

## 54 ${ }^{\text {th }}$ INTERNATIONAL

## CHEMISTRY OLYMPIAD

## 2022

## UK Round One

## STUDENT QUESTION BOOKLET

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}

- The time allowed is two hours.
- Attempt all six 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 page of this question booklet includes a copy of the periodic table and some useful physical constants and quantities.
- 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 | 6 | Total |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks <br> Available | 9 | 9 | 24 | 13 | 19 | 12 | $\mathbf{8 6}$ |

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 E 10 petrol

To help tackle the causes of climate change, in September 2021 the UK government changed the standard petrol grade at fuel pumps from E5 to E10 petrol. These E values refer to the percentage of ethanol in the ethanol-hydrocarbon fuel mixture. It has been argued that the change from E5 to E10 was one contributing factor to the petrol shortage in October 2021 as retailers attempted to remove their
 stock supplies of E5.

E values and octane numbers are both displayed on petrol pumps. There is only a small proportion of the straight chain isomer of octane in petrol as this tends to "knock" in the engine. Knocking is where the fuel ignites prematurely and this reduces engine efficiency. Branched chain isomers of octane knock much less and a lot of these are found in petrol. One major isomer is 2,2,4-trimethylpentane.
(a) Draw the skeletal formula of 2,2,4-trimethylpentane.

Blending ethanol into fuel mixtures such as in E5 and E10 also reduces knocking. Ethanol is a biofuel and is often produced by fermenting sugar from crop plants. The plants capture carbon dioxide from the atmosphere and convert this into sugars such as glucose, $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}$, through photosynthesis.
(b) Write the equation for the formation of glucose in photosynthesis from carbon dioxide.

The anaerobic fermentation of glucose produces ethanol and carbon dioxide.
(c) Write the equation for the anaerobic fermentation of glucose.

One of the characteristics of an effective fuel is the amount of energy it releases, or its enthalpy of combustion. One method to determine this is to use average bond enthalpies. Some average bond enthalpies are given below.

| Bond | Average bond enthalpy $/ \mathbf{k J ~ m o l}^{-\mathbf{1}}$ |
| :---: | :---: |
| $\mathrm{C}-\mathrm{C}$ | 347 |
| $\mathrm{C}-\mathrm{H}$ | 413 |
| $\mathrm{O}=\mathrm{O}$ | 498 |
| $\mathrm{C}-\mathrm{O}$ | 358 |
| $\mathrm{C}=\mathrm{O}$ | 805 |
| $\mathrm{O}-\mathrm{H}$ | 464 |

When calculated by this method, all the different isomers of octane have the same value.
(d) Calculate the enthalpy of combustion of an isomer of octane.

Assume that 1 litre of E10 fuel contains 100 mL of ethanol and 900 mL of octane isomers, and that 1 litre of E5 fuel contains 50 mL of ethanol and 950 mL of octane isomers. The density of pure ethanol is $0.789 \mathrm{~g} \mathrm{~cm}^{-3}$ and the density of pure octane isomers is $0.703 \mathrm{~g} \mathrm{~cm}^{-3}$. You can assume that there is no volume change on mixing.
The enthalpy of combustion of ethanol using average bond enthalpies is $-1276 \mathrm{~kJ} \mathrm{~mol}^{-1}$.
(e) For both E5 and E10 fuels, calculate the energy, in kJ, released when 1 litre of the fuel is burnt.
If you did not get an answer for part (d) then you may use a value of $-6666 \mathrm{~kJ} \mathrm{~mol}^{-1}$ for the enthalpy of combustion of octane isomers in this calculation.
(f) Taking the energy released from burning 1 litre of E5 as 100\%, calculate the percentage of the energy released from burning 1 litre of E10 fuel.

All the carbon dioxide released by the combustion of ethanol is offset by the carbon dioxide captured when the plants are grown. As such, the contribution from the ethanol is not counted when the $\mathrm{CO}_{2}$ footprints of the E5 and E10 fuels are compared.
(g) Taking the $\mathrm{CO}_{2}$ produced from burning 1 litre of E 5 fuel as $100 \%$, calculate the percentage of $\mathrm{CO}_{2}$ produced from burning 1 litre of E 10 fuel. Consider only $\mathrm{CO}_{2}$ formed from the combustion of octane isomers.

## 2. This question is about the chemistry of nitrous oxide

Nitrous oxide, $\mathrm{N}_{2} \mathrm{O}$, is used as a propellant in whipped cream, as a fuel additive to improve combustion in car engines, and as an anaesthetic in medicine and dentistry. When inhaled, nitrous oxide can result in hysterical euphoria, which led to the nickname "laughing gas". It is now known that there are serious health risks associated with using nitrous oxide recreationally.


Nitrous oxide can be formed from nitrous acid, $\mathrm{HNO}_{2}$, a weak acid, that is used in the production of dyes.
(a) Draw the dot and cross diagram for $\mathrm{HNO}_{2}$.

Nitrous acid can be converted into nitrous oxide by two different methods. The first method is shown below. Firstly nitrous acid reacts with $\mathrm{O}_{2}$ to form molecule A. Molecule A then reacts with ammonia to form a salt $\left[\mathrm{B}^{+}\right]\left[\mathbf{C}^{-}\right]$, which subsequently thermally decomposes into nitrous oxide and water.

$$
\mathrm{HNO}_{2} \xrightarrow{\mathrm{O}_{2}} \mathbf{A} \xrightarrow{\mathrm{NH}_{3}}\left[\mathbf{B}^{+}\right]\left[\mathrm{C}^{-}\right] \xrightarrow{\text { heat }} \mathrm{N}_{2} \mathrm{O}+2 \mathrm{H}_{2} \mathrm{O}
$$

Elemental analysis shows that A contains $1.60 \%$ hydrogen and $22.23 \%$ nitrogen by mass.
(b) Determine the formula of $\mathbf{A}$.
(c) Draw the ions $\mathbf{B}^{+}$and $\mathbf{C}^{-}$clearly showing their shape.

The second method thermally decomposes nitrous acid. For every two molecules of nitrous acid, one molecule each of $\mathbf{D}, \mathbf{E}$, and water are formed. $\mathbf{E}$ is a brownish-red gas in equilibrium with a colourless gas $\mathbf{X}$.
$\mathbf{D}$ and $\mathbf{E}$ then react with each other to form molecule $\mathbf{F}$, which then thermally decomposes to form nitrous oxide and oxygen.
(d) Write the formulae of $\mathbf{D}, \mathbf{E}, \mathbf{F}$, and $\mathbf{X}$.

Nitrous oxide is a linear molecule with a nitrogen atom in the middle.
(e) Draw the structure for $\mathrm{N}_{2} \mathrm{O}$.

## 3. This question is about cubane

Platonic solids are three-dimensional shapes where all faces, edges, and angles are congruent (identical). There are only five such solids. Plato hypothesised that the classical elements - air, earth, fire, and water - each corresponded to one of the shapes.
With the advances in chemistry in the last 2360 years, we no longer think that there are four elements or that they are made of Platonic solids. However, we can make a Platonic solid out of elements.

One such molecule, cubane, is of interest and potential use because of its unusual structure.


Skeletal formula of cubane
(a) State the molecular formula of cubane.

One synthesis of cubane proceeds via cubane-1,4-dicarboxylic acid. The structures of cubanecarboxylic acid and the three isomers of cubane-dicarboxylic acid are shown below.


Cubane-
carboxylic acid


Cubane-1,2-
dicarboxylic acid


Cubane-1,3dicarboxylic acid


Cubane-1,4dicarboxylic acid
(b) Complete the table in the answer booklet with the number of peaks in the ${ }^{13} \mathrm{C}$ NMR spectrum of:
(i) Cubane
(ii) Cubane-carboxylic acid
(iii) Cubane-1,2-dicarboxylic acid
(iv) Cubane-1,3-dicarboxylic acid
(v) Cubane-1,4-dicarboxylic acid.

The start of the cubane synthesis is shown below.


A was treated with three equivalents of $\mathrm{Br}_{2}$ to form $\mathbf{B}$. $\operatorname{In} \mathbf{B}$, which has the molecular formula $\mathrm{C}_{7} \mathrm{H}_{9} \mathrm{O}_{2} \mathrm{Br}_{3}$, each of the three bromine atoms are exactly three bonds away from the two oxygen atoms.

B was then reacted with excess sodium hydroxide. This reaction is proposed to proceed via intermediate $\mathbf{C}$, which then reacts with another molecule of itself to form compound $\mathbf{D}$.
(c) Draw the structures of $\mathbf{A}$ and $\mathbf{B}$.

The reaction from intermediate $\mathbf{C}$ to $\mathbf{D}$ is known as a Diels-Alder cycloaddition. The simplest example of a Diels-Alder cycloaddition, between butadiene and ethene, is shown on the right.

Three other examples of Diels-Alder cycloadditions are shown below:

(d) Draw the structures of products $\mathbf{W}$ and $\mathbf{X}$.

Y dimerises via a Diels-Alder reaction to produce the product shown.
(e) Draw the structure of starting material $\mathbf{Y}$.
(f) Based on this knowledge of the Diels-Alder reaction, draw the structure of intermediate C.

D


IR: $1795 \mathrm{~cm}^{-1}$
Compound $\mathbf{D}$ reacts with aqueous acid to form compound $\mathbf{E}$, which on exposure to UV light, reacts intramolecularly to form compound $\mathbf{F}$. Compound $\mathbf{F}$ contains two four-membered rings.

Lastly, compound $\mathbf{F}$ is reacted with sodium hydroxide followed by hydrochloric acid. This results in a reaction known as the Favorskii Rearrangement. The general reaction for a Favorskii Rearrangement is shown here:

(g) On the structure in the answer booklet, circle the electrophilic carbon atom(s).
(h) Using the frameworks provided in the answer booklet, draw the structures of $\mathbf{E}$ and $\mathbf{F}$.

This dicarboxylic acid can be chemically converted to cubane.

(i) Using the frameworks provided in the answer booklet, draw the structures of $\mathbf{G}$ and $\mathbf{H}$.

An isomer of cubane, barrelene, can also be constructed using a Diels-Alder reaction.


The two starting materials undergo a Diels-Alder reaction to form $\mathbf{Q}$. An additional ring is formed to give product $\mathbf{R}$, which then reacts to give three products, one of which is shown. Compound $\mathbf{S}$ is a gas, and compound $\mathbf{T}$ when treated with NaOH gives barrelene-1,2-dicarboxylic acid.
(j) Using the frameworks provided in the answer booklet, draw the structures of $\mathbf{Q}, \mathbf{R}, \mathbf{S}$, and T .

## Q4 This question is about coronavirus testing

A typical lateral flow test works by a sample liquid flowing along a paper medium (from left-to-right in the picture). Lateral flow tests for COVID-19 use the strong binding between spike proteins on the surface of virus particles and antibodies to detect coronavirus. The
 red/pink colour in many lateral flow tests is from gold nanoparticles coated with antibodies.

To use a particular lateral flow test, a swab is taken and placed in $1.0 \mathrm{~cm}^{3}$ extraction solution containing $7.3 \mathrm{mmol} \mathrm{dm}^{-3} \mathrm{Na}_{2} \mathrm{HPO}_{4}$ and $4.6 \mathrm{mmol} \mathrm{dm}^{-3} \mathrm{KH}_{2} \mathrm{PO}_{4}$ at pH 7.4 at $25^{\circ} \mathrm{C}$.
(a) What is the purpose of these chemicals in the extraction solution? Tick the correct answer in the answer booklet.

| Make a very acidic | Make a neutral <br> solution | Make a very alkaline <br> solution | Make a buffered <br> solution |
| :--- | :--- | :--- | :--- |

(b) If $1.0 \mathrm{~cm}^{3}$ of $0.10 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HCl}$ were then added to the extraction solution, what pH would the resulting solution be? Tick the correct answer in the answer booklet.
$\begin{array}{llll}\text { Very Acidic } & \text { pH } 7.4 & \text { Very Alkaline }\end{array}$
During the test a person swabs their nose/throat and places it in the extraction solution. The resulting solution is called the test solution. A test sample of a few drops $\left(0.10 \mathrm{~cm}^{3}\right)$ of the test solution are placed on the sample pad.
If the person taking the test has COVID-19, there will typically be $7.1 \times 10^{6}$ virus particles per $\mathrm{cm}^{3}$ in the test solution. Each virus particle has approximately 20 spike proteins on its surface.
(c) What is the concentration of spike proteins, [SP], in the test sample placed on the pad in $\mathrm{mol} \mathrm{dm}{ }^{-3}$ ?

If you do not get an answer, use $[S P]=1.0 \times 10^{-11} \mathrm{~mol} \mathrm{dm}$ in subsequent calculations.
Once the sample passes the conjugate pad, it becomes saturated with red-coloured antibody-coated Au nanoparticles (NP), to a concentration $1.6 \times 10^{12} \mathrm{NP}$ per $\mathrm{cm}^{3}$.
An equilibrium is set up where the NP bind to any spike proteins, SP. Assume that any binding that takes place between spike proteins and nanoparticles is $1: 1$.

$$
\begin{gathered}
\mathrm{SP}(\mathrm{aq})+\mathrm{NP}(\mathrm{aq}) \rightleftharpoons \mathrm{SPNP}(\mathrm{aq}) \\
K=\frac{[\mathrm{SPNP}]}{[\mathrm{NP}][\mathrm{SP}]}=1.2 \times 10^{10} \mathrm{~mol}^{-1} \mathrm{dm}^{3}
\end{gathered}
$$

(d) As there is a large excess of nanoparticles, you can assume that the concentration of nanoparticles at equilibrium is still $1.6 \times 10^{12} \mathrm{NP}$ per $\mathrm{cm}^{3}$
Determine [SPNP] at equilibrium in $\mathrm{mol} \mathrm{dm}^{-3}$.
If you do not get an answer, use $[S P N P]=1.0 \times 10^{-11} \mathrm{~mol} \mathrm{dm}^{-3}$ in subsequent calculations.

The resulting mixture flows over the test strip which contains surface-immobilized antibodies (AB). When considering the amount of a substance on a surface, we use surface density, $\sigma_{\mathrm{A}}$, instead of concentration.
The test strip is 3.0 mm long, 1.0 mm wide and 0.10 mm deep, with a surface density of antibodies, $\sigma_{A B}=1.2 \times 10^{9} \mathrm{~mm}^{-2}$.
(e) (i) Calculate how many surface-immobilized antibodies, AB , there are on the test strip surface.
(ii) Calculate how many free spike proteins, SP, and how many nanoparticle-bound spike proteins, SPNP, are present in a volume of solution of the size of the test strip before any interaction with the test strip.

The surface-immobilized antibodies, AB, bind to any spike protein present (free SP and nanoparticle-bound SPNP) with the following equilibria:

$$
\begin{gathered}
\mathrm{AB}(\text { surface })+\mathrm{SP}(\mathrm{aq}) \\
\mathrm{AB}(\text { surface })+\mathrm{ABSP}(\text { surface }) \\
\mathrm{SPN}(\mathrm{aq})
\end{gathered} \stackrel{\operatorname{ABSPNP}(\text { surface })}{ }
$$

These have the same equilibrium constant:

$$
K=\frac{\sigma_{\mathrm{ABSP}}}{\sigma_{\mathrm{AB}}[\mathrm{SP}]}=\frac{\sigma_{\mathrm{ABSPNP}}}{\sigma_{\mathrm{AB}}[\mathrm{SPNP}]}=3.3 \times 10^{10} \mathrm{~mol}^{-1} \mathrm{dm}^{3}
$$

(f) Determine the number of nanoparticles immobilized on the test strip, ABSPNP, once the whole $0.10 \mathrm{~cm}^{3}$ test sample has fully flowed past.

The visibility of the test line depends on the number of nanoparticles which become immobilized on it. Nanoparticles are visible down to a surface density of $3 \times 10^{6} \mathrm{NP}$ per $\mathrm{mm}^{2}$.
(g) Determine the minimum number of virus particles present in the test sample which would give a positive result.

## 5. This question is about making the smallest Chinese knot

The 2022 International Chemistry Olympiad is being organised by Tianjin University in China. Traditional Chinese culture often features decorative knots tied from strands of cord or material. In 2021, researchers managed to tie a molecule into the smallest ever Chinese knot.

They first synthesised an organic ligand to act as the strands of thread. Coordination of atoms on these organic ligands to metal ions produced a $(3 \times 3)$ interwoven grid as shown below. The twelve strand ends were joined with a chemical reaction and the metal ions were then removed to give a purely organic Chinese knot.


A Chinese knot from rope

The synthesis of one of the organic strands can begin from two different starting materials: A or $\mathbf{B}$ which can both be converted into 3-fluoro-4-nitrophenol.

(a) (i) Draw the structure of $\mathbf{A}$.
(ii) Draw the structure of the active electrophile formed when $\mathbf{A}$ reacts to form 3 -fluoro-4-nitrophenol.

Elemental Analysis of B revealed: C 51.81\%; H 3.62\%; N 10.07\%.
(b) Draw the structure of $\mathbf{B}$.

3-Fluoro-4-nitrophenol is converted into compound $\mathbf{D}$. In the reaction of $\mathbf{C}$ to $\mathbf{D}$, a primary amine $\left(\mathrm{RNH}_{2}\right)$ is used, where R is an alkyl group.
(c) (i) Draw the structure of $\mathbf{C}$.
(ii) Draw the structure of $\mathbf{D}$. Use the abbreviation R for the alkyl group from the primary amine.

Compound $\mathbf{D}$ is converted into the organic strand in three steps. The final two steps use the same palladium catalyst mix. Treating compound $\mathbf{E}$ and thiazolothiazole with this mix gives compound $\mathbf{F}$. Treating compound $\mathbf{F}$ and reagent $\mathbf{G}$ with this mix gives the organic strand.

(d) Draw the structures of compound $\mathbf{E}$ and reagent $\mathbf{G}$.

In the ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{D}$, the signals from the alkyl group R are as follows:
$3.26 \mathrm{ppm}(2 \mathrm{H}$, doublet of triplets); 1.77 ppm ( 1 H , multiplet); $1.63 \mathrm{ppm}(2 \mathrm{H}$, doublet of triplets) 0.98 ppm (6H, doublet).
(e) Draw the structure of the primary amine $\left(\mathrm{RNH}_{2}\right)$ used to synthesise $\mathbf{D}$.

Atoms in each strand coordinate to transition metal ions to form the $(3 \times 3)$ grid.
(f) On the structure of the strand in the answer booklet, draw in the place of the metal ions and show which atoms coordinate to each metal ion. Use the style of the picture on the right, where the metal ion is represented by a letter $M$ in a circle, and the atoms which are coordinating have an arrow to show which metal they coordinate to.

(g) What is the overall coordination geometry around each metal ion in this $3 \times 3$ grid best described as? Tick the correct answer in the answer booklet.

| tetrahedral | trigonal planar | square planar |
| :---: | :---: | :---: |
| octahedral | square pyramidal | hexagonal planar |

The formula of the metal salt added to form the grid can be written as $\mathbf{M X}_{2}{ }^{\bullet} 6 \mathrm{H}_{2} \mathbf{O}$, where $\mathbf{M}^{\mathbf{2 +}}$ is a divalent cation of a first-row transition metal, $\mathrm{X}^{-}$is a tetrahedral anion of charge -1 , and there are six molecules of water of crystallisation in the salt. Upon shaking the salt in aqueous sodium hydroxide, a green precipitate is formed that upon standing turns brown. Upon gentle heating of the salt, there is a $32.0 \%$ loss in mass. Anion $\mathbf{X}^{-}$contains two different elements, neither of which is oxygen.
(h) Identify $\mathbf{M}^{\mathbf{2 +}}$ and draw the structure of anion $\mathbf{X}^{-}$.

The $3 \times 3$ grid is then subjected to a reaction known as alkene metathesis, which joins two terminal alkenes into a disubstituted alkene, producing ethene as a by-product. Due to the rigid structure of the grid, only adjacent strands can be joined in this reaction.



Although this reaction only joins adjacent strand ends, there are still many possibilities of which ends can be joined. Depending on which ends join first, sometimes some ends are left too far away from other ends to be joined at all. Once the alkene metathesis reaction is complete, the metal ions are removed by addition of EDTA. After metal ion removal, four different types of organic structure remain, depending on which ends join: (i) Chinese knots; (ii) two interlinked rings; (iii) individual rings; (iv) linear organic molecules.



Individual ring



Linear
(i) In the answer booklet tick which of the four structures will be present after the following connections are made between the strand ends and then the metal ions removed.
(i) $\quad(1,2)(3,4)(5,6)(7,8)(9,10)(11,12)$
(ii) $(1,2)(4,5)(6,7)(8,9)(10,11)(3$ and 12 remain unjoined)
(iii) $(1,2)(3,4)(5,6)(8,9)(10,11)(7$ and 12 remain unjoined)
(iv) $(2,3)(4,5)(6,7)(8,9)(10,11)(12,1)$

## 6. This question is about storing vaccines

Because of degradation of components, vaccines need to be refrigerated, which increases their cost and makes distribution difficult. A recently developed process called "ensilication" can drastically improve the vaccines' stability. Ensilicated vaccine components can be stored at room temperature and withstand heating up to $100^{\circ} \mathrm{C}$.


The ensilication process begins with the hydrolysis of ethyl orthosilicate, $\mathrm{Si}\left(\mathrm{OCH}_{2} \mathrm{CH}_{3}\right)_{4}$, to form orthosilicic acid, $\mathrm{Si}(\mathrm{OH})_{4}$, (process 1). This is added to a solution of the protein/antibody, which catalyses the decomposition of the acid into silica, $\mathrm{SiO}_{2}$ (process 2 ).
(a) Write the chemical equations for processes 1 and 2.

At the end of the process a suspension of silica nanoparticles loaded with protein is formed. The protein can be released using a solution of NaF and HCl , which breaks up the silica (process 3).

$$
\mathrm{SiO}_{2}+6 \mathrm{NaF}+6 \mathrm{HCl} \rightarrow \mathrm{H}_{2} \mathrm{SiF}_{6}+6 \mathrm{NaCl}+2 \mathrm{H}_{2} \mathrm{O}
$$

(b) Calculate the standard enthalpy change of this reaction given the following data:

$$
\begin{array}{ll}
\mathrm{NaOH}+\mathrm{HCl} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O} & \Delta H^{\ominus}=-56.7 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
\mathrm{SiO}_{2}+6 \mathrm{HF} \rightarrow \mathrm{H}_{2} \mathrm{SiF}_{6}+2 \mathrm{H}_{2} \mathrm{O} & \Delta H^{\ominus}=-100.3 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
\mathrm{NaOH}+\mathrm{HF} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{NaF} & \Delta H^{\ominus}=-61.5 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{array}
$$

Process 2 is thermodynamically favoured but slow, which is why it requires a catalyst. The equilibrium constant for this reaction is

$$
K_{\mathrm{eq}}=1 /\left[\mathrm{Si}(\mathrm{OH})_{4}\right]
$$

and

$$
\ln \left[\mathrm{Si}(\mathrm{OH})_{4}\right]=-\frac{1680}{T}-0.605
$$

where $\left[\mathrm{Si}(\mathrm{OH})_{4}\right]$ is the equilibrium concentration in $\mathrm{mol}_{\mathrm{dm}}{ }^{-3}$, and $T$ is the temperature in K .
(c) Calculate the molar enthalpy change, $\Delta H^{\ominus}$, and molar entropy change, $\Delta S^{\ominus}$, for process 2.

Dynamic light scattering can be used to determine the size of the nanoparticles. Assume our solution contains spherical particles of only two types: ensilicated protein with radius $r_{1}$ and free protein with radius $r_{2}$. The intensity of the light scattered by these particles can be converted into an autocorrelation function, $c$.

$$
c=\left(1-\frac{\Gamma t}{r_{1}}+\frac{1}{2}\left(\frac{\Gamma t}{r_{1}}\right)^{2}\right)+A\left(1-\frac{\Gamma t}{r_{2}}+\frac{1}{2}\left(\frac{\Gamma t}{r_{2}}\right)^{2}\right)
$$

where $A$ is a dimensionless constant, $t$ is time in $\mu \mathrm{s}, r_{1}$ and $r_{2}$ are the radii in nm and $\Gamma=0.170713 \mathrm{~nm} \mu \mathrm{~s}^{-1}$. Note: the following calculations are sensitive to rounding error. Work to the specified number of significant figures in (d)-(f).
(d) Calculate the constant $A$, given that at $t=0$, the autocorrelation function $c_{0}=1.56744$. If you do not get an answer, use $A=0.50000$ in subsequent calculations.

The equation for $c$ can be rearranged into the form $f=a \times t-b$, where

$$
f=\frac{c-c_{0}}{\Gamma t}, \quad a=\frac{1}{2} \Gamma\left(r_{1}^{-2}+A r_{2}^{-2}\right), \quad b=r_{1}^{-1}+A r_{2}^{-1}
$$

(e) Calculate the values of the slope $a$ and intercept $b$, given that $c=1.54289$ at $t=1 \mu \mathrm{~s}$ and $c=1.51937$ at $t=2 \mu \mathrm{~s}$.
If you do not get an answer, use $a=0.00250 \mathrm{~nm}^{-1} \mu \mathrm{~s}^{-1}$ and $b=0.12500 \mathrm{~nm}^{-1}$ in subsequent calculations.
(f) Hence calculate the radii $r_{1}$ and $r_{2}$. Consider first solving for $x_{1}=r_{1}^{-1}$ and $x_{2}=r_{2}^{-1}$.

## Acknowledgements \& References

Q1 The image is © Dr Ben Pilgrim
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Mark Jordan (Royal Society of Chemistry)
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Dr Penny Robotham (The National Mathematics and Science College)
Dr Andy Taylor (King Edward VI Camp Hill School for Boys)
Dr Alex Thom (Girton College, University of Cambridge)
Dr George Trenins (ETH Zürich)

## Physical Constants \& 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 | $m_{e}$ | $9.109 \times 10^{-31} \mathrm{~kg}$ |
|  |  |  |
|  | $1 \mathrm{~nm}=1 \times 10^{-9} \mathrm{~m}$ |  |
|  | $1 \AA=1 \times 10^{-10} \mathrm{~m}$ |  |
| $0{ }^{\circ} \mathrm{C}=273 \mathrm{~K}$ |  |  |
|  |  |  |
|  | $\Delta G^{\ominus}=\Delta H^{\ominus}-T \Delta S^{\ominus}$ |  |
| $\Delta G^{\ominus}=-n F E^{\ominus}$ |  |  |


| $\begin{gathered} 1 \\ \mathrm{H} \\ 1.008 \end{gathered}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | ${ }^{2} \mathrm{He}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} 3 \\ \begin{array}{c} 10.00 \\ 6.94 \\ \hline \end{array} \\ \hline \end{gathered}$ | $\begin{array}{\|l\|} \hline 4 \\ \mathrm{Be} \\ 9.01 \\ \hline \end{array}$ |  |  |  |  |  |  |  |  |  |  | $\begin{array}{\|c\|} \hline 5 \\ \mathrm{~B} \\ 10.81 \\ \hline \end{array}$ | $\begin{array}{\|c} \hline 6 \\ \mathrm{C} \\ 12.01 \\ \hline \end{array}$ | $\begin{array}{\|c} \hline 7 \\ \mathrm{~N} \\ 14.01 \\ \hline \end{array}$ | $\begin{array}{\|c} \hline 8 \\ \mathrm{O} \\ 16.00 \\ \hline \end{array}$ | $\begin{gathered} 9 \\ F \\ 19.00 \\ \hline \end{gathered}$ | $\begin{aligned} & \hline 10 \\ & \mathrm{Ne} \\ & 20.18 \end{aligned}$ |
| $\begin{gathered} 11 \\ \mathrm{Na} \\ 22.99 \end{gathered}$ | 12 <br> Mg |  |  |  |  |  |  |  |  |  |  | $\begin{gathered} 13 \\ \mathrm{Al} \\ 26.98 \end{gathered}$ | $\begin{gathered} \hline 14 \\ \mathrm{Si} \\ 28.09 \end{gathered}$ | $\begin{gathered} 15 \\ \mathrm{P} \\ 30.97 \end{gathered}$ | $\begin{gathered} 16 \\ \mathrm{~S} \\ 32.06 \end{gathered}$ | $\begin{gathered} 17 \\ \mathrm{Cl} \\ 35.45 \end{gathered}$ | $\begin{gathered} 18 \\ \mathrm{Ar} \\ 39.95 \end{gathered}$ |
| $\begin{gathered} 19 \\ \mathrm{~K} \\ 39.102 \end{gathered}$ | $\begin{array}{\|c} \hline 20 \\ \mathrm{Ca} \\ 40.08 \\ \hline \end{array}$ | $\begin{gathered} 21 \\ \mathrm{Sc} \\ \hline 44.96 \end{gathered}$ | $\begin{array}{\|l} \hline 22 \\ \mathrm{Ti} \\ 47.87 \\ \hline \end{array}$ | $\begin{gathered} 23 \\ \vee \\ \mathrm{~V}, 94 \end{gathered}$ | $\begin{gathered} 24 \\ \mathrm{Cr} \\ 52.00 \end{gathered}$ | $\begin{aligned} & 25 \\ & \mathrm{Mn} \\ & 54.94 \end{aligned}$ | $\begin{array}{\|l\|} \hline 26 \\ \mathrm{Fe} \\ 55.85 \end{array}$ | $\begin{array}{\|c\|} \hline 27 \\ \mathrm{Co} \\ 58.93 \end{array}$ | $\begin{gathered} 28 \\ \mathrm{Ni} \\ 58.69 \end{gathered}$ | $\begin{array}{\|c} \hline 29 \\ \mathrm{Cu} \\ 63.55 \\ \hline \end{array}$ | $\begin{array}{\|l\|} \hline 30 \\ \mathrm{Zn} \\ 65.38 \end{array}$ | 31 Ga 69.72 | $\begin{gathered} 32 \\ \mathrm{Ge} \\ 72.63 \\ \hline \end{gathered}$ | $\begin{gathered} 33 \\ \text { As } \\ 74.92 \end{gathered}$ | $\begin{gathered} 34 \\ \mathrm{Se} \\ 78.97 \\ \hline \end{gathered}$ | $\begin{aligned} & 35 \\ & \mathrm{Br} \\ & 79.904 \end{aligned}$ | $\begin{gathered} 36 \\ \mathrm{Kr} \\ 83.80 \end{gathered}$ |
| $\begin{gathered} 37 \\ R \mathrm{Rb} \\ 85.47 \end{gathered}$ | $\begin{gathered} 38 \\ \mathrm{Sr} \\ 87.62 \end{gathered}$ | $\begin{gathered} 39 \\ Y \\ 88.91 \end{gathered}$ | $\begin{aligned} & \hline 40 \\ & \mathrm{Zr} \\ & 91.22 \end{aligned}$ | $\begin{gathered} 41 \\ \mathrm{Nb} \\ 92.91 \end{gathered}$ | $\begin{gathered} \hline 42 \\ \mathrm{Mo} \\ 95.95 \\ \hline \end{gathered}$ | 43 Tc | $\begin{aligned} & 44 \\ & \mathrm{Ru} \\ & 101.07 \end{aligned}$ | $\begin{gathered} 45 \\ R h \\ 102.91 \end{gathered}$ | $\begin{array}{\|c\|} \hline 46 \\ \mathrm{Pd} \\ 106.42 \\ \hline \end{array}$ | 47 <br> Ag 107.87 | $\begin{aligned} & 48 \\ & \mathrm{Cd} \\ & 112.41 \end{aligned}$ | $\begin{aligned} & \hline 49 \\ & \ln \\ & 114.82 \\ & \hline \end{aligned}$ | $\begin{gathered} 50 \\ \text { Sn } \\ 118.71 \end{gathered}$ | $\begin{gathered} \hline 51 \\ \mathrm{Sb} \\ 121.76 \\ \hline \end{gathered}$ | $\begin{array}{\|l\|} \hline 52 \\ \mathrm{Te} \\ 127.60 \\ \hline \end{array}$ | $\begin{aligned} & \hline 53 \\ & \text { I } \\ & 126.90 \\ & \hline \end{aligned}$ | $\begin{gathered} 54 \\ \mathrm{Xe} \\ 131.29 \end{gathered}$ |
| $\begin{gathered} 55 \\ \mathrm{Cs} \\ 132.91 \end{gathered}$ | $\begin{array}{\|c\|} \hline 56 \\ \mathrm{Ba} \\ 137.33 \\ \hline \end{array}$ | $\begin{gathered} \hline 57 \\ \mathrm{La} \\ 138.91 \end{gathered}$ | $\begin{array}{\|c\|} \hline 72 \\ \mathrm{Hf} \\ 178.49 \\ \hline \end{array}$ | $\begin{gathered} \hline 73 \\ \mathrm{Ta} \\ 180.95 \\ \hline \end{gathered}$ | $\begin{gathered} \hline 74 \\ \mathrm{~W} \\ 183.84 \\ \hline \end{gathered}$ | $\begin{aligned} & \hline 75 \\ & R e \\ & 186.21 \end{aligned}$ | $\begin{aligned} & 76 \\ & \mathrm{Os} \\ & 190.23 \end{aligned}$ | $\begin{array}{\|l\|} \hline 77 \\ \text { Ir } \\ 192.22 \\ \hline \end{array}$ | $\begin{gathered} 78 \\ \mathrm{Pt} \\ 195.08 \end{gathered}$ | 79 Au 196.97 | $\begin{array}{\|l\|} \hline 80 \\ \mathrm{Hg} \\ 200.59 \\ \hline \end{array}$ | $\begin{aligned} & \hline 81 \\ & \mathrm{TI} \\ & 204.38 \\ & \hline \end{aligned}$ | $\begin{array}{\|l\|} \hline 82 \\ \mathrm{~Pb} \\ 207.2 \\ \hline \end{array}$ | $\begin{aligned} & \hline 83 \\ & \mathrm{Bi} \\ & 208.98 \\ & \hline \end{aligned}$ | $\begin{array}{\|l\|} \hline 84 \\ \mathrm{Po} \end{array}$ | $\begin{array}{\|l\|} \hline 85 \\ \mathrm{At} \end{array}$ | 86 |
| ${ }^{87} \mathrm{Fr}$ | 88 Ra | 89 Ac | 104 $R f$ | 105 | 106 Sg | 107 | 108 Hs | 109 Mt | 110 Ds | 111 Rg | 112 $C n$ | 113 Nh | 114 FI | 115 Mc | 116 Lv | $\begin{gathered} 117 \\ \text { Ts } \end{gathered}$ | 118 Og |


| Lanthanides | $\begin{gathered} 58 \\ \mathrm{Ce} \\ 140.12 \end{gathered}$ | $\begin{array}{\|c\|} \hline 59 \\ \mathrm{Pr}_{140} \end{array}$ | $\begin{gathered} \hline 60 \\ \mathrm{Nd} \\ 144.24 \end{gathered}$ | $\begin{gathered} \hline 61 \\ \mathrm{Pm} \end{gathered}$ | $\begin{array}{\|l\|} \hline 62 \\ \mathrm{Sm} \\ 150.4 \end{array}$ | $\begin{gathered} 63 \\ \text { Eu } \\ 151.96 \end{gathered}$ | $\begin{gathered} 64 \\ \text { Gd } \\ 157.25 \end{gathered}$ | $\begin{gathered} \hline 65 \\ \mathrm{~Tb} \\ 158.93 \end{gathered}$ | $\begin{gathered} 66 \\ \text { Dy } \\ 162.50 \end{gathered}$ | $\begin{gathered} \hline 67 \\ \text { Ho } \\ 164.93 \end{gathered}$ | $\begin{aligned} & 68 \\ & \begin{array}{l} \text { Er } \\ 167.26 \end{array} \end{aligned}$ | $\begin{gathered} \hline 69 \\ \mathrm{Tm} \\ 168.93 \end{gathered}$ | $\begin{gathered} 70 \\ \mathrm{Yb} \\ 173.05 \end{gathered}$ | $\begin{gathered} \hline 71 \\ \text { Lu } \\ 174.97 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Actinides | $\begin{gathered} 90 \\ \text { Th } \\ 232.04 \end{gathered}$ | $\begin{gathered} 91 \\ \mathrm{~Pa} \\ 231 \end{gathered}$ | $\begin{gathered} 92 \\ \mathrm{U} \\ 238.03 \end{gathered}$ | $\begin{gathered} 93 \\ \mathrm{~Np} \end{gathered}$ | $\begin{gathered} 94 \\ \mathrm{Pu} \end{gathered}$ | $\begin{gathered} 95 \\ \text { Am } \end{gathered}$ | $\begin{gathered} 96 \\ \mathrm{Cm} \end{gathered}$ | $\begin{gathered} 97 \\ \text { Bk } \end{gathered}$ | $98$ | $\begin{gathered} 99 \\ \text { Es } \end{gathered}$ | $\begin{gathered} 100 \\ \text { Fm } \end{gathered}$ | $\begin{gathered} 101 \\ \mathrm{Md} \end{gathered}$ | $\begin{aligned} & 102 \\ & \text { No } \end{aligned}$ | $\begin{gathered} 103 \\ \mathrm{Lr} \end{gathered}$ |

