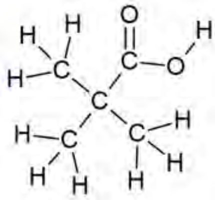
A. 

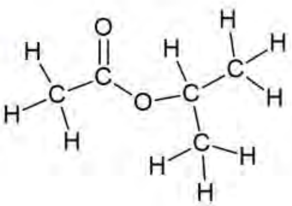
B. 

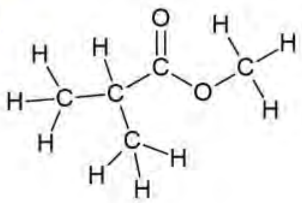
C. 

D. 

E. 

F. 

G. 

H. 

(o) Using the identifying letters, which of the above molecules would you expect to give the following ^{1}H NMR data?

Hydrogen atom environment	Relative number of hydrogen atoms	Chemical shift
I	9	1.2
II	1	11.5

F

(p) Using the identifying letters, which of the above molecules would you expect to give the following ^{1}H NMR data?

Hydrogen atom environment	Relative number of hydrogen atoms	Chemical shift
I	6	1.2
II	1	2.6
III	3	3.7

H

(q) Using the identifying letters, which of the above molecules would you expect to give the following ^{1}H NMR data? Select all that apply.

Hydrogen atom environment	Relative number of hydrogen atoms	Chemical shift
I	3	1.0
II	2	1.7
III	3	2.5
IV	2	4.0

B

(r) Using the identifying letters, which of the above molecules would you expect to give the following ^{1}H NMR data? Select all that apply.

Hydrogen atom environment	Relative number of hydrogen atoms	Chemical shift
I	3	2.2
II	2	2.7
III	3	3.3
IV	2	3.6

D

Question 18

Let us consider the simplest types of reaction, those that happen in one step. We call these reactions elementary. For elementary reactions, the reaction rate (denoted by v) is dependent on the concentrations of each of the reactants.

For example, the elementary reaction aA + bB → cC has the rate law $v = k[A]^a[B]^b$, where k is a constant called the rate constant.

Consider the reaction between carbon monoxide and nitrogen trioxide:

$CO(g) + NO_3(g) \rightarrow CO_2(g) + NO_2(g)$

(a) What is the rate law for this reaction?

(i) $v = k[CO_2][NO_2]$

(ii) $v = k[NO_2]$

(iii) $v = k[NO_3]$

(iv) $v = k[CO_2]$

(v) $v = k[CO][NO_3]$

(vi) $v = k[CO]$

The exponents of the concentration terms in the rate law are known as the partial orders of the reaction. In the rate law $v = k[A]^a[B]^b$, reactant A has an order of a and reactant B has an order of b.

The overall reaction order is the sum of each reactant's order. In the above example, the overall reaction order is a + b.

(b) For the elementary reaction $CO(g) + NO_3(g) \rightarrow CO_2(g) + NO_2(g)$, identify the following:

(i) Partial reaction order of CO. **1**

(ii) Partial reaction order of NO_3. **1**

(iii) Overall reaction order. **2**

(c) For the elementary reaction $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$, identify the following:

(i) Partial reaction order of NO. **2**

(ii) Partial reaction order of O_2. **1**

(iii) Overall reaction order. **3**

(d) For the elementary reaction $CO(g) + NO_3(g) \rightarrow CO_2(g) + NO_2(g)$: calculate the rate constant, k, if the reaction rate is 0.00491 mol L^{-1} s^{-1} when the [CO] is 0.137 mol L^{-1} and $[NO_3]$ is 0.229 mol L^{-1}. Express your answer in L mol^{-1} s^{-1}.

k = 0.00491 / (0.137 × 0.229) = 0.157 L mol^{-1} s^{-1}

(e) Which of the following can increase the rate of a chemical reaction?

(i) Increasing the surface area of a solid reactant.

(ii) Decreasing the temperature.

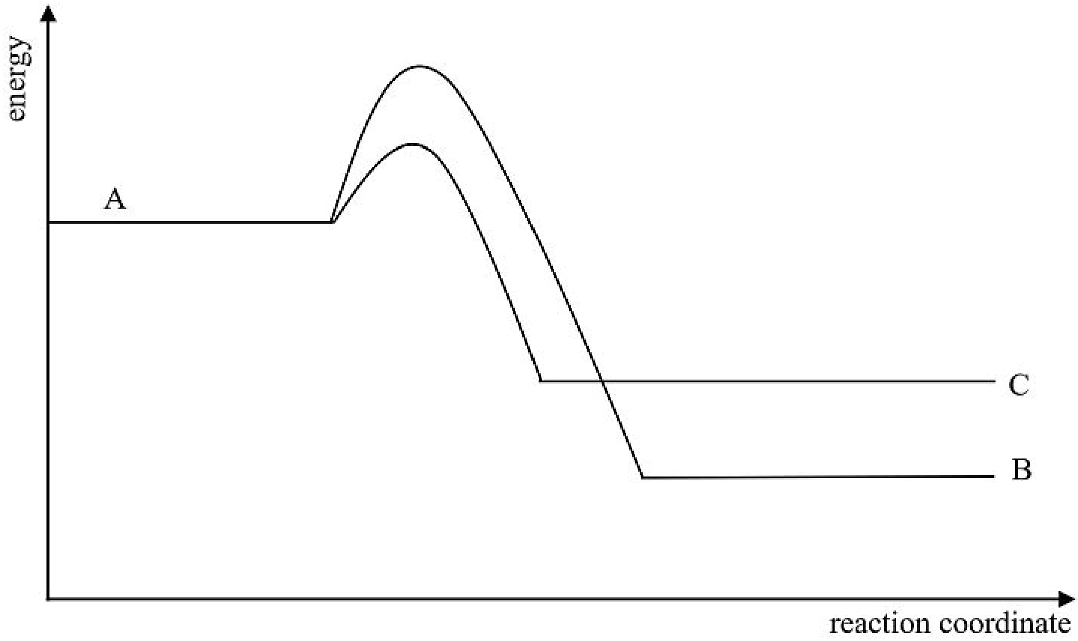
(iii) Using a catalyst.

(iv) For a gaseous reaction, decreasing the volume of a closed reaction vessel.

(v) For an aqueous reaction, increasing the concentration of products.

The activation energy for a chemical reaction, E_A, represents the minimum energy that must be provided to the reactants for a chemical reaction to occur. Collision theory states that for a successful reaction to occur, reactant molecules must collide in the correct orientation and with energy that exceeds the activation energy.

The following energy profile diagram shows two possible products, B and C, that can be produced from reactant A.



(f) What is the major product when the reaction is allowed to run for 30 seconds at a low temperature?

C

(g) What is the major product when the reaction is allowed to run for 48 hours at a high temperature?

B

Collision theory states that for a successful reaction to occur, reactant molecules must collide in the correct orientation and with energy that exceeds the activation energy. The rate of reaction is proportional to the frequency of successful collisions. This can be represented by the following formula. The rate constant, k, is proportional to the reaction rate.

$$k = Ae^{-\frac{E_A}{RT}}$$

E_A = activation energy (J), R = Universal Gas Constant, T = temperature (K), k = rate constant.

A is the pre-exponential factor, and is given by the formula:

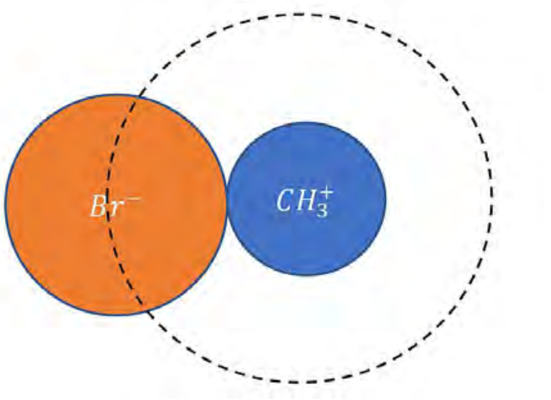
$$A = P \times N_A \times \sigma \times v$$

N_A = Avogadro's constant; the other terms will be explained below.

Consider the following reaction: $CH_3^+ + Br^- \rightarrow CH_3Br$.

For this reaction to occur, a CH_3^+ ion, with radius r_C, must come into contact with a Br^- ion, with radius r_B.

The σ term represents the area in which the two ions are close enough to collide, and can be calculated as the area of the dotted circle shown below.



(h) Select the correct expression for σ for this reaction (the area of a circle is πr^2).

(i) $\pi(r_C - r_B)^2$

(ii) $2\pi r_C^2$

(iii) $\pi r_C^2 - \pi r_B^2$

(iv) $\pi r_B^2 + \pi r_C^2$

(v) $\pi(r_B + r_C)^2$

(i) Select the molecular geometry of CH_3^+.

(i) tetrahedral

(ii) linear

(iii) trigonal planar

(iv) trigonal pyramidal

(v) T-shaped

(j) Using the fact that the radii of CH_3^+ and Br^- are 140 pm and 195 pm respectively, calculate σ for the reaction, in m^2.

$$\sigma = \pi \times (195 \times 10^{-12} + 140 \times 10^{-12})^2$$
$$= 3.5256 \ldots \times 10^{-19}$$
$$= 3.53 \times 10^{-19}\ m^2$$

The v term represents the velocity (in ms^{-1}) of the particles as they collide, and is given by:

$$v = \sqrt{\frac{8k_BT}{\pi\mu}}$$

In this formula, μ is the reduced mass, in kg, given by:

$$\mu = \frac{m_1m_2}{m_1 + m_2}$$

where m_1 and m_2 are the masses of the colliding ions.

(k) Calculate the mass (in kg) of a Br^- ion.

$$m_{Br^-} = \frac{79.90\ g}{1\ mol} \times \frac{1\ kg}{1000\ g} \times \frac{1\ mol}{6.022 \times 10^{23}}$$
$$= 1.326 \ldots \times 10^{-25}\ kg$$

(l) Calculate the mass (in kg) of a CH_3^+ ion.

$$m_{CH_3^+} = \frac{15.034\ g}{1\ mol} \times \frac{1\ kg}{1000\ g} \times \frac{1\ mol}{6.022 \times 10^{23}}$$
$$= 2.4965 \ldots \times 10^{-26}\ kg$$

(m) Calculate the reduced mass (μ) for this reaction.

$$\mu = \frac{m_1m_2}{m_1 + m_2}$$
$$\mu = 2.10115 \ldots \times 10^{-26}\ kg$$
$$= 2.10 \times 10^{-26}\ kg\ (3sf)$$

(n) Calculate v at 298 K for the above reaction, given that $k_B = 1.381 \times 10^{-23}\ m^2\ kg\ s^{-2}\ K^{-1}$.

$$v = \sqrt{\frac{8 \times 1.381 \times 10^{-23} \times 298}{\pi \times 2.10115 \ldots \times 10^{-26}}}$$
$$= 706.229 \ldots ms^{-1}$$
$$= 706\ ms^{-1} (3sf)$$

Recall the following formulae:

$$k = Ae^{-\frac{E_A}{RT}}$$

E_A = activation energy (J), R = Universal Gas Constant, T = temperature (K), k = rate constant.

A is the pre-exponential factor, and is given by the formula:

$$A = P \times N_A \times \sigma \times v$$

(o) Given that ρ = 0.9 and E_A= −123 kJ mol^{-1}, calculate the value of k for this reaction at 298 K.

$$k = 0.9 \times 6.022 \times 10^{23} \times 3.5256 \ldots \times 10^{-19} \times 706.229 \ldots \times e^{\frac{123000}{8.314 \times 298}}$$
$$= 4.9077 \ldots \times 10^{29}$$
$$= 4.91 \times 10^{29}\ (3sf)$$

Reaction rates of enzymes can be described by the Michaelis-Menten equation:

$$v = \frac{V_{\max}[\mathrm{S}]}{K_{\mathrm{m}} + [\mathrm{S}]}$$

- v_ is the rate of reaction
- V_{max} is the maximum reaction rate
- [S] is the concentration of the enzyme's substrate (reactant)
- K_m is a constant

For the following changes, select the effect (if any) on the rate of reaction.

(p) What effect does increasing the concentration of substrate from below K_m to above K_m have on the reaction rate?

Increases reaction rate.

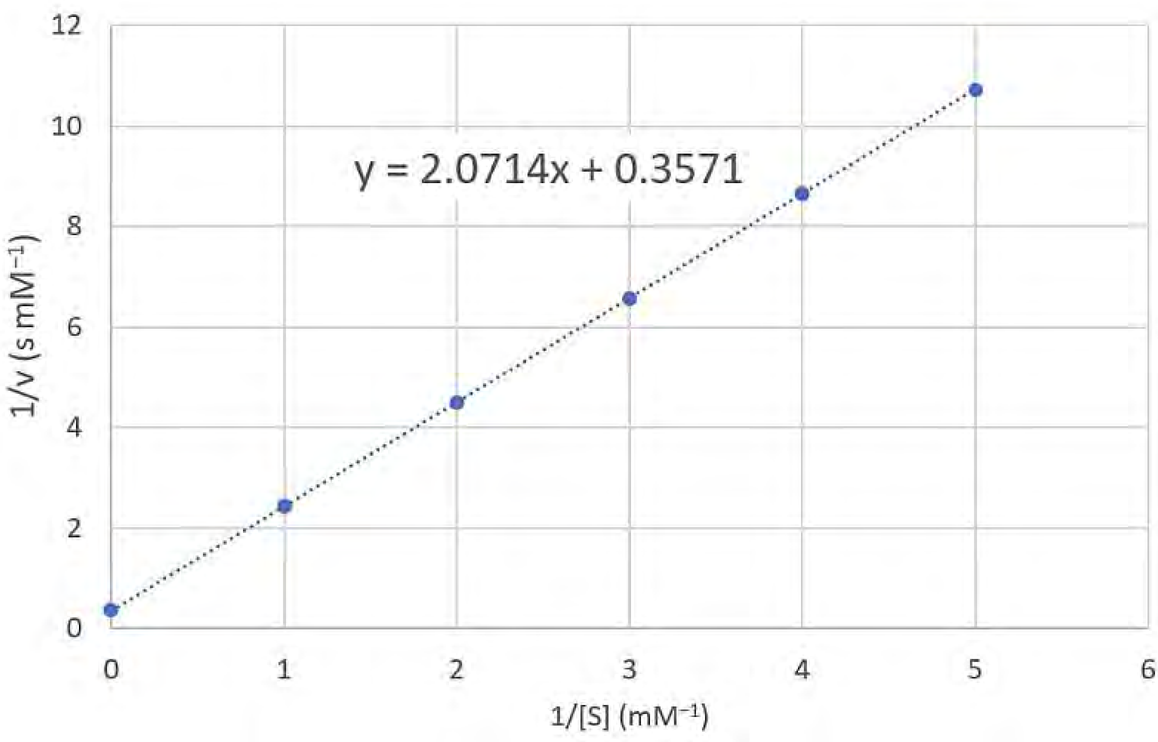
(q) What effect does using a different enzyme with a smaller K_m value have on the reaction rate?

Increases reaction rate.

The Michaelis-Menten equation can be re-written as follows:

$$\frac{1}{v} = \frac{K_m}{V_{max}} \cdot \frac{1}{[S]} + \frac{1}{V_{max}}$$

A plot of 1/v_ against 1/[S] for a certain enzyme is shown below:



(r) What is the value of V_{max} for this enzyme?

V_{max} = 1/0.3571 = 2.800 mM s^{-1}

(s) What is the value of K_m for this enzyme?

K_m = 2.0714 × 2.800 = 5.8 mM

(t) At what [S] is the reaction rate equal to half V_{max}?

When v = half V_{max}, [S] = K_m = 5.8 mM

END OF EXAM