

## 55 ${ }^{\text {th }}$ INTERNATIONAL

## CHEMISTRY OLYMPIAD

## 2023

## UK Round One

## STUDENT QUESTION BOOKLET

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}

- The time allowed is two hours.
- Attempt all five questions.
- Write your answers in the student answer booklet.
- Write only the essential steps of your calculations in the answer booklet.
- Always give the appropriate unit and number of significant figures.
- The final pages of this question booklet include a copy of the periodic table and some useful physical constants and formulae.
- Do NOT write anything in the right-hand margin of the answer booklet.
- The marks available for each question are shown below. These may be helpful when dividing your time between questions.

| Question | 1 | 2 | 3 | 4 | 5 | Total |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks <br> Available | 7 | 20 | 18 | 20 | 20 | 85 |

Some of the questions will contain material you will not be familiar with. However, you should be able to work through the problems by applying the skills you have learnt as a chemist. There are different ways to approach the tasks - even if you cannot complete certain parts of a question, you may find later parts straightforward.

## Q1 This question is about rocket fuels

The NASA Artemis uses liquid oxygen (LOX) and liquid hydrogen fuel sources. These fuels ensure the rocket mass is low and alongside their large enthalpy change of combustion enable a rocket to overcome gravity.

In 2022 there were a number of failed launch attempts due to a leak in the hydrogen fuel.


In the rocket engine the fuel components are first vaporised before reacting to form water.
(a) Write an equation for the reaction between gaseous hydrogen and oxygen.

The bond enthalpy of $\mathrm{H}-\mathrm{H}$ is $432 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and the average bond enthalpy of $\mathrm{O}-\mathrm{H}$ is $460 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Assume the enthalpy change for the reaction in part (a) is -241 kJ per mole of hydrogen gas.
(b) Calculate the bond enthalpy of the $\mathrm{O}=\mathrm{O}$ bond in $\mathrm{kJ} \mathrm{mol}^{-1}$.

The density of liquid hydrogen is $0.071 \mathrm{~g} \mathrm{~cm}^{-3}$.
(c) (i) Calculate the number of moles of hydrogen molecules in $1 \mathrm{dm}^{3}$ of liquid hydrogen.
(ii) Calculate the energy released when the gas formed from $1 \mathrm{dm}^{3}$ of liquid hydrogen is combusted.

SpaceX's aim to colonise Mars leads to the choice of methane as an alternative to hydrogen. Methane can be formed using Mars' natural resources via the Sabatier process as the atmosphere of the planet is made up of $95.3 \%$ carbon dioxide by volume. In the Sabatier process methane and water are formed from the reaction of carbon dioxide and hydrogen gas.
(d) (i) Write an equation for the Sabatier process.
(ii) State the oxidation number of carbon and hydrogen in the reactants and products.

SpaceX has recently developed a new engine, the Raptor, that uses liquid methane and LOX. Energy is required to turn them into the gaseous phase before they react. The enthalpy change of vaporisation of methane is $+8.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and the enthalpy change of vaporisation of oxygen is $+6.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$. The enthalpy change of combustion of methane, shown below, is $-890.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$.

$$
\mathrm{CH}_{4(\mathrm{~g})}+2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{CO}_{2(\mathrm{~g})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}
$$

(e) Calculate the enthalpy change of reaction, in kJ , when one mole of liquid methane reacts with liquid oxygen to form gaseous carbon dioxide and gaseous water.

Q2 This question is about electronegativity, bonding and structure

2022 was the $90^{\text {th }}$ anniversary of Linus Pauling proposing the concept of electronegativity. His book The nature of the chemical bond is considered the most influential chemistry book of $20^{\text {th }}$ century, and he was awarded the 1954 Nobel prize in chemistry for his work.
Electronegativity, $\chi$, is a measure of the ability of an atom to attract a pair of electrons in a covalent bond.


Pauling used thermodynamic data to calculate the difference in electronegativity between two atoms A and B. All electronegativity values are positive with no units, and atom $A$ has a higher electronegativity than atom $B$.

$$
\chi_{A}-\chi_{B}=0.102 \sqrt{\mathrm{~B}_{d}(A B)-\frac{\mathrm{B}_{d}(A A)+\mathrm{B}_{d}(B B)}{2}}
$$

$B_{d}$ represents the bond dissociation energies, in $\mathrm{kJ} \mathrm{mol}^{-1}$, of the $\mathrm{A}-\mathrm{A}, \mathrm{B}-\mathrm{B}$ and $\mathrm{A}-\mathrm{B}$ bonds.
(a) Calculate the difference in electronegativity between Cl and H , given that

$$
\mathrm{B}_{d}\left(\mathrm{H}_{2}\right)=432 \mathrm{~kJ} \mathrm{~mol}^{-1}, \mathrm{~B}_{d}\left(\mathrm{Cl}_{2}\right)=244 \mathrm{~kJ} \mathrm{~mol}^{-1} \text { and } \mathrm{B}_{d}(\mathrm{HCl})=427 \mathrm{~kJ} \mathrm{~mol}^{-1} .
$$

As this method gives a difference in electronegativity it is necesssary to choose a reference point in order to gain values for individual elements. Pauling originally chose hydrogen as the reference, with a value of 2.20 .
(b) Using this reference and your knowledge of trends in electronegativity in the periodic table, calculate the electronegativity value for chlorine.

Other scientists suggested other methods to determine the electronegativity of an element, which can be adjusted to be consistent with those determined by Pauling. Robert Mulliken calculated the value from the first ionisation energy $\left(\mathrm{E}_{i}\right)$ and first electron affinity ( $\mathrm{E}_{e a}$ ) of an atom.

$$
\chi_{A}=0.00197\left(\mathrm{E}_{i}+\mathrm{E}_{e a}\right)+0.19
$$

In this equation $\mathrm{E}_{i}$ and $\mathrm{E}_{e a}$ are in $\mathrm{kJ} \mathrm{mol}^{-1}$, although $\mathrm{E}_{i}$ is often measured in electronvolts (eV). $1 \mathrm{eV}=96.49 \mathrm{~kJ} \mathrm{~mol}^{-1}$.
(c) Calculate the adjusted Mulliken electronegativity of nitrogen given that $\mathrm{E}_{i}(\mathrm{~N})=14.5 \mathrm{eV}$ and $\mathrm{E}_{e a}(\mathrm{~N})=6.80 \mathrm{~kJ} \mathrm{~mol}^{-1}$.

Electronegativity has been used by scientists to rationalise differences in bonding.
Van Arkel-Ketelaar triangles allow a simple visualisation of the degrees of ionic, metallic, and covalent bonding found in a binary compound (AB).

In the triangle the average electronegativity of $A$ and $B$, $\bar{\chi}$, is plotted against the difference in electronegativity, $\chi_{A}-\chi_{B}$.


The electronegativities of ten elements are given in the table below.

| Element | H | C | O | F | Al | P | Si | Cs | Hg | Br |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Electronegativity | 2.20 | 2.55 | 3.44 | 3.98 | 1.61 | 2.19 | 1.90 | 0.79 | 2.00 | 2.96 |

Consider the van Arkel-Ketelaar plot below.

(d) Identify the letter in the answer booklet which represents the position of the following substances.
(i) AIP
(iv) HgO
(ii) CsH
(v) $\quad \mathrm{SiC}$
(iii) BrF
(e) Identify which of the five substances in part (d) displays the greatest degree of metallic character in its bonding.
(f) Three substances, $\mathrm{Cs}, \mathrm{CsBr}$, and CO have been marked on the van Arkel-Ketelaar plot below. Based on your knowledge of trends in electronegativity in the periodic table, identify which point A-P describes where the following substances would be located.
(i) CsCl
(iii) GaN
(ii) NaK


Boron nitride sits in a central position within the van Arkel-Ketelaar triangle exhibiting elements of all three bonding types.

It can be formed by reaction (1) of boric acid $\left(\mathrm{H}_{3} \mathrm{BO}_{3}\right)$ and ammonia.
It can also be formed by reaction (2) of boron trioxide ( $\mathrm{B}_{2} \mathrm{O}_{3}$ ), nitrogen, and calcium hexaboride $\left(\mathrm{CaB}_{6}\right)$, which produces calcium oxide as a by-product.

(g) (i) Write the equation of reaction (1).
(ii) Write the equation of reaction (2).

Boron nitride has several crystalline forms. This includes a cubic form (c-BN), a hexagonal layered structure similar to graphite ( $\mathrm{h}-\mathrm{BN}$ ), and a wurtzite structure ( $\mathrm{w}-\mathrm{BN}$ ). The different forms can be interconverted by changing the pressure and temperature. Diagrams of the three different structures are shown below.


Unit cell of c-BN


Layer structure of h-BN


Unit cell of w-BN
The unit cell of $c-B N$ is cubic, with cell parameters of $a=3.63 \AA$.

The unit cell of $\mathrm{h}-\mathrm{BN}$ is a right regular hexagonal prism, with cell parameters of $\mathrm{b}=1.47 \AA$ And $\mathrm{c}=6.66 \AA$.

The unit cell of $w-\mathrm{BN}$ is a right rhombic prism, with cell parameters of $d=2.54 \AA$ and $e=3.63 \AA$ and interior angles of $60^{\circ}$ and $120^{\circ}$.


Unit cell of h-BN

You may find it helpful to refer to the physical constants and formulae page for useful equations for the next part of this question.
(h) (i) Calculate the volume of the $\mathrm{c}-\mathrm{BN}$ unit cell in $\mathrm{cm}^{3}$.
(ii) Calculate the density of $\mathrm{c}-\mathrm{BN}$ in $\mathrm{g} \mathrm{cm}^{-3}$.
(iii) Calculate the volume of the $\mathrm{h}-\mathrm{BN}$ unit cell in $\mathrm{cm}^{3}$.
(iv) Calculate the density of $\mathrm{h}-\mathrm{BN}$ in $\mathrm{g} \mathrm{cm}^{-3}$.
(v) Calculate the number of B atoms and N atoms in the unit cell of $\mathrm{w}-\mathrm{BN}$.

## Q3 This question is about amino acid complexes

Copper bisglycinate (or copper(II) glycinate) is used as a dietary supplement for copper. It is one of many metal coordination complexes of amino acids.

Amino acids have the general structure shown here, and contain an acidic carboxyl group and a basic amino group. The R substituent can contain a range of different functional groups.


The essential amino acid isoleucine ( $\mathrm{R}=\mathrm{CH}\left(\mathrm{CH}_{3}\right) \mathrm{CH}_{2} \mathrm{CH}_{3}$ ) has a $\mathrm{p} K_{\mathrm{a}}$ value of 9.60 , and its hydrochloride salt has a $\mathrm{p} K_{\mathrm{a}}$ value of 2.36.
(a) (i) Draw the skeletal structure of isoleucine in an aqueous solution at $\mathrm{pH}=2$.
(ii) Draw the skeletal structure of isoleucine in an aqueous solution at $\mathrm{pH}=11$.

The isoelectric point is the pH at which the overall charge in a molecule is zero.
(b) (i) Draw the skeletal structure of isoleucine at the isoelectric point.
(ii) Calculate the isoelectric point of isoleucine.

To confirm the $\mathrm{p} K_{\mathrm{a}}$ values, a $50 \mathrm{~cm}^{3}$ sample of a $0.025 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of isoleucine hydrochloride is titrated with $40 \mathrm{~cm}^{3}$ of a $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of NaOH .
(c) Identify in the answer booklet which of the following titration curves best describes the titration.







When the amino acid is fully deprotonated, the carboxylate ion of the amino acid,
$\mathrm{RCH}\left(\mathrm{NH}_{2}\right) \mathrm{COO}^{-}$, is able to coordinate to metal ions as a bidentate ligand through the nitrogen and carboxylate oxygen as shown on the right.

(Other ligands on metal ion M and charges not shown)
Copper(II) glycinate is formed when the amino acid glycine $(\mathrm{R}=\mathrm{H})$ is added to an aqueous solution of copper(II) ethanoate. A blue precipitate of the square pyramidal copper(II) glycinate $\left(\mathrm{C}_{4} \mathrm{H}_{10} \mathrm{CuN}_{2} \mathrm{O}_{5}\right)$ is formed which contains one coordinated water molecule.
When heated, this precipitate undergoes isomerism between different stereoisomers, however the water molecule remains in the axial position as shown.

(d) Complete the structures of the stereoisomers of copper(II) glycinate in the answer booklet, representing the bidentate ligand as shown on the right.

The amino acid methionine ( $\mathrm{R}=\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{SCH}_{3}$ ) forms a methionine anion ( $\mathrm{Mt}^{-}$) when deprotonated. In octahedral metal complexes $\left(\mathrm{MMt}_{3}\right)$, assume the methionine anion $\left(\mathrm{Mt}^{-}\right)$, acts as a bidentate ligand through the nitrogen and carboxylate oxygen.
(e) Complete the structures of the stereoisomers of $\mathrm{MMt}_{3}$ in the answer booklet, representing the bidentate ligand as shown on the right.

If the stereoisomer is chiral, you should only draw one enantiomer.

In an octahedral transition metal complex, the d-orbitals are not degenerate (of equal energy) but split into two levels.

split d-orbitals

When d-electrons fill the orbitals they can take one of two arrangements, described as high spin or low spin, depending on the number of $d$-electrons.
In the high spin arrangement, all the d-orbitals are filled singularly with electrons of parallel spin before any electrons are paired.
In the low spin arrangement, the lower energy d-orbitals are filled completely before any electrons fill the higher energy d-orbitals.
$\mathrm{FeMt}_{3}$ is an $\mathrm{Fe}(\mathrm{III})$ compound. The iron ion has a charge of +3 and there are five d-electrons to fill the diagram, leading to the high spin and low spin arrangements below.


High spin arrangement for Fe (III)


Low spin arrangement for Fe (III)

The high and low spin arrangements can be differentiated between by calculating the theoretical spin magnetic moment ( $\mu$ ) of the complex (measured in units of Bohr magnetons, BM ) and comparing it to experimental values.

$$
\mu=\sqrt{n(n+2)}
$$

where $n=$ number of unpaired electrons
$\mathrm{RhMt}_{3}$ is an octahedral Rh (III) complex where each $\mathrm{Mt}^{-}$ligand makes two bonds to the metal. $\mathrm{CuMt}_{2}$ is an octahedral $\mathrm{Cu}(\mathrm{II})$ complex where each $\mathrm{Mt}^{-}$ligand makes three bonds to the metal.
(f) Complete in the answer booklet the following information for both $\mathrm{RhMt}_{3}$ and $\mathrm{CuMt}_{2}$ :

- The number of d-electrons in the outer shell of the metal ion.
- Fill in the electrons in the d-orbital diagrams. If there is the possibility of high and low spin arrangements draw them both. Otherwise just fill in the one possible arrangement.
- For each electronic arrangement drawn calculate the spin magnetic moment of that complex.

The spin magnetic moment observed experimentally for Fe (III) complex $\mathrm{FeMt}_{3}$ is 5.63 BM .
(g) Determine whether the metal ion in $\mathrm{FeMt}_{3}$ is high spin or low spin.

Q4 This question is about vaping

From April 2019 to February 2020 there were 68 deaths from Vaping Associated Lung Injury (VALI) in the USA. The majority of the vape liquids linked to VALI cases at the time contained vitamin E acetate. When ingested, vitamin E acetate is harmless. When heated to high temperatures, however, it can break down into a highly toxic compound.


(a) (i) Which functional group(s) does vitamin E acetate contain? Tick the correct answer(s) in the answer booklet.

Nitrile
Alcohol
Ester
Ketone
Ether

## Carboxylic

Acid
(ii) Vitamin $E$ acetate has a molecular formula of $\mathrm{C}_{\mathrm{x}} \mathrm{H}_{52} \mathrm{O}_{3}$. Determine x .

A variety of analytical techniques were used to investigate the toxic product.
In the mass spectrum of vitamin $E$ acetate, the peak at $\mathrm{m} / \mathrm{z}=165.2$ comes from the ion resulting from the loss of the toxic product from the ion that gives the peak at $\mathrm{m} / \mathrm{z}=207.2$.
The ${ }^{1} \mathrm{H}$ NMR spectrum in $\mathrm{CDCl}_{3}$ of the toxic product has 1 signal.
The ${ }^{13} \mathrm{C}$ NMR spectrum in $\mathrm{D}_{2} \mathrm{O}$ of the toxic product has 2 signals.
Four possible structures for the toxic product are shown below. Only one of these is correct.



(b) In the table in the answer booklet, indicate (with $\checkmark$ or $\boldsymbol{x}$ ) whether each structure is consistent with the data from each analytical technique.

A synthesis of vitamin E acetate involves the Wittig reaction. In this reaction an aldehyde (or ketone) reacts with a phosphonium ylide to produce an alkene.


$$
\mathrm{Ph}=\mathrm{C}_{6} \mathrm{H}_{5}
$$

If there is a $\mathrm{C}=\mathrm{O}$ or $\mathrm{C}=\mathrm{C}$ bond adjacent to the negatively charged carbon on the phosphonium ylide, the major alkene product is the $E$-isomer. Otherwise, the major alkene product is the $Z$ isomer. Two examples of the reactants and major product from the Wittig reaction are shown in the table below.

| aldehyde/ketone | phosphonium ylide | major alkene product |
| :---: | :---: | :---: |
|  |  |  |

(c) Complete the following table of Wittig reactions in the answer booklet.


The first part of the synthesis of vitamin E acetate is shown below.

(d) Draw the structures of $\mathbf{A}, \mathbf{B}, \mathbf{C}$ and $\mathbf{D}$.

Upon the addition of $\mathrm{HCl}_{(\mathrm{aq})}$, $\mathbf{D}$ reacts intramolecularly to form a ring and a molecule of water. This reaction occurs via an intermediate tertiary carbocation.
(e) Draw the structure of this carbocation.

The second part of the synthesis of vitamin E acetate is shown below.


The reaction which transforms molecule $\mathbf{W}$ into molecule $\mathbf{X}$ and by-product $\mathbf{Y}$ is called ozonolysis. The general reaction scheme for ozonolysis, using ozone gas $\left(\mathrm{O}_{3}\right)$ and Zn , is shown below.

(f) Draw the structures of $\mathbf{W}, \mathbf{X}$, by-product $\mathbf{Y}$, and reagent $\mathbf{Z}$.

## Q5 This question is about cheese

Former Prime Minister Liz Truss once said that "We import two thirds of our cheese. That is a disgrace."

When we started writing this paper in summer 2022, we thought a question on cheese would be timely, given that the 2023 International Chemistry Olympiad is being held in Switzerland (a country with many famous cheeses) and that Liz Truss would be the Prime Minister at the time of Round 1.

While there are many differences in the process of cheese manufacture, the conversion of lactose to lactic acid during fermentation is a key chemical process wherever the cheese is from.

lactic acid


(a) Lactic acid has an acid dissociation constant, $K_{\mathrm{a}}=1.38 \times 10^{-4}$.
(i) Draw the conjugate base of lactic acid.
(ii) Calculate the $\mathrm{p} K_{a}$ of lactic acid.

Lactic acid is more acidic than propanoic acid. This is due to a hydrogen bond which stabilises its conjugate base.
(b) Draw out the structure of the conjugate base of lactic acid showing this hydrogen bond.

Lactose, the starting sugar in milk, is a disaccharide with formula $\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}$. In the first step of the conversion to lactic acid, lactose is converted into two monosaccharides.

(c) (i) How would you classify the reaction of lactose to form the two monosaccharides. Tick the correct answer(s) in the answer booklet.

Oxidation Reduction Condensation Hydrolysis Isomerisation Elimination
(ii) Write the names of monosaccharide sugars ( A and B ) that make up lactose.

The conversion of lactose to lactic acid is accomplished by bacteria in a complex biochemical process, however lactic acid is often the sole product.
(d) Write an equation for the conversion of lactose to lactic acid.

Many varities of Swiss cheese, such as Emmental, are famous for the holes or 'eyes' that appear in the cheese. To produce the holes another species of bacteria, Propionibacterium freudenreichii is important. This bacterium carries out the reaction of lactic acid to propanoic acid, ethanoic acid, carbon dioxide and water. The production of carbon dioxide causes the bubbles to appear.

(e) Write an equation for the production of carbon dioxide carried out by this bacterium. In the net reaction, lactic acid is the sole reagent, and ethanoic acid and carbon dioxide are produced in equal amounts.

Assume during fermentation at $21^{\circ} \mathrm{C}$, a spherical bubble of diameter 1.5 cm appears in the cheese.
(f) (i) Calculate the volume of this bubble in $\mathrm{m}^{3}$.
(ii) Assuming the bubble is pure $\mathrm{CO}_{2}$ at atmospheric pressure, $p_{\mathrm{atm}}=101325 \mathrm{~Pa}$, calculate the mass of lactic acid which was fermented by the bacteria to produce this bubble. For the calculation assume that $\mathrm{CO}_{2}$ obeys the ideal gas law,

$$
p V=n R T
$$

Note: the state symbol for cheese is (ch).
Carbon dioxide dissolved in cheese can exist in two forms: dissolved gaseous carbon dioxide, $\mathrm{CO}_{2\left(\text { (ch ) , or dissolved hydrogen carbonate, } \mathrm{HCO}_{3}^{-} \text {(ch). }\right.}$

$$
\mathrm{CO}_{2(\text { ch })}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HCO}_{3}^{-}(\mathrm{ch})+\mathrm{H}_{(\text {ch })}^{+}, \quad K=\frac{\left[\mathrm{H}_{(\text {ch })}^{+}\right]\left[\mathrm{HCO}_{3(\text { ch })}^{-}\right]}{\left[\mathrm{CO}_{2(\text { ch })}\right]}=4.47 \times 10^{-7} \mathrm{~mol} \mathrm{dm}^{-3},
$$

At the end of the fermentation, $\left[\mathrm{CO}_{2 \text { (ch) })}\right]+\left[\mathrm{HCO}_{3}{ }^{-}\right.$(ch) $]=3.70 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3}$, and $\mathrm{pH}=5.20$
(g) Calculate the equilibrium concentration of carbon dioxide dissolved in cheese, $\left[\mathrm{CO}_{2 \text { (ch) })}\right.$.

We now examine how $\mathrm{CO}_{2}$ bubbles ("eyes") of a certain size are formed in the early stages of fermentation. Suppose a bubble of radius $r$ is in contact with a fixed volume of cheese $V_{\text {ch }}$ at temperature $T$. The pressure of $\mathrm{CO}_{2}$ inside the bubble, $p_{\mathrm{b}}$, is related to the concentration of dissolved $\mathrm{CO}_{2}$ by Henry's law,

$$
\left[\mathrm{CO}_{2(\mathrm{ch})}\right]=k_{\mathrm{H}} p_{\mathrm{b}}
$$

(h) In the table in the answer booklet, tick which expression gives the molar amounts of $\mathrm{CO}_{2(\mathrm{~g})}, \mathrm{CO}_{2(\text { ch })}$ and $\mathrm{HCO}_{3}^{-}$(ch), in terms of $p_{\mathrm{b}}, r, k_{\mathrm{H}}, V_{\mathrm{ch}}, T, \mathrm{pH}$, and relevant constants.

| $k_{\mathrm{H}} V_{\mathrm{ch}} p_{\mathrm{b}}$ | $\frac{4 \pi r^{3} p_{\mathrm{b}}}{3 R T}$ | $\frac{4 \pi r^{3} p_{\mathrm{b}}}{3 R T} K \cdot 10^{\mathrm{pH}}$ | $K \cdot 10^{\mathrm{pH}} k_{\mathrm{H}} V_{\mathrm{ch}} p_{\mathrm{b}}$ | $\frac{V_{\mathrm{ch}} p_{\mathrm{b}}}{3 R T}$ | $K \cdot 10^{-\mathrm{pH}} k_{\mathrm{H}} V_{\mathrm{ch}} p_{\mathrm{b}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |

The sum of molar amounts in part ( $\mathbf{h}$ ) is a constant, labelled $\eta$, and the pressure inside the bubble is modelled by the equation

$$
p_{b}=p_{a t m}+\frac{\gamma}{r}
$$

where $\gamma$ is a constant.
(i) Substituting this expression for $p_{\mathrm{b}}$, express the sum of molar amounts as

$$
\left(a+b r^{3}\right)\left(p_{a t m}+\frac{\gamma}{r}\right)=\eta
$$

giving $a$ and $b$ in terms of $k_{H}, V_{\mathrm{ch}}, K, T, \mathrm{pH}$, and relevant constants.
This equation gives the bubble size, $r$, but is too complicated to solve by hand. Instead, we use the smallness of $\frac{\gamma}{r}$ compared to $p_{\text {atm }}$ to approximate it with the simpler equation

$$
r=\left(\frac{d}{b}\right)^{\frac{1}{3}}\left(1-\frac{r \eta}{3 p_{\mathrm{atm}}^{2} d} \cdot \frac{1}{r}\right) \text {, where } d=\frac{\eta}{p_{a t m}}-a
$$

At this stage of the fermentation:
$a=1.70 \times 10^{-9} \mathrm{~mol} \mathrm{~Pa}^{-1}$
$b=1.75 \times 10^{-3} \mathrm{~mol} \mathrm{~Pa}^{-1} \mathrm{~m}^{-3}$
$\eta=2.35 \times 10^{-4} \mathrm{~mol}$
$\gamma=9.28 \mathrm{~Pa} \mathrm{~m}$
(j) Calculate the two possible values of $r$ that satisfy the simplified equation and state which is the correct physical solution consistent with $\frac{\gamma}{r}$ being small compared to $p_{\text {atm }}$.

## Acknowledgements \& References

References will be added to the version of the paper uploaded to the web later.
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## Physical Constants and Formulae

| Avogadro's constant | $N_{A}$ | $6.02 \times 10^{23} \mathrm{~mol}^{-1}$ |
| :--- | :--- | :--- |
| molar gas constant | $R$ | $8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ |
| Faraday constant | $F$ | $96485 \mathrm{C} \mathrm{mol}^{-1}$ |
| Planck constant | $H$ | $6.626 \times 10^{-34} \mathrm{~m}^{2} \mathrm{~kg} \mathrm{~s}^{-1}$ |
| speed of light in vacuum | $C$ | $2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$ |
| mass of electron | $m_{e}$ | $9.109 \times 10^{-31} \mathrm{~kg}$ |
|  |  |  |
|  | $1 \mathrm{~nm}=1 \times 10^{-9} \mathrm{~m}$ |  |
|  | $\left.1 \AA \begin{array}{l}\text { A }\end{array}\right) \times 10^{-10} \mathrm{~m}$ |  |
|  | $0^{\circ} \mathrm{C}=273 \mathrm{~K}$ |  |
|  |  |  |
|  | $\Delta G^{\ominus}=\Delta H^{\ominus}-T \Delta S^{\ominus}$ |  |
| $\Delta G^{\ominus}=-n F E^{\ominus}$ |  |  |

volume of cube $=(\text { side length })^{3}$
volume of sphere $=\frac{4}{3} \pi \times(\text { radius })^{3}$
volume of right prism $=($ area of base $) \times($ height $)$
area of equilateral triangle $=\frac{\sqrt{3}}{4} \times(\text { side length })^{2}$
area of regular hexagon $=\frac{3 \sqrt{3}}{2} \times(\text { side length })^{2}$

| $\begin{gathered} 1 \\ \mathrm{H} \\ 1.008 \end{gathered}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | $\begin{gathered} 2 \\ \mathrm{He} \\ 4.003 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & 3 \\ & \mathrm{Li} \\ & 6.94 \\ & \hline \end{aligned}$ | $\begin{aligned} & \hline 4 \\ & \mathrm{Be} \\ & 9.01 \\ & \hline \end{aligned}$ |  |  |  |  |  |  |  |  |  |  | $\begin{array}{\|l} \hline 5 \\ \text { B } \\ 10.81 \\ \hline \end{array}$ | $\begin{gathered} 6 \\ \mathrm{C} \\ 12.01 \\ \hline \end{gathered}$ | $\begin{array}{\|c} \hline 7 \\ \mathrm{~N} \\ 14.01 \\ \hline \end{array}$ | $\begin{gathered} 8 \\ \mathrm{O} \\ 16.00 \\ \hline \end{gathered}$ | $\begin{array}{\|c\|} \hline 9 \\ \text { F } \\ 19.00 \\ \hline \end{array}$ | $\begin{aligned} & 10 \\ & \mathrm{Ne} \\ & 2018 \end{aligned}$ |
| $\begin{gathered} 11 \\ \mathrm{Na} \\ 22.99 \end{gathered}$ | $\begin{gathered} 12 \\ \mathrm{Mg} \\ 24 \end{gathered}$ |  |  |  |  |  |  |  |  |  |  | $\begin{gathered} 13 \\ \mathrm{Al} \\ 26.98 \\ \hline \end{gathered}$ | $\begin{gathered} 14 \\ \mathrm{Si} \\ 28.09 \end{gathered}$ | $\begin{gathered} 15 \\ \mathrm{P} \\ 30.97 \end{gathered}$ | $\begin{gathered} 16 \\ \mathrm{~S} \\ 32.06 \end{gathered}$ | $\begin{gathered} 17 \\ \mathrm{Cl} \\ 35.45 \end{gathered}$ | $\begin{gathered} 18 \\ \mathrm{Ar} \\ 39.95 \end{gathered}$ |
| $\begin{gathered} 19 \\ \mathrm{~K} \\ 39.102 \end{gathered}$ | $\begin{gathered} 20 \\ \mathrm{Ca} \\ 40.08 \end{gathered}$ | $\begin{gathered} 21 \\ \mathrm{Sc} \\ \hline 44.96 \end{gathered}$ | $\begin{gathered} \hline 22 \\ \mathrm{Ti} \\ 47.87 \end{gathered}$ | $\begin{gathered} 23 \\ V \\ 50.94 \end{gathered}$ | $\begin{gathered} 24 \\ \mathrm{Cr} \\ 52.00 \end{gathered}$ | $\begin{gathered} \hline 25 \\ \mathrm{Mn} \\ 54.94 \end{gathered}$ | $\begin{aligned} & \hline 26 \\ & \mathrm{Fe} \\ & 55.85 \end{aligned}$ | $\begin{gathered} 27 \\ \mathrm{Co} \\ 58.93 \end{gathered}$ | $\begin{gathered} 28 \\ \mathrm{Ni} \\ 58.69 \end{gathered}$ | $\begin{gathered} 29 \\ \mathrm{Cu} \\ 63.55 \end{gathered}$ | $\begin{gathered} 30 \\ \mathrm{Zn} \\ 65.38 \end{gathered}$ | 31 $G a$ 69.72 | $\begin{gathered} 32 \\ \mathrm{Ge} \\ 72.63 \end{gathered}$ | $\begin{gathered} 33 \\ \text { As } \\ 74.92 \end{gathered}$ | $\begin{gathered} 34 \\ \mathrm{Se} \\ 78.97 \end{gathered}$ | $\begin{aligned} & \hline 35 \\ & \mathrm{Br} \\ & 79.904 \end{aligned}$ | $\begin{gathered} 36 \\ \mathrm{Kr} \\ 83.80 \end{gathered}$ |
| $\begin{gathered} 37 \\ \mathrm{Rb} \\ 85.47 \end{gathered}$ | $38$ $87.62$ | $\begin{gathered} 39 \\ Y \\ 88.91 \end{gathered}$ | $\begin{aligned} & 40 \\ & \mathrm{Zr} \\ & 91.22 \\ & \hline \end{aligned}$ | $\begin{gathered} 41 \\ \mathrm{Nb} \\ 92.91 \end{gathered}$ | $\begin{gathered} 42 \\ \mathrm{Mo} \\ 95.95 \end{gathered}$ | $\begin{gathered} 43 \\ \text { Tc } \end{gathered}$ | $\begin{gathered} 44 \\ \mathrm{Ru} \end{gathered}$ $101.07$ | $\begin{gathered} 45 \\ R h \\ 102.91 \end{gathered}$ | $\begin{aligned} & 46 \\ & \mathrm{Pd} \\ & 106.42 \end{aligned}$ | 47 <br> Ag 107.87 | $\begin{aligned} & 48 \\ & \text { Cd } \\ & 112.41 \end{aligned}$ | $\begin{aligned} & 49 \\ & \ln \\ & 114.82 \\ & \hline \end{aligned}$ | $\begin{gathered} 50 \\ \mathrm{Sn} \\ 118.71 \end{gathered}$ | $\stackrel{51}{\mathrm{Sb}_{121.76}}$ | $\begin{array}{\|c\|} \hline 52 \\ \mathrm{Te} \\ 127.60 \\ \hline \end{array}$ | $\begin{array}{\|l\|} \hline 53 \\ \text { I } \\ 126.90 \\ \hline \end{array}$ | $\begin{gathered} 54 \\ \mathrm{Xe} \\ 131.29 \end{gathered}$ |
| $\begin{gathered} 55 \\ \mathrm{Cs} \\ 132.91 \end{gathered}$ | $\begin{gathered} 56 \\ \mathrm{Ba} \\ 137.33 \end{gathered}$ | $\begin{gathered} 57 \\ \text { La } \\ 138.91 \end{gathered}$ | $\begin{gathered} 72 \\ \mathrm{Hf} \\ 178.49 \end{gathered}$ | $\begin{gathered} 73 \\ \mathrm{Ta} \\ 180.95 \end{gathered}$ | $\begin{gathered} 74 \\ \mathrm{~W} \\ 183.84 \end{gathered}$ | $\begin{aligned} & \hline 75 \\ & R e \\ & 186.21 \end{aligned}$ | $\begin{gathered} 76 \\ \text { Os } \\ 190.23 \end{gathered}$ | $\begin{aligned} & 77 \\ & \text { Ir } \\ & 192.22 \end{aligned}$ | $\begin{gathered} 78 \\ \mathrm{Pt} \\ 195.08 \end{gathered}$ | $\begin{gathered} 79 \\ \mathrm{Au} \end{gathered}$ $196.97$ | $\begin{gathered} 80 \\ \mathrm{Hg} \\ 200.59 \end{gathered}$ | $\begin{gathered} 81 \\ \mathrm{TI} \\ 204.38 \end{gathered}$ | $\begin{gathered} 82 \\ \mathrm{~Pb} \\ 207,2 \end{gathered}$ | $\begin{gathered} 83 \\ \mathrm{Bi} \\ 208.98 \end{gathered}$ | $\begin{gathered} 84 \\ \mathrm{Po} \end{gathered}$ | $\begin{gathered} 85 \\ \mathrm{At} \end{gathered}$ | $\begin{gathered} 86 \\ R n \end{gathered}$ |
| ${ }^{87} \mathrm{Fr}$ | 88 | 89 Ac | 104 $R f$ | 105 | 106 $S g$ | 107 | 108 Hs | 109 Mt | 110 Ds | 111 $R g$ | 112 <br> $C n$ | 113 Nh | 114 Fl | 115 Mc | 116 Lv | $\begin{gathered} 117 \\ \mathrm{Ts} \end{gathered}$ | 118 Og |


| Lanthanides | $58$ | $59$ $140.91$ | $\begin{aligned} & 60 \\ & \mathrm{Nd} \\ & 144.24 \end{aligned}$ | $\begin{aligned} & 61 \\ & \mathrm{Pm} \end{aligned}$ | $\begin{array}{\|l} \hline 62 \\ \text { Sm } \\ 150.4 \end{array}$ | $\begin{gathered} 63 \\ { }_{151.96}^{\mathrm{Eu}} \end{gathered}$ | $\begin{gathered} 64 \\ \underset{157.25}{\mathrm{Gd}} \end{gathered}$ | $\begin{gathered} 65 \\ \mathrm{~Tb} \\ 158.93 \end{gathered}$ | $\begin{aligned} & 66 \\ & \text { Dy } \\ & 162.50 \end{aligned}$ | $\begin{gathered} 67 \\ \text { Ho } \\ 164.93 \end{gathered}$ | $\begin{aligned} & 68 \\ & \text { Er } \\ & 167.26 \\ & \hline \end{aligned}$ | $\begin{gathered} \hline 69 \\ \mathrm{Tm} \\ 168.93 \\ \hline \end{gathered}$ | $\begin{gathered} 70 \\ \mathrm{Yb} \\ 173.05 \\ \hline \end{gathered}$ | $\begin{array}{\|c} \hline 71 \\ \mathrm{Lu} \\ 174.97 \end{array}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Actinides | $\begin{gathered} 90 \\ \text { Th } \\ 232.04 \end{gathered}$ | $\begin{gathered} 91 \\ \mathrm{~Pa} \\ 231.04 \end{gathered}$ | $\begin{gathered} 92 \\ \mathrm{U} \\ 238.03 \end{gathered}$ | $\stackrel{93}{\mathrm{~Np}}^{\text {¢ }}$ | $\begin{gathered} 94 \\ \mathrm{Pu} \end{gathered}$ | $\begin{gathered} 95 \\ \text { Am } \end{gathered}$ | $\begin{gathered} 96 \\ \mathrm{Cm} \end{gathered}$ | $\begin{gathered} 97 \\ \mathrm{Bk} \end{gathered}$ | $98$ | 99 | 100 Fm | 101 Md | 102 No | 103 Lr |

