2019 AUSTRALIAN SCIENCE OLYMPIAD EXAM

CHEMISTRY

TO BE COMPLETED BY THE STUDENT. USE CAPITAL LETTERS.

First Name: ……………….….………… Last Name………………………………….

Date of Birth: ……/…..../..….

☐ Male ☐ Female ☐ Unspecified Year 10 ☐ Year 11 ☐ Other: …….

Name of School: …………………………………….………………..**State:** ……...

Examiners Use Only:

2019 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-graphics calculator, pens, pencils, erasers and a ruler.
- Answer SECTION A on the Multiple Choice Answer Sheet provided. **Use a pencil.**
- Answer SECTION B in the spaces provided in this paper. Write in pen and use a pencil only for graphs.
- Ensure that your diagrams are clear and labelled.
- All numerical answers must have correct units.
- Marks will be awarded for correct answers, not deducted for incorrect answers.
- Note that it may be possible to complete some later parts of short answer questions without having completed earlier parts.
- Rough working may be done on page 33 and 34 of this booklet.
- Data that may be required for a question may be found on page 3.
- Do **not** staple the multiple choice answer sheet to this booklet.

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

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 coulomb = 1 $A\ s^{-1}$	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 $K_a = \{[H^+]\,[A^-]\} / [HA]$ $pH = pK_a + \log_{10}\{[A^-] / [HA]\}$ $PV = nRT$ $E = h\nu$
Surface area of sphere $A = 4\pi r^2$	$c = \nu\lambda$

Periodic table of the Elements

1 — Atomic number
H
1.008 — Atomic mass

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											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 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	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 72.59	33 As 74.92	34 Se 78.96	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 95.94	43 Tc (98)	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 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	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 (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac (227)	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds								

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	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
90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Atomic mass values given here are to four significant figures. A value given in parentheses denotes the mass of the longest-lived isotope.

SECTION A: MULTIPLE CHOICE
USE THE ANSWER SHEET PROVIDED

1. What is the formula for the compound formed by barium and nitrogen?

(a) BaN
(b) Ba_2N
(c) BaN_2
(d) Ba_2N_3
(e) Ba_3N_2

2. Which of the following compounds exists as linear molecules at room temperature and pressure?

(a) CO_2
(b) SiO_2
(c) NaCl
(d) OF_2
(e) H_2O

3. When liquid methane (CH_4) is vapourised, which bonds or forces are broken?

(a) covalent bonds
(b) dipole-dipole interactions
(c) dispersion forces
(d) hydrogen bonds
(e) ionic bonds

4. The molar masses of C_2H_6, CH_3OH and CH_3F are similar. Which of the following lists these compounds in order of increasing boiling point?

(a) $C_2H_6 < CH_3OH < CH_3F$
(b) $CH_3F < CH_3OH < C_2H_6$
(c) $CH_3OH < CH_3F < C_2H_6$
(d) $C_2H_6 < CH_3F < CH_3OH$
(e) $CH_3F < C_2H_6 < CH_3OH$

5. Which of the following species contains 21 neutrons and 19 electrons?

(a) ${}^{41}_{20}\mathrm{Ca}^{2+}$

(b) ${}^{41}_{20}\mathrm{Ca}^{+}$

(c) ${}^{40}_{19}\mathrm{K}^{+}$

(d) ${}^{40}_{21}\mathrm{Sc}^{2+}$

(e) ${}^{38}_{17}\mathrm{Cl}^{-}$

6. Which of the following elements has the highest **fourth** ionisation energy?

(a) helium
(b) lithium
(c) boron
(d) carbon
(e) nitrogen

7. Jarosite is a white mineral of formula $KAl_3X_2(OH)_6$, where X is an unspecified species. Which of the following could X be?

(a) HCO_3^-
(b) Ca^{2+}
(c) Ag^+
(d) SO_4^{2-}
(e) PO_4^{3-}

8. How many atoms are present in a 1.0 g sample of the dimethylaminoxyl radical, $(CH_3)_2NO$?

(a) 1.0×10^{22}
(b) 6.0×10^{22}
(c) 1.0×10^{23}
(d) 6.0×10^{23}
(e) 6.0×10^{24}

9. Silver oxide (Ag_2O) decomposes to silver and oxygen upon heating. The molar mass of silver oxide is approximately 232 g mol^{-1}.

   What amount of oxygen gas is produced when 4.64 g of silver oxide decomposes?

   (a) 0.005 mol
   (b) 0.01 mol
   (c) 0.02 mol
   (d) 0.04 mol
   (e) 0.08 mol

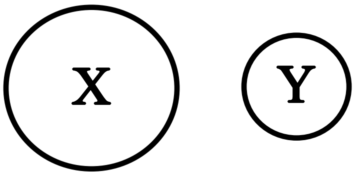
10. Iron can be produced by reducing iron(III) oxide with carbon monoxide, as described by the following balanced chemical equation:

    $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

    What mass of carbon dioxide is produced by the complete reduction of 16.0 g of iron(III) oxide?

    (a) 1.5 g
    (b) 4.4 g
    (c) 6.6 g
    (d) 8.8 g
    (e) 13.2 g

11. The following diagram shows the relative atomic radii of two elements, **X** and **Y**.



    Elements X and Y are **non-metals** and are in the **same group** of the Periodic Table

    Which of the following statements must be true?

    (a) Element X has a higher first ionisation energy than element Y.
    (b) Element X is more reactive than element Y.
    (c) Element Y has greater electron shielding than element X.
    (d) Element Y has a higher electronegativity than element X.
    (e) Element X has a higher effective nuclear charge than Y.

12. A mixture of calcium carbonate and sodium chloride contains 10% carbon by mass. What is the percentage by mass of sodium chloride in the sample?

(a) 10%
(b) 17%
(c) 50%
(d) 83%
(e) 90%

13. When the following unbalanced equation is balanced, how many $O_2(g)$ molecules are consumed for every $CO_2(g)$ produced?

$$C_3H_7OH(l) + \quad O_2(g) \rightarrow \quad CO_2(g) + \quad H_2O(l)$$

(a) 0.67
(b) 0.75
(c) 1.00
(d) 1.33
(e) 1.5

14. When aluminium reacts with hydrochloric acid, aluminium chloride and hydrogen gas are produced. The volume of one mole of hydrogen gas at 25 °C and 100 kPa is 24.79 L.

When 2.70 g of aluminium reacts with 50.0 mL of 5.00 mol L^{-1} hydrochloric acid, what volume of hydrogen gas is produced, when measured at 25 °C and 100 kPa?

(a) 2.48 L
(b) 3.10 L
(c) 3.72 L
(d) 4.96 L
(e) 6.20 L

15. A nucleophile is a chemical species that forms a covalent bond by donating a pair of electrons to another species. Which of the following would you expect to be the best nucleophile?

(a) Na^+
(b) I^-
(c) Ca
(d) Ca^{2+}
(e) CH_4

END OF SECTION A
SECTION B COMMENCES OVERLEAF

SECTION B
ANSWER IN THE SPACES PROVIDED

Question 16

Intermolecular forces and bonding affect many bulk properties of chemicals, including melting point, freezing point and solubility. There are a range of units used for solubility, including molarity (moles of solute per litre of **solution**, mol L^{-1}), g/100 mL (grams of solute per 100 mL of **solution**) and molality (moles of solute per kilogram of **solvent,** mol kg^{-1}).

A sample of 15.0 g of caffeine was partially dissolved in water and the remaining solid was filtered off, leaving 500 mL of solution. The water from the resulting saturated caffeine solution was boiled off and the dissolved caffeine was recovered and weighed. 4.5 g of caffeine was recovered.

(a) Calculate the solubility of caffeine in water, in g/100 mL.

m(caffeine dissolved) = 15.0 g – 4.5 g = 10.5 g

Solubility = 10.5 g / 5 = 2.10 g/100 mL

Hansen solubility parameters (HSPs) can be used to predict if a solute will dissolve in a solvent. Each molecule is given three parameters:

- δ_D is related to the dispersion forces between molecules. These come from the rearrangement of electrons forming instantaneous dipoles.
- δ_P is related to the dipole-dipole forces between molecules. These come from the static dipoles in polar molecules.
- δ_H is related to the hydrogen bonding between molecules. These come from the interaction of highly polarised bonds to hydrogen and lone pairs.

Larger values for these parameters correspond to stronger forces.

(b) Explain why the values for δ_P and δ_H for hexane (C_6H_{14}) are zero.

Hexane is non-polar, so has no dipole-dipole forces or hydrogen bonding between its molecules. Accordingly, δ_P and δ_H are zero.

HSPs for caffeine and water are shown in the table below:

	δ_D	δ_P	δ_H
Caffeine	19.5	10.1	13
Water	15.5	16	42.3

We can predict the solubility from the HSPs by computing the parameter R, using the following formula:

$$R^2 = 4(\delta_{D,1} - \delta_{D,2})^2 + (\delta_{P,1} - \delta_{P,2})^2 + (\delta_{H,1} - \delta_{H,2})^2$$

R is a measure of how different the two molecules are. The **smaller** the value of R for a solute-solvent pair, the more likely the solute is soluble in the solvent. From experimental evidence, $R < 7$ generally means the solute is soluble in the solvent.

(c) Calculate the value of R for caffeine in water.

$$R^2 = 4(\delta_{D,1} - \delta_{D,2})^2 + (\delta_{P,1} - \delta_{P,2})^2 + (\delta_{H,1} - \delta_{H,2})^2$$

$$R^2 = 4(19.5 - 15.5)^2 + (10.1 - 16)^2 + (13 - 42.3)^2 = 957.3$$

$$R = 30.9$$

(d) The same experiment as in a) was conducted with using dichloromethane instead of water. The solubility of caffeine in dichloromethane was found to be 140 mg mL^{-1} and the corresponding R value was calculated to be 8.22. Do the values of R agree with the observed solubilities for dichloromethane and water?

140 mg mL^{-1} = 14 g/100 mL.

Thus caffeine is more soluble in dichloromethane (14 g/100 mL) than it is in water (2.1 g/100 mL, from part (a)).

R for caffeine in dichloromethane is 8.22, which is smaller than R for caffeine in water (30.9, from part (b)).

Accordingly, caffeine should be more soluble in dichloromethane than in water, which agrees with the observed solubilities.

Hansen solubility parameters can also be used to understand the properties of mixed solvents. The HSPs for a solvent mixture are the weighted averages of the HSPs for the pure components.

(e) Using the information in the table below:

	δ_D	δ_P	δ_H
Nitromethane	15.8	18.8	6.0
Benzene	18.4	0	2.0
PMMA	18.6	10.5	5.1

i. Calculate the Hansen solubility parameters for a 1:1 mixture of nitromethane and benzene.

$\delta_D = (15.8 + 18.4)/2 = 17.1$

$\delta_P = (18.8 + 0)/2 = 9.4$

$\delta_H = (6.0 + 2.0)/2 = 4.0$

ii. Calculate R for PMMA in 1:1 nitromethane/benzene.

$R^2 = 4(18.6 - 17.1)^2 + (10.5 - 9.4)^2 + (5.1 - 4.0)^2 = 11.4$

$R = 3.38$

iii. R for PMMA in benzene is 10.96 and for PMMA in nitromethane is 10.06. Based off these R values, would PMMA be most likely to dissolve in benzene, nitromethane or 1:1 nitromethane/benzene?

The 1:1 nitromethane/benzene mixture (R for the mixture is lowest).

Colligative properties of solutions are properties that depend upon the concentration of solute molecules or ions but not upon the identity of this solute. One such property is freezing-point depression.

The freezing point of a liquid decreases when a solute is added. Historically, molecular weights were calculated empirically by using this property.

Freezing-point depression is directly proportional to the *molality* of the solute. Molality (moles of solute per kilogram of **solvent,** mol kg^{-1}) should not be confused with molarity (moles of solute per litre of **solution**, mol L^{-1}).

106.5 g of urea (CH_4N_2O, molar mass 60.062 g mol^{-1}) is dissolved in 195.4 mL of water at 60 °C. The density of water at 60 °C is 0.9832 g mL^{-1}.

(f) What is the molality (in mol kg^{-1}) of the solution?

$$n(urea) = \frac{106.5\ \mathrm{g}}{60.062\ \mathrm{g\ mol^{-1}}} = 1.773\ \mathrm{mol}$$

$$m(H_2O) = 0.1954\ \mathrm{L}\ \times 0.9832\ \mathrm{kg\ L^{-1}} = 0.1921\ \mathrm{kg}$$

$$molality = \frac{1.773\ \mathrm{mol}}{0.1921\ \mathrm{kg}} = 9.230\ \mathrm{mol\ kg^{-1}}$$

(g) A saturated solution of glucose ($C_6H_{12}O_6$) in water at 60 °C has a molarity of 8.25 mol L^{-1} and a density of 2.47 g mL^{-1}. What is the molality of a saturated solution of glucose in water at 60 °C?

$$n(glucose\ per\ \mathrm{L}) = 8.25\ \mathrm{mol}$$

$$m(glucose\ per\ \mathrm{L}) = 8.25\ \mathrm{mol}\ \times 180.156\ \mathrm{g\ mol^{-1}} = 1486\ \mathrm{g} = 1.49\ \mathrm{kg}$$

$$m(1\ \mathrm{L\ solution}) = 2.47\ \mathrm{g\ mL^{-1}} \times 1000\ \mathrm{mL}\ = 2470\ \mathrm{g} = 2.47\ \mathrm{kg}$$

$$m(water\ per\ \mathrm{L}) = 2.47\ \mathrm{kg} - 1.49\ \mathrm{kg} = 0.98\ \mathrm{kg}$$

$$molality = \frac{8.25\ \mathrm{mol}}{0.98\ \mathrm{kg}} = 8.4\ \mathrm{mol\ kg^{-1}}$$

The change in freezing point of the solution can be calculated using the following equation:

$$T_F(solution) - T_F(pure\ solvent) = \Delta T_F = -iK_F m$$

- T_F is the freezing temperature in K
- ΔT_F is the change in freezing temperature in K
- i is the van't Hoff factor (more information below)
- K_f is the cryoscopic constant equal to 1.86 K kg mol^{-1}
- m is the molality of the solution in mol kg^{-1}.

The van't Hoff factor, i, is the number of discrete particles (e.g. molecules, ions) released into solution per formula unit. For species that do not dissociate, such as urea, $i = 1$.

A particularly useful application of freezing point depression is in making ice baths that are colder than 0 ºC whilst still using ice and water. One such salt used is sodium chloride, which dissolves as follows:

$$\mathrm{NaCl}(s) \rightarrow \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq)$$

(h) What is the theoretical van't Hoff factor for sodium chloride?

2

(i) Sodium chloride is added to ice (freezing point 0.0 ºC) to make a bath with a freezing point of −20.0 ºC. If 2.457 kg of ice is used, what mass of sodium chloride must be added?

$$m = \frac{-\Delta T_\mathrm{f}}{iK_\mathrm{f}} = \frac{20.0\ \mathrm{K}}{2 \times 1.86\ \mathrm{K\ kg\ mol^{-1}}} = 5.38\ \mathrm{mol\ kg^{-1}}$$

$$n(NaCl) = 5.38\ \mathrm{mol\ kg^{-1}} \times 2.457\ \mathrm{kg} = 13.2\ \mathrm{mol}$$

$$m(NaCl) = 13.2\ \mathrm{mol} \times 58.44\ \mathrm{g\ mol^{-1}} = 772\ \mathrm{g}$$

In winter, salts are often spread on top of icy roads to melt ice and make driving safer. Calcium chloride hexahydrate is often used for this purpose as it is very cheap and effective.

(j) The concentration of a saturated solution of calcium chloride in water at 0 °C is 60.93 g/100 mL, the density of this solution is 1.366 g mL^{-1} and the density of water at 0 °C is 1.000 g mL^{-1}.

i. What is the freezing point of saturated calcium chloride solution?

$$\mathrm{m(100\ mL\ saturated\ CaCl_2\ solution)} = 100 \times 1.366 = 136.6\ \mathrm{g} = 0.1366\ \mathrm{kg}$$

$$\mathrm{m(water\ in\ 100\ mL\ saturated\ CaCl_2\ solution)} = 136.6\ \mathrm{g} - 60.93\ \mathrm{g} = 75.67\ \mathrm{g} = 0.07567\ \mathrm{kg}$$

$$\mathrm{n(CaCl_2\ in\ 100\ mL\ solution)} = \frac{60.93}{40.08 + 2 \times 35.45} = \frac{60.93}{110.98} = 0.5490\ \mathrm{mol}$$

$$\mathrm{molality(saturated\ CaCl_2\ solution)} = \frac{0.5490\ \mathrm{mol}}{0.07567\ \mathrm{kg}} = 7.255\ \mathrm{mol\ kg^{-1}}$$

$$T_F(solution) = T_F(pure\ solvent) - iK_F m$$

$$T_F(solution) = 0 - 3 \times 1.86 \times 7.255 = -40.5\ °\mathrm{C}$$

ii. What mass of calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) needs to be added to 100 mL of water to make a saturated solution? (Hint: consider the water present in the added solid.)

1 mol of $CaCl_2 \cdot 6H_2O$ liberates 6 mol of H_2O, i.e. 6 × 18.016 = 108.096 g of H_2O

From (j), the molality of saturated $CaCl_2$ solution is 7.255 mol kg^{-1}.

Dissolving 7.255 mol of $CaCl_2 \cdot 6H_2O$ liberates 7.255 × 108.096 = 784 g of H_2O

So to prepare a saturated $CaCl_2$ solution, we need to add 7.255 mol of $CaCl_2 \cdot 6H_2O$ to 1000 – 784.3 = 215.7 g H_2O.

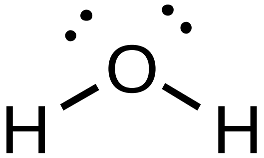
From (j), m(100 mL water) = 100 g.We can prepare a saturated $CaCl_2$ solution by dissolving 7.255 mol of $CaCl_2 \cdot 6H_2O$ in 215.7 g of H_2O, so if we have 100 g H_2O, we need: $\frac{100}{215.7} \times 7.255 \text{ mol} = 3.363 \text{ mol}$

So m($CaCl_2 \cdot 6H_2O$ required) = 3.36 × 219.076 = 737 g

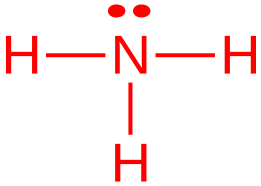
Question 17

The properties of different compounds can be used to separate or distinguish them in a mixture. These properties can often be predicted by looking at molecular structures.

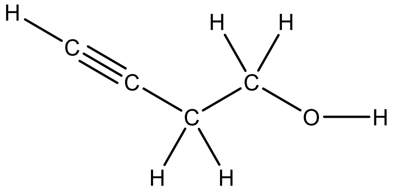
An example of a Lewis structure is shown below for water.

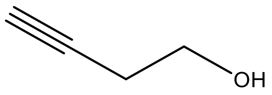


(a) Draw Lewis structures for the following molecules:

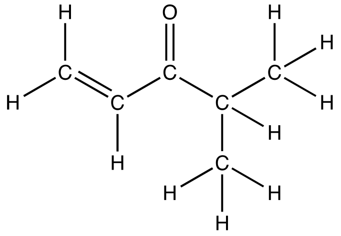
(i) hydrogen gas (H_2)	$H-H$
(ii) nitrogen gas (N_2)	$:N\equiv N:$
(iii) ammonia (NH_3)	

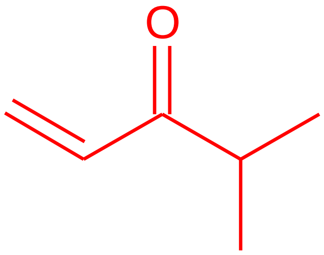
The structural formula of organic (carbon-based) molecules can be represented by skeletal formula notation. In this notation, bonds are represented by lines, with carbon atoms located at the end of each line segment or meeting point of line segments. Hydrogen atoms connected to carbon atoms are implied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





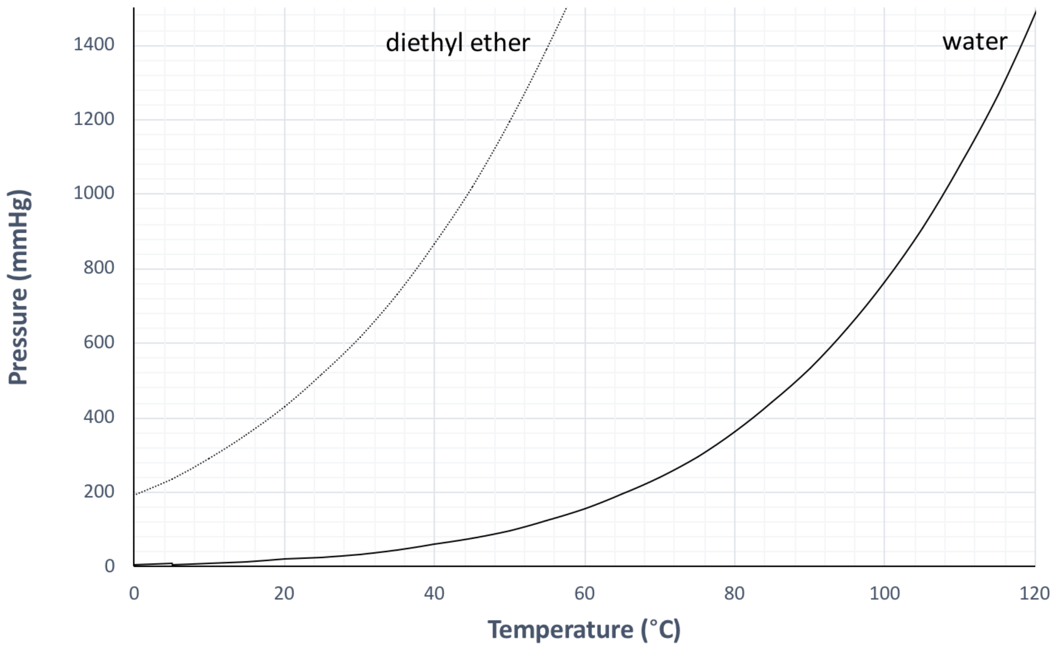
(b) Draw the skeletal formula for the following structure:





When a compound is in a liquid state, at any given time, some fraction of the molecules have enough kinetic energy to evaporate into the gas phase. The pressure of this gas phase at a given temperature is known as vapour pressure.

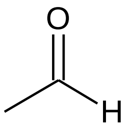
The boiling point is the temperature at which the vapour pressure of the compound is equal to atmospheric pressure. The graph below shows the relationship between vapour pressure and temperature for water and diethyl ether.

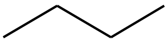


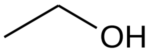
(c) If water boils at 100 °C under normal pressure, what is the boiling point of diethyl ether under the same conditions?

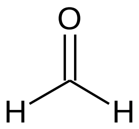
36 °C

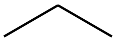
The structures of some simple compounds are shown below.

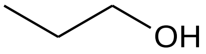

acetaldehyde

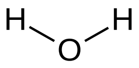

butane


ethanol


formaldehyde


propane


propan-1-ol


water

Substances that have lower boiling points tend to have higher vapour pressures at any given temperature.

(d) For each of the following pairs of compounds, tick the one with the **higher** vapour pressure at 20 °C. Explain your reasoning, **identifying the relevant intermolecular forces** involved.

i. Higher vapour pressure: ☐ butane ☒ propane

Reasoning:

The dispersion forces between propane molecules are weaker than the dispersion forces between butane molecules, hence propane has a higher vapour pressure than butane.

ii. Higher vapour pressure: ☒ acetaldehyde ☐ ethanol

Reasoning:

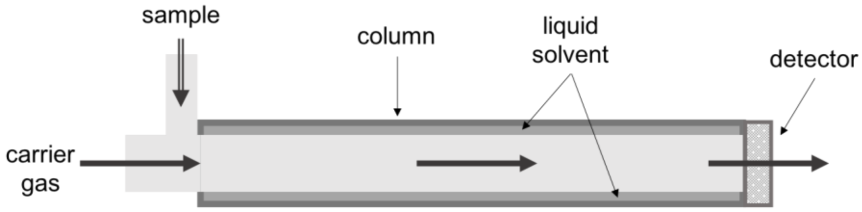
The dipole-dipole interactions between acetaldehyde molecules are weaker than the hydrogen bonds between ethanol molecules, hence acetaldehyde has a higher vapour pressure than ethanol.

The differences in vapour pressure of different compounds can be used to separate them. One such technique that uses this is gas chromatography.

(e) Rank the above compounds from the previous figure in terms of their vapour pressure at 20 °C. Three boxes have been filled out for you.

(high vapour pressure) 1	propane
2	formaldehyde
3	butane
4	acetaldehyde
5	ethanol
6	propan-1-ol
7 (low vapour pressure)	water

To analyse a sample by gas chromatography, the sample is first heated, and the vapours produced are transferred to one end of a tube known as the column. The column is lined with a liquid solvent, and a carrier gas flows through the tube. This allows compounds to travel through the column in the gaseous phase, eventually reaching a detector at the other end.



The length of time a substance spends in the column is known as its **retention time**.

The higher a substance's vapour pressure, the longer it spends in the gas phase (rather than dissolved in the liquid solvent), so the faster it proceeds through the column.

(f) If a sample of butane and formaldehyde were run in gas chromatography, which sample would have the **longer** retention time, assuming that they interact identically with the liquid solvent?

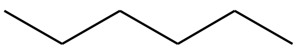
☒ butane ☐ formaldehyde

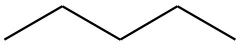
(g) For each row, select the class of compound expected to have the **longer** retention time with the given liquid solvent, assuming that we are comparing polar and non-polar compounds with similar vapour pressures.

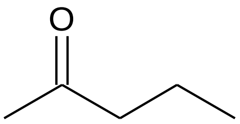
Liquid solvent polarity	**Longer** retention time		
i. Polar solvent	☒ Polar compound	☐ Non-polar compound	☐ Neither
ii. Non-polar solvent	☐ Polar compound	☒ Non-polar compound	☐ Neither

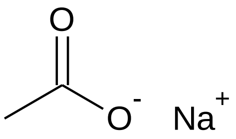
The detector produces a signal when the gaseous compounds pass by. The resulting graph is called a chromatogram, showing the time and size of the signals from the detector.

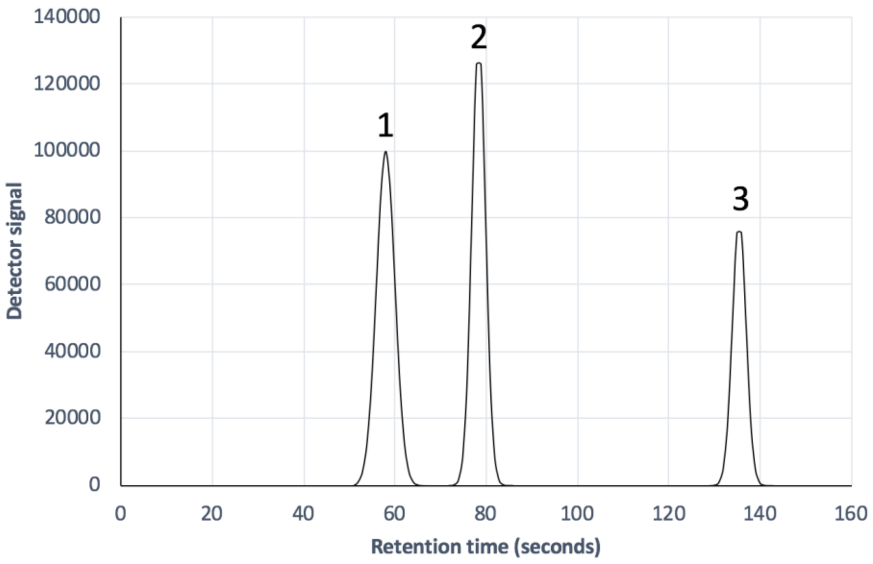
Gas chromatography of a sample containing the following four compounds was performed using a **polar liquid solvent**. The resulting chromatogram is shown on the next page.


hexane


pentane


pentan-2-one


sodium acetate



(h) Assign the compounds to the peaks observed. Note: one of the four compounds does not appear.

	Peak 1	Peak 2	Peak 3
Compound	pentane	hexane	pentan-2-one

(i) Which of the four compounds did not appear on the chromatogram? Why?

Sodium acetate. There are strong electrostatic interactions between the sodium and acetate ions in its crystal lattice, hence sodium acetate has a much smaller vapour pressure than the other (molecular) compounds.

(j) If the liquid solvent was non-polar, can the order of compound peaks still be predicted? If yes, what would the order be? If no, why not?

No. The non-polar substances (with the lowest vapour pressures and shortest retention times) will now have increased retention times due to increased interaction with the non-polar solvent. The retention time for each molecule will depend on which of these factors is more important.

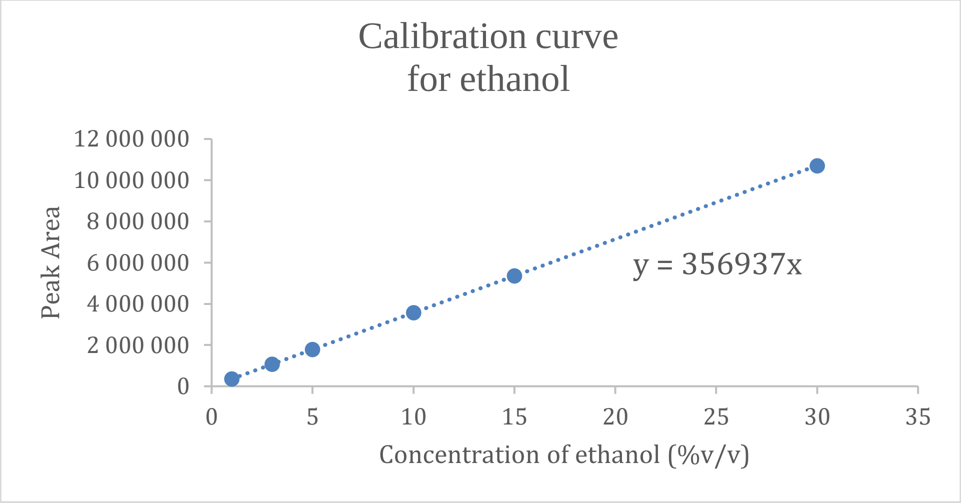
The conditions under which gas chromatography is performed can be optimised to improve the quality of the chromatogram. For example, one common issue is peak separation in the chromatogram, which is important to differentiate compounds. Peak separation is defined as the difference in retention time between two peaks.

(k) Tick the box corresponding to the conditions which would change peak separation.

Condition	**Peak separation**		
a) Increased flow rate of carrier gas	☒ Decrease	☐ No change	☐ Increase
b) Increased temperature	☒ Decrease	☐ No change	☐ Increase
c) Increased column length	☐ Decrease	☐ No change	☒ Increase

In addition to separating and identifying compounds, gas chromatography can be used to determine the concentration of a compound in an unknown sample. In general, the area of the peak corresponding to a particular compound in a chromatogram is proportional to the concentration of that compound in the sample.

To do this, a calibration curve must first be produced by analysing a series of solutions of known concentration. A calibration curve for aqueous solutions of ethanol is shown below, including the equation of the line of best fit.



An ethanol-water mixture of unknown concentration is analysed, and the corresponding chromatogram has a single peak with an area of 5.31 × 10^6.

(l) Determine the percentage by volume of ethanol in the unknown sample.

$$\%(v/v) = \frac{5.31\times 10^6}{356937} = 14.9\%$$

(m) Given that ethanol has a density of 0.789 g mL^{-1}, calculate the concentration of ethanol (in mol L^{-1}) in the unknown ethanol-water mixture. (If you do not get an answer to the previous question, assume that the percentage by volume of ethanol in the unknown sample is 14.0%(v/v)).

$$m(ethanol\ in\ 1\ \mathrm{L}) = 0.789\ \mathrm{g\ mL^{-1}} \times 14.9\ \mathrm{g/100\ mL} \times\ 10 = 117\ \mathrm{g}$$

$$n(ethanol) = \frac{117\ \mathrm{g}}{46.068\ \mathrm{g\ mol^{-1}}} = 2.55\ \mathrm{mol}$$

So [ethanol] = 2.55 mol L^{-1}

Often, samples contain many different compounds besides the compound being analysed. These additional compounds are termed the matrix. The matrix can have a significant effect on gas chromatography, and using standard solutions with a different matrix to the sample being analysed can lead to errors. One strategy for overcoming these "matrix effects" is standard addition. The premise of this technique involves ensuring that the standard solutions contain the same matrix present in the sample to be analysed.

Petrol is a complex mixture of non-polar hydrocarbons, and ethanol is sometimes added to improve combustion. Standard addition can be used to determine the concentration of ethanol by gas chromatography.

Five samples of petrol are taken, and a different volume of ethanol is added to each, as shown in the following table. Each sample is then diluted with hexane to a final volume of 1.2 mL.

Sample Code	Volume petrol (mL)	Volume ethanol (mL)	Concentration of added ethanol (%(v/v))
A	1.00	0.00	0.00
B	1.00	0.05	4.17
C	1.00	0.10	8.34
D	1.00	0.15	12.5
E	1.00	0.20	16.7

(n) Complete the table by calculating the concentration of ethanol added to sample C (working space is provided below).

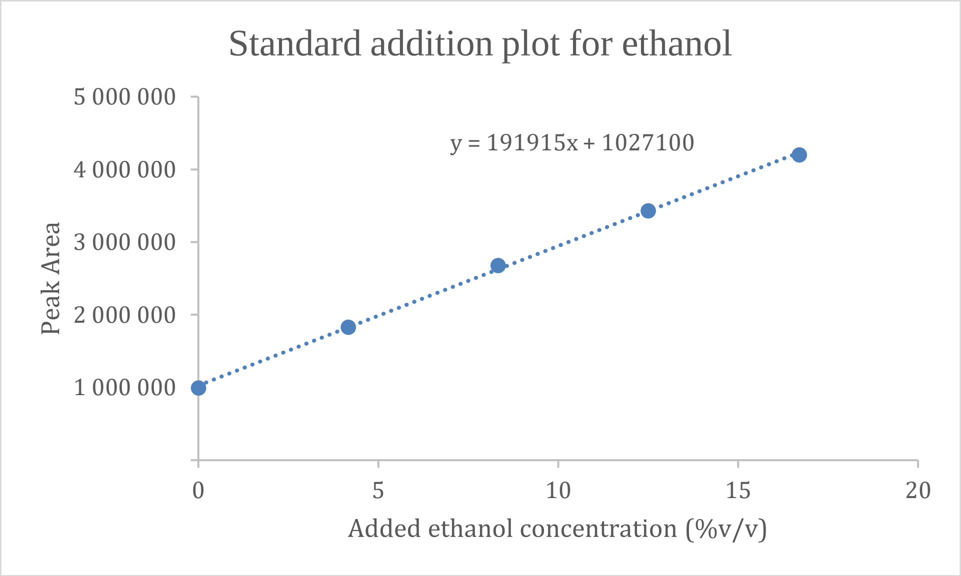
(o) Explain why each sample is diluted to constant volume.

- makes calculations easier
- allows for the samples to be compared directly, since the unknown is of constant concentration across them

(p) Would water be an appropriate solvent to dilute the samples with, instead of hexane? Explain why or why not.

No, as water is not miscible with the non-polar hydrocarbons in petrol.

Samples A – E are analysed by gas chromatography as before, and the ethanol peak areas are plotted against the concentration of added ethanol. The plot is shown below, again including the equation of the line of best fit.



(q) Calculate the percentage by volume of ethanol in the petrol sample.

Peak area for 0% added ethanol = 1027100

$$[ethanol] = \frac{1027100}{191915} \times \frac{1.2}{1.0} = 5.35\%$$

Question 18

The energy of a photon of light is given by the following equation:

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

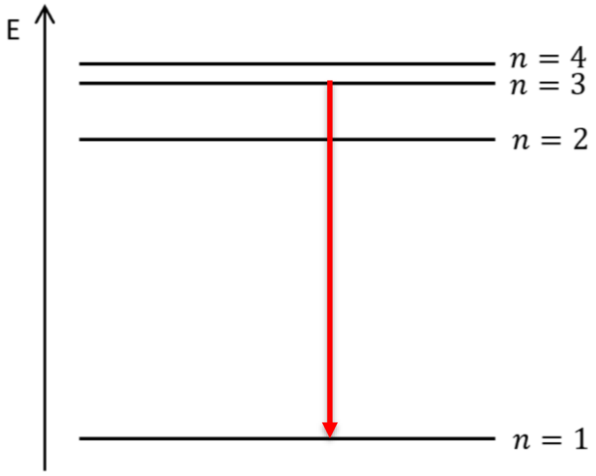
- E is the energy of the photon (in J)
- λ is the wavelength of light (in m)
- h is Planck's constant (6.626×10^{-34} J s)
- c is the speed of light (2.998×10^{8} m s^{-1})

(a) Calculate the energy of a photon of light with wavelength 500.0 nm (500.0×10^{-9} m).

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{500.0 \times 10^{-9}} = 3.973 \times 10^{-19}\ \mathrm{J}$$

The Bohr Model of the atom describes the different discrete energy levels that electrons can occupy. For example, the energy levels of the hydrogen atom are shown in the diagram below. An electron can change energy levels by absorbing or emitting a photon of light that has the same energy as the energy difference between the two levels. Atoms *fluoresce* when they move from an excited energy level to the *ground state* (i.e. lowest) energy level, releasing energy in the form of light.

(b) In the hydrogen atom, an electron absorbs a photon and moves from the $n = 2$ to $n = 3$ energy level, and then fluoresces. Draw an arrow that represents the transition of the electron during **fluorescence** on the energy diagram below.



(c) Will the wavelength of the photon emitted by fluorescence be higher, lower or the same as the photon absorbed by the electron initially? Briefly explain your answer.

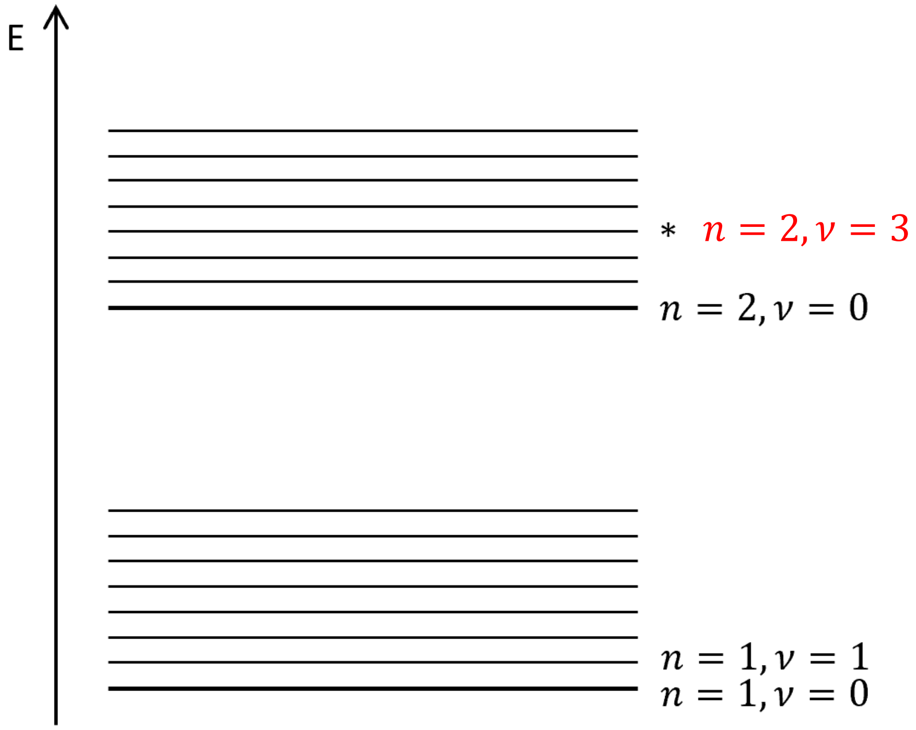
The energy difference is greater for fluorescence, so the wavelength will be lower.

Atoms are not the only species that can fluoresce. Molecules can fluoresce as well, however their energy diagrams are far more complex than for atoms:

- Molecules contain both electronic energy levels (like those in the hydrogen atom examined above) and vibrational energy levels.
- The overall energy of the molecule is the sum of the electronic and vibrational energies.
- The energy gap between vibrational energy levels is much smaller than the gap between electronic energy levels.
- A molecule can be in any combination of excited electronic and vibrational states.

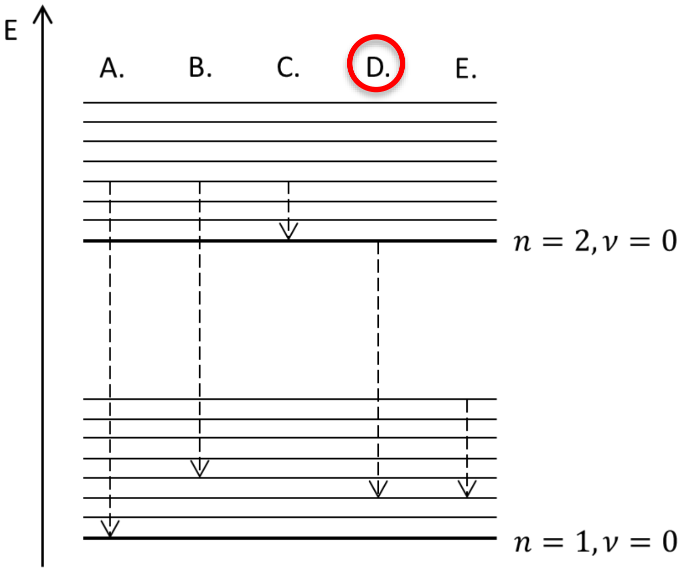
Each of these energy levels can be represented as a line on a *Jablonski* diagram, shown below, and is labelled based on the electronic energy level (labelled from the ground state up by $n = 1, 2, 3, \ldots$) and the vibrational energy level (labelled from the ground state up by $\nu = 0, 1, 2, \ldots$).
For example, in the diagram below, the bold lines represent the electronic energy levels ($n = 1, 2, 3, \ldots$) in the lowest vibrational energy level ($\nu = 0$). The ground state of the entire system is labelled $n = 1, \nu = 0$.

(d) Write the corresponding n and ν numbers next to the energy level labelled $*$ below. Some other energy levels have been labelled for your convenience.



Molecules can also move between different vibrational energy levels by emitting energy as heat, without emitting photons. Typically, if a molecule is in a state with $\nu \neq 0$, it will quickly release heat through this process to reach the $\nu = 0$ state. After this, a molecule can *fluoresce* by releasing a photon of light, ending up in a state with $n = 1$, before again releasing heat to return it to the $n = 1, \nu = 0$ state.

(e) One of the following transitions on the Jablonksi diagram below corresponds to the release of a photon from a molecule that is fluorescing, as described in the paragraph above. Circle the letter corresponding to this transition.



A molecule initially in the ground state absorbs a photon of light with a wavelength of 350.0 nm (350.0×10^{-9} m) and undergoes fluorescence. In the process, it releases 1.351×10^{-19} J of heat to the environment.

(f) Calculate the wavelength of the emitted photon of light.

Recall from (a) that the energy of a photon of light is given by the following equation:

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

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{350.0 \times 10^{-9}} = 5.676 \times 10^{-19}\ \mathrm{J}$$

$$E_{fluorescence} = 5.676 \times 10^{-19}\ \mathrm{J} - 1.351 \times 10^{-19}\ \mathrm{J} = 4.325 \times 10^{-19}\ \mathrm{J}$$

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{4.325 \times 10^{-19}} = 4.593 \times 10^{-7}\ \mathrm{m} = 459.3\ \mathrm{nm}$$

Another process that a molecule can undergo is internal conversion, which allows the molecule to decay from the $n = 2, \nu = 0$ energy level to the $n = 1, \nu = 0$ energy level by emitting energy only as heat, without releasing a photon. This process occurs more frequently when the molecule concerned collides more frequently with other molecules. We define the quantum yield, Φ, of a molecule as the number of photons emitted in fluorescence divided by the number of photons absorbed.

(g) What is the range of possible values for Φ?

0-1

(h) As temperature increases, will Φ increase or decrease? *Briefly explain your answer.*

As temperature increases, the molecules will collide more frequently with each other, so the rate of internal conversion increases. Accordingly, Φ decreases.

(i) 200.0 J of light with wavelength 700 nm (700.0×10^{-9} m) is shone onto a material. Calculate the number of photons in the light.

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{700.0 \times 10^{-9}} = 2.838 \times 10^{-19}\ \mathrm{J}$$

$$\text{Number of photons} = \frac{200\ \mathrm{J}}{2.838 \times 10^{-19}\ \mathrm{J}} = 7.048 \times 10^{20}\ \text{photons}$$

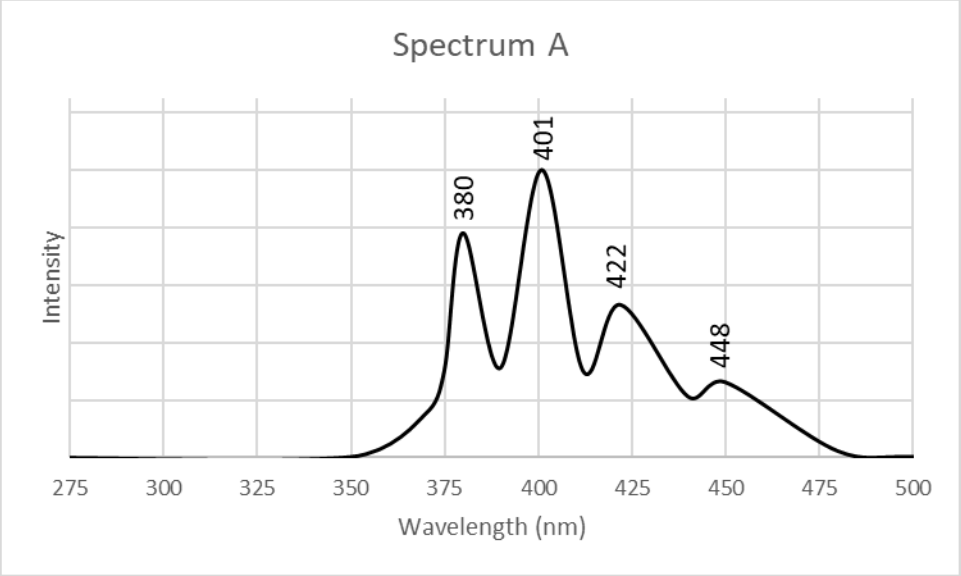
(j) The quantum yield of the event is 0.993954. Calculate the number of photons emitted by fluorescence.

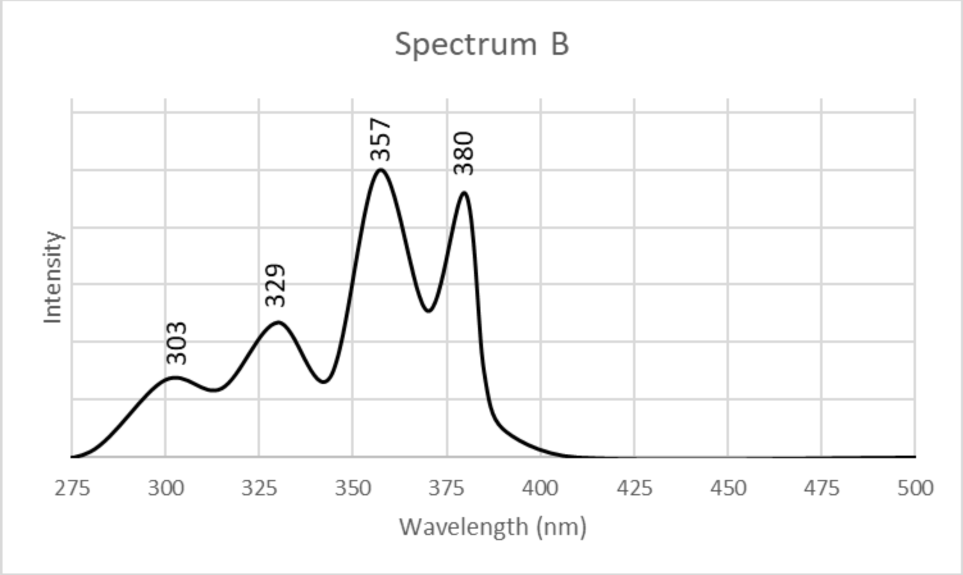
$$\text{Number of photons} = 0.993954 \times 7.048 \times 10^{20} = 7.005 \times 10^{20}\ \text{photons}$$

The fluorescence of a molecule or atom can be measured by exciting a sample with light of a wavelength λ_{excite} and detecting the intensity of light that the sample emits by fluorescence at wavelength λ_{detect}.

There are two different ways of displaying this data: in an **excitation** spectrum, the excitation wavelength λ_{excite} is varied and the detection wavelength λ_{detect} is held constant; in an **emission** spectrum, the excitation wavelength is λ_{excite} held constant and the detection wavelength λ_{detect} is varied. In each case, the spectrum is presented as a graph of intensity (on the y-axis) vs varied wavelength (λ_{excite} or λ_{detect}) on the x-axis.

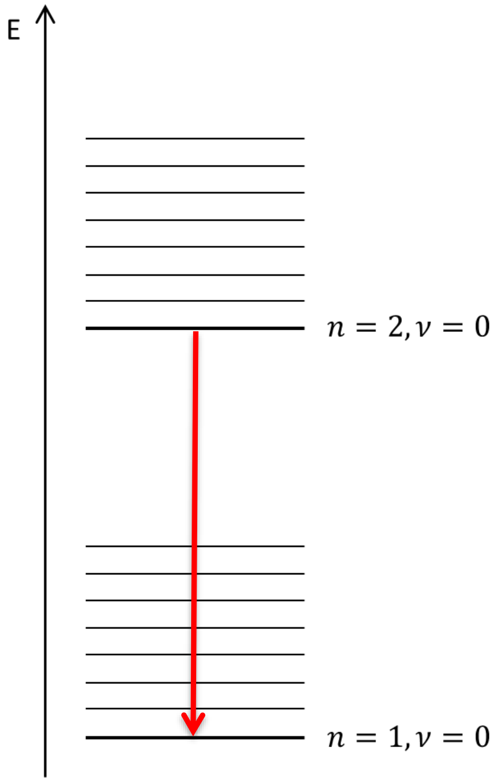
The emission and excitation spectra of a molecule are provided below (1 nm = 1 × 10^{-9} m).



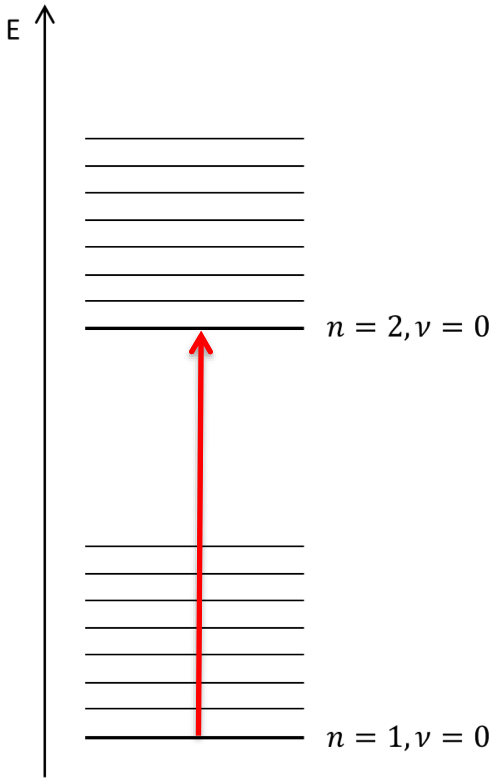


(k) On the Jablonski diagrams below, draw the transition corresponding to the following peaks:

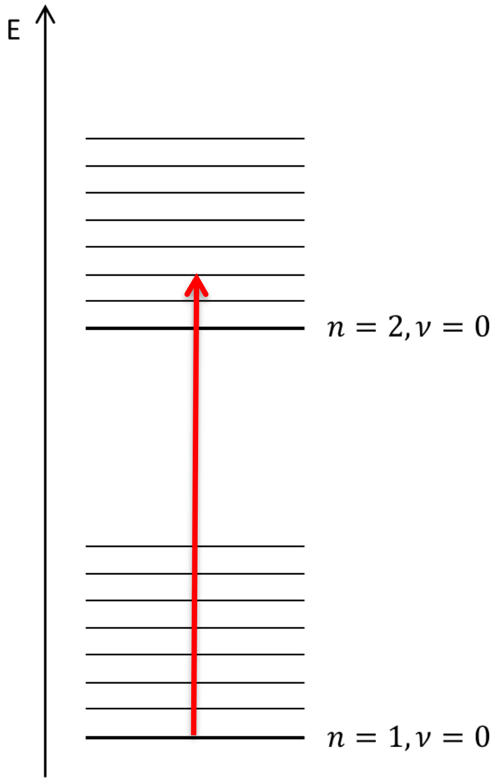
i. 380 nm in Spectrum **A**.



ii. 380 nm in Spectrum **B**.



iii. 329 nm in Spectrum **B**.



(l) The emission spectrum of the molecule as shown above was produced at an excitation wavelength of $\lambda_{\text{excite}} = 380$ nm. What would happen to the emission spectrum if the excitation wavelength was changed to $\lambda_{\text{excite}} = 329$ nm? (Circle all that apply)

A. The spectrum will be shifted towards larger wavelengths.

B. The spectrum will be shifted towards shorter wavelengths.

C. The spectrum will be shifted to higher intensities.

D. The spectrum will be shifted to lower intensities.

E. There will be no change to the spectrum.

(m) Calculate the energy difference between $n = 1, v = 1$ and $n = 2, v = 3$ energy levels.

The $n = 1, v = 0$ to $n = 2, v = 3$ transition occurs at 303 nm in Spectrum B.

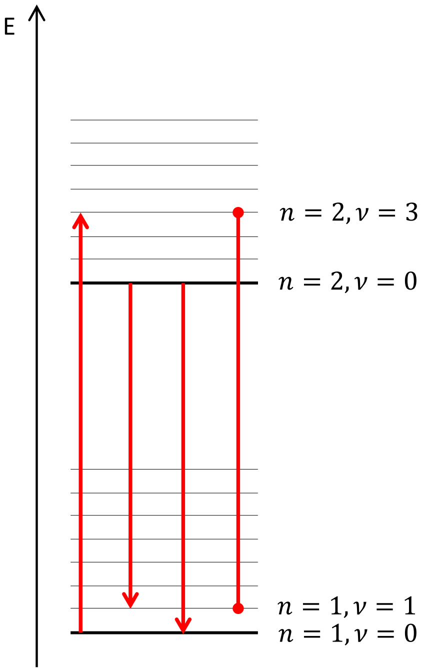
$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{303.0 \times 10^{-9}} = 6.556 \times 10^{-19}\ \text{J}$$

The $n = 2, v = 0$ to $n = 1, v = 1$ transition occurs at 401 nm in Spectrum A.

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{401.0 \times 10^{-9}} = 4.954 \times 10^{-19}\ \text{J}$$

The $n = 1, v = 0$ to $n = 2, v = 0$ transition occurs at 380 nm in Spectrum A.

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{380.0 \times 10^{-9}} = 5.228 \times 10^{-19}\ \text{J}$$



So for the $n = 1, v = 1$ to $n = 2, v = 3$ transition:

$$E = 6.556 \times 10^{-19}\ \text{J} + 4.954 \times 10^{-19}\ \text{J} - 5.228 \times 10^{-19}\ \text{J} = 6.282 \times 10^{-19}\ \text{J}$$

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Integrity of Competition

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