



Singapore Chemistry League 2023



Core Problems and Solutions



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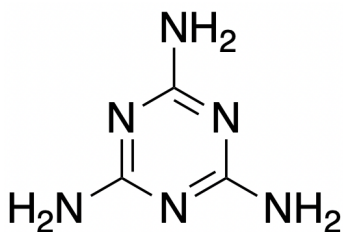
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Problem 1: The Melamine Milk Scandal**[5 points]**

In 2008, the melamine milk scandal saw the Sanlu group dope infant milk formula with melamine ($C_3H_6N_6$) to artificially increase the nitrogen content and return higher protein concentrations in order to pass quality control checks. Unfortunately, it also resulted in widespread occurrences of kidney damage in some 300,000 infants.



The chemical structure of melamine

In the milk industry, protein content has traditionally been measured by the **Kjeldahl method**. It leverages the fact that the amino acids in proteins are some of the only nitrogen-containing biomolecules in the body, and calculates the percentage by mass of nitrogen in the sample. This number is termed the N-value. The Crude Protein (CP) content is obtained by multiplying the N-value by 6.38.

(a) What is the percentage by mass of nitrogen in melamine?

Leave your answer in 3 significant figures. [2 points]

A sample of milk was tested and found to have a CP of 2.50. To pass quality control checks, the milk needs to have a minimum CP of 3.00. The manufacturer (illegally) adds melamine to this milk to fulfil quality control requirements.

(b) What is the percentage by mass of melamine in this final mixture?

Leave your answer in 3 significant figures. [3 points]

Solution:

(a) 66.6%

With the chemical formula, $C_3H_6N_6$, provided, finding percentage by mass of N becomes a straightforward application of formula:

$$\begin{aligned} \% \text{ by mass of N} &= \frac{\text{Mass of N in compound}}{\text{Relative molar mass of compound}} \times 100\% \\ &= \frac{6 \times 14.01}{3 \times 12.01 + 6 \times 1.008 + 6 \times 14.01} \times 100\% \\ &= 66.641\% \text{ (5 s.f.)} \\ &= 66.6\% \text{ (3 s.f.)} \end{aligned}$$

(b) 28.5%

Originally, the milk had a measured CP of 2.50, which corresponds to an N-value of 2.50/6.38. The N-value we need to reach in order to hit a CP of 3.00 is 3.00/6.38.

Recall that the N-value was defined as the percentage by mass of nitrogen in the sample. Now, let's imagine a hypothetical setup where exactly 1g of milk is used, and x g is the volume of melamine that needs to be added to the milk to reach a CP of 3.00. We can write an equation as follows:

$$\begin{aligned} \frac{\text{Mass of N in mixture}}{\text{Total mass of mixture}} &= \text{required N value} = \frac{3.00}{6.38} \\ \frac{\text{Mass of N from milk} + \text{Mass of N from melamine}}{\text{Total mass of mixture}} &= \text{required N value} = \frac{3.00}{6.38} \\ \frac{\frac{2.50}{6.38} \times 1 + \frac{6 \times 14.01}{3 \times 12.01 + 6 \times 1.008 + 6 \times 14.01} x}{1 + x} &= \frac{3.00}{6.38} \end{aligned}$$

Solving this, we obtain $x = 0.39945$ (5 s.f.) The % by mass of melamine in the final mixture is found from the expression $\frac{x}{1+x} \times 100\%$. Substituting the value of x found gives us the final value, 28.5% (3 s.f.)

Problem 2: Unit To Stop**[7 points]**

In this problem, you may assume all gases are ideal gases.

Ariel is from Singapore but enjoys travelling the world and making new friends. She and a few of her close friends enjoy collecting gases. However, Ariel sometimes struggles to communicate with these friends, especially when they use weird units she does not understand. She has 0.548 kg of chlorine, under atmospheric pressure and at a temperature of 298 K.

(a) What volume of chlorine does Ariel have?

Leave your answer in 3 significant figures in units of dm^3 . [2 points]

Barry is from the United States. He has 1.21lb of nitrogen gas, under a temperature of 79°F and a pressure of 35 pounds per square inch (PSI).

Charles is from the UK. He has 0.617 stone of xenon gas, under a temperature of 518°R and a pressure of 676 mmHg.

Dewei is from China. She has 3.45 *jīn* (斤) of methane gas at 25°C and a pressure of 14500 mmH₂O.

(b) For their annual get-together in Las Vegas, Ariel wants to gather all four collections of gases together in a room. What is the sum of the volumes of the four gases?

Leave your answer in 3 significant figures in units of cubic yards. [3 points]

Ariel wants to rent a function room for everyone to meet, but the proprietor wants to make sure the pressure of all the gases is not too much for the walls of the room to handle before renting the room out. Strangely, the proprietor operates in the centimeter-gram-second (CGS) unit system, and wants Ariel to report the pressure in the CGS unit of barye. He tells Ariel that the function room has dimensions of 280 cm by 580 cm by 740 cm, and is under room temperature. You may assume the gases do not react.

(c) Calculate the final pressure of the room when all 4 gas collections are present.

Leave your answer in 3 significant figures in units of barye. [2 points]

Use the following values on the next page when solving this problem.

Mass:

Pound: 1lb = 453.59 g

1 stone = 14 pounds

1jin = 500g

Length:

1 inch = 2.54 cm

1 foot = 12 inches

1 yard = 3 feet

Temperature:Fahrenheit: $^{\circ}\text{F} = ^{\circ}\text{C} \times \frac{5}{9} + 32$ ¹Rankine: $1^{\circ}\text{R} = 5/9 \text{ K}^2$ **Pressure:**

1 PSI is the pressure resulting from the gravitational force exerted by 1 pound on the surface of earth applied to an area of one square inch.

1 barye = $1 \text{ g cm}^{-1} \text{ s}^{-2}$ Density of mercury = 13.5 g cm^{-3} Density of water = 1 g cm^{-3} Gravitational field strength at Earth's surface = 9.81 kg m s^{-2}

¹ Erratum: The correct conversion is $^{\circ}\text{F} = ^{\circ}\text{C} \times 9/5 + 32$.

² Erratum: The correct conversion is $1^{\circ}\text{R} = 9/5 \text{ K}$. Teams are notified of the errata after the start of the competition.

Solution:

(a) 189 dm³

$$n = \frac{0.548 \times 10^3}{2(35.45)} = 7.7292 \text{ mol}$$

$$V = \frac{nRT}{p} = \frac{7.7292(8.3145)(298)}{101325} = 0.18900 \text{ m}^3 = 189.00 \text{ dm}^3$$

(b) 4.01 yd³

To solve this question, it is best to convert everything to SI base units first before working out the volumes.

Barry:

$$\text{Mass} = 1.21(453.59) = 548.8439 \text{ g}$$

$$\text{Amount} = \frac{548.8394}{2(14.01)} = 19.588 \text{ mol}$$

$$T = 79^\circ\text{F} = (79 - 32)\left(\frac{5}{9}\right)^\circ\text{C} = 26.111^\circ\text{C} = 299.26\text{K}$$

$$\text{pressure} = 35 \times \frac{453.59 \times 10^{-3} \times 9.81}{(2.54 \times 10^{-2})^2} = 241397 \text{ Pa}$$

$$V = \frac{19.588(8.3145)(299.26)}{241397} = 0.20190 \text{ m}^3$$

Charles:

$$\text{Mass} = 0.617(14)(453.59) = 3918.1 \text{ g}$$

$$\text{Amount} = \frac{3918.1}{131.3} = 29.841 \text{ mol}$$

$$T = \frac{5}{9}(518) = 287.78\text{K}$$

$$\text{pressure} = (13.5 \times 10^3)(9.81)(676 \times 10^{-3}) = 89526 \text{ Pa}$$

$$V = \frac{29.841(8.3145)(287.78)}{89526} = 0.79756 \text{ m}^3$$

Dewei:

$$\text{Mass} = 500(3.45) = 1725 \text{ g}$$

$$\text{Amount} = \frac{1725}{12.01 + 4(1.008)} = 107.53 \text{ mol}$$

$$T = 298.15\text{K}$$

$$\text{pressure} = (1 \times 10^3)(9.81)(14500 \times 10^{-3}) = 142245 \text{ Pa}$$

$$V = \frac{107.53(8.3145)(298.15)}{142245} = 1.8740 \text{ m}^3$$

$$\text{Total volume} = 0.18900 + 0.20190 + 0.79756 + 1.8740 = 3.06246 \text{ m}^3$$

$$1 \text{ cubic yard} = (36 \times 2.54 \times 10^{-2})^3 = 0.76455 \text{ m}^3$$

$$\text{Total volume} = \frac{3.06246}{0.76455} = 4.0056 \text{ yd}^3 = 4.01 \text{ yd}^3 \text{ (3 s.f.)}$$

(c) 34000 barye

$$\text{Total amount of gas} = 7.7292 + 19.588 + 29.841 + 107.53 = 164.69 \text{ mol}$$

$$\text{Volume of room} = (280 \times 10^{-2})(580 \times 10^{-2})(740 \times 10^{-2}) = 120.18 \text{ m}^3$$

$$\text{Pressure} = \frac{164.69(8.3145)(298.15)}{120.18} = 3397.1 \text{ Pa}$$

$$1 \text{ barye} = \frac{10^{-3}}{10^{-2}} = 10^{-1} \text{ Pa}$$

$$\text{Pressure} = 33971 \text{ barye} = 34000 \text{ barye (3 s.f.)}$$

Note: I hope this question has served as an insight into the importance of a standardised system of units (SI).

Problem 3: Transmutation and Vanishing Crystals**[4 points]**

In physics (as well as nuclear chemistry), there are 3 common types of radioactive decay: Alpha, Beta minus and Beta plus.

Name	Equation
Alpha	${}^A_ZX \rightarrow {}^{A-4}_{Z-2}X + {}^4_2He$
Beta minus	${}^A_ZX \rightarrow {}^A_{Z+1}X + e^- + \text{antineutrino}$
Beta plus	${}^A_ZX \rightarrow {}^A_{Z-1}X + \text{positron} + \text{neutrino}$

It is given that the end product of a long decay chain is lead-206. During the decay chain, a total of 6 helium-4 nuclei and 4 electrons were observed to be emitted.

(a) What is the sum of the nucleon number and proton number of the starting element?

[2 points]

Radioactive decay occurs at varying rates for different substances, as, just as in kinetics, is measured by the half-life, $t_{1/2}$. The half-life is defined as the length of time it takes for half of the radioactive atoms of a specific radionuclide to decay.

Ammie is immortal and spends her time collecting elements. On her 19th birthday, she collected a bismuth crystal that weighs exactly 100g. After eons had passed, she was shocked to find that her once-majestic crystal had diminished to just 10g - what in the world happened?

Contrary to popular belief, bismuth is not a stable element - its most stable isotope, ${}^{209}\text{Bi}$, has a half-life of 2.01×10^{19} years.



Ooh, bismuth crystals!

And while we're at it... Ammie really is immortal, isn't she? When this happened she would have been $n \times 10^m$ years old.

(b) What is the value of $n+m$?

Leave your answer to 3 significant figures, and assume that the crystal constitutes of entirely ^{209}Bi . [2 points]

Solution:

(a) 320

Lead-206 has nuclide notation ${}_{82}^{206}\text{Pb}$.

Emission of 6 helium-4 nuclei indicates that 6 alpha decays have occurred, while emission of 4 electrons indicates 4 beta-minus decay steps have occurred.

Each alpha decay results in a decrease in nucleon number of 4 while beta-minus decay does not affect nucleon number; the nucleon number of the starting compound is thus $206 + 6(4) = 230$.

Each alpha decay results in a decrease in proton number of 2 while beta-minus decay increases proton number by 1; the proton number of the starting compound is thus $82 + 6(2) - 4(1) = 90$.

The starting compound was ${}_{90}^{230}\text{Th}$, and the sum of the nucleon and protons numbers is $230 + 90 = 320$.

(b) 25.7

To find how many years has transpired since Ammie's glorious 100g crystal decayed to just 10g, we first find n , the number of half-lives that have passed:

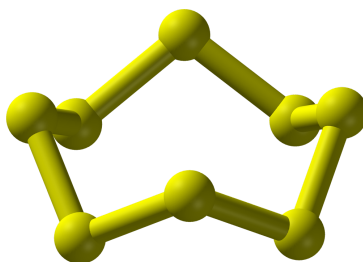
$$\begin{aligned}\left(\frac{1}{2}\right)^n &= \frac{1}{10} \\ n(\ln(\frac{1}{2})) &= \ln(\frac{1}{10}) \\ n &= 3.3219 \text{ (3 s.f.)}\end{aligned}$$

Thus, a total of $3.3219 \times 2.01 \times 10^{19} = 6.6770 \times 10^{19}$ (5 s.f.) years have passed since Ammie obtained the bismuth crystal. She would have been $6.6770 \times 10^{19} + 19 \approx 6.6770 \times 10^{19}$ years old!

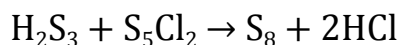
Thus $n = 6.6770$ (5 s.f.) and $m = 19$.

Problem 4: What's That Smell?**[3 points]**

Sulfur is one of the elements that exist naturally in the most number of different allotropes (forms). Many forms of elemental sulfur involve its atoms bonded to each other like a ring - these are generally known as cyclo-sulfur allotropes. For example, S_8 , the most common form of sulfur, has a structure which looks almost like a crown:



These cyclo-sulfur rings may look reactive, but they are actually really stable! In fact, they can be made in the lab, by reacting a hydrogen polysulfide (H_2S_x) with a polysulfide dichloride (S_yCl_2), where $x, y \geq 2$. For example, S_8 could theoretically be made by reacting H_2S_3 with S_5Cl_2 , in the following reaction:

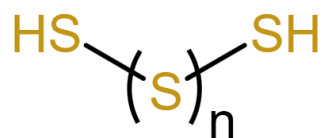


Note that it is also possible to produce S_8 by reacting H_2S_4 with S_4Cl_2 , or reacting H_2S_5 with S_3Cl_2 and so on, as long as the total number of sulfur atoms found in the reactants is consistent.

With this knowledge, find the minimum ring size of a cyclo-sulfur ring such that its enthalpy change of formation is endothermic. If you believe that the enthalpy change of formation is always exothermic for cyclo-sulfur rings of all sizes, input your answer as "0".

You may use this data:Bond energy (H-S) = 347 kJmol^{-1} Bond energy (S-Cl) = 250 kJmol^{-1} Bond energy (S-S) = 264 kJmol^{-1} Bond energy (H-Cl) = 431 kJmol^{-1}

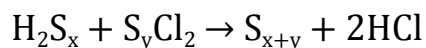
Hint: Hydrogen polysulfides and polysulfide dichlorides have the following general structures respectively:



Solution:

0

We can reframe the problem by considering the general form of the equation which produces a cyclo-sulfur ring of a certain ring size,



To calculate the enthalpy change of formation for S_{x+y} , we can examine the bonds broken and formed in the reaction.

The bonds broken are 2 H–S bonds and 2 S–Cl bonds, found at each end of the polysulfide chain (refer to the hint for its structures). The actual polysulfide component of each reactant remains unaffected, as only the ends are joined together to form the final cyclo-sulfur ring.

The bonds formed are hence 2 S–S bonds and 2 H–Cl bonds. We can calculate the ΔH_r as follows:

$$\begin{aligned}\Delta H &= \sum BE(\text{bonds broken}) - \sum BE(\text{bonds formed}) \\ \Delta H &= [2BE(\text{H-S}) + 2BE(\text{S-Cl})] - [2BE(\text{S-S}) + 2BE(\text{H-Cl})] \\ &= [2(347) + 2(250)] - [2(264) + 2(431)] \\ &= -196 \text{ kJ mol}^{-1}\end{aligned}$$

Surprisingly, we did not have to consider x or y in our calculations, as the length of the polysulfide chains in the reactants does not affect the reaction enthalpy. It is safe to say that the enthalpy change of reaction remains constant at -196 kJ mol^{-1} regardless of the size of the cyclo-sulfur ring formed - hence the enthalpy change is never endothermic!

Problem 5: Don't Try This At Home!**[3 points]**

One day, Lowry the calm scientist decides to make a high-pressure vial (To play with? To look at? Who knows? Only he). The idea is that he would fill a small glass vial with a gas at high pressure and then seal it off to maintain the pressure inside. But how can he secure the vial without the gas escaping when he removes the pump, or the pressure inside bursting off the seal? Lowry is in a pickle.

Thankfully, the pickle reminds him of something. After some hard work thinking it through, Lowry learns he can make a high-pressure vial by placing a sublimable solid inside a glass vial, then sealing it into an ampoule using a blowtorch³. With the ampoule sealed, the solid sublimates into a gas, and with the gas trapped inside, the pressure builds up over time.

Being peace-loving and aware of the dangers with the ampoule dropping or exploding, Lowry chooses a non-toxic gas. What better candidate than CO₂!

Starting at atmospheric pressure, Lowry weighs 2g of dry ice, but to minimise sublimation, he spoons it in an empty glass vial immersed in liquid nitrogen at -195.8°C . Then, he quickly takes the vial out and seals it into an ampoule. Assume no dry ice sublimates during this process and no gas in the vial escapes. Using a displacement can, he estimates the interior volume of the ampoule to be 20 cm³.

Lowry allows the dry ice to completely sublime to CO₂ at 30°C. Find the final gas pressure in the ampoule in kPa.

Density of dry ice = 1.6 gcm⁻³

Leave your answer in 3 significant figures.

³ In ampoule-making, the glass at the mouth of the container melts under the heat of the blowtorch, allowing it to fuse together and create an airtight seal. Granted, some solid will sublime from the heat and some gas in the vial will escape, but as Lowry is an expert amateur chemist, we accord him our trust.

Solution:

6100 kPa

$$M_r \text{ of CO}_2 = 12.01 + 2(16.00) = 44.01$$

$$\text{Amount of CO}_2 \text{ added} = \frac{2}{44.01} \text{ mol}$$

Note that the final pressure in the ampoule is contributed not only by the sublimated CO₂, but also by the gas already present in the vial after Lowry added the dry ice. We can find the volume of preexisting gas by subtracting the volume taken up by the dry ice from the total interior volume of the container.

$$\text{Volume of dry ice} = \frac{2}{1.6} = 1.25 \text{ cm}^3$$

$$\text{Volume of preexisting gas} = 20 - 1.25 = 18.75 \text{ cm}^3$$

Under atmospheric pressure 101325 Pa and at temperature -195.8°C ,

$$\text{Using } pV = nRT,$$

$$\text{Amount of preexisting gas} = \frac{(101325)\left(\frac{18.75}{10^6}\right)}{(8.3145)(273.15 - 195.8)} = 0.0029541 \text{ mol (5 s.f.)}$$

$$\text{Total amount of gas in ampoule} = \left(\frac{2}{44.01} + 0.0029541\right) \text{ mol}$$

At temperature 30°C and volume 20 cm^3 ,

$$\text{Using } pV = nRT,$$

$$\text{Total pressure} = \frac{\left(\frac{2}{44.01} + 0.0029541\right)(8.3145)(273.15 + 30)}{\frac{20}{10^6}} = 6099500 \text{ Pa (5 s.f.)} = 6100 \text{ kPa (3 s.f.)}$$

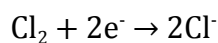
That is over 60 times atmospheric pressure! Much caution is needed. Just a little more pressure and the CO₂ would reach its critical point ($\sim 73 \text{ atm}$), beyond which it would transition into a supercritical fluid. Maybe Lowry would have liked that more... that's a story for another day.

Problem 6: The Mighty Ox and The Crimson Cat**[4 points]**

The concept of oxidation states is something that tends to be glossed over in high school. Doubtless you have been exposed to a variety of redox reactions, but what does it really mean when something is oxidised or reduced?

In truth, oxidation states are an invented concept, just a way of bookkeeping. It's a quick and convenient way to keep track of electron distributions, where a species at higher oxidation state is more electron-deficient, and a species at lower oxidation state more electron-rich.

This concept is quite easily illustrated in the case of ions. Consider the following reaction:



The oxidation state of chlorine has changed from 0 to -1 here, and simultaneously it has gained an electron, thus becoming more electron-rich.

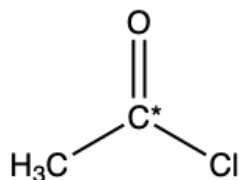
However, so far we have only been looking at ionic species. What do we make of atoms that are covalently bonded? In fact, we do have a system to keep track of oxidation states in covalent compounds. In general, there are just two rules to follow:

1. For every single bond between an element X is bonded and a more electronegative element Y, the oxidation state of X increases by 1 and the oxidation state of Y decreases by 1. This means that double and triple bonds will cause an increase/decrease in oxidation states by 2 and 3 respectively.
2. When an element X is bonded to the same element, there is no change in oxidation state of either element as they are at the same electronegativity.

Let's get some practice applying these rules. For the rest of the question, use the Pauling electronegativity scale (a.k.a the one you'd be familiar with).

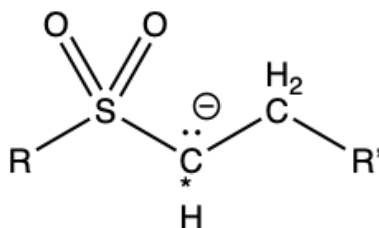
- (a) What is the oxidation state of the carbon labelled with an asterisk in the following molecule?

You may omit the + sign for positive oxidation states. **[2 points]**



Now, let's give this another try, but this time we're doing something different - we're mixing both covalent and ionic bonds!

- (b) A sulfonium ylide is a chemical species which has a carbanion (a carbon with a negative charge) adjacent to an $-\text{SO}_2\text{R}$ group (a.k.a a sulfonium group), as illustrated below. What is the oxidation state of the carbon labelled with an asterisk? *You may omit the + sign for positive oxidation states.* **[2 points]**



R and R' are hydrogen, alkyl or aryl groups, and are basically a common way to denote an arbitrary group in organic molecules. For this question, their exact identity is irrelevant.

Solution:

(a) 3

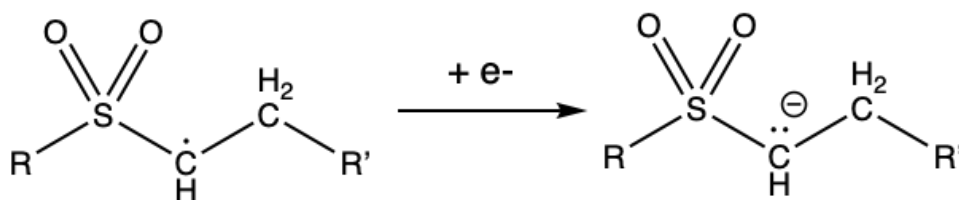
We observe that the carbon has a C=O bond, a C–C bond and a C–Cl bond. Since oxygen and chlorine are both more electronegative than carbon, this means that the C=O bond increases the O.S. of C by 2, the C–Cl bond increases it by 1, and the C–C bond has no effect on oxidation state. Thus, the overall oxidation state of carbon is +3.

(b) -1

Let's focus on the covalent bonds first. The carbon in question has 1 C–S bond, 1 C–H bond and 1 C–C bond. Sulfur very slightly ekes out carbon in electronegativity, with a Pauling electronegativity of 2.58 compared to 2.55, while hydrogen is decidedly less electronegative than C, at 2.20.

Thus, the C–S bond increases carbon's oxidation state by 1, the C–H bond decreases it by 1, and the C–C bond has no effect, for a net change of 0 (so far).

Now, let's consider the ionic side of things. Carbon has a -1 charge localised on itself, which effectively resulted from it gaining an electron. One could think of it this way:



Remember the central tenet of oxidation states? *An increase in electron density results in a decrease in oxidation state.* In this case, the carbon has thus decreased in oxidation state by 1, from 0, for an overall oxidation state of -1.

Problem 7: From Table Salt To Superconductors**[3 points]**

Within the field of solid state chemistry, the concept of a unit cell dominates: Simply put, it is the smallest section of a crystal lattice structure that can express the structure of the entire crystal. In other words, by identifying the unit cell, we are able to elucidate the structure of the entire crystal by translating the unit cell in all three axes. For instance, consider the familiar NaCl, whose crystal structure (Diagram 1) and unit cell (Diagram 2) are shown:

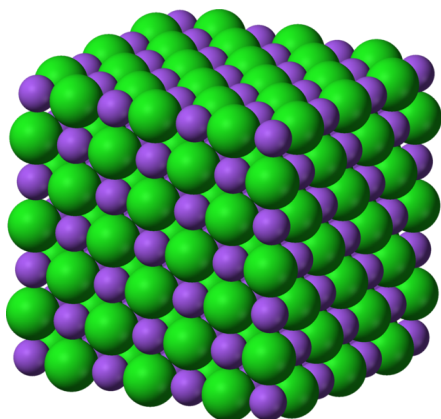


Diagram 1

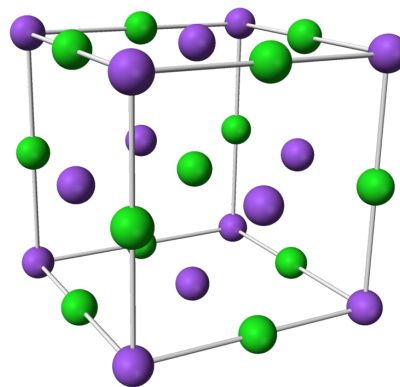
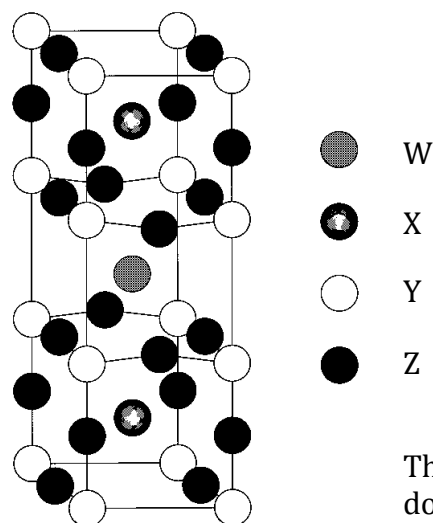


Diagram 2

In addition, we can elucidate the empirical formula of a chemical compound from the unit cell alone.

NaCl is the paragon of an ionic lattice but hardly representative - other crystal structures can prove much more complicated. Consider the unit cell of a certain superconductor shown below:



The letters are simply labels and do not correspond to actual chemical elements.

Suggest the empirical formula of the compound shown above, based on its unit cell.

Present your answer in the form $abcd$, where a , b , c and d are the stoichiometric amounts of W , X , Y and Z respectively. For instance, if you think the formula is $W_2X_3Y_4Z_5$, input your answer as 2345.

Hint: Do not take the unit cell at face value. Atoms located at the edges and vertices of the cell do NOT contribute a full equivalent of an atom to the unit cell! For example, does the unit cell of NaCl have the same number of Na and Cl atoms?

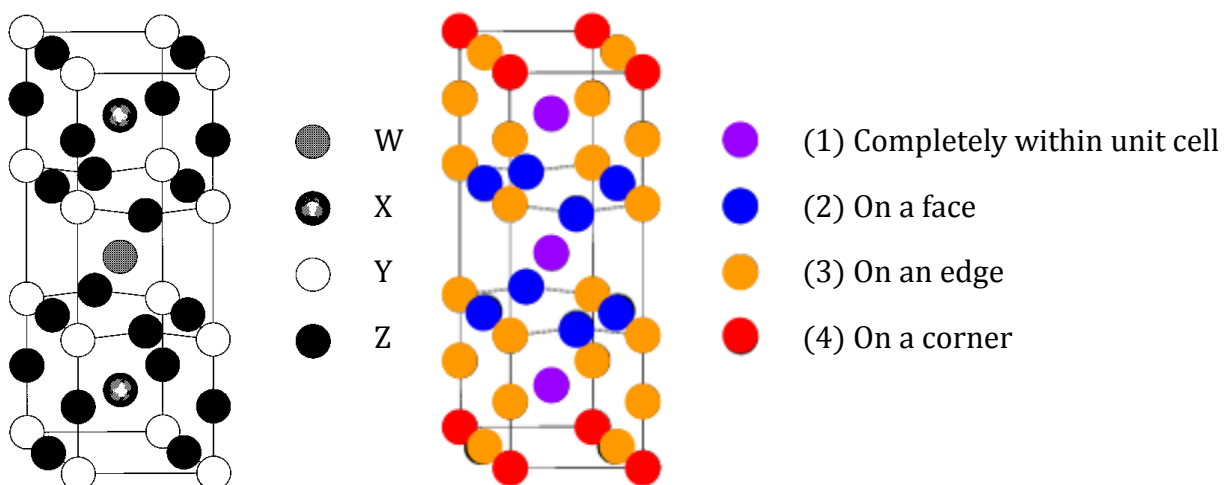
Solution:

1237

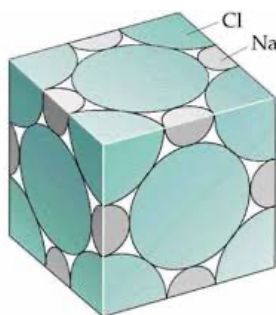
The stoichiometric ratios are $WX_2Y_3Z_7$.

While your first instinct upon seeing the unit cell may have been to count the number of respective atoms (which would give you $WX_2Y_{16}Z_{20}$, or 121620), this would not give you the answer because *each atom does not always contribute a full equivalent to the unit cell*.

We may divide the atoms into four types, atoms found (1) completely within the unit cell (2) on a face of the unit cell (3) on an edge of the unit cell, and (4) on a corner of the unit cell, as illustrated below:



Now consider that, for instance, an atom of type (3) would be shared between 4 unit cells - as the edge is necessarily in contact with four other cells. As a result, each atom would contribute only $\frac{1}{4}$ of an atom to any individual unit cell. To leverage NaCl once again, you could have visualised the unit cell as a perfect square, in which case each Na atom (of type (3)) would have appeared as such:



In a similar vein, atoms of type (1), (2) and (4) would contribute 1, $\frac{1}{2}$ and $\frac{1}{8}$ of an atom to each unit cell respectively.

Armed with this knowledge, we may now return to the problem at hand. Atoms W and X are the most straightforward, since they are both fully contained within the unit cell and are hence of type 1. There is 1 atom W and 2 atom Y, hence 1 and 2 equivalents respectively, per unit cell.

Atom Y has 8 corner atoms and 8 edge atoms, giving $8 * \frac{1}{8} + 8 * \frac{1}{4} = 3$ equivalents per unit cell.

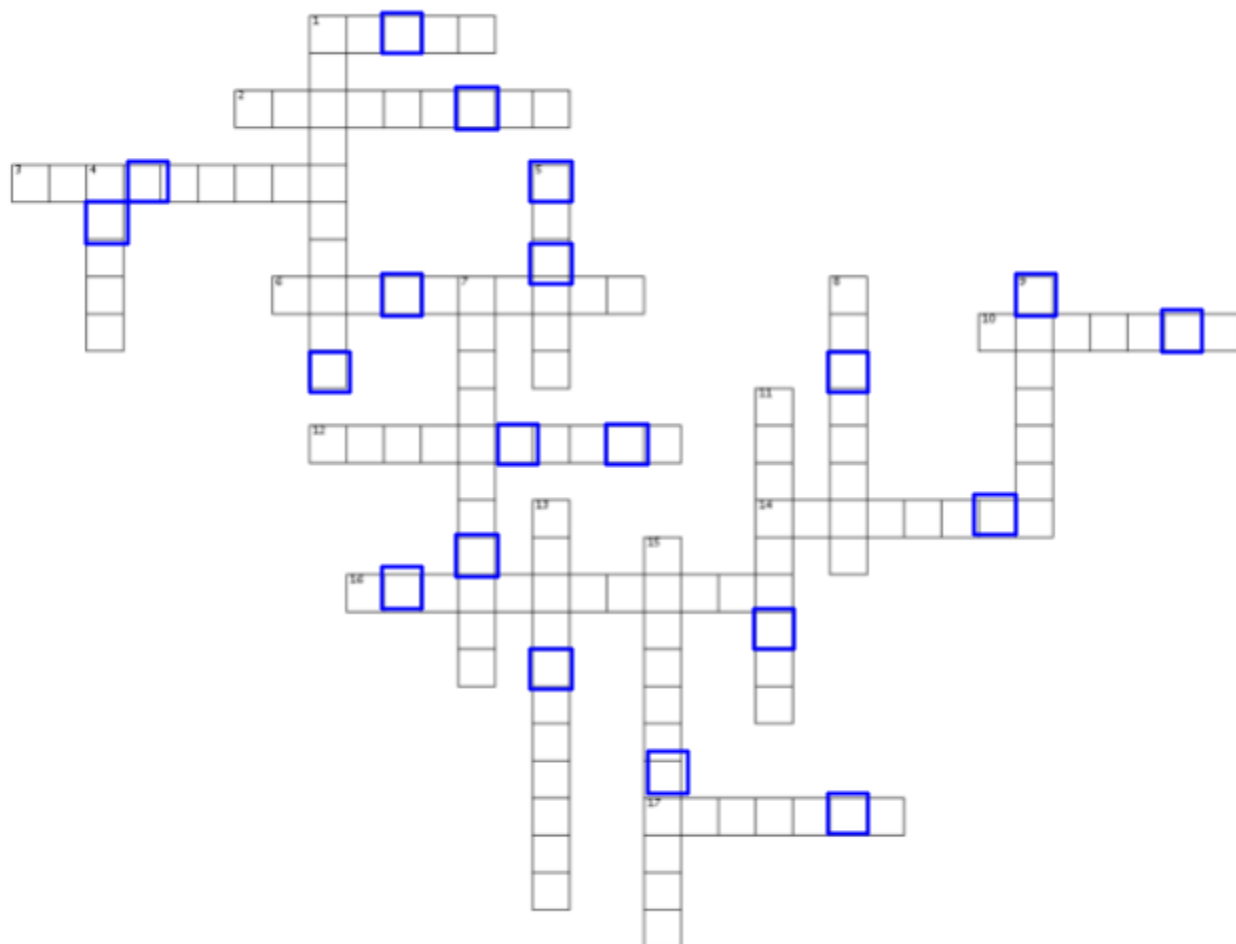
Atom Z has 12 edge atoms and 8 face atoms, giving $12 * \frac{1}{4} + 8 * \frac{1}{2} = 7$ equivalents per unit cell.

Thus the simplest ratio is 1:2:3:7.

For interest: The compound is Yttrium Barium Copper Oxide, commonly abbreviated to YBCO. In reality, the oxygen content tends to be lower than the stoichiometric amount of 7, due to defects in the crystal lattice structure (another common branch of study in solid state chemistry).

Problem 8: Take a break, let's talk lore**[5 points]**

With a healthy mixture of key words, basic jargon and some historical facts, let's enjoy one of your childhood pastimes in quite a different context. First, let's complete a crossword.

**ACROSS**

1. Bringer of both life and death, a German chemist responsible for developing both the reaction that would usher in the agricultural revolution, and a deadly chemical warfare agent that killed thousands in WW1.
2. A straight-chain molecule.
3. A common biopolymer found only in plant cells.
6. The first element in the periodic table to have no stable isotopes.
10. Biological catalysts.
12. A neutral molecule that has both positive and negative charges.
14. In their lavish, hedonistic banquets, Romans used to drink from _____ cups to induce vomiting and thus consume more food.

16. The common name for methanal, and also the substance commonly used to preserve organic specimens.
17. Fluorine is assigned a value of 3.98 on which electronegativity scale?

DOWN

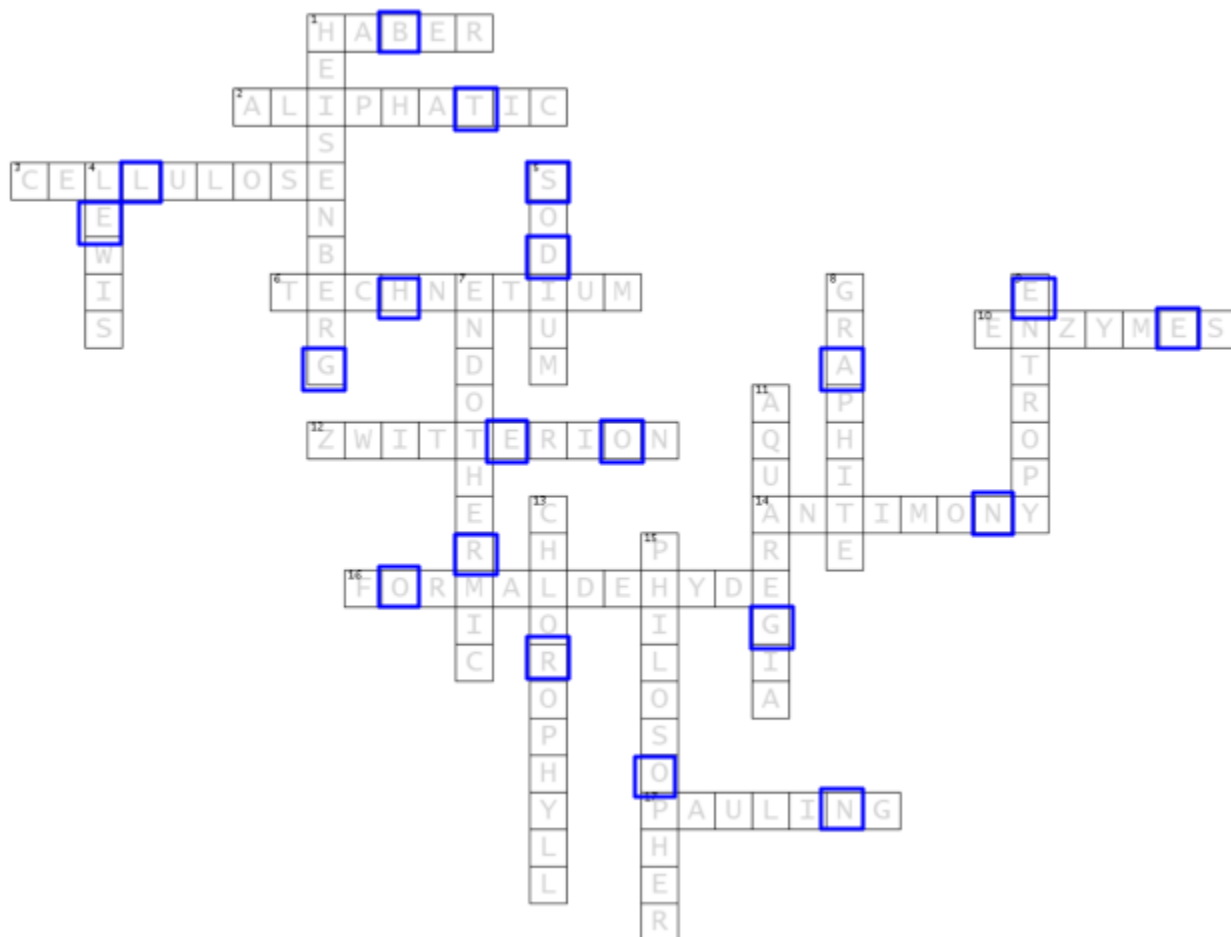
1. A name shared by both a German quantum physicist and a character from a famous Netflix series, although only pseudonymously by the latter.
4. The broadest classification of acid.
5. An element with a characteristic 589nm emission which saw widespread usage in street lamps in the late 20th century.
7. Bond-breaking is an _____ process.
8. A diamond isn't forever - it will slowly convert into another allotrope of carbon.
9. Ultimately, all reactions are driven by an increase in _____.
11. A mixture of two common acids which derives its name from its ability to dissolve gold.
13. The compound responsible for the green colour of plants.
15. Chemistry began with the quest for the _____'s stone, which was purported to have been able to convert lead to gold.

Now, you may have noticed that some boxes have been outlined in blue. As it turns out, the letters in these boxes spell the full name of a certain Nobel laureate in chemistry.

Which **year** was this Nobel laureate awarded the Nobel Prize?

Solution:

1951



The Nobel laureate is Glenn Theodore Seaborg, who, along with Edwin Macmillan, was awarded the 1951 Nobel Prize in Chemistry "for their discoveries in the chemistry of transuranium elements".

Problem 9: Imma Be Real With You**[5 points]**

Ammie was taught that ideal gases would occupy a molar volume of 22.4 dm³ at standard temperature and pressure, and 24.0 dm³ at room temperature and pressure. Being fastidious, she decides to test this out for herself with one mole of gas X, and obtains the results as follows:

Amount of gas / mol	Temperature / K	Pressure / Pa	Volume / dm ³
1	273.15	10 ⁵	22.475
1	293.15	101325	23.840

Table 1

The deviation from an ideal gas makes her wonder if there are equations that can model the properties of real gases better than the familiar $pV = nRT$. There are, in fact, multiple that have been proposed, one of which is the **Van der Waals equation**:

$$p = \frac{nRT}{V-bn} - \frac{an^2}{V^2}$$

Where a , b are experimentally determined constants.

The $-\frac{an^2}{V^2}$ term accounts for intermolecular attractive forces, which effectively decreases pressure exerted against the container. You can visualise this as the particles “pulling” together, hence bouncing against the walls of the container less frequently, resulting in less force exerted on the walls of the container and subsequently less pressure.

The $-bn$ term accounts for the volume occupied by a real gas, by modelling the gas particles as hard spheres that take up a finite volume. Hence, the actual volume available in the container is modified to be less than the total volume of the container.

- (a) Let us attempt a rudimentary modelling of such a system. Xenon has a Van der Waals radius of 216 pm. Based on the assumption that each gas particle is a perfect, hard sphere, what would the value of the coefficient b for Xenon be, expressed in m³mol⁻¹?
Leave your answer to 3 significant figures, in decimal form. [2 points]

(b) Let a_x and b_x be the Van der Waals coefficients of Ammie's gas X, expressed in $\text{J m}^3 \text{mol}^{-2}$ and $\text{m}^3 \text{mol}^{-1}$ respectively. What is the value of $a_x \times b_x$?

Leave your answer to 3 significant figures, in decimal form. [3 points]

Solution:

(a) 0.0000254 m³mol⁻¹

First, we obtain the volume of each Xenon atom. As 1 pm = 10⁻¹² m,

$$\text{Volume} = \frac{4}{3}\pi(216 \times 10^{-12})^3 \text{ m}^3$$

We then multiply by Avogadro's Number to obtain the average volume of one mole of Xenon gas particles:

$$\text{Molar volume} = \frac{4}{3}\pi(216 \times 10^{-12})^3 (6.0221 \times 10^{23}) \text{ m}^3$$

Which gives us 2.542130 x 10⁻⁵ m³mol⁻¹ (7 s.f.) upon solving.

(b) 0.0000433

Solving this is a matter of utilising simultaneous equations. As we are dealing with one mole of gas X, the Van der Waals equation can first be simplified as follows:

$$p = \frac{(1)RT}{V-b(1)} - \frac{a(1)^2}{V^2} = \frac{RT}{V-b} - \frac{a}{V^2}$$

We then express a in terms of b:

$$\begin{aligned} p &= \frac{RT}{V-b} - \frac{a}{V^2} \\ \frac{a}{V^2} &= \frac{RT}{V-b} - p \\ a &= \frac{RTV^2}{V-b} - pV^2 \end{aligned}$$

By substituting R = 8.3145 and the values in Table 1, we obtain a system of two linear equations:

$$\begin{aligned} a_X &= \frac{8.3145(273.15)(0.022475)^2}{0.022475-b_X} - 10^5(0.022475)^2 \\ a_X &= \frac{8.3145(293.15)(0.023840)^2}{0.023840-b_X} - 101325(0.023840)^2 \end{aligned}$$

Equating them will give a single solution set $(a_x, b_x) = (0.67624, 6.3971 \times 10^{-5})$, from which the final answer is derived.

Problem 10: How Familiar Are You With Euclidean Geometry?**[4 points]**

For how simple it is, the VSEPR model has incredible predictive power. As a result, despite the emergence of the newer, more versatile molecular orbital (MO) theory based on quantum chemical calculations, the VSEPR theory remains a valuable tool.

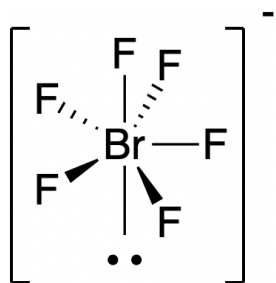
- (a) Of the following five molecules, there is one that has a different electron-pair geometry from the other four. Suggest which molecule this is.

Input the number corresponding to the molecule. [2 points]

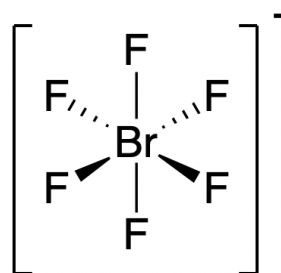
$[\text{I}_3]^-$	BrF_3	XeCl_4	SbCl_5	TeF_4
1	2	3	4	5

As with all theories, the VSEPR model has its limitations. For example, it fails at predicting the geometry of heavier d-block compounds, where *stereochemically inactive lone pairs* come into play. In simpler terms, this means that there are valence lone pairs that are effectively ignored when determining the geometry of the molecule, as they are buried in a deeper *s* subshell.

For example, the Br in $[\text{BrF}_6]^-$ has 1 lone pair and 6 bond pairs, for which VSEPR would predict a pentagonal bipyramidal electron-pair geometry as shown. However, it is octahedral in reality.



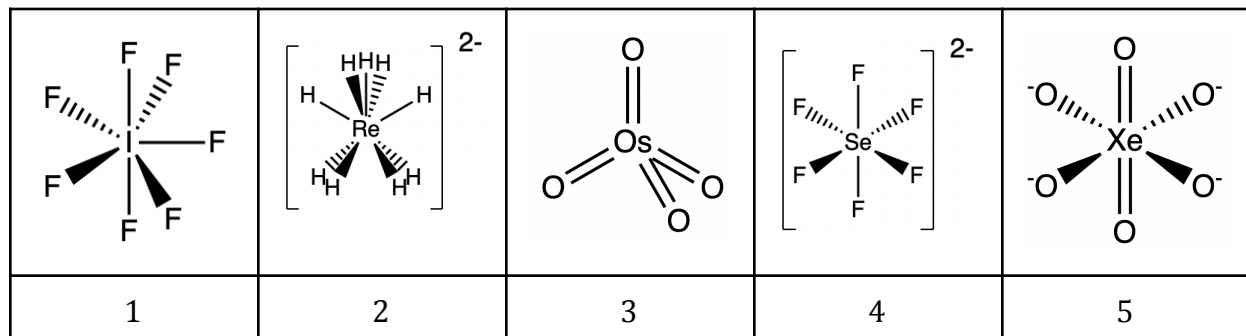
(Expected) Pentagonal bipyramidal



(Actual) Octahedral

(b) The geometry of a series of molecules are shown below. One and only one of them possess a stereochemically inactive lone pair. Which molecule is this?

Input the number corresponding to the molecule. **[2 points]**



Hint: In transition metals, we consider the outermost s and d subshells to be the valence shell. For example, palladium (0) is considered to have $2+8=10$ valence electrons..

Hint #2: For species with an overall charge, it helps, as a matter of bookkeeping, to "assign" the extra electrons to the central atom. Effectively, they are included into the valence shell of the central atom.

Solution:

(a) 3

All of the molecules except for 3 have a trigonal bipyramidal electron-pair geometry. XeCl_4 is the only one that has an octahedral electron-pair geometry.

	1	2	3	4	5
Molecule	$[\text{I}_3]^-$	BrF_3	XeCl_4	SbCl_5	TeF_4
Molecular geometry	Linear	T-shaped	Square planar	Trigonal pyramidal	See-saw
Lone pairs	3	2	2	0	1
Bond pairs	2	3	4	5	4
Regions of electron density	5	5	6	5	5

(b) 4

We will first have to identify the expected geometry of each molecule under VSEPR theory, and then compare that to the actual geometry shown. If the actual structure has one less region of electron density than expected, that would be the molecule exhibiting a stereochemically inactive lone pair.

The following table shows the reasoning for each of the molecules:

	1	2	3	4	5
Formula	IF_7	$[\text{ReH}_9]^{2-}$	OsO_4	$[\text{SeF}_6]^{2-}$	$[\text{XeO}_6]^{4+}$
Charge	0	2-	0	2-	4-
Valence electrons of central atom*	7	$7 + 2 = 9$	8	$6 + 2 = 8$	8
Valence	7	9	8	6	8

electrons participating in bonding					
Lone pairs	$\frac{7-7}{2} = 0$	$\frac{9-9}{2} = 0$	$\frac{8-8}{2} = 0$	$\frac{8-6}{2} = 1$	$\frac{8-8}{2} = 0$
Expected geometry	Pentagonal bipyramidal	Tricapped trigonal prismatic	Tetrahedral	Pentagonal bipyramidal	Octahedral
Actual geometry				Octahedral	
Inert lone pair?	N	N	N	Y	N

*As a matter of bookkeeping, we “assign” the additional electrons gained in forming the anion to the central atom, even though in reality they are not necessarily located there. The $[\text{XeO}_6]^{4-}$ is an exception, as we’re able to assign them to the oxygens instead. Ultimately, regardless of where you assign the additional electrons, the important thing is to draw reasonable Lewis structures where octets are fulfilled as much as possible (for the side atoms, at least), and all electrons are accounted for.

Problem 11: The Iodoform Test**[6 points]**

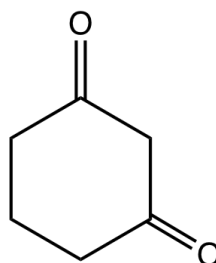
The iodoform test is commonly known as a test for organic compounds containing the following functional groups: $-\text{CH}(\text{CH}_3)\text{OH}$ and $-\text{COCH}_3$. First used by Lieben in 1870, the test has been around for over 150 years. In the iodoform test, the substance of interest is heated in an alkaline solution containing aqueous iodine. A positive test is indicated by the precipitation of the yellow solid, CHI_3 , also known as iodoform.

The iodoform test exploits the acidity of the protons on the carbon atom that is adjacent to the carbonyl group, as well as the keto-enol equilibrium of the methyl ketone:

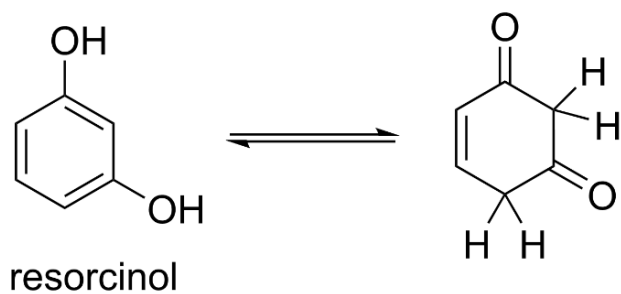


With the alkene $\text{C}=\text{C}$ bond present, it is not difficult to see the potential for substitution of H atoms by I atoms to occur on this carbon atom. After three substitutions, nucleophilic addition-elimination process takes place on the carbonyl group to finally form the iodoform precipitate and complete the reaction.

- (a) In the reaction of acetone in the iodoform test, intermediate A with $M_r = 435.75$ is formed. Provide the structure of intermediate A. **[2 points]**
- (b) Interestingly, 1,3-cyclohexanedione also gives a positive iodoform test result. At the end of the reaction, organic product B and iodoform precipitate are formed. Provide the structure of product B, which is uncharged and purely covalent. **[2 points]**



- (c) Even more interestingly, in 1959, Seelye & Turney observed that resorcinol, or 1,3-dihydroxybenzene, also gave a positive result in the iodoform test after a prolonged duration. At first glance, this may seem like a rather curious result but in fact, it can be explained by first considering keto-enol tautomerism of resorcinol:

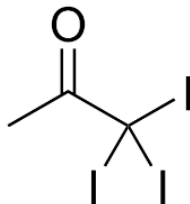


At the end of the reaction, organic product C and iodoform precipitate are formed. Provide the structure of the uncharged and purely covalent product C with formula $C_5H_6O_4$.

Provide the structure of the more stable stereoisomer. [2 points]

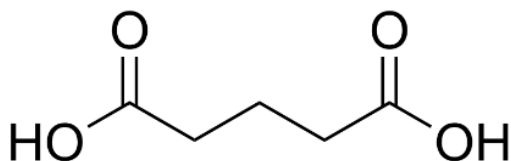
Solution:

(a)



The iodoform reaction involves stepwise substitution of the hydrogen atoms at the alpha position before the Cl_3^- ion leaves as the leaving group. Thus, considering the molar mass of the intermediate provided (435.75), the intermediate must be the one formed after 3 substitutions (i.e. with three I atoms bonded to the carbon at alpha position to the ketone).

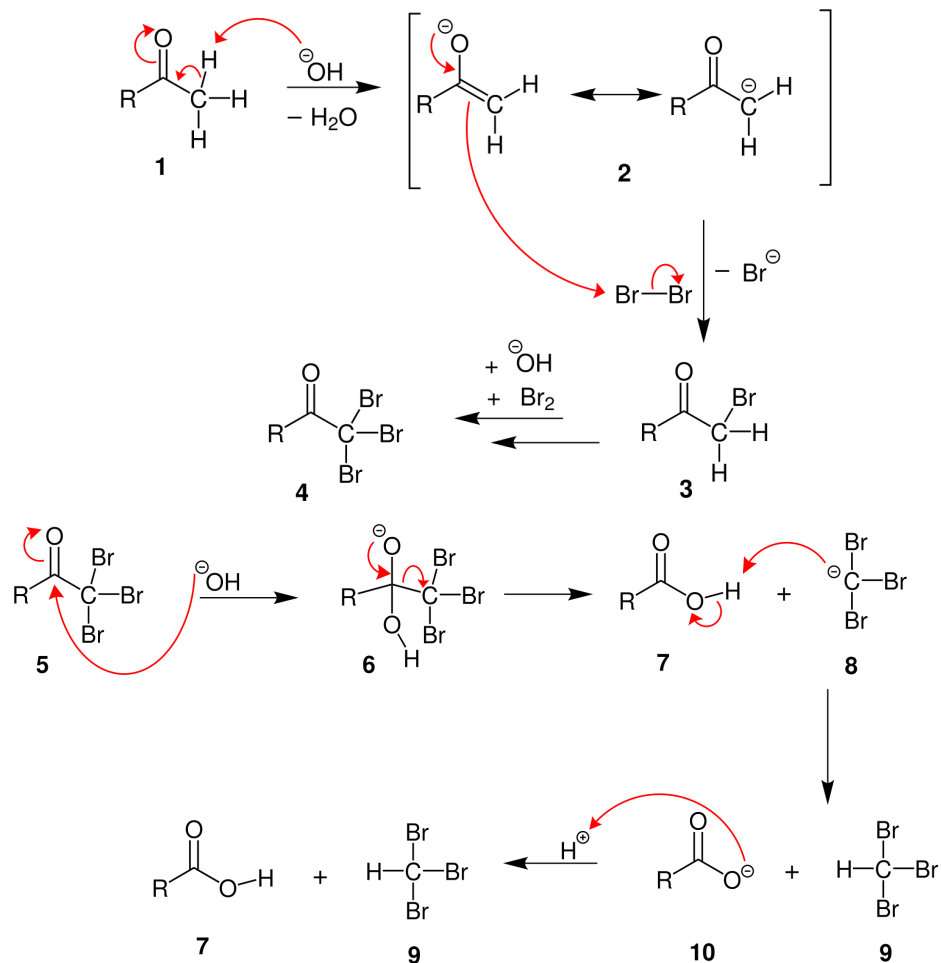
(b)



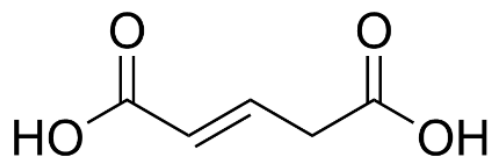
To successfully solve this question requires a good understanding of the mechanism of the iodoform reaction, which is shown below.

The most acidic protons on the 1,3-cyclohexanedione molecule are the two that are alpha to both $\text{C}=\text{O}$ groups. Thus, two substitutions of H atoms with I atoms would take place there. After the substitutions, a hydroxide ion attacks one of the carbonyl carbons, forcing the $-\text{CI}_2^-$ group to leave and as a result, one of the carbonyl groups becomes a carboxylic acid group. The $-\text{CI}_2^-$ group can be first protonated or it could also immediately attack an electrophilic I_2 molecule, converting itself into $-\text{CI}_3$. The hydroxide ion would then attack the remaining carbonyl group to convert it into a carboxylic acid group as well.

To help with understanding the solution, the mechanism for the haloform reaction on a typical methyl ketone substrate is shown below, involving Br atoms instead of I atoms as an example. The same mechanism takes place for iodine as a reactant.



(c)



The iodoform reaction on 1,3-dihydroxybenzene follows a similar pattern to that described in (b).

Problem 12: Quantum isn't scary, I promise**[6 points]**

Chemists are great lovers of systematisation - we like to have numbers and labels for everything. This is also the case with our very own atomic orbitals - instead of the familiar *spdf* terminology generally encountered, the (electrons in) orbitals are more rigorously classified according to a set of four **quantum numbers**:

Quantum number	Symbol	Possible values	Relationship to <i>spdf</i> terminology
Principal	n	1,2,...	Corresponds to the atomic <u>shell</u> - e.g. the $3d_{xy}$ orbital belongs to the 3rd shell hence has $n = 3$, $2p_x$ has $n = 2$, and so on.
Angular momentum	l	0,1,... $n-1$	Corresponds to the <u>subshells</u> , i.e the <i>spdf</i> classification, where $l=0$ is the s subshell, $l=1$ is the p subshell, and so on.
Magnetic	m_l	$-l, -(l-1), \dots, 0, \dots, l-1, l$	Corresponds to the exact <u>orbitals</u> - for instance, the only difference between the $2p_x$ and $2p_z$ orbitals are their m_l numbers. There's no systematic way to relate our conventional naming of the orbitals to their magnetic quantum numbers.
Spin	m_s	$-\frac{1}{2}, \frac{1}{2}$	Determines the spin orientation of the electron occupying the orbital. Remember how the Pauli Exclusion Principle states that each orbital can only hold 2 electrons? This is the fancy way of arriving at the same conclusion.

Table 1

Seeing so many new terms at once may be intimidating, but do not be deterred - let us walk through this slowly. For a start, you may have noticed that the possible values of each quantum number (the third column of the table above) depends on the exact value of the previous quantum numbers (except for the spin quantum number, which is always either $\frac{1}{2}$ or $-\frac{1}{2}$). For instance, when principal quantum number $n=2$, the possible angular momentum quantum numbers, l , are 0 and 1, because the highest possible value of l was $n-1$.

- (a) A similar logic follows for the possible values of the magnetic quantum number, m_l . Suppose that $l = 3$. How many possible values of m_l are there? **[2 points]**

Now, let's get some practice converting between *spdf* notation and quantum number notation.

- (b) What are the principal and angular momentum quantum numbers of the $4d_{yz}$ orbital?

*Express your answer as a concatenated 2-digit number \overline{nl} , where n is the principal quantum number and l the angular momentum quantum number. **[2 points]***

Let's try converting between notations again, but in a slightly different manner.

- (c) How many orbitals are there with $n=3$? **[2 points]**

Solution:

(a) 7

The range of values of m_l is $-l, -(l-1), \dots, 0, \dots, l-1, l$. We've been given that $l=3$. Thus, the possible values of m_l are $-3, -2, -1, 0, 1, 2, 3$. This gives us a total of 7 possible values.

(b) 42

The principal quantum number is rather more of a giveaway, as it is already present in the name! The $4d_{yz}$ orbital belongs to the 4th shell, and hence $n=4$.

In Table 1, it was given that “ $l=0$ is the s subshell, $l=1$ is the p subshell, and so on.” By extrapolating just a bit further, we can deduce that $l=2$ corresponds to the d subshell (and $l=3$ to the f subshell).

Thus the required number \overline{nl} would be 42.

(c) 9

In effect, the question is asking how many orbitals are in the 3rd atomic shell. The most straightforward solution is to brute-force this: Within the 3rd shell we have the 3s, 3p and 3d subshells. We have 3 p orbitals and 5 d orbitals (note that this is regardless of the atomic shell!), giving us a total of $5+3+1 = 9$ orbitals in all.

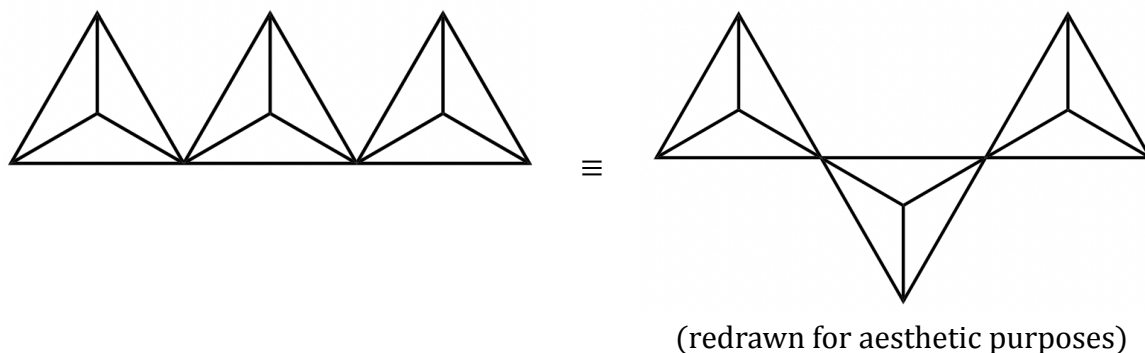
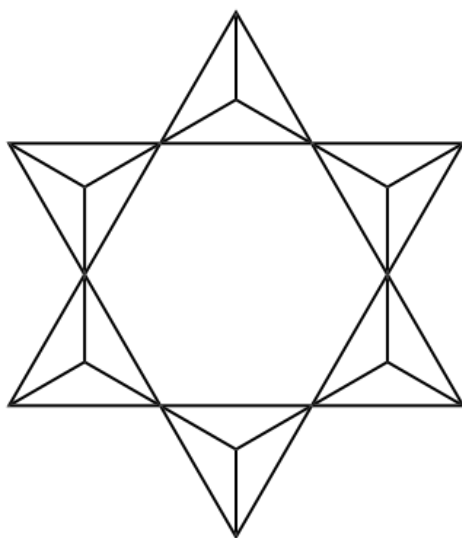


Figure 4

- (a) Let the chemical formula of the following silicate be $[\text{Si}_x\text{O}_y]^{z-}$. What is the value of the concatenated number \overline{xy} ? **[2 points]**



- (b) With reference to the silicate in part (a), suggest the value of z , where $z-$ is the charge of the silicate. **[2 points]**

Hint: In general, any oxygen that is bonded to only 1 Si bears a 1- charge, while any oxygen bonded to 2 Si bears no charge.

Inosilicates are a subset of silicates that have a chain-like structure. The diagram below shows the structure of what is known as a *single-chain inosilicate* with an unknown number of $[\text{SiO}_4]$ units:

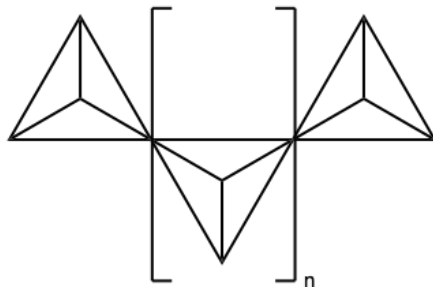


Figure 5

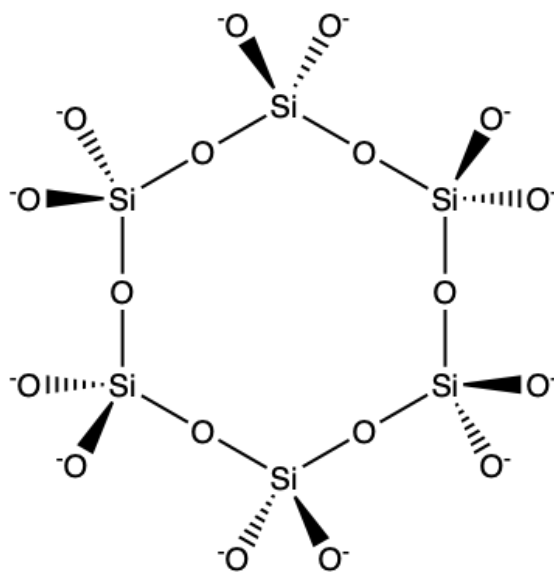
The bracket with n denotes that the basic unit found inside is repeated many times to form a polymeric structure.

- (c) One particular single-chain inosilicate, with a polymeric structure as shown in figure 5, has a total charge of 20^- . How many silicon atoms are found in the inosilicate? **[2 points]**

Solution:

(a) 618

The simplified structure represents the following cyclic silicate, where some Si-O-Si bond angle-accuracy has been sacrificed for the sake of clarity:



As can be seen, there are 6 silicon atoms and 18 oxygen atoms, thus $x = 6$ and $y = 18$.

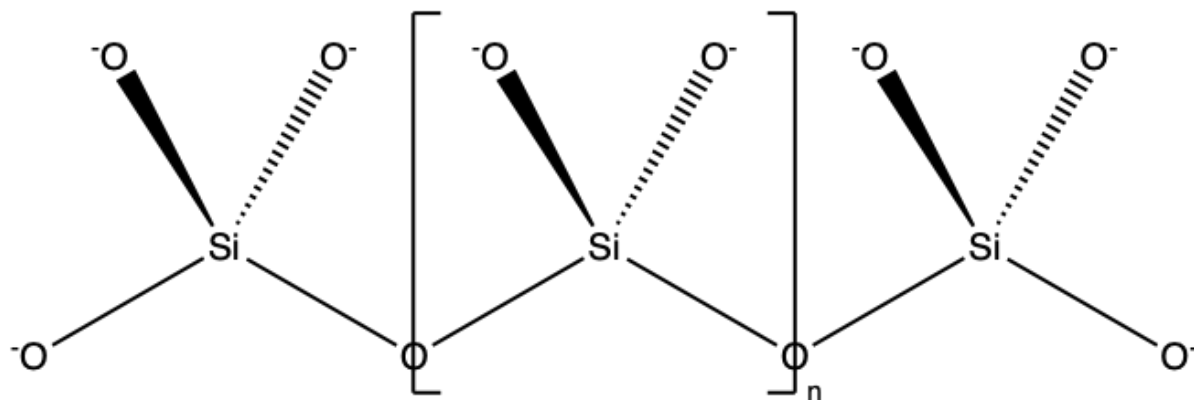
(b) 12

Similarly, had you successfully arrived at the structure of the cyclic silicate above, the charge could be easily deduced. There are only 12 oxygen atoms bonded to only one Si, for an overall charge of 12-.

The information in the hint is a manifestation of the convenient (but not infallible!) rule of thumb that atoms in a molecule will attempt to fulfil octet state. An oxygen with 2 single covalent bonds already has 8 electrons in its valence shell, while an oxygen with only 1 single bond has only 7 valence electrons. Thus, it “gains” an electron to fulfil octet, thus conferring upon it a negative charge.

(c) 9

It is perhaps more convenient to convert the tetrahedral simplification into the actual structure of the inosilicate, which is shown below:



Notice that the “terminal” silicons are bonded to 3 oxygen atoms with 1- charge each, while the “middle” silicon atoms are each connected to 2 oxygen atoms with 1- charge each. Thus, an equation can be constructed:

Total charge on “middle” silicons + total charge on “terminal” silicons = total charge of silicate

$$2n + 3 \times 2 = 20$$

$$n = 7$$

Hence, there are 7 “middle” silicons, and adding the two “terminal” silicons, we obtain a total of 9 silicons in this inosilicate.

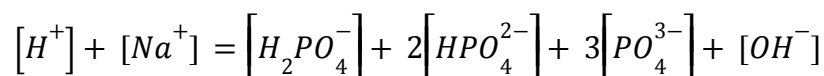
Problem 14: CHAAARGE!!!!**[3 points]**

In solving complex equilibria, we often have to bring in various balance equations, including mass balance, charge balance and proton balance. Of these, charge balance equations (CBEs) are some of the most useful.

To set up a charge balance equation, we need to identify the ions that could be present in that solution, and then equate all the positive charges to the negative charges. Thus, the general form of a charge balance equation is:

$$\begin{aligned} \text{Total positive charges} &= \text{total negative charges} \\ [Cation\ 1] + [Cation\ 2] + \dots &= [Anion\ 1] + [Anion\ 2] + \dots \end{aligned}$$

As an example, consider a solution of Na_3PO_4 . The CBE for the system is as follows:



Notice that any multiply charged anions, such as $[HPO_4^{2-}]$ and $[PO_4^{3-}]$, will have a coefficient in front corresponding to their charge. This is because each of these anions will contribute more than 1 charge, hence a coefficient is needed to balance their charges.

Consider a solution of HCl. Determine the value of $\frac{dpH}{d[Cl^-]}$ when $[Cl^-] = 2 \times 10^{-7} M$.

Leave your answer in 3 significant figures.

Solution:

-1540000

We can set up the CBE as:

$$[H^+] = [Cl^-] + [OH^-]$$

We want to put things in terms of $[H^+]$:

$$[H^+] = [Cl^-] + \frac{K_w}{[H^+]}$$

First, we find the values we need.

$$[H^+] = 2 \times 10^{-7} + \frac{K_w}{[H^+]}$$

$$[H^+]^2 - 2 \times 10^{-7}[H^+] - K_w = 0$$

$[H^+] = 2.4142 \times 10^{-7}$ M. Now, we do our differentiation:

$$[Cl^-] = [H^+] - \frac{K_w}{[H^+]}$$

$$\frac{d[Cl^-]}{d[H^+]} = 1 + \frac{K_w}{[H^+]^2}$$

$$\frac{d[Cl^-]}{d[H^+]} = 1.17157$$

$$pH = -\lg [H^+] = -\frac{\ln [H^+]}{\ln 10}$$

$$\frac{dpH}{d[H^+]} = -\frac{1}{[H^+] \ln 10}$$

$$\frac{dpH}{d[H^+]} = -1.7989 \times 10^6$$

$$\frac{dpH}{d[Cl^-]} = \frac{dpH}{d[H^+]} \div \frac{d[Cl^-]}{d[H^+]} = \frac{-1.7989 \times 10^6}{1.17157} = -1535463 = -1540000 \text{ (3 s.f.)}$$

Problem 15: Si Vis Pacem, Para Bellum**[6 points]**

In a way, we can thank Chemistry for making the John Wick series happen. It is thanks to Chemistry that we have Kevlar, which John's bulletproof suit is made of. Kevlar is just one of many polymers, and its structure is shown below. The secret behind its incredible tensile strength-to-weight ratio lies in both the hydrogen bonding between amide groups and the aromatic pi stacking of the phenyl rings.

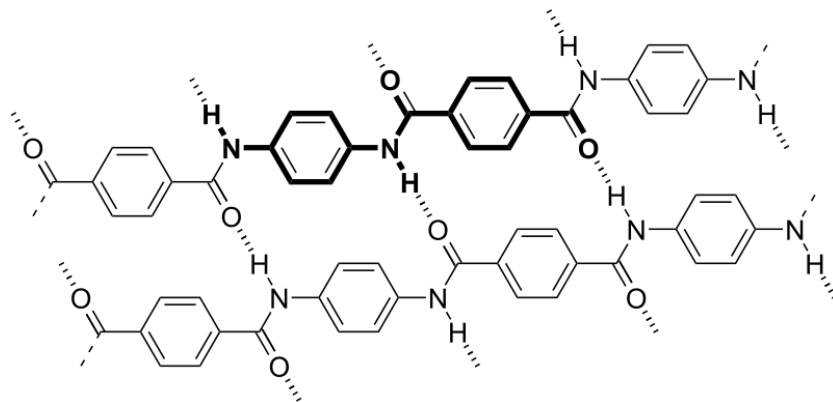


Figure 2: The structure of Kevlar

The empirical formula of Kevlar is C_7H_7NO - to derive this, one needs only isolate the repeating unit that makes up the polymer. For Kevlar, it's the portion bolded out - Which has formula $C_{14}H_{14}N_2O_2$ (make a count yourself), which then simplifies to the empirical formula.

- (a) It is given that the empirical formula of the following polymer is of the form $C_aH_bO_cF_d$. Give the concatenated number \overline{abcd} . **[2 points]**

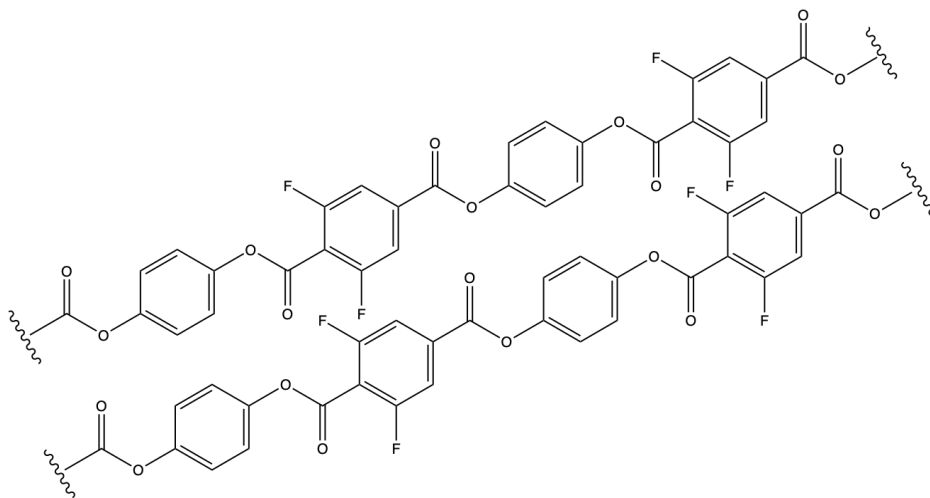


Figure 3: An unknown polymer

Certain polymers, especially inorganic polymers, have no obvious monomeric unit. However, we can still determine their empirical formula by observing the simplest repeating unit.

- (b) The polymer below is a silicate mineral of empirical formula $[\text{Si}_x\text{O}_y]^{n-}$. What is the concatenated number \overline{xy} ? **[2 points]**

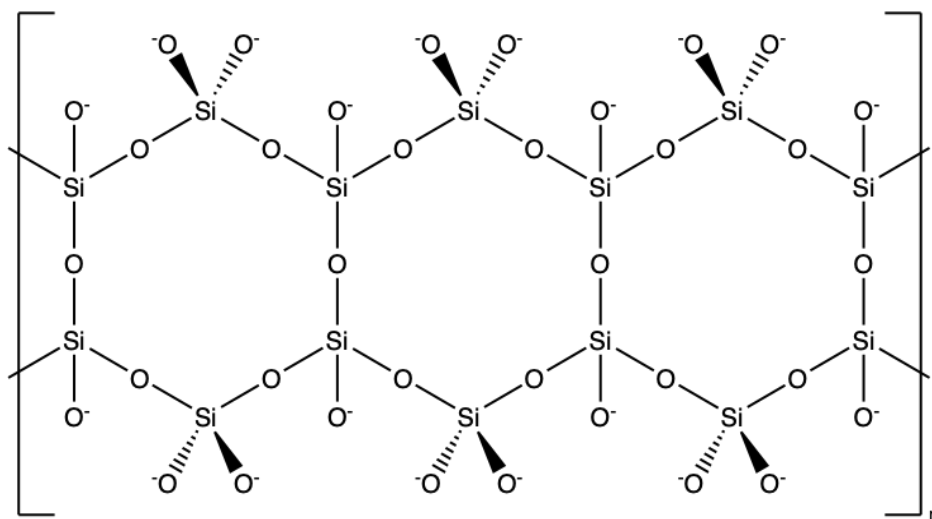


Figure 4: A silicate polymer

Nature's equivalent of Kevlar is cellulose, which is shown below. It also possesses extraordinary tensile strength due to the interlinking of cellulose fibrils via intermolecular hydrogen bonding. Unlike Kevlar, cellulose is made from only one monomer - the cyclic beta-glucose molecule.

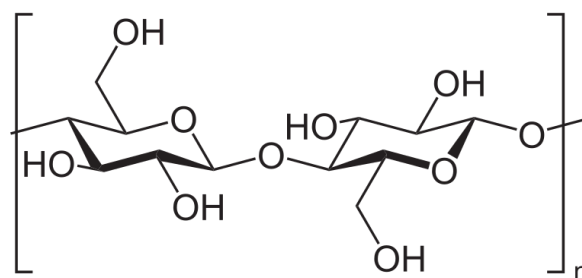


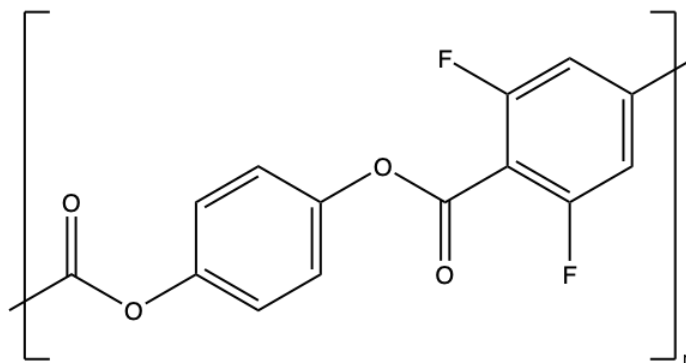
Figure 5: The structure of cellulose

- (c) What is the maximum average number of hydrogen bonds that can be formed per glucose monomer in cellulose? **[2 points]**

Solution:

(a) 7321

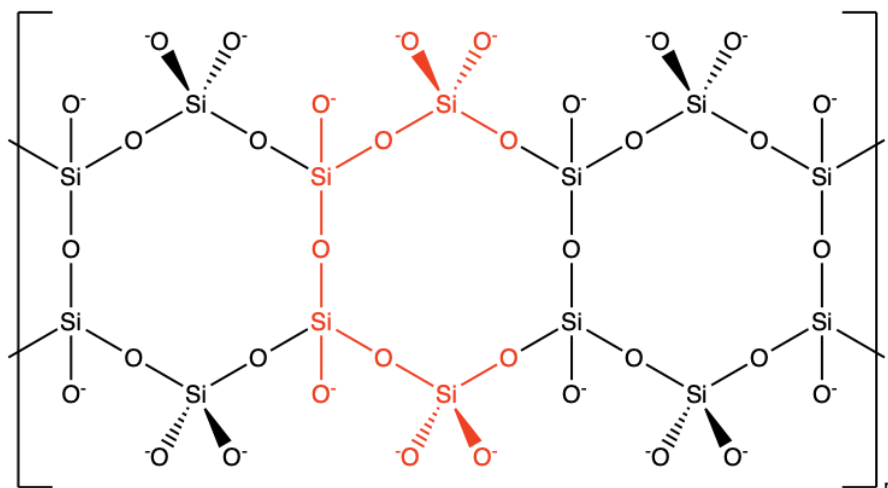
The repeating unit is the following:



Which has chemical formula $C_{14}H_6O_4F_2$, which simplifies to an empirical formula of $C_7H_3O_2F$.

(b) 411

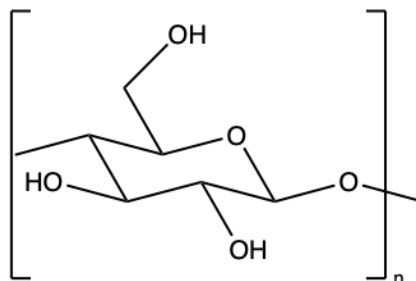
Given its hexagonal motif, we observe that the repeating pattern is the portion shaded in red. Translating it horizontally for an arbitrary number of times will give the resulting polymer.



The chemical formula of the red portion is $[Si_4O_{11}]^{6-}$. Thus, $x = 4$, $y = 11$, and the concatenated number \overline{xy} would be 411.

(c) 3

A beta-glucose monomer is shown:



First we count the number of lone pairs available for hydrogen-bonding. There are 3 -OH groups, and 2 C-O-C groups. On each oxygen there are 2 lone pairs. Thus, each beta-glucose monomer possesses 10 lone pairs available for hydrogen bonding.

As there are 3 -OH groups and no other hydrogen atoms bonded to electronegative atoms, we have 3 hydrogen atoms available for hydrogen bonding.

The number of hydrogen atoms available for hydrogen bonding is less than the number of lone pairs available, and hence it is the number of hydrogen atoms that limits the maximum number of hydrogen bonds possible. Thus we conclude that each beta glucose monomer can only form a maximum of 3 hydrogen bonds.

Problem 16: A Pair of Hands**[4 points]**

A central concept of organic chemistry, especially biochemistry, is *chirality*. Doubtless the more senior among us will be familiar with this concept, but let us return to fundamentals and dissect one of its fundamental tenets - *planes of symmetry*.

In chemistry, we are taught that a molecule is chiral when it does not have a plane of symmetry. A plane of symmetry is an imaginary plane that cuts an object into two mirror-image portions. To use an everyday example, forks and spoons are not chiral, because they do possess a plane of symmetry, running along the length of the cutlery. Conversely, objects like your hand, or a leather boot, cannot be cut into two mirror-image portions by a plane, hence do not possess planes of symmetry.

Frequently, an object can possess multiple planes of symmetry.

(a) How many planes of symmetry does a cube have? **[2 points]**

Soldiers, onwards to organic molecules! Adamantane is a chemical molecule with formula $C_{10}H_{16}$. Every carbon has a tetrahedral arrangement of atoms around it (exactly the desired conformation), leading to an exceptionally stable molecule. You could visualise it as a molecule with 4 sides, each side the shape of a hexagon.

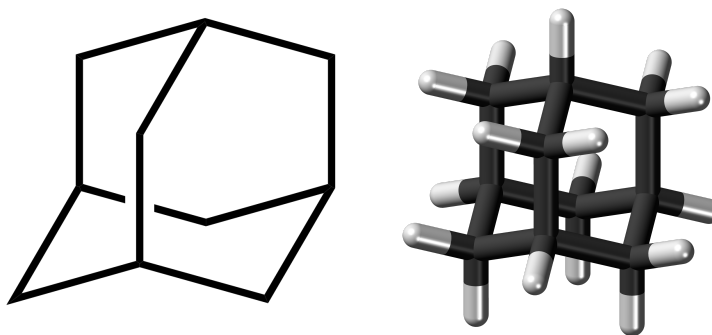


Diagram 1: Two depictions of adamantane.

Amantadine is identical with adamantane, except that one hydrogen has been replaced with an amino ($-NH_2$) group.

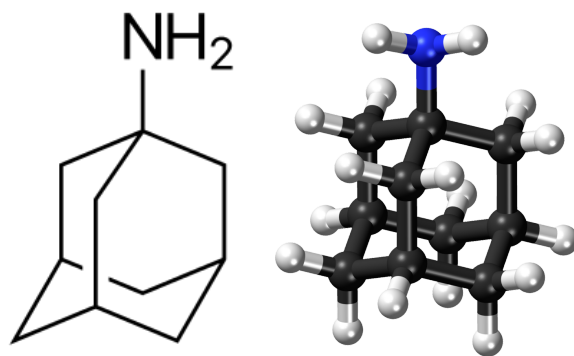


Diagram 2: The structure of amantadine

Let the number of planes of symmetry in adamantane be x and amantadine be y .

(b) What is the concatenated number \overline{xy} ? **[2 points]**

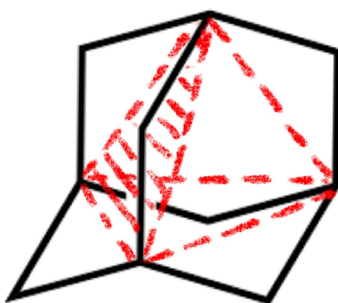
Solution:

(a) 9

As the many machinations of copyright infringement are at work, the setter has unfortunately been unable to attach an image as reference. However, a search online (or a concerted attempt at visualising a cube) would reveal that there are 3 planes of symmetry that cut parallel to the faces of the cube, and 6 that cut diagonally, for a total of 9.

(b) 63

Adamantane has similar symmetry to a tetrahedron - both have 4 identical faces and 4 vertices (in adamantane, only the carbons bonded to 3 other carbons are taken as a "vertex"). An illustration of this geometric similarity is shown:



Just as a tetrahedron has 6 planes of symmetry, adamantane will have 6.

This symmetry is disrupted in the case of amantadine. With one of the vertices now different from the other 3, this is analogous to a trigonal pyramid, which is obtained by elongating 1 of the 4 vertices of a tetrahedron (hopefully you can see the similarity in this "elongation" process to the attachment of an -NH_2 group to a carbon in adamantane). There are 3 planes of symmetry, all of them running through the C-N bond, and each bisecting one hexagonal face in half.

Problem 17: 2 Roads, 1 Destination**[4 points]**

Fu Xuan has just learnt about binary nitrogen compounds in organic chemistry class. She is currently reading about hydrazoic acid, HN_3 , a weak acid that reacts in interesting manners with certain organic functional groups. In this question, HN_3 reacts with carbonyls to install a nitrogen group adjacent to it.

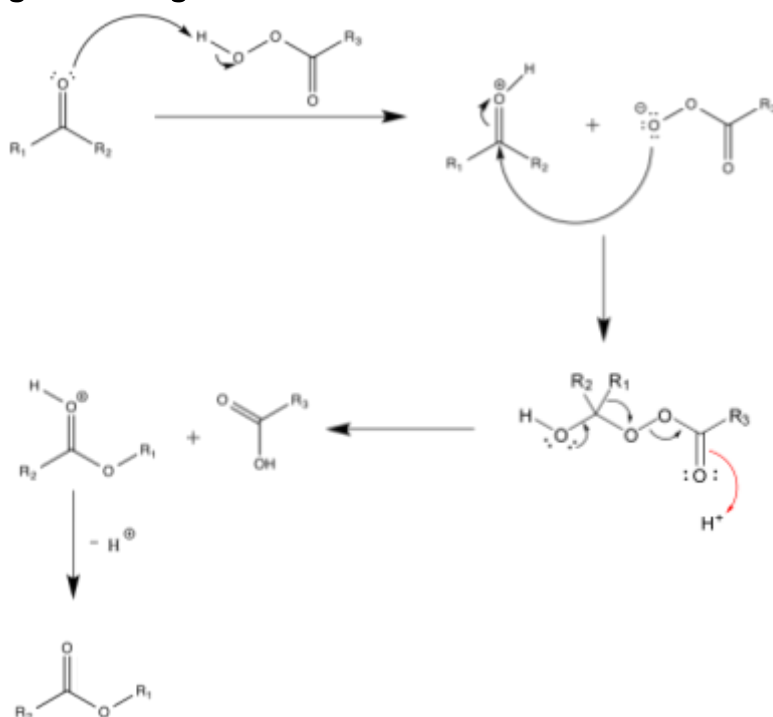
(a) Name the functional group that is formed in this reaction. Select only *one* option.

Input the letter corresponding to the correct answer. The answer is case-sensitive.

[2 points]

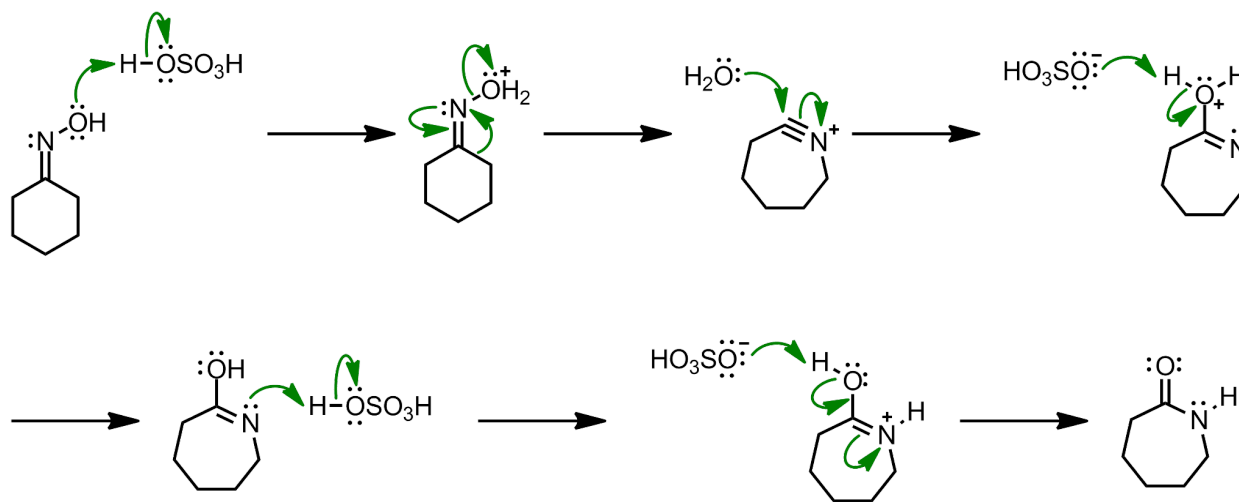
- A) Amine
- B) Amide
- C) Imine
- D) Amino acid

In synthetic chemistry, the Schmidt reaction is a well-known synthetic reaction that can follow 2 pathways. They are similar to 2 other named reactions: the *Beckmann Rearrangement* and the *Baeyer-Villiger Rearrangement*, which are both rearrangement reactions which involve an alkyl group migrating.

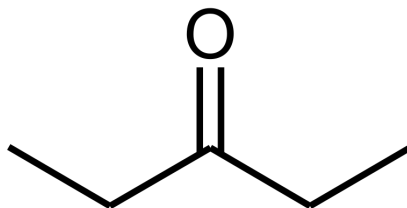
Baeyer-Villiger Rearrangement

Beckmann Rearrangement

In this example, the cyclohexane ring is taken to be the R-group.



- (b) Fu Xuan wants to try out the Schmidt reaction. With reference to either mechanism, draw **one** possible product of the Schmidt reaction using the substrate below. **[2 points]**

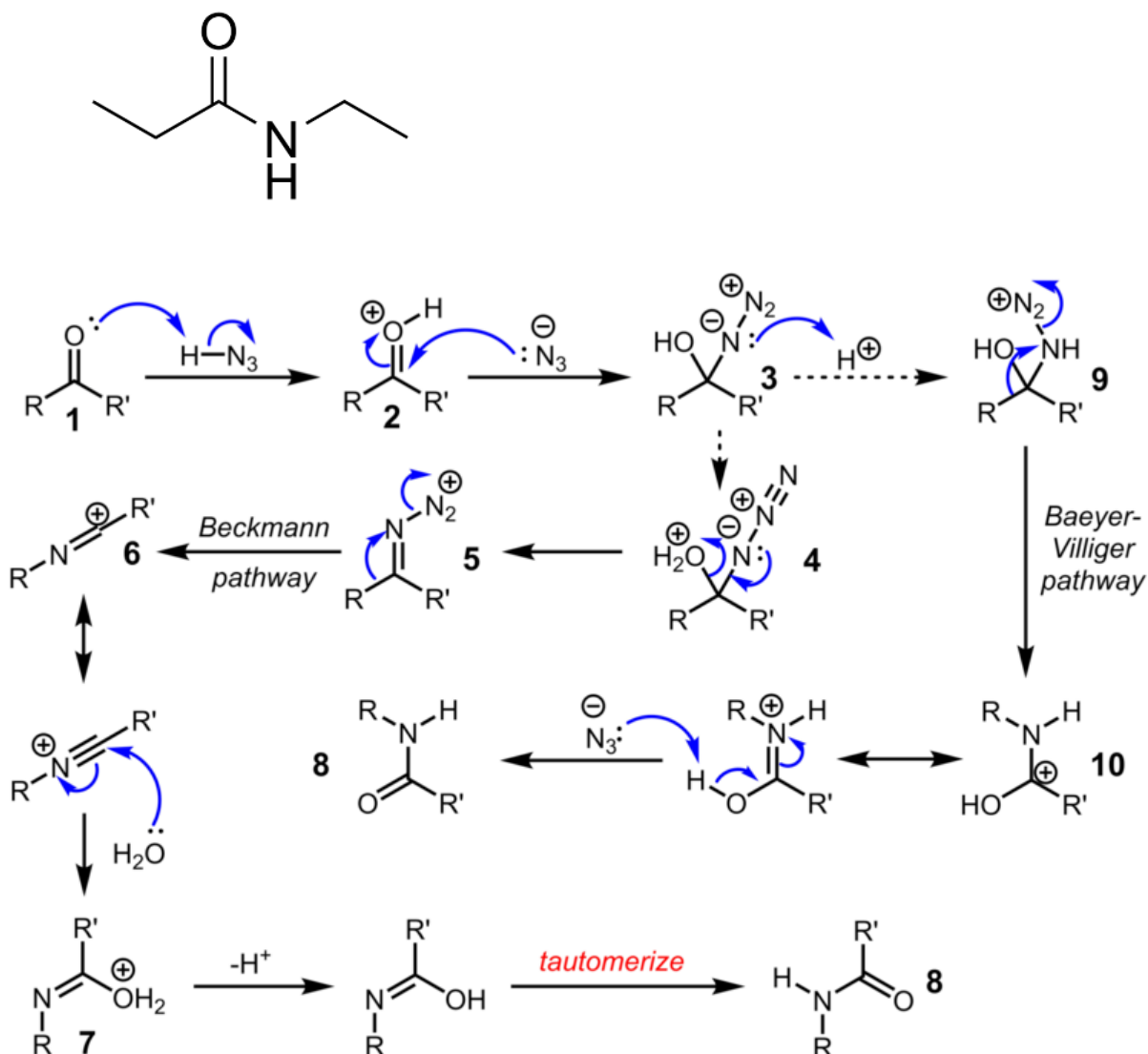


Solution:

(a) B

The amide group has the chemical structure $-(C=O)-NR_2$, and is what would be obtained after a nitrogen atom is inserted into the C–C bond adjacent to the carbonyl group.

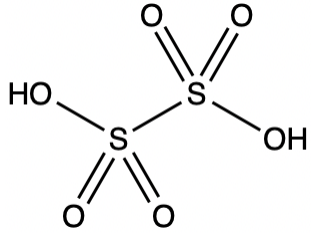
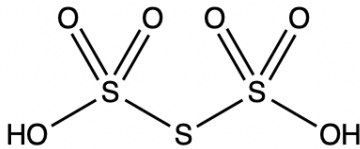
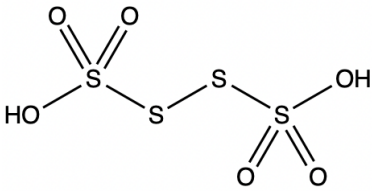
(b)



The above diagram shows a proposed reaction mechanism pathway for Schmidt reaction which is analogous to the Beckmann and Baeyer-Villiger pathways. Since R and R' groups are identical for the substrate above, we do not need to worry about which alkyl group migrates. The end result is that the carbonyl is converted into an **amide**.

Problem 18: I am yellow, I burn blue, I bleed red.**[5 points]**

Jorge has just learnt about wonderful sulfuric acid in high school and wishes to know more. He discovers that sulfur forms a remarkable range of oxo-acids, with the sulfur existing in a range of oxidation states. For example, due to its tendency to catenate (form bonds with itself), polythionic acids of general formula $H_2S_nO_6$ can exist, up to $n = 6$. The first 3 members, dithionic acid, trithionic acid and the more familiar tetrathionic acid are shown below, along with the average oxidation state of sulfur in each compound.

		
Dithionic acid	Trithionic acid	Tetrathionic acid
+5	$+\frac{10}{3}$	+2.5

Let us conduct a thought experiment. Imagine that the series of polythionic acids is continuously extended for increasing integral values of n .

- (a) What is the value of n for the first acid in this series with an average sulfur oxidation state smaller than $+\frac{1}{2023}$?

If you think the average oxidation state never decreases beyond $+\frac{1}{2023}$, put 0 as your answer. [2 points]

Jorge decides (against all sensible judgement) to collect a range of sulfur compounds with sulfur in various oxidation states. The compounds that he wishes to collect are as follows:

DMS	Tetrathionic acid	DMSO
SF_6	Cystine	Thionyl chloride

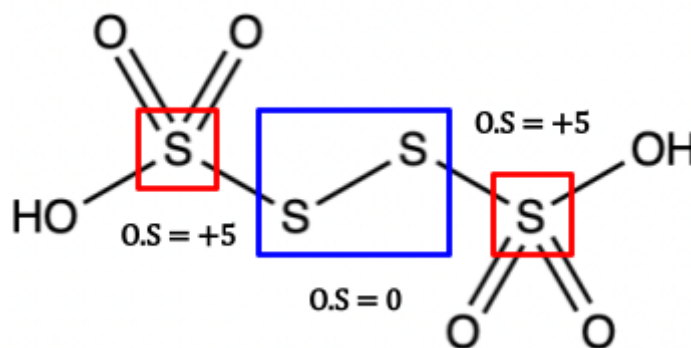
As whimsical as a Murakami novel, Jorge decides that he'd like to collect the chemicals in order of ascending average oxidation state of sulfur in the compound.

- (b) Let the average oxidation state of sulfur in the first, third and last compound he collects be x , y and z respectively. What is the value of $x+y+z$?
If $x+y+z$ is positive, you may omit the + sign. [3 points]

Solution:

(a) 20231

It is necessary to first derive a formula for average oxidation state, in terms of n . For the polythionic acids, we can divide the sulfur atoms into two types: **Terminal sulfur atoms** and **bridging sulfur atoms**. The **terminal sulfur atoms** are, as the name suggests, found at the end of the sulfur chains. Every polythionic acid will have exactly 2 **terminal sulfur atoms**, and a variable number of **bridging sulfur atoms**.



Tetrathionic acid as an example of the classification of sulfur atoms

To deduce the oxidation states of individual sulfur atoms, we count the elements that it is bonded to, and compare the electronegativities. Each bond to a more electronegative element has the effect of increasing the sulfur's oxidation state by 1, while each bond to another sulfur (which has the same electronegativity) does not change either sulfur's oxidation state in any way.

Let us get down to the business of bond-counting. Each **terminal sulfur atom** has 6 bonds in total: 5 S-O bonds (each S=O bond is counted as two equivalents) and 1 S-S bond. As O is more electronegative than S, the oxidation state of each **terminal sulfur atom** is +5.

Each **bridging sulfur atom** has only 2 bonds, and both are S-S bonds. As a result, the oxidation state is deduced to be 0.

The average oxidation state of sulfur in any particular compound with multiple sulfur atoms is the sum of oxidation states of each individual sulfur atom, divided by the total number of sulfur atoms. Notice that for *any* polythionic acid, only terminal sulfur atoms have a non-zero oxidation state; thus, the sum of oxidation states of each individual sulfur atom is always $+5 \times 2 = +10$.

Thus, the general formula for average oxidation state of sulfur in a polythionic acid is $+10/n$, where n is the total number of sulfur atoms in that acid.

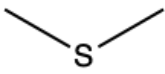
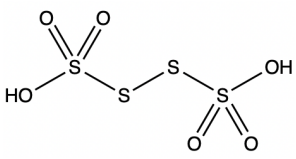
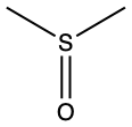
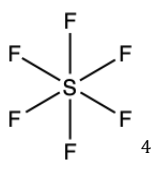
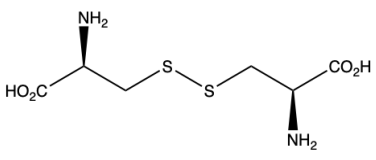
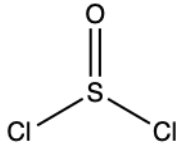
The inequality we have to solve is as follows:

$$\begin{aligned} \text{Average O.S of sulfur} &< \frac{1}{2023} \\ \frac{10}{n} &< \frac{1}{2023} \\ n &> 20230 \end{aligned}$$

Thus the minimum value of n is 20231.

(b)4

The structure of each of the sulfur compounds are shown below, as well as the average oxidation state of sulfur for each compound. In much the same fashion as we did for part (a), the oxidation state of each individual sulfur atom can be found by counting the number of bonds formed by each sulfur atom to 1. More electronegative elements 2. Other S 3. Less electronegative elements.

DMS	Tetrathionic acid	DMSO
		
-2	+2.5	0
SF ₆	Cystine	Thionyl chloride
		
+6	-1	+4

⁴ Lewis structure purists will argue that a more accurate representation would be an S²⁺ atom covalently bonded to 4 fluorine at any one time, and ionically bonded to 2 F⁻ atoms. The good news is that going about the structure this way also gives the same oxidation state of sulfur.

Thus, the first, third and last element Jorge collected would have been DMS, DMSO and SF₆.
 $x = -2$, $y = 0$ and $z = +6$, so $x + y + z = 4$.

Problem 19: Drop That Base**[5 points]**

In organic chemistry, the class of intramolecular reactions that convert open-chain molecules into ring compounds is known as cyclisation or ring-closure reactions. When designing syntheses for cyclic molecules, chemists examine its open-chain precursor, ensuring that the correct nucleophilic and electrophilic sites react to form the desired ring. Yet, owing to a mixture of steric and electronic factors, some rings which appear possible at first glance are not formed favourably in practice.

Baldwin's Rules, proposed by British chemist Sir Jack Baldwin in 1976, is a simplified set of empirical guidelines that suggest which cyclisation reactions are favourable, and which are less likely to occur.

Baldwin's Rules are also important because it gives us a way to name and identify different cyclisation reactions. This nomenclature includes:

1. The number of atoms formed in the ring,
2. Whether the reaction is *exo* or *endo*: *exo* meaning a bond is broken outside of the formed ring, and *endo* meaning a bond is broken within the formed ring, and
3. The geometry of the electrophilic carbon atom that is being attacked: *tet* if the carbon is sp^3 hybridised (tetrahedral), *trig* for sp^2 hybridised (trigonal), and *dig* for sp hybridised (diagonal)

in that order.

Hence, the name *5-exo-tet* means an *exo* ring closure results from an attack on a *tet* carbon to form a 5-membered ring, and may be used to describe the S_N2 reaction in Fig. 1:

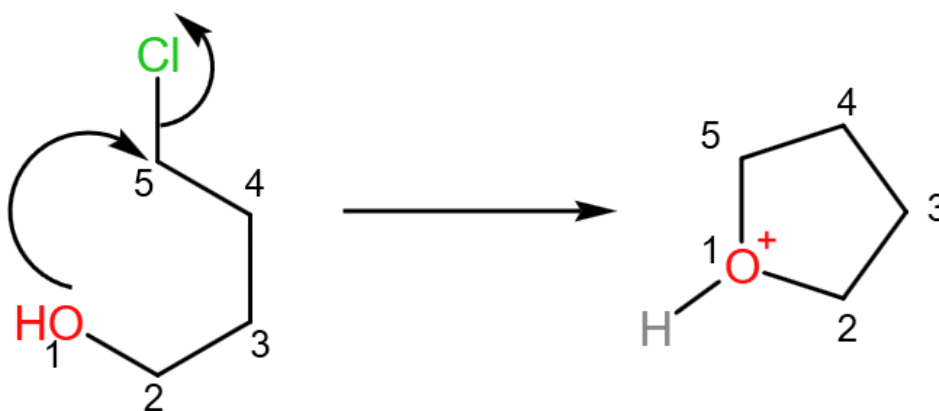
**Fig. 1**

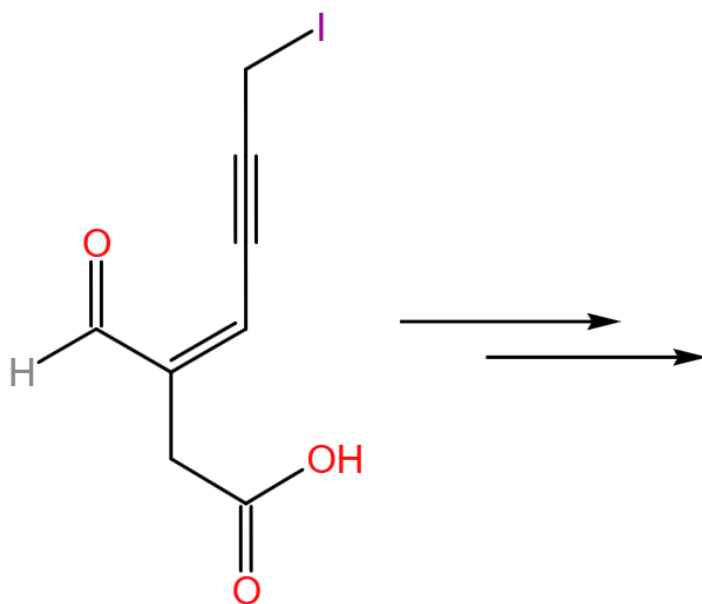
Table 1 then describes the reactions that are favoured. For example, *5-exo-tet* and *7-endo-trig* reactions are favoured, but *3-exo-dig* and *6-endo-tet* reactions are disfavoured.

	Exo		Endo	
	Favoured	Disfavoured	Favoured	Disfavoured
Tet	3 / 4 / 5 / 6 / 7	-	-	3 / 4 / 5 / 6 / 7
Trig	3 / 4 / 5 / 6 / 7	-	6 / 7	3 / 4 / 5
Dig	5 / 6 / 7	3 / 4	3 / 4 / 5 / 6 / 7	-

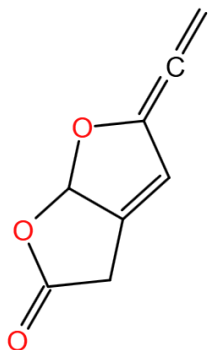
Table 1

The following compound is refluxed in a suitable basic medium till completion, and the final product extracted after acidic workup. Using Baldwin's Rules and given that reaction conditions allow only for cyclisation to take place, give the theoretical final product of this reaction, assuming no exceptions to the above rules.

Hint: Locate the nucleophilic and electrophilic centres in the molecule.

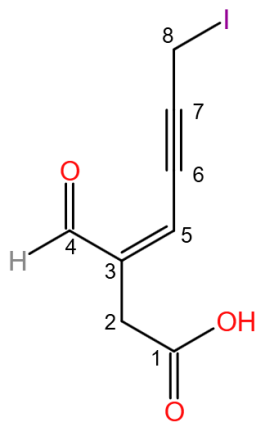


Solution:



When proposing organic mechanisms, it is a helpful practice to locate all nucleophilic (electron sources) and electrophilic sites (electron sinks) on a molecule as these contribute to its reactivity the most. A reaction always involves the interaction of a nucleophile with an electrophile; less reactive sites remain unchanged. This gives us a sense of the reactions that can occur and the products that can be formed.

It is also helpful to number the carbon atoms before we begin:



The most acidic proton is the labile H on the carboxylic acid group. Basic medium facilitates the removal of this proton from the molecule to form its conjugate base.

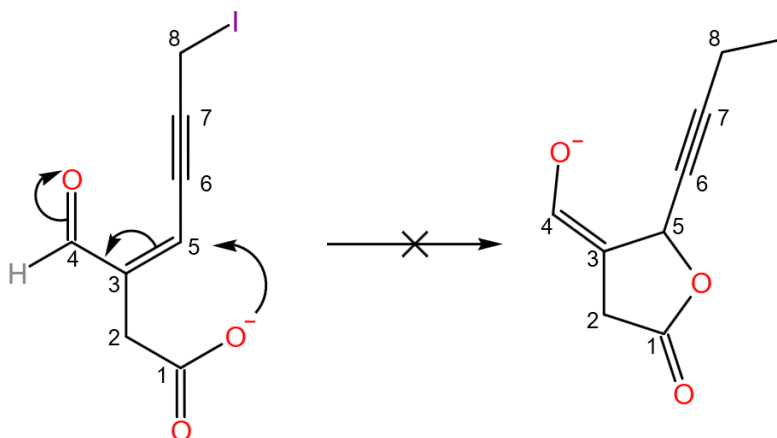
The resulting carboxylate anion has high electron density and is the strongest nucleophilic site on the molecule. The regiochemistry of the reaction is predicted by comparing the electrophilic sites, and its favourability determined using Baldwin's Rules.

Electron-deficient carbon atoms are C4, C5, C7 and C8 (excluding C1, which is directly bonded to nucleophilic O). Carbonyl C4 is directly bonded to an electronegative O atom. C5 and C7 are electron-deficient due to the electron-withdrawing effect of the carbonyl group

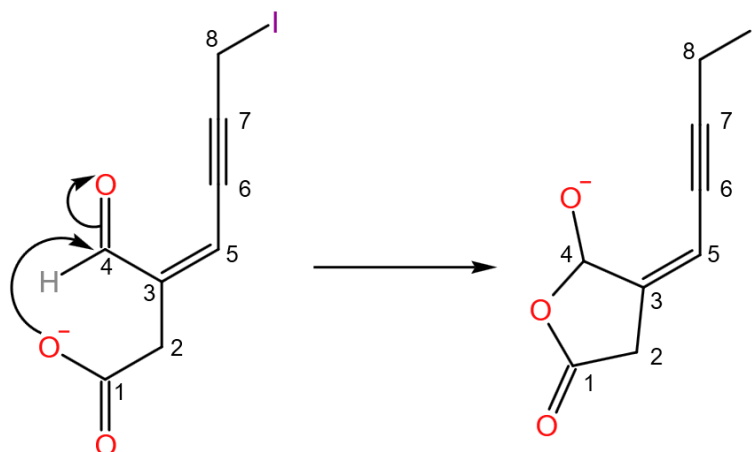
(visualised by drawing its resonance structures). C8 is directly bonded to an electronegative I atom. We discuss the invalidity of C2 and C6 as electrophilic sites below.

Given the restricted rotation about the C3=C5 double bond, it is unlikely for the carboxylate nucleophile to perform nucleophilic attack on C7 or C8. Likewise, C6 is located too far from the carboxylate to react favourably as they are located on opposite sides of the C3=C5 bond (E conformation). C2 is part of a $-\text{CH}_2-$ group which does not contain any polar bonds, hence it is not electrophilic. Baldwin's Rules help us to decide whether nucleophilic attack on C4 or C5 is more favourable. It then helps for us to name the two cyclisation reactions that would occur upon attack on C4 and C5 using the rules we have just learnt.

Attack on C5 follows a conjugate addition mechanism forming a 5-membered ring. As the reaction causes a π -bond in C3=C5 to be broken within the newly-formed ring, the ring closure is *endo*. As C5 is sp^2 hybridised and has a trigonal planar geometry, the attack is *trig*. Hence the reaction is *5-endo-trig*, which is disfavoured.



Attack on C4 follows a nucleophilic addition mechanism forming a 5-membered ring. As the reaction causes a π -bond in C4=O to be broken outside the newly-formed ring, the ring closure is *exo*. As the carbonyl C4 attacked is sp^2 hybridised and has a trigonal planar geometry, the attack is *trig*. Hence the reaction is *5-exo-trig*, and is favoured.



Hence attack on C4 occurs preferentially, forming the above intermediate.

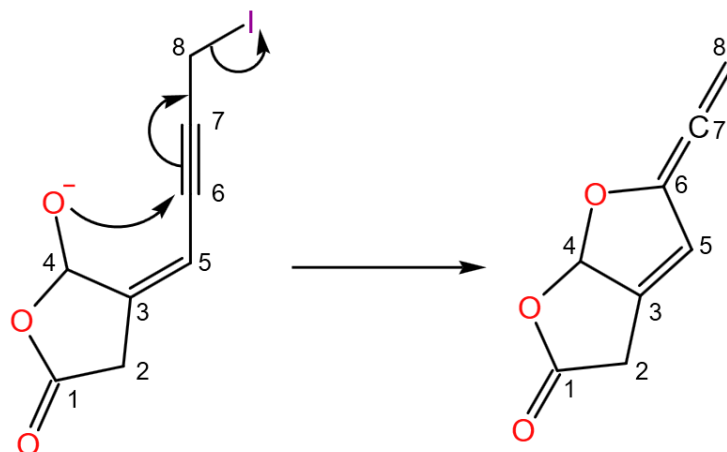
The strongest nucleophile on the intermediate is the newly-formed alkoxide group. The issue is determining whether subsequent cyclisations are favourable. A common answer may be to end the reaction at this stage, upon which acidic workup yields the final hydroxy lactone.

But it is worth examining whether the molecule contains further electrophilic sites which the alkoxide may attack. C2 is non-electrophilic while C8 is too far from the alkoxide to form a stable ring. Of the remaining carbon atoms, C3, C5, C6 and C7 form electron-rich π -bonds in the respective conjugated alkene and alkyne, which would repel incoming nucleophiles. This leaves us to test C1.

Yet, drawing a nucleophilic acyl substitution mechanism reveals that as the nucleophile attacks and displaces the existing alkoxide moiety, the reaction forms and cleaves an ester bond at the exact same position. The result is that the structure of the molecule remains unchanged; nucleophilic attack on C1 does not produce a new molecule.

Is this the end of the road?

We have yet to consider a possibility - the nature of the I atom as a good leaving group. Given its large anionic radius of I⁻, its negative charge is well-stabilised. This means that a reaction that displaces the I atom whilst forming a ring at the same time can be favourable, so long as it follows Baldwin's Rules. Displacing the I atom, in addition to backside attack on C8 via the S_N2 mechanism, is also possible via a **nucleophilic conjugate substitution** (S_N2 prime) mechanism. The I atom is located at alpha-position relative to the alkyne, which means an attack on C6 could displace the I atom as below.



This means despite the $C6\equiv C7$ bond being electron-rich, driving out a leaving group produces an electron “hole” on C6 when a new π -bond forms on $C7-C8$, allowing nucleophilic attack to occur on C6. This reaction is favourable by Baldwin’s Rules as it forms a 5-membered ring with *exo* ring closure and *dig* attack (attack on sp hybridised carbon atom), hence *5-exo-dig*.* Despite the peculiarity and relative instability of allene formation, its synthesis via a similar mechanism with appreciable yield is documented in a study by Gilmore, Mohamed and Alabugin⁵. The reaction is entropically driven by the loss of the I atom which renders it irreversible, giving the final theoretical product as shown.

*Given that the alkene is also in conjugation with the alkyne, why is nucleophilic attack on C3 unfavourable, if its reaction can be found to be *3-exo-trig* and favoured by Baldwin’s Rules? This can be explained electronically by the alignment of molecular orbitals in the alkoxide and trigonal planar C3. Computational studies find that attack on a trigonal planar carbon occurs most readily when the angle of attack of the nucleophile is $105\pm 5^\circ$ with respect to the π -bond, above or below the plane of the carbon atom, when the overlap of molecular orbitals between reactants is maximised; this is known as the Bürgi-Dunitz angle. The presence of the ring which C3–C4 is part of distorts this angle beyond the ideal, making it difficult for the alkoxide to attack C3. Furthermore, attack on C3 forms a butatriene group which is even more unstable. In comparison, an attack on C6 is more feasible.

On a side note, does the product not look like a cute bass guitar?

⁵ Gilmore, K, Mohamed, R. K., & Alabugin, I. V. (2016). The Baldwin rules: revised and extended. *WIREs Comput Mol Sci*. doi: 10.1002/wcms.1261. Extracted from https://www.researchgate.net/profile/Kerry-Gilmore/publication/301705299_The_Baldwin_rules_revised_and_extended_Baldwin_Revised_Extended/links/5748518808ae2301b0b9803b/The-Baldwin-rules-revised-and-extended-Baldwin-Revised-Extended.pdf?sg%5B0%5D=started_experiment_milestone&origin=journalDetail

Problem 20: Obsessive Dilution**[3 points]**

Timmy has an irrational fear of acids. Upon seeing any acid, he feels an uncontrollable urge to dilute them until they are almost neutral.

However, Timmy knows only one method of dilution: pouring away half the solution, topping up back to its original volume with pure water, while stirring to ensure homogeneity.

Timmy has 250 cm^3 of 3 mol dm^{-3} ethanoic acid. His electronic pH metre displays values rounded to the nearest 2 dp. What is the **least** number of times Timmy must perform his dilution for his pH metre to show a reading of 7.00?

The pKa of ethanoic acid is 4.76.

Leave your answer as an integer.

Solution:

31

Since the precision of the pH metre is 2 d.p, the minimum pH required for the metre to display 7.00 is 6.995. The corresponding $[H^+] = 10^{-6.995} \text{ mol dm}^{-3}$.

Since $K_w = [H^+][OH^-]$,
 $[OH^-] = 10^{-7.005} \text{ mol dm}^{-3}$.

We can use a charge balance equation, which makes use of the fact that the sum of the positive charges equals the sum of the negative charges in solution.

$$[AcO^-] + [OH^-] = [H^+]$$

Therefore, $[AcO^-] = 10^{-6.995} - 10^{-7.005} \text{ mol dm}^{-3}$.

$K_a = \frac{[H^+][AcO^-]}{[AcOH]}$, and by rearranging this equation,

$$[AcOH] = \frac{[H^+][AcO^-]}{K_a} = 1.340371802 \times 10^{-11} \text{ mol dm}^{-3}.$$

Total concentration of ethanoic acid
 $= 10^{-6.995} - 10^{-7.005} + 1.340371802 \times 10^{-11}$
 $= 2.316039678 \times 10^{-9} \text{ mol dm}^{-3}$.

Let N be the number of dilutions needed to reach the required $[AcOH]$.

Given that the initial $[AcOH] = 3 \text{ mol dm}^{-3}$, and that the concentration is halved with every dilution,

$$3 \times (0.5)^N = 2.316039678 \times 10^{-9}$$

$$N = \frac{\ln\left(\frac{2.316039678 \times 10^{-9}}{3}\right)}{\ln(0.5)} = 30.27$$

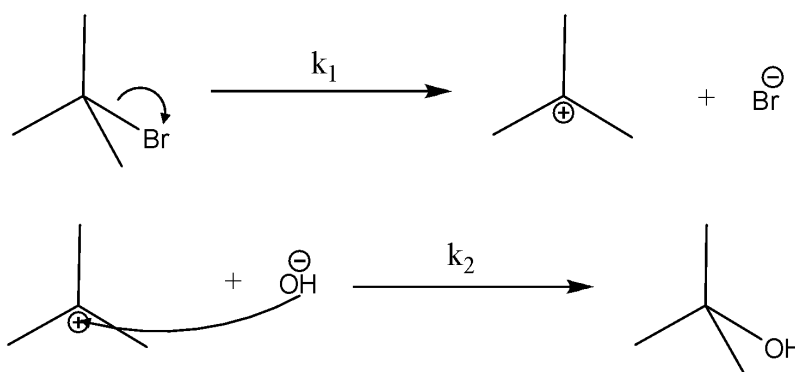
Hence, at least 31 dilutions are needed.

Problem 21: Steady Lah!**[3 points]**

Reaction kinetics is an important field of physical chemistry where we study how the rates of reactions vary with various concentrations. To help us investigate the kinetics of complex mechanisms, we employ the *steady-state approximation*, which assumes that the concentrations of intermediates are constant when we approach the steady state. In other words, we assume the following equation to hold for any intermediate:

$$\frac{d[X]}{dt} = \text{rate of formation of } X - \text{rate of consumption of } X = 0$$

As an example, let us consider a simplified mechanism for the S_N1 reaction.



To solve for the rate of formation of the alcohol, we carry out the steady state approximation on the carbocation intermediate:

$$\frac{d[(CH_3)_3C^+]}{dt} = k_1[(CH_3)_3CBr] - k_2[(CH_3)_3C^+][OH^-] = 0$$

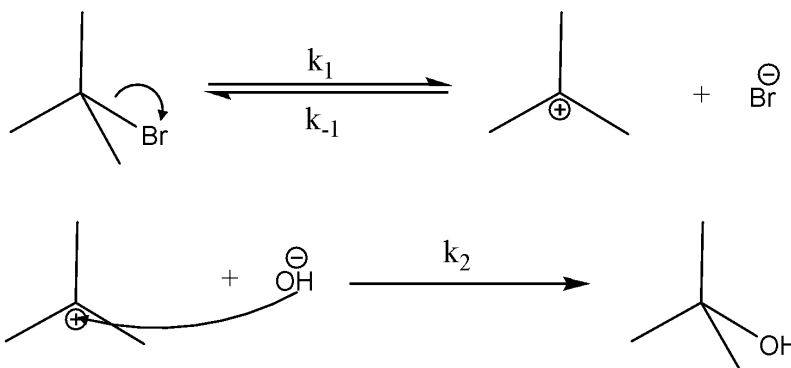
$$[(CH_3)_3C^+] = \frac{k_1[(CH_3)_3CBr]}{k_2[OH^-]}$$

$$\frac{d[(CH_3)_3COH]}{dt} = k_2[(CH_3)_3C^+][OH^-] = k_2 \left(\frac{k_1[(CH_3)_3CBr]}{k_2[OH^-]} \right) [OH^-]$$

$$\frac{d[(CH_3)_3COH]}{dt} = k_1[(CH_3)_3CBr]$$

We can deduce that the reaction is first order with respect to the halogenoalkane, but independent of the nucleophile, which is what we conventionally understand. Things

become slightly more complicated if we consider the first step to be reversible, as we have to consider the reverse reaction in the steady-state approximation.



We can simplify the rate into two cases: when $[\text{Br}^-] \gg [\text{OH}^-]$ and when $[\text{OH}^-] \gg [\text{Br}^-]$.

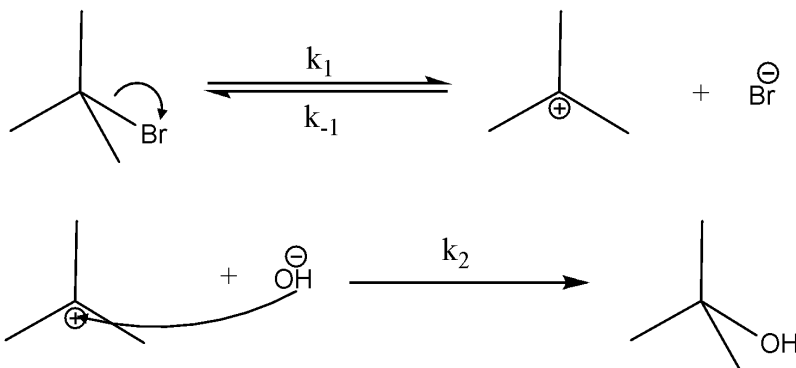
Case	Order with respect to $[(\text{CH}_3)_3\text{CBr}]$	Order with respect to $[\text{Br}^-]$	Order with respect to $[\text{OH}^-]$
$[\text{Br}^-] \gg [\text{OH}^-]$			
$[\text{OH}^-] \gg [\text{Br}^-]$			

Using the steady-state approximation, fill in the above table.

Key in your answer as a concatenated number of the orders from left to right, with the first row before the second row. If any orders are negative, represent the negative sign as a 0 before the number. If any orders are fractional, represent the number as a decimal to 1dp. For example, if you believe the orders are 1 with respect to $[(\text{CH}_3)_3\text{CBr}]$, $-3/2$ with respect to $[\text{Br}^-]$ and 2 with respect to $[\text{OH}^-]$ for both cases, key in **101.52101.52**.

Solution:

1011100



$$\frac{d[(\text{CH}_3)_3\text{C}^+]}{dt} = k_1[(\text{CH}_3)_3\text{CBr}] - k_{-1}[(\text{CH}_3)_3\text{C}^+][\text{Br}^-] - k_2[(\text{CH}_3)_3\text{C}^+][\text{OH}^-] = 0$$

$$\left[(\text{CH}_3)_3\text{C}^+ \right] = \frac{k_1[(\text{CH}_3)_3\text{CBr}]}{k_{-1}[\text{Br}^-] + k_2[\text{OH}^-]}$$

$$\frac{d[(\text{CH}_3)_3\text{COH}]}{dt} = k_2 \left[(\text{CH}_3)_3\text{C}^+ \right] [\text{OH}^-] = k_2 \left(\frac{k_1[(\text{CH}_3)_3\text{CBr}]}{k_{-1}[\text{Br}^-] + k_2[\text{OH}^-]} \right) [\text{OH}^-]$$

$$\frac{d[(\text{CH}_3)_3\text{COH}]}{dt} = \frac{k_1 k_2 [(\text{CH}_3)_3\text{CBr}] [\text{OH}^-]}{k_{-1}[\text{Br}^-] + k_2[\text{OH}^-]}$$

Now, we consider the two cases.

When $[\text{Br}^-] \gg [\text{OH}^-]$, the $k_2[\text{OH}^-]$ term is negligible and we can remove it from the denominator.

$$\frac{d[(\text{CH}_3)_3\text{COH}]}{dt} = \frac{k_1 k_2 [(\text{CH}_3)_3\text{CBr}] [\text{OH}^-]}{k_{-1}[\text{Br}^-]}$$

This results in first order for both the bromoalkene and OH^- , but negative first order for Br^- (which serves as an inhibitor, consuming the carbocation fast enough before it can react with the nucleophile).

When $[\text{OH}^-] \gg [\text{Br}^-]$, the $k_{-1}[\text{Br}^-]$ term is negligible:

$$\frac{d[(CH_3)_3COH]}{dt} = \frac{k_1 k_2 [(CH_3)_3CBr][OH^-]}{k_2 [OH^-]} = k_1 [(CH_3)_3CBr]$$

This results in first order for the bromoalkene but zeroth order for OH^- and Br^- (this is the same as the initial situation, as there is so much nucleophile that the second reaction will proceed before the reverse reaction can).

We fill in the table:

Case	Order with respect to $[(CH_3)_3CBr]$	Order with respect to $[Br^-]$	Order with respect to $[OH^-]$
$[Br^-] \gg [OH^-]$	1	-1	1
$[OH^-] \gg [Br^-]$	1	0	0

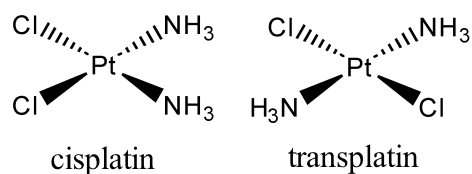
We key in 1011100.

Problem 22: Same Same But Different**[5 points]**

For the purposes of this question, you may assume all complexes in part (a) and (b) adopt a perfect octahedral geometry without any Jahn-Teller distortion.

Isomerism is a concept that is relevant not only to organic compounds but also to coordination complexes. It is often useful to determine the number of isomers of a complex.

One of the common types of isomerism is stereoisomerism, where different complexes have the same formulae and the same ligands with the same coordination modes, but differ in the 3-dimensional arrangements of the atoms. For instance, cisplatin and transplatin, displayed below, are stereoisomers.



- (a) Consider the complex $[\text{FeBrCl}(\text{en})_2]^+$. Determine the number of stereoisomers it has.
[2 points]


Another type of isomerism is termed coordination isomerism, which arises when a compound has multiple complexes inside. In such compounds, complexes may “exchange” their ligands.

- (b) Consider the ionic compound $\text{FeCo}(\text{NH}_3)_6(\text{CN})_6$. Determine the total number of isomers (both stereoisomers and coordination isomers). **[3 points]**

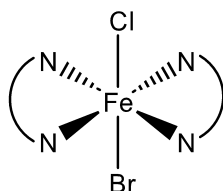
Solution:

(a) 3

It is easiest to do this question by drawing out all the isomers. To keep track, it helps to note which ligands are trans to which ligands. After drawing out a structure, we need to also check if it has a plane of symmetry, and if it does not, we need to consider the enantiomer.

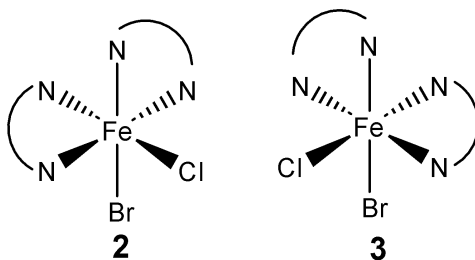
For simplicity, all en ligands are represented by .

We first consider the ethylenediamine ligand, with both nitrogen atoms trans to each other.



We term this isomer **1**. **1** has a plane of symmetry and does not have an enantiomer.

Next, we consider if one pair of nitrogen atoms are cis to each other. This product lacks a mirror plane and has an enantiomer.



Hence, there are 3 total isomers.

(b) 12

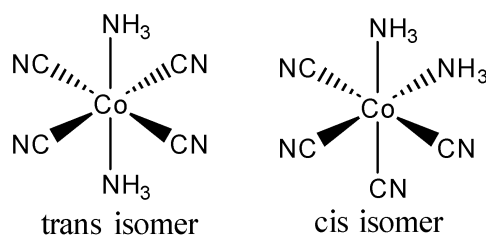
We first work out the number of possible coordination isomers. All the possible isomers are below:

- $[\text{Fe}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{CN})_6]^{3-}$
- $[\text{Fe}(\text{NH}_3)_5(\text{CN})]^{2+}[\text{Co}(\text{CN})_5(\text{NH}_3)]^{2-}$
- $[\text{Fe}(\text{NH}_3)_4(\text{CN})_2]^+[\text{Co}(\text{CN})_4(\text{NH}_3)_2]^-$
- $[\text{Co}(\text{NH}_3)_4(\text{CN})_2]^+[\text{Fe}(\text{CN})_4(\text{NH}_3)_2]^-$
- $[\text{Co}(\text{NH}_3)_5(\text{CN})]^{2+}[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{2-}$
- $[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Fe}(\text{CN})_6]^{3-}$

Note that $[\text{Co}(\text{NH}_3)_3(\text{CN})_3][\text{Fe}(\text{CN})_3(\text{NH}_3)_3]$ is invalid as both complexes are uncharged the compound is no longer ionic.

Now, we consider the geometrical isomers.

- $[\text{Fe}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Fe}(\text{CN})_6]^{3-}$ are MA_6 for each ligand and have no geometrical isomers. This gives 2 isomers.
- $[\text{Fe}(\text{NH}_3)_5(\text{CN})]^{2+}[\text{Co}(\text{CN})_5(\text{NH}_3)]^{2-}$ and $[\text{Co}(\text{NH}_3)_5(\text{CN})]^{2+}[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{2-}$ are MA_5B and have no geometrical isomers (the axial and equatorial positions for octahedral are equivalent). These provide 2 isomers.
- $[\text{Fe}(\text{NH}_3)_4(\text{CN})_2]^+[\text{Co}(\text{CN})_4(\text{NH}_3)_2]^-$ and $[\text{Co}(\text{NH}_3)_4(\text{CN})_2]^+[\text{Fe}(\text{CN})_4(\text{NH}_3)_2]^-$ are MA_4B_2 . Each ligand has a pair of cis-trans isomers. Hence, there are $2(2)(2) = 8$ isomers from these.

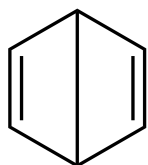


Hence, we have a total of $2 + 2 + 8 = 12$ isomers.

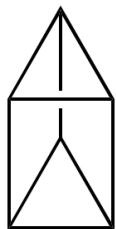
Problem 23: What's Another Word For Fragrant?**[7 points]**

Of all the aromatic molecules benzene is doubtless the most well-known, so much so as to be almost representative of organic chemistry in the public mind. The familiar Kekulé structure is taken for granted now, and we often neglect to appreciate the many proposed structures of benzene following the elucidation of its molecular formula.

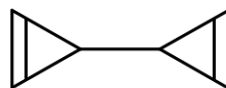
C_6H_6 isomers such as Dewar benzene (1) and prismane (2) have been successfully synthesised despite their great instability, and others like bicyclopropenyl (3) are proposed to be possible metastable species. Of course, a few isomers are impossible, such as Claus benzene (4).



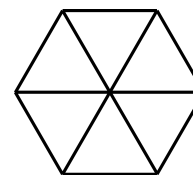
1



2



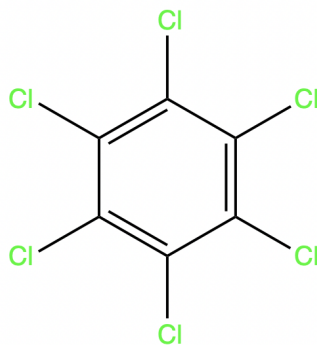
3



4

(a) Identify the number of σ bonds in prismane. **[2 points]**

Hexachlorobenzene (5) is obtained on an industrial scale by the complete chlorination of benzene via electrophilic aromatic substitution.



5

(b) Let the ratio of the intensity of the base peak to the molecular ion peak in the mass spectrum of hexachlorobenzene be $m:n$. Find m/n .

Assume that no fragmentation occurs, and that the isotopic abundance of $^{35}\text{Cl} : ^{37}\text{Cl}$ is 3 : 1.

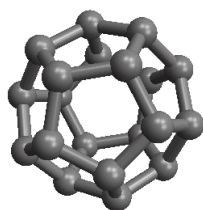
Give your answer to 0d.p. **[2 points]**

Benzene has now become a recurring structural motif in a diverse range of molecules, from biomolecules to transition metal complexes. Of particular interest to nanochemistry are the fullerenes, allotropes of carbon that come in a wide variety of geometrical shapes.

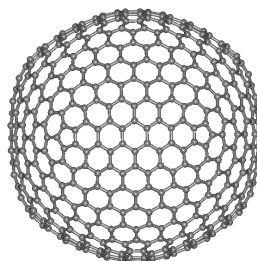
Buckminsterfullerene (**6**) belongs to a class of closed fullerenes affectionately called “buckyballs”. Members vary in size from C_{20} (**7**) to C_{720} (**8**). Some, like C_{70} (**9**) are not perfect spheres and are instead slightly elongated. However, all spherical closed fullerenes vary on a common structural theme of an icosahedral geometry. There is one pentagon found on each vertex of the icosahedron, for a total of 12 pentagons in each fullerene. The remainder of the molecule is composed of intertwined benzene rings in a honeycomb pattern between them.



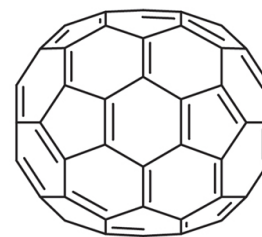
6



7



8



9

(c) Identify the number of benzene rings in C_{720} . **[3 points]**

Solution:

(a) 15

Prismane consists of 6 chemically equivalent carbons, each with 1 C–H bond and 3 C–C bonds. Thus, there are 9 C–C σ bonds and 6 C–H σ bonds for a total of 15 σ bonds.

(b) 2

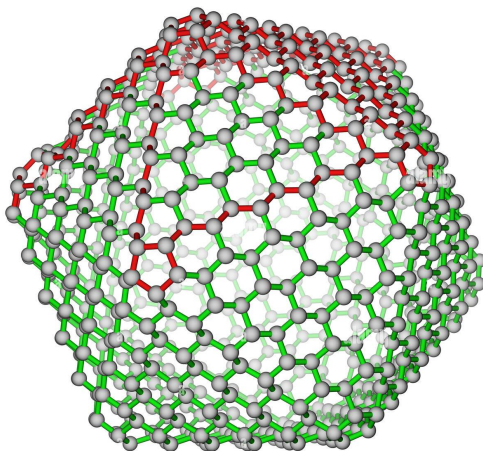
There would be a total of 7 peaks (no fragment peaks are present), with the M^+ peak corresponding to $C_6^{35}Cl_6$ (i.e all chlorines are chlorine-35), $M+2$ corresponding to $C_6^{35}Cl_5^{37}Cl$ (1 chlorine-37 and 5 chlorine-35), ... and so on until the $M+12$ peak, which corresponds to $C_6^{37}Cl_6$. The relative intensities are proportional to the relative abundance of these 7 species.

The relative abundances of the species, in turn, follows a binomial distribution, where the probability, $P(n)$, of a species with n chlorine-37 atoms occurring is $P(n) = {}^6C_n \left(\frac{3}{4}\right)^{6-n} \left(\frac{1}{4}\right)^n$. This value is highest when $n = 1$, and $P(1) = 0.356$.

To obtain the ratio of the base peak to the M^+ peak, we will also need to obtain $P(0) = 0.178$, which is the relative abundance of $C_6^{35}Cl_6$. Thus, the answer is $\frac{P(1)}{P(0)} = \frac{0.356}{0.178} = 2$.

(c) 350

Diagram 9 below more clearly shows the icosahedral geometry of C_{720} :



Let us classify the benzene rings into 2 types: **type A** are found along the edges of the icosahedral shape, and **type B** within a face of the icosahedron.

As there are 30 edges in an icosahedron and 5 benzene rings lining each edge, there are 150 **type A** benzenes. As there are 20 faces in an icosahedron and 10 benzenes fully contained within each face, this gives 200 **type B** benzenes.

Thus there are a total of $200 + 150 = 350$ benzene rings in C_{720} .

Problem 24: Concentration Cell**[4 points]**

A *concentration cell* is a kind of electrochemical cell where each half-cell contains the same redox solution but at different concentrations.

Suppose 2 lead half-cells at 25°C are connected by a very sensitive voltmeter. Both half-cells have lead electrodes and 300 cm³ of 0.050 mol dm⁻³ Pb(NO₃)₂ (aq). The reduction potential of the Pb²⁺|Pb half-cell is -0.13 V.

Aqueous NaI of concentration 0.40 mol dm⁻³ is slowly added into one half-cell. The half-cells are constantly stirred to ensure homogeneity.

Calculate the volume of NaI (aq), in cm³, that must be added for the cell potential to reach 50 mV.

(K_{sp} of PbI₂ = 9.80 × 10⁻⁹ at 25°C)

Assume that any solid precipitated does not affect the volume of water present.

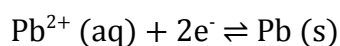
Leave your answer in 3 significant figures.

Solution:

76.0 cm³

Let the half-cells be **A** and **B**. Suppose NaI (aq) was added into half-cell **B**, which would cause PbI₂ (s) to precipitate and [Pb²⁺] to decrease. The reduction potential of **B** hence becomes more negative. Since [Pb²⁺] and reduction potential are constant in **A**, a potential difference would form and slowly increase between the half-cells.

Using the Nernst equation to calculate the reduction potential of **A**,



$$E_A = -0.13 - \frac{8.3145 \times 298.15}{2 \times 96485} \ln\left(\frac{1}{0.050}\right) = -0.1684843 \text{ V}$$

Since **B** has a more negative reduction potential than **A**,

$$E_B = -0.1684843 - 0.05$$

$$= -0.2184843$$

$$= -0.13 - \frac{RT}{nF} \ln\left(\frac{1}{[\text{Pb}^{2+}]}\right)$$

$$[\text{Pb}^{2+}] = \frac{1}{e^{\frac{2 \times 96485 \times 0.0884843}{8.3145 \times 298.15}}} = 0.001020082 \text{ mol dm}^{-3}$$

Since $K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^{-}]^2$,

$$[\text{I}^{-}] = \sqrt{\frac{9.80 \times 10^{-9}}{0.001020082}} = 0.003099528 \text{ mol dm}^{-3}$$

Now let

x = volume of 0.40 mol dm⁻³ NaI added to **B**, in dm³

y = amount of PbI₂ (s) precipitated in **B**, in mol

Suppose all the PbI₂ remains dissolved in solution after NaI (aq) was added.

$$\text{Initial } [\text{Pb}^{2+}] = \frac{0.05 \times 0.3}{0.3+x} = \frac{0.015}{0.3+x}$$

$$\text{Initial } [\text{I}^{-}] = \frac{0.40 \times x}{0.3+x} = \frac{0.4x}{0.3+x}$$

Concentrations (mol dm ⁻³)	Pb ²⁺ (aq)	+ 2 I ⁻ (aq)	⇌ PbI ₂ (s)
Init.	$\frac{0.015}{0.3+x}$	$\frac{0.4x}{0.3+x}$	
Change	$-\frac{y}{0.3+x}$	$-\frac{2y}{0.3+x}$	
Eqm.	0.001020082	0.003099528	

$$\frac{0.015-y}{0.3+x} = 0.001020082 \quad (1)$$

$$\frac{0.4x-2y}{0.3+x} = 0.003099528 \quad (2)$$

Solving these simultaneous equations, we find

$$x = 0.075996 \text{ dm}^3 \approx 76.0 \text{ cm}^3 \text{ (3 s.f.)}$$

Problem 25: Alai & Kayla's Shenanigans!**[7 points]**

Alai & Kayla are roommates boarding at 'Yrtsimehc' High School. Their dormitory is unusual as it consists of multiple airtight vacuum compartments.



- (a) Alai has bought a blimp to travel to school, as shown above. The blimp contains an internal combustion engine and is stored outside their dorms. The engine operates between 300K and 800K, calculate the maximum efficiency of it.

Leave your answer as a decimal in 2 significant figures. [2 points]

- (b) Kayla has filled one of their dorm rooms with 25000 mol of Kr(g). Suppose the gas occupies 72 dm³ at 300K and expands isothermally to occupy 100dm³, calculate the change in entropy for this process in units of J K⁻¹.⁶

Leave your answer in 5 significant figures. [2 points]

Note: Part (c) is unrelated to part (b).

Kayla requires help to complete her 'Dyermothnamics' homework question.

The constant-pressure heat capacity (in units of J) of a given sample of a perfect gas was found to have the following relationship with temperature across the temperature range of 100K to 250K:

$$C_p = 3.667 + 0.9823 T$$

At temperatures above 250K, the perfect gas follows the below correlation instead:

$$C_p = -0.8822T^2 + 5.881 T + 2.344$$

Where T is denoted as temperature in Kelvin.

⁶ Erratum: The question originally asked for an answer in units of J mol⁻¹ K⁻¹. All teams who raised a ticket regarding incorrect answers arising from this confusion have had their marks amended accordingly.

- (c) Find the heat, q , associated with the process when the temperature is lowered from 400K to 150K under constant pressure in units of J.

Leave your answer in 5 significant figures. [3 points]

Solution:

(a) 0.63

Max efficiency means the heat engine is actually a Carnot engine in disguise.

Using the formula for efficiency of a Carnot engine:

$$\eta = 1 - \frac{T_c}{T_h} = 1 - 300/800 = 0.63 \text{ (2 s.f.)}$$

(b) 68284 J mol⁻¹ K⁻¹

$\Delta U = q + w$, $\Delta U = 0$ since $\Delta T = 0$ (isothermal process)

$$dq = -dw = PdV$$

$$\Delta U = \int dS = \int PdV = \int \frac{nRT}{V} dV$$

$$= nR(\ln V_2 - \ln V_1) = nR(\ln V_2 - \ln V_1)$$

$$= 25000 \times 8.3145 \times \ln(100/72)$$

$$= 68284 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (5 s.f.)}$$

(c) 13918000 J

By definition, $q = \Delta H$

$$\int dH = \int C_p dT$$

$$= \int_{400}^{250} (-0.8822T^2 + 5.881T + 2.344) dT + \int_{250}^{150} (3.667 + 0.9823T) dT$$

$$= 13918000 \text{ J (5 s.f.)}$$

Problem 26: Chemical Connections**[6 points]**

In the British quiz show Only Connect, hosted by Victoria Coren Mitchell, contestants race to find the hidden connections in groups of items. The hardest stage in the show is dubbed the “Connect Wall” and is presented as a wall of 16 words. Contestants must find the unique division of these words into 4 groups of 4 words each. (Note that some words may fit into more than one group, but there is only one set of four groupings). In an additional twist on Connect Walls, sometimes there is a hidden word that is connected by all 4 groups that one must find.

As an example, consider the connect wall below:

Grigory Rasputin	Clemens Winkler	Ernest Lawrence	Lecoq de Boisbaudran
Catherine the Great	John Bardeen	Walter Brattain	Leo Tolstoy
Nicolaus Copernicus	Theodor Benfey	Albert Einstein	Charles Janet
Timothy Stowe	Yuri Oganessian	Enrico Fermi	Paul Giguère

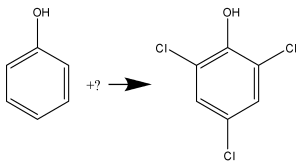
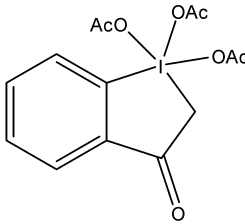
The unique grouping is as follows:

- Russians: Grigory Rasputin, Catherine the Great, Leo Tolstoy, Yuri Oganessian
- People related with Germanium: Clemens Winkler (discovered it), Lecoq de Boisbaudran (confirmed its atomic mass), John Bardeen, Walter Brattain (built the first germanium transistor)
- People with Elements named after them: Ernest Lawrence, Albert Einstein, Enrico Fermi, Nicolaus Copernicus
- People who proposed periodic tables: Theodor Benfey, Charles Janet, Timothy Stowe, Paul Giguère

What connects all four groups? Well, a certain Russian chemist has an element named after him, predicted the existence of Germanium and proposed *the* periodic table. The final answer to this connect wall is **Dmitri Mendeleev**.

(Note that Yuri Oganessian also has an element named after him, but he can't go in that group as the Russians group will be lacking a person).

Now consider the following connect wall. The 4 groups uniquely point to a common anion.

$\arccos(-1/3)$	$I_2(g)$		$\rho = 1313.0 \text{ kg m}^{-3}$ at s.t.p. $C_p = 4R$ at low T $C_p = 13R$ at high T
conc. HNO_3	Baking soda	$[V(H_2O)_6]^{2+}$	Superglue
$\omega(W) = 38.90\%$ $\omega(X) = 18.00\%$ $\omega(Y) = 15.91\%$ $\omega(Z) = 27.19\%$		$ATP + H_2O \rightarrow AMP + ?$	Dominica, El Salvador and Nicaragua
Green algae, Excavata, Oomyctes	T_d	$V = \frac{a^3}{6\sqrt{2}}$	$(NH_4)_2[Ce(NO_3)_6]$

ω refers to the mass fraction of that element in the compound.

Hints:

Ammie, one of our mascots, thinks this anion is normally served with potato. She's not quite right.

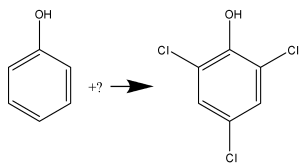
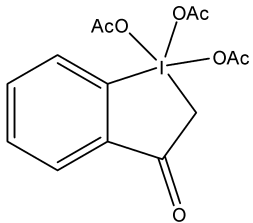
Deduce the **hidden anion** in this connect wall.

Give your answer in the form of the CAS Registry Number of the anion, omitting any dashes. You may find this database helpful: <https://commonchemistry.cas.org/> (note that this database cannot search by formula, so you need to key in the full name). For example, if you believe the anion is the sulfide anion, which has a CAS Registry Number of 18496-25-8, key in 18496258.

Solution:

14333132

The items in the wall are labelled for ease of reference.

	A	B	C	D
1	$\arccos(-1/3)$	$I_2(g)$		$\rho = 1313.0 \text{ kg m}^{-3}$ at s.t.p. $C_p = 4R$ at low T $C_p = 13R$ at high T
2	conc. HNO_3	Baking soda	$[V(H_2O)_6]^{2+}$	Superglue
3	$\omega(W) = 38.89\%$ $\omega(X) = 18.00\%$ $\omega(Y) = 15.91\%$ $\omega(Z) = 27.19\%$		$ATP + H_2O \rightarrow AMP + ?$	Dominica, El Salvador and Nicaragua
4	Green algae, Excavata, Oomyctes	T_d	$V = \frac{a^3}{6\sqrt{2}}$	$(NH_4)_2[Ce(NO_3)_6]$

The groups are:

- Purple: $I_2(g)$, $[V(H_2O)_6]^{2+}$, A3 ($BaCuSi_2O_6$, the pigment Han purple), Dominica, El Salvador and Nicaragua (the only countries with purple in their flag)
- Oxidising agents: C1 (aqueous Cl_2), conc. HNO_3 , B3 (Dess-Martin periodinane), $(NH_4)_2[Ce(NO_3)_6]$ (also known as ceric ammonium nitrate/CAN)
- Ends in -ate: Baking soda (sodium bicarbonate), Superglue (cyanoacrylate), C3 (forms pyrophosphate), Green algae, Excavata, Oomyctes (flagellates)
- Tetrahedral: $\arccos(-1/3)$ ($=109.47^\circ$, the tetrahedral angle), D1 (SiH_4), T_d , $V = \frac{a^3}{6\sqrt{2}}$
(volume of a tetrahedron)

A certain common purple oxidising agent (which is an anion) ends in -ate and has a tetrahedral structure. It is none other than MnO_4^- (note in the linked database, you have to search "permanganate", whereas "Manganate" or "MnO4-" will not show results). Permanganate has a CAS number of 14333-13-2, so we key in 14333132.

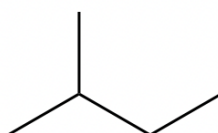
Problem 27: Escher's Tessellations**[7 points]**

MC Escher was well known for his almost surrealistic tessellation art; from a simple shape he was able to create works of art by duplicating it *ad infinitum*. This is the essence of tessellation: Repeating the same unit to give rise to impossible complexity.

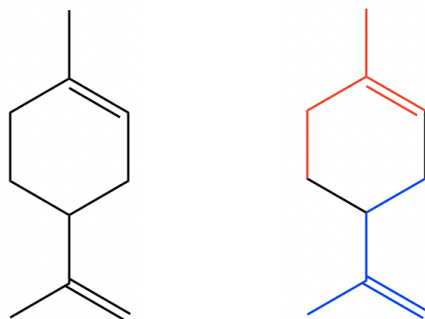


An MC Escher-inspired tessellation that looks suspiciously like terpenes...

In plant biology, there is a class of organic compounds called **terpenes** which play a crucial role in mediating ecological processes such as disease prevention, flowering and plant-plant conversation. This class of compounds is special from an organic chemist's perspective because *they are tessellations*, built from a repetition of the same basic carbon skeleton:

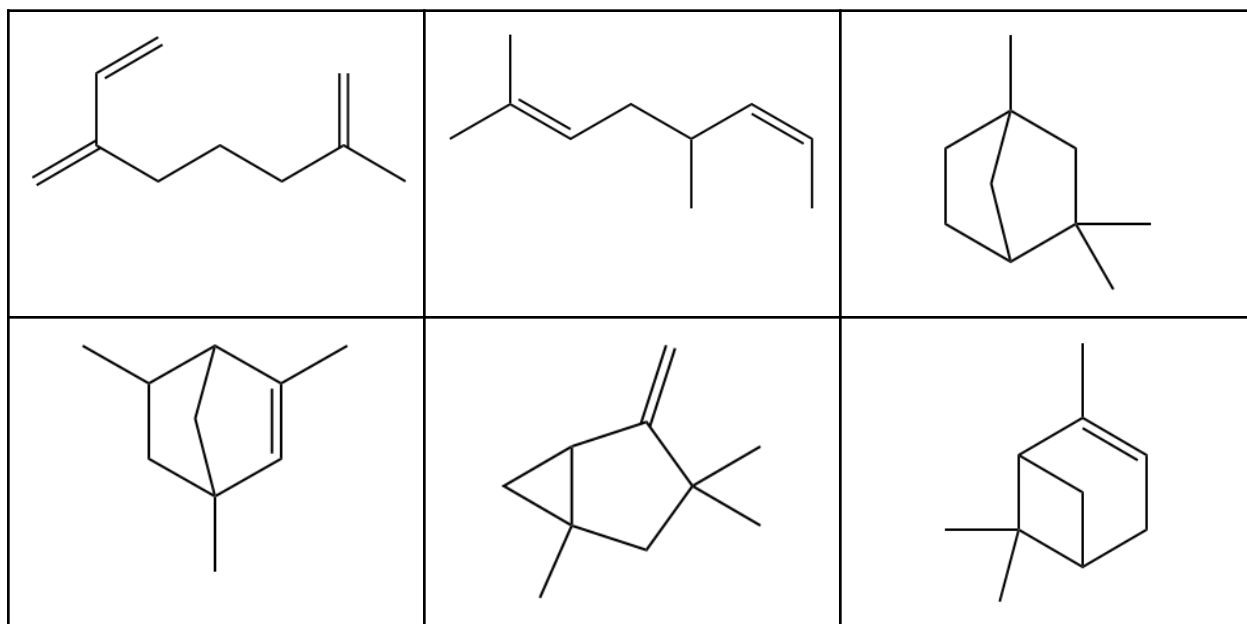


In other words, the carbon skeleton in the terpene must be constructible from repeating units of this 5C structural motif, colloquially called an isoprene unit. An example is limonene, which is constructed from 2 such units:

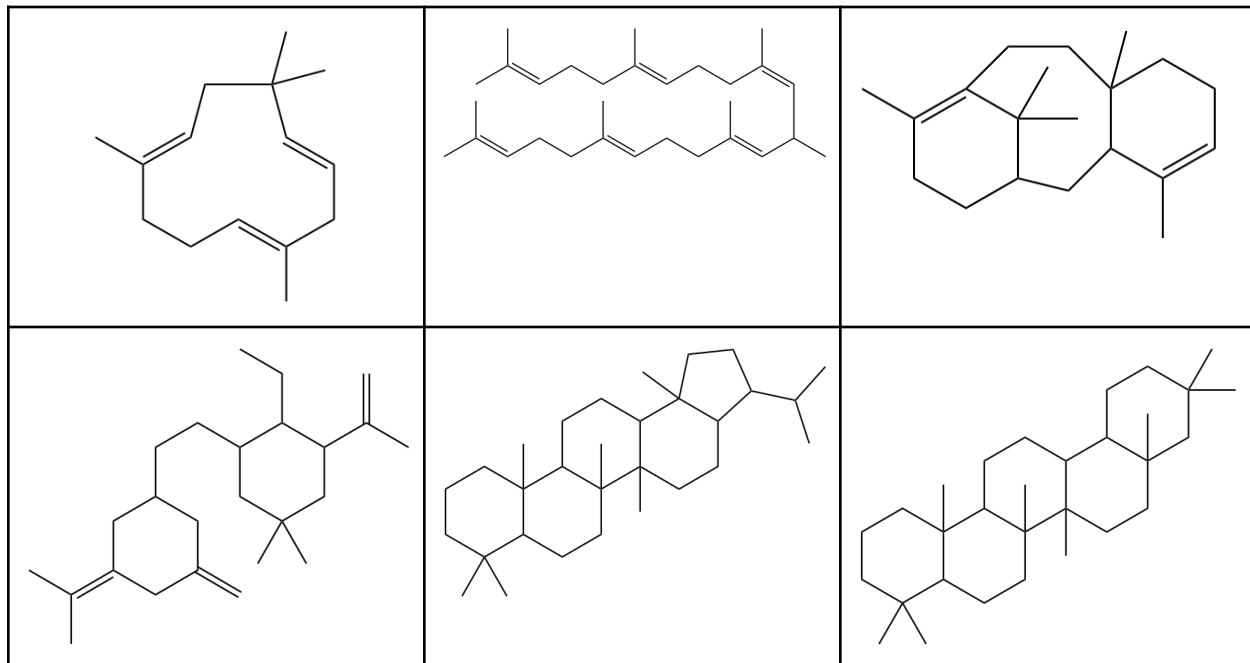


Depending on the number of basic isoprene units they are constructed from, terpenes are called monoterpenes, diterpenes and triterpenes for 2, 4 and 6 isoprene units respectively.

(a) Fancy yourself an up-and-coming MC Escher? A series of 10C molecules are shown - how many of them are the carbon skeletons of monoterpenes? **[3 points]**



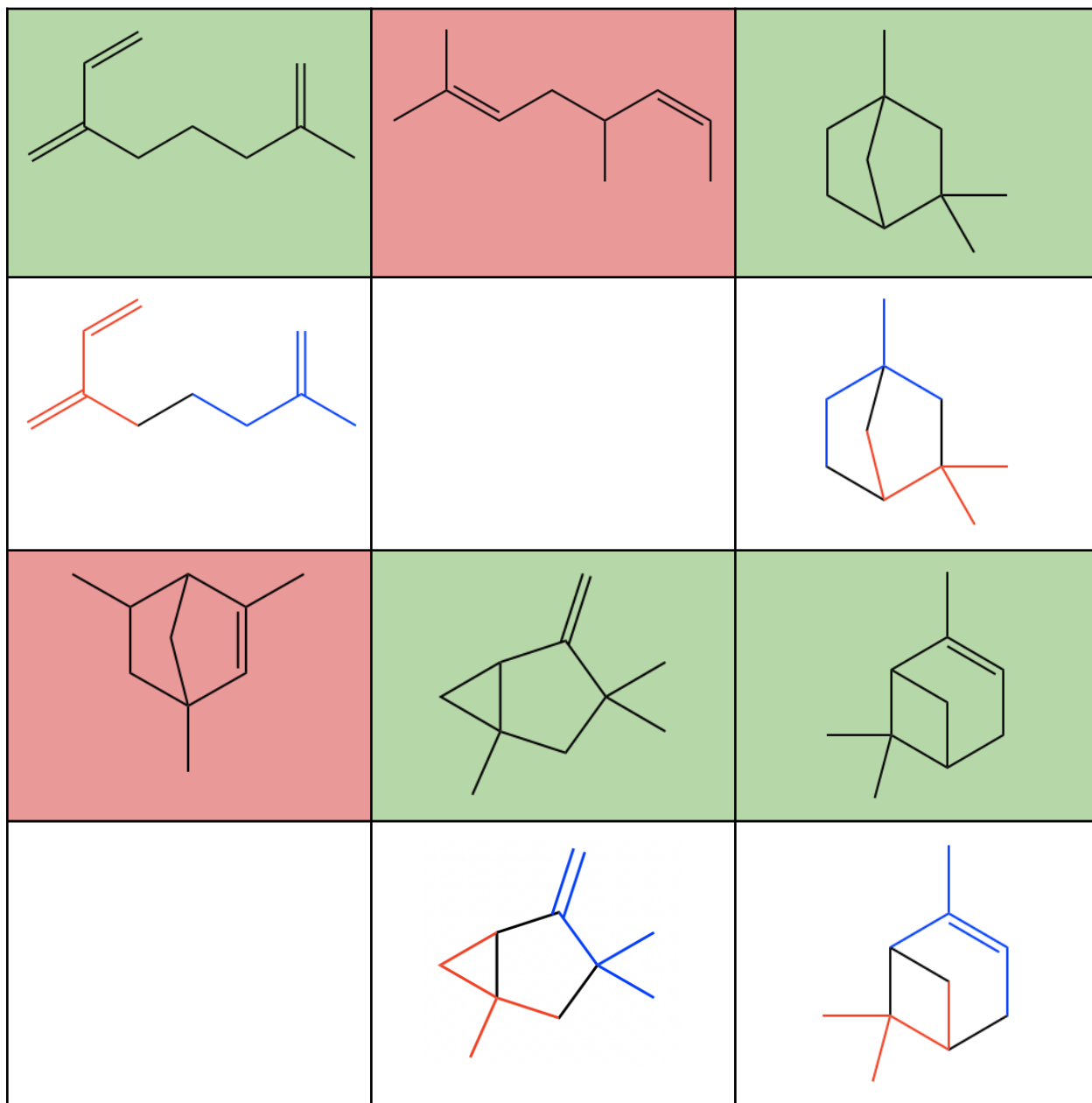
(b) Nature is a supremely sublime artist, capable of producing works of astounding complexity. How many of the following C_{20} and C_{30} molecules are the carbon skeletons of diterpenes or triterpenes? **[4 points]**



Solution:

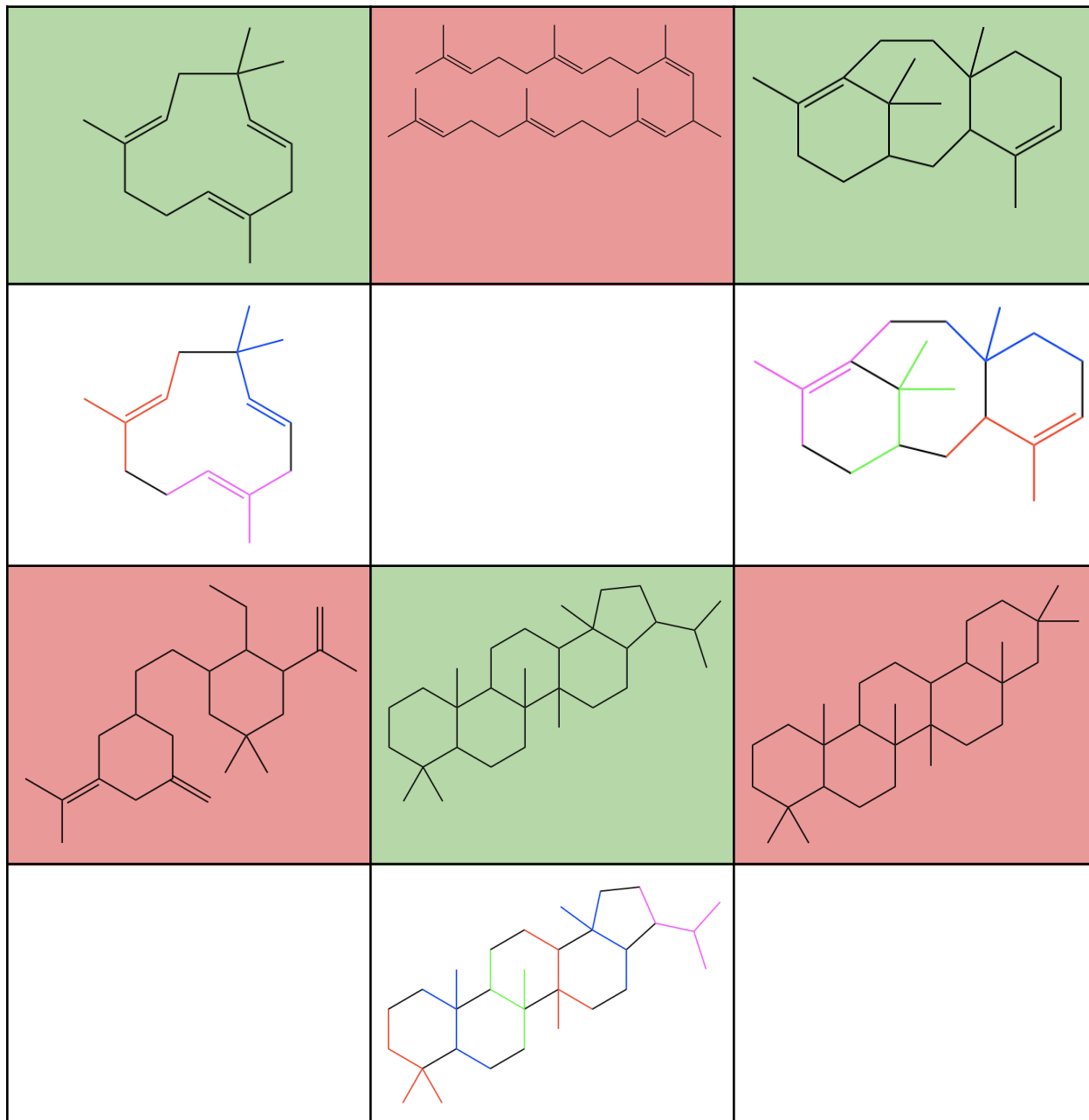
(a) 4

A hallmark of a monoterpene is that the carbon skeleton is constructible from two isoprene units. The carbon skeletons that pass this test are identified below, along with the isoprene units they are built from:



(b) 3

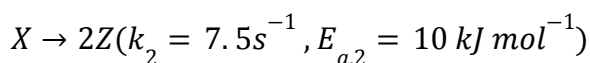
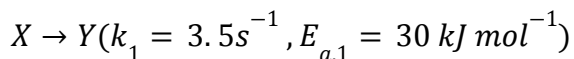
A similar process is applied in part (b), and the results shown below:



Problem 28: First-Order, But Higher-Order**[7 points]**

First-order reactions are one of the most fundamental in the study of kinetics. These reactions may be used as 'basic building blocks' in considering more complex reactions in certain circumstances.

- (a) We begin by exploring parallel first-order reactions, where one reactant concurrently via different first-order pathways becomes different sets of products. Consider the following reaction scheme (both reactions occur concurrently):



- (i) Given that the effective rate constant $k_{eff} = k_1 + k_2$, and that k_{eff} satisfies any relation that both k_1 and k_2 do, determine the effective activation energy $E_{a,eff}$ (in kJ mol^{-1})

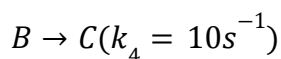
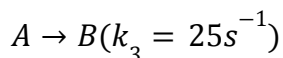
Leave your answer in 3 significant figures. [2 points]

Hint: You may need to differentiate exponential functions

- (ii) The rate constants above (k_1 and k_2) are given for 298K. By considering the relationship between the ratio of products Y and Z that will be formed and the rate constants of each reaction, find the temperature T (in K) when the mole ratio of Y to Z produced is 2:1. Assume that activation energy remains constant with temperature.

Leave your answer in 3 significant figures. [2 points]

- (b) We continue by exploring consecutive first-order reactions. This is where many elementary first order steps in a mechanism occur consecutively to form an overall reaction sequence. Consider this reaction scheme now:



B is an intermediate in this reaction scheme. As A is converted to C, the concentration of B will initially increase to a maximum at time t_{max} before decreasing. Find t_{max} .

Leave your answer in 3 significant figures. [3 points]

Hint 1:

To find a time where [B] is maximum, the rate of change of [B] must be ____.

Hint 2:

To solve a linear differential equation of the form $\frac{dy}{dx} + f(x)y = g(x)$,

multiply throughout by the integrating factor $\mu(x) = e^{\int f(x)dx}$ and the solution will be

$$y(x) = \frac{\int \mu(x)g(x)dx}{\mu(x)}.$$

Solution:

(a) (i) 16.4 kJmol⁻¹

The trick is to use the Arrhenius equation $k = Ae^{-\frac{E_a}{RT}}$ and substitute this into the given equation.

$$k_{eff} = k_1 + k_2 \text{ can hence be converted to the form } A_{eff} e^{-\frac{E_{a,eff}}{RT}} = A_1 e^{-\frac{E_{a,1}}{RT}} + A_2 e^{-\frac{E_{a,2}}{RT}}$$

Now we can employ the hint and differentiate to get

$$\left(-\frac{E_{a,eff}}{RT^2}\right) A_{eff} e^{-\frac{E_{a,eff}}{RT}} = \left(-\frac{E_{a,1}}{RT^2}\right) A_1 e^{-\frac{E_{a,1}}{RT}} + \left(-\frac{E_{a,2}}{RT^2}\right) A_2 e^{-\frac{E_{a,2}}{RT}}$$

This is simply equivalent to $k_{eff} E_{a,eff} = k_1 E_{a,1} + k_2 E_{a,2}$ if you substitute back the rate constants for their Arrhenius forms.

$$\text{Hence, } E_{a,eff} = \frac{k_1 E_{a,1} + k_2 E_{a,2}}{k_1 + k_2} \text{ (i.e. simply their weighted sums)} = 16.363 = 16.4 \text{ (3 s.f.)}$$

(ii) 406 K

Let the rate constants at temperature T be k_1' and k_2' .

As both are first-order reactions, $\frac{k_1'}{k_1' + k_2'}$ of X will form Y and $\frac{k_2'}{k_1' + k_2'}$ of X will form Z.

Hence, $\frac{[Y]}{[Z]} = \frac{k_1'}{2k_2'}$. Since $[Y] = 2[Z]$, $k_1' = 4k_2'$.

Using the Arrhenius equation, we obtain $\frac{k_1'}{k_2'} = e^{\frac{E_{a,1}}{R} \left(\frac{1}{T} - \frac{1}{298}\right)}$ and $\frac{k_2'}{k_2'} = e^{\frac{E_{a,2}}{R} \left(\frac{1}{T} - \frac{1}{298}\right)}$

Dividing the two equations obtained, $\frac{k_1' k_2'}{k_1' k_2'} = e^{\frac{E_{a,1} - E_{a,2}}{R} \left(\frac{1}{T} - \frac{1}{298}\right)}$

Substituting $k_1' = 4k_2'$, and the values of k_1' , k_2' , $E_{a,1}$, $E_{a,2}$ and R, we can obtain a value for T.

$$T = 406.09\text{K} = 406\text{K} \text{ (3 s.f.)}$$

(b) 0.0611 s

This question is a little more complicated. We start with something simple.

$$\frac{d[B]}{dt} = k_3[A] - k_4[B] \text{ and since } A \text{ is only consumed, } [A] = [A]_0 e^{-k_3 t}$$

Substituting this result back into the equation, we will obtain a linear differential equation

$$\frac{d[B]}{dt} + k_4[B] = k_3[A]_0 e^{-k_3 t} \text{ which can be solved using the hint to give}$$

$$[B] = [A]_0 \left(\frac{k_3}{k_4 - k_3} \right) (e^{-k_3 t} - e^{-k_4 t})$$

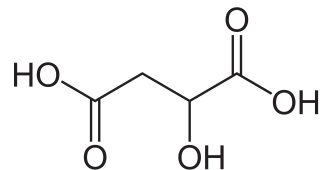
$$\text{This can be then differentiated to give } \frac{d[B]}{dt} = [A]_0 \left(\frac{k_3}{k_4 - k_3} \right) (-k_3 e^{-k_3 t} + k_4 e^{-k_4 t})$$

$$\text{Now, we can set } \frac{d[B]}{dt} = 0 \text{ and obtain, after some manipulation, } t_{max} = \frac{1}{(k_3 - k_4)} \ln\left(\frac{k_3}{k_4}\right).$$

$$\text{Hence, substituting } k_3 \text{ and } k_4, \text{ we obtain } t_{max} = 0.061086 = 0.0611\text{s (3 s.f.)}$$

Problem 29: Jorge's Marvellous Medicine**[7 points]**

Malic acid is an organic acid found naturally in apples and grapes. Notably, it is a key intermediate in the Krebs Cycle during aerobic respiration, is widely used as a food additive, and is investigated for its role in supporting muscle function and cardiovascular health. It is a dibasic weak acid with chemical formula $C_4H_6O_5$ and the following structure:



To prepare for his trip at sea, Jorge buys a pack of effervescent malic acid tablets. From the packaging, he learns that each tablet contains exactly 1g of malic acid.

- (a) As directed by the packaging, Jorge drops 1 tablet into 200cm^3 of water. The tablet fully dissolves under standard conditions (298K, 1 bar).

To estimate the pH of the resultant solution, he first assumes that malic acid is a monoprotic weak acid with $\text{p}K_a = 3.40$.

Find the pH of the solution.

Leave your answer in 2 significant figures. [2 points]

- (b) Jorge then recalculates the pH, knowing that malic acid is actually a dibasic acid with two acid dissociation reactions (let $\text{p}K_{a,1} = 3.40$, $\text{p}K_{a,2} = 5.10$).

Find the actual pH of the solution.

Leave your answer in 5 significant figures. [3 points]

- (c) Jorge wants his solution to have a pH of 3. What volume of water, in cm^3 , should he dissolve one tablet in?

Leave your answer in 3 significant figures. [2 points]

Solution:

(a) 2.4

Expressing malic acid as H_2A ,

Molecular formula of $H_2A = C_4H_6O_5$

M_r of $H_2A = 4(12.01) + 6(1.008) + 5(16.00) = 134.088$

Given mass of H_2A in 1 tablet = 1g,

Amount of $H_2A = \frac{1}{134.088}$ mol

Initial concentration of H_2A , $c_o = \frac{\frac{1}{134.088}}{0.200} = \frac{5}{134.088}$ M (5 s.f. gives same ans for (a))

Calculating pH of a monoprotic weak acid, we use

$$[H^+] \approx \sqrt{K_a [H_2A]}$$

Given $pK_a = 3.40$,

$$\Rightarrow pH = -\lg \sqrt{K_a [H_2A]} = -\lg \sqrt{10^{-3.40} \left(\frac{5}{134.088}\right)} = 2.41 \text{ (3 s.f.)} = 2.4 \text{ (2 s.f.)}$$

OR

Using ICE table (let $[H^+] = x$),

$$K_a = \frac{[H^+][HA^-]}{[H_2A]} = \frac{(x)(x)}{\left(\frac{5}{134.088} - x\right)} = 10^{-3.40}$$

Solve for x,

$$x = [H^+] = 0.0036590053 \text{ M}$$

$$\Rightarrow pH = -\lg[H^+] = -\lg(0.0036590053) = 2.4366 \text{ (5 s.f.)} = 2.4 \text{ (2 s.f.)}$$

(b) 2.4357

Writing and rearranging $K_{a,1}$ and $K_{a,2}$ expressions,

$$K_{a,2} = \frac{[H^+][A^{2-}]}{[HA^-]} \Rightarrow [HA^-] = \frac{[H^+][A^{2-}]}{K_{a,2}} \text{-----(1)}$$

$$K_{a,1} = \frac{[H^+][HA^-]}{[H_2A]} \Rightarrow [H_2A] = \frac{[H^+][HA^-]}{K_{a,1}} = \frac{[H^+]^2[A^{2-}]}{K_{a,1}K_{a,2}} \text{-----(2)}$$

Making use of the following balance equations,

$$\text{MBE: } c_o = [H_2A] + [HA^-] + [A^{2-}]$$

$$\text{CBE: } [\text{H}^+] = [\text{HA}^-] + 2[\text{A}^{2-}]^7$$

Sub expressions for $[\text{H}_2\text{A}]$ and $[\text{HA}^-]$ obtained above

Into MBE:

$$c_o = \frac{[\text{H}^+]^2[\text{A}^{2-}]}{K_{a,1}K_{a,2}} + \frac{[\text{H}^+][\text{A}^{2-}]}{K_{a,2}} + [\text{A}^{2-}]$$

Making $[\text{A}^{2-}]$ the subject,

$$[\text{A}^{2-}] = \frac{c_o}{\frac{[\text{H}^+]^2}{K_{a,1}K_{a,2}} + \frac{[\text{H}^+]}{K_{a,2}} + 1} \text{-----(3)}$$

Into CBE:

$$[\text{H}^+] = \frac{[\text{H}^+][\text{A}^{2-}]}{K_{a,2}} + 2[\text{A}^{2-}]$$

Making $[\text{A}^{2-}]$ the subject,

$$[\text{A}^{2-}] = \frac{[\text{H}^+]}{\frac{[\text{H}^+]}{K_{a,2}} + 2} \text{-----(4)}$$

Equating (3) and (4),

$$\begin{aligned} \frac{c_o}{\frac{[\text{H}^+]^2}{K_{a,1}K_{a,2}} + \frac{[\text{H}^+]}{K_{a,2}} + 1} &= \frac{[\text{H}^+]}{\frac{[\text{H}^+]}{K_{a,2}} + 2} \Rightarrow \frac{c_o[\text{H}^+]}{K_{a,2}} + 2c_o = \frac{[\text{H}^+]^3}{K_{a,1}K_{a,2}} + \frac{[\text{H}^+]^2}{K_{a,2}} + [\text{H}^+] \\ \Rightarrow \frac{[\text{H}^+]^3}{K_{a,1}K_{a,2}} + \frac{[\text{H}^+]^2}{K_{a,2}} + \left(1 - \frac{c_o}{K_{a,2}}\right)[\text{H}^+] - 2c_o &= 0 \end{aligned}$$

Given $\text{p}K_{a,1} = 3.40$, $\text{p}K_{a,2} = 5.10$, $c_o = \frac{5}{134.088} \text{ M}$ (note that using 5s.f. intermediate for c_o when answer is given in 5s.f. is not appropriate⁸), solving the cubic for $[\text{H}^+]$,

$$[\text{H}^+] = 0.0036669224 \text{ M}$$

$$\Rightarrow \text{pH} = -\lg[\text{H}^+] = -\lg(0.0036669224) = 2.4357 \text{ (5 s.f.)}$$

(c) 2150 cm³

Given $\text{pH} = 3$, $[\text{H}^+] = 10^{-3} \text{ M}$

From (4),

$$[\text{A}^{2-}] = \frac{10^{-3}}{\frac{10^{-3}}{K_{a,2}} + 2} = 7.819064 \times 10^{-6} \text{ M}$$

Sub value of $[\text{A}^{2-}]$ into (1),

$$[\text{HA}^-] = \frac{(10^{-3})(7.819064 \times 10^{-6})}{K_{a,2}} = 9.843618 \times 10^{-4} \text{ M}$$

⁷ $[\text{OH}^-]$ is excluded from CBE to simplify the equation. Given that the solution is mildly acidic (from (a)), it is safe to assume $[\text{OH}^-]$ is negligible. Including $[\text{OH}^-]$ in calculations yields the same value of $[\text{H}^+]$ when rounded to 8 s.f.

⁸ However, using 6s.f. intermediate for both c_o and the value of $[\text{H}^+]$ found subsequently yields the same result of 2.4357, hence it may be taken as the only correct answer. Common practice is to leave intermediates in working to at least 1 or 2 more s.f. than expected in the final answer, so this consideration should be maintained throughout.

Sub value of $[A^{2-}]$ into (2),

$$[H_2A] = \frac{(10^{-3})^2 (7.819064 \times 10^{-6})}{K_{a,1} K_{a,2}} = 0.002472605 \text{ M}$$

Sub values into MBE,

$$c_0 = [H_2A] + [HA^-] + [A^{2-}]$$

$$= 0.002472605 + 9.843618 \times 10^{-4} + 7.819064 \times 10^{-6}$$

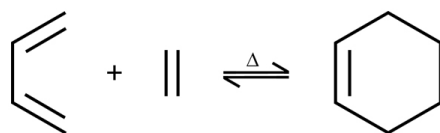
$$= 0.003464786 \text{ M}$$

Given amount of $H_2A = \frac{1}{134.088} \text{ mol}$,

$$\Rightarrow \text{Volume of water} = \frac{\frac{1}{134.088}}{c_0} = \frac{\frac{1}{134.088}}{0.003464786} = 2.15 \text{ dm}^3 = 2150 \text{ cm}^3 \text{ (3 s.f.)}$$

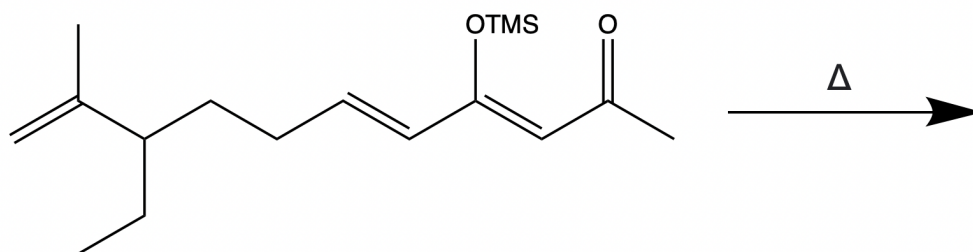
Problem 30: One Pericyclic Reaction To Rule Them All**[7 points]**

The Diels-Alder reaction is a [4+2] cycloaddition that falls under a class of reaction called pericyclic reactions. It proceeds via the following mechanism:



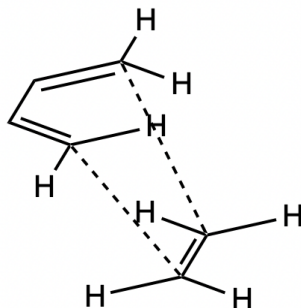
Within the field of natural product synthesis, it is highly valued for its atom economy, the rapid increase in complexity it brings about, and the ability to generate multiple chiral centres simultaneously.

(a) Predict the product of the following reaction, disregarding stereochemistry for now.

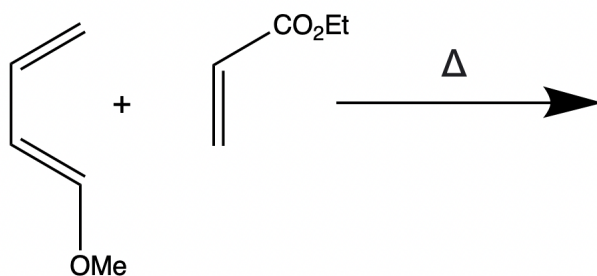
[3 points]

The reaction can be made to proceed in higher yield if electron-donating substituents are present on the diene, and electron-withdrawing substituents are present on the dienophile. However, this also means multiple products are possible depending on how the reactants approach each other.

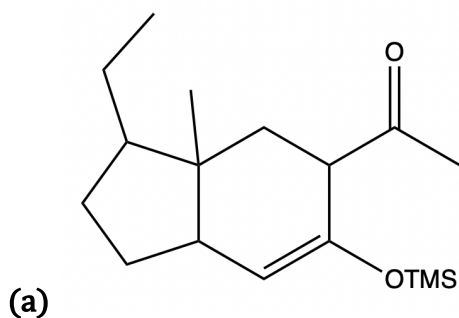
The multiple possible stereochemical outcomes arise as a result of the geometry of the transition state. It is not planar as a simple arrow-pushing mechanism may suggest. Rather, the diene will approach above or below the dienophile, as shown:



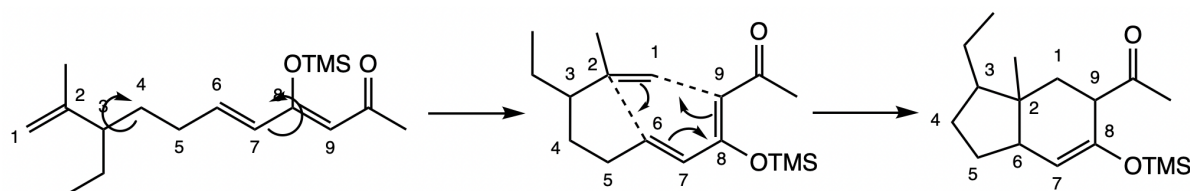
- (b) How many different products can *theoretically* be formed from the following Diels-Alder reaction, including stereochemical considerations? (While in reality the reactants will approach each other with a specific orientation due to the directing effects of the substituents, you may disregard this.) **[4 points]**



Solution:

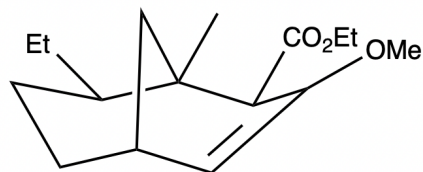


The reaction is made easier to visualise by rotating and bending some bonds as follows, after which the hexagonal arrangement of the diene and dienophile becomes more apparent:



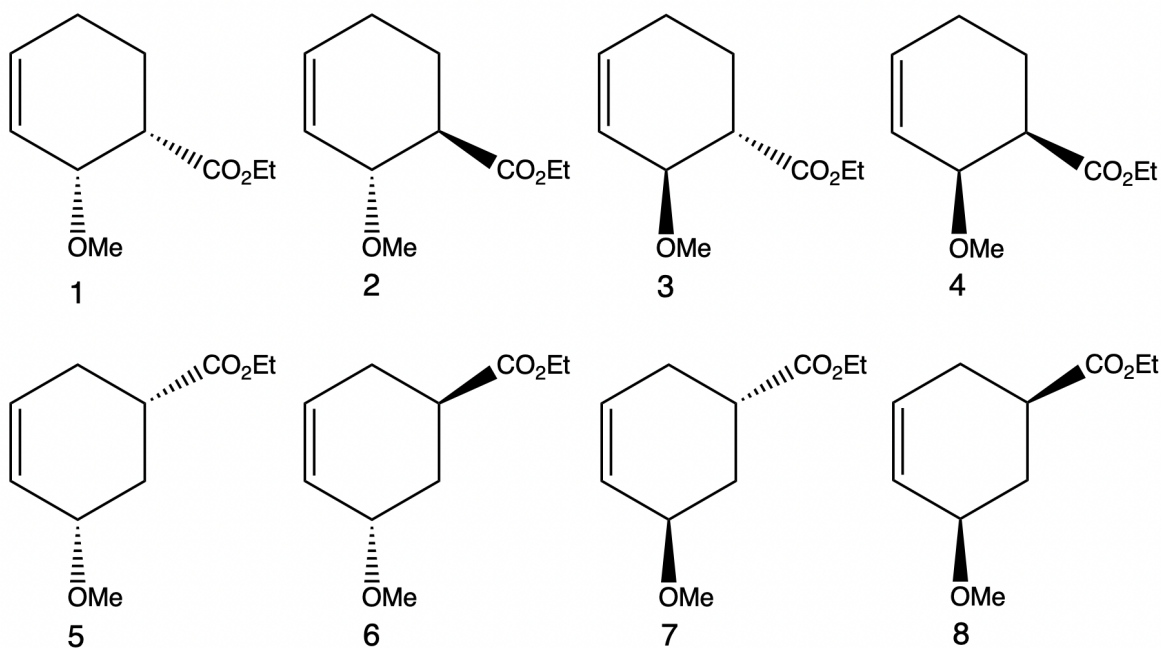
The importance of pattern recognition cannot be emphasised enough; that the diene and the dienophile are connected to each other by a carbon chain does not change the basic mechanism. It is important to focus on the critical elements of the reaction and not be distracted by the fact that it so happens to be intramolecular instead of intermolecular.

There is an alternative connectivity with the diene in the opposite orientation to the dienophile. However, the carbon tether joining them is unlikely to be long enough to enable the dienophile to reach all the way across and twist in a way as to allow the orbitals to line up and the reaction to proceed. On top of that, the resulting product, a bridged bicyclic structure (shown below), is less stable than the fused bicyclic product.



(b) 8

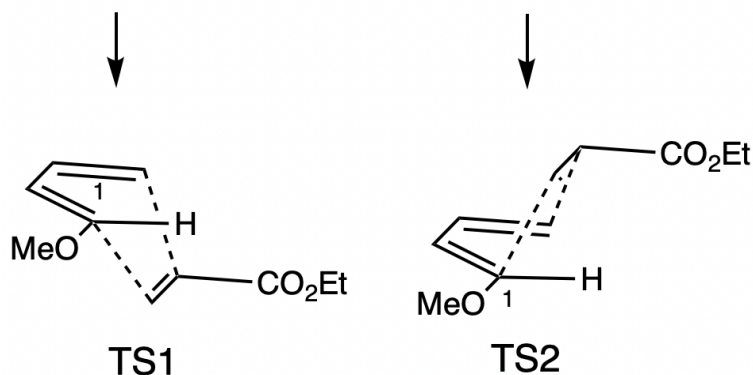
The 8 possible products are shown below:



It is entirely possible to arrive at this answer just by iterating through all possible permutations of the product (well, kudos to your team if you made an educated guess like this), but a more detailed examination requires us to enlist our understanding of two concepts: Regiochemistry and stereochemistry.

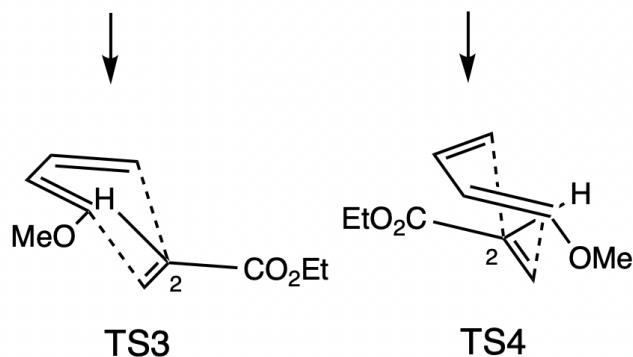
Regiochemistry relates to the location of the substituents relative to each other - compounds **1-4** are 1,2 substituted, while **5-8** are 1,3 substituted. In reality, the 1,2 product would predominate as the largest LUMO and HOMO coefficients would line up with each other - but that is ignored for the sake of the question. Stereochemistry, on the other hand, relates to the 3-dimensional placement of the substituents and is expressed in the various permutations of the wedge/dashes in the compounds above.

Let us consider stereochemistry in more detail. Firstly, the stereochemistry of the -OMe group depends on whether the diene approaches above or below the dienophile, as shown:



Imagine the bonds forming along the dotted lines as the reaction progresses. The carbon **C1** (to which the -OMe is attached) becomes sp^3 and tetrahedral in the final product. When viewed from above (in the direction of the arrow), you will observe that in **TS1**, the C1-H bond is found “above” the cyclohexene, projecting towards you, and the C1-O bond below the projecting downwards. As a result, the C1-O bond is expressed as a dash in the skeletal structure. Vice versa for **TS2**. This might take some visualisation!

Now, the problem shifts to how the stereochemistry of the CO_2Et is determined. Observe that the dienophile (the alkene) will orient the CO_2Et in one of two possible ways: with the $-CO_2Et$ pointing “towards” the diene (**TS3**), or “away” from the diene (**TS4**).



Now do the same process of following the reaction to the product, observing from above, and notice the relative placements of the C2-H and C2- CO_2Et group. **TS3** corresponds to compound **6** and **TS4** to compound **5**. In chemical terminology, compound **5** would be called the *endo product* and compound **6** the *exo product*, which are important concepts in undergraduate chemistry. Whether the reaction prefers one or the other would depend on the exact conditions employed.

Problem 31: Halo-gen**[9 points]**

Diatomic halogen gases such as I_2 exist in equilibrium with their atoms, as shown by this equilibrium: $I_2(g) \rightleftharpoons 2I(g)$

Empirical data collected for such a reaction can be used to determine the bond energy of the halogens. However, as the forward reaction only proceeds appreciably when the temperature is high (above 1000K), the bond energy found through this method has to be corrected for the large difference in temperature to obtain an accurate value.

A chemist performed an experiment at two different temperatures and his results are summarised below.

T/K	1100	1200
$P_{I_2, \text{initial}}/\text{bar}$	0.0494	0.0609
$P_{\text{total, equilibrium}}/\text{bar}$	0.0619	0.0859

- (a) Using the given data, and assuming that within the temperature range above ΔH and ΔS are constants, find, within this temperature range,
- (i) ΔH (in kJ mol^{-1}) **[2 points]**
- (ii) ΔS (in $\text{J mol}^{-1}\text{K}^{-1}$) **[2 points]**

Leave your answer in 3 significant figures.

- (b) Assuming now that I_2 and I are both ideal gases, determine the bond energy of I_2 at 298K (in kJ mol^{-1}).

Leave your answer in 3 significant figures. [2 points]

- (c) The bond energy for chlorine and bromine gas at 298K are also given as follows.

$$\text{BE}(\text{Cl}-\text{Cl}) = +243 \text{ kJ mol}^{-1}$$

$$\text{BE}(\text{Br}-\text{Br}) = +193 \text{ kJ mol}^{-1}$$

A physicist uses these three halogen gases in an experiment investigating the wavelengths of different light. He creates equal, separate samples of each of the three halogen gases and shines visible light of wavelength x nm through any two of these samples (randomly chosen from the three) at 298K. (Assume that

$400 \leq x \leq 700$, and x is equally likely to take any real value within this continuous range.)

If the halogen gas dissociates in exactly one of two of these samples, he considers the experiment a success, and a failure otherwise. Find the probability that the experiment is a success.

Leave your answer in 3 significant figures. [3 points]

[Hint: To determine whether the halogen gas dissociates, assume one photon has just enough energy to break one X–X bond, where X is the halogen.]

Solution:

(a) (i) 155 kJmol⁻¹ (ii) 107 Jmol⁻¹K⁻¹

We need to find a way to convert the given data into useful thermodynamic information. The first thing that comes to mind is equilibrium constant K .

To determine the relations between the given information, we realise that $P_{I2, equilibrium} + P_{I, equilibrium} = P_{total, equilibrium}$ and $P_{I, equilibrium} = 2(P_{I2, initial} - P_{I2, equilibrium})$ to derive the relation $P_{I, equilibrium} = 2(P_{total, equilibrium} - P_{I2, initial})$.

We then calculate $P_{I, equilibrium}$ and find $K_p = \frac{P_{I, equilibrium}^2}{P_{I2, equilibrium}} = \frac{P_{I, equilibrium}^2}{P_{total, equilibrium} - P_{I, equilibrium}}$.

At 1100K, $P_{I, equilibrium} = 0.0250$ and $K_p = 0.016937$

At 1200K, $P_{I, equilibrium} = 0.0500$ and $K_p = 0.069637$

From here, we may use van't Hoff's equation to find ΔH directly: $\ln \frac{K_2}{K_1} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$$\Delta H = + 1.5517 \times 10^5 \text{ J mol}^{-1} = + 155 \text{ kJ mol}^{-1} \text{ (3 s.f.)}$$

We may then calculate ΔG at either temperature to find ΔS .

At 1100K, $\Delta G = -RT \ln K_p = + 37300 \text{ J mol}^{-1}$

$$\Delta S = \frac{1}{T} (\Delta H - \Delta G) = + 107.15 \text{ J mol}^{-1} \text{K}^{-1} = + 107 \text{ J mol}^{-1} \text{K}^{-1} \text{ (3 s.f.)}$$

(b) 145 kJmol⁻¹

As there is a change in temperature, ΔH can no longer be assumed to be constant. We simply use Kirchoff's Law: $\Delta H_{298} = \Delta H_{1100} + \Delta C_p \Delta T$, and use equipartition principle for C_p (2.5R for monatomic and 3.5R for diatomic gases, hence $\Delta C_p = 2(2.5R) - 3.5R = 1.5R$)

We get $\Delta H_{298} = + 1.4517 \times 10^5 \text{ J mol}^{-1} = + 145 \text{ kJ mol}^{-1} \text{ (3 s.f.)}$

(c) 0.516

Bond energy is the amount of energy required to break one mole of X-X bonds. With this understanding and the hint provided, $BE(X - X) = \frac{N_A hc}{\lambda}$.

Hence, $\lambda_{I_2} = 824.04nm$, $\lambda_{Br_2} = 619.82nm$, $\lambda_{Cl_2} = 492.29nm$.

Now the problem is simply mathematical. The probability of dissociating is:

$$P(Cl_2 \text{ will dissociate}) = \frac{492.29-400}{700-400} = 0.30763$$

$$P(Br_2 \text{ will dissociate}) = \frac{619.82-400}{700-400} = 0.73273$$

$$P(I_2 \text{ will dissociate}) = 1$$

Consider the three cases:

Case 1: Cl_2 and Br_2

$P(\text{success in Case 1}) = P(Cl_2 \text{ will dissociate})P(Br_2 \text{ will not dissociate}) + P(Cl_2 \text{ will not dissociate})P(Br_2 \text{ will dissociate})$

$$= (0.30763)(1 - 0.73273) + (0.73273)(1 - 0.30763) = 0.58954$$

Case 2: Cl_2 and I_2

As I_2 will definitely dissociate, the experiment will be a success if Cl_2 does not dissociate.

$$P(Cl_2 \text{ will not dissociate}) = 1 - 0.30763 = 0.69237$$

Case 3: Br_2 and I_2

A similar logic as Case 2 applies.

$$P(Br_2 \text{ will not dissociate}) = 1 - 0.73273 = 0.26727$$

As there is an equal chance of each of the three cases occurring,

$$P(\text{success}) = \frac{1}{3} (0.58954 + 0.69237 + 0.26727) = 0.51639 = 0.516 \text{ (3 s.f.)}$$

Problem 32: Feeling A Little Gassy**[5 points]**

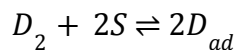
Many reactions that have important applications involve gases reacting by adsorbing onto a surface. The kinetics of such reactions are investigated using a model called the Langmuir isotherm. Several assumptions are used in the isotherm, which makes it an imperfect model, but it nonetheless is useful. A simple depiction of the Langmuir considers only one gas A.

$$\begin{aligned}
 A_g + S &\rightleftharpoons A_{ad} \\
 K &= \frac{[A_{ad}]}{p_A[S]} \\
 [S]_0 &= [S] + [A_{ad}] \\
 [S]_0 &= \frac{[A_{ad}]}{p_A K} + [A_{ad}] = [A_{ad}] \left(\frac{1}{p_A K} + 1 \right) \\
 \theta &= \frac{[A_{ad}]}{[S]_0} = \frac{1}{\frac{1}{K p_A} + 1} = \frac{p_A K}{1 + p_A K}
 \end{aligned}$$

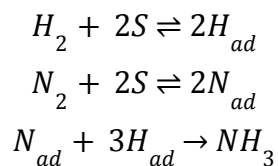
where A_g is A in the gaseous unadsorbed form, A_{ad} is A in the adsorbed form, S is an empty adsorption location on the surface, K is the relevant equilibrium constant. θ is fractional coverage of the surface of the metal.

For a simple reaction $A_g + S \rightleftharpoons A_{ad} \rightarrow P$, if we assume the final reaction step is rapid compared to the adsorption step, we can then denote rate by an expression of the form $k\theta$.

The model above suffices for a unimolecular gas. For bimolecular gases, the reaction scheme must be slightly modified to the following scheme.



Consider the common Haber process. Assume the reaction proceeds as follows:

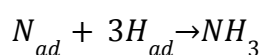
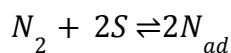
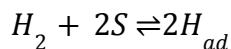


Assume the equilibrium constants for the adsorption of nitrogen and hydrogen have a ratio of 2:1. Determine the ratio of the pressures of nitrogen to hydrogen at which the rate of production of ammonia is maximised. Assume that the product $K_H p_{H_2} = 3$.

Leave your answer in 3 significant figures.

Solution:

0.138



$$K_H = \frac{[H_{ad}]^2}{p_{H_2}[S]^2} K_N = \frac{[N_{ad}]^2}{p_{N_2}[S]^2}$$

$$[S]_0 = [S] + [H_{ad}] + [N_{ad}]$$

$$[S]_0 = [S] + \sqrt{K_H p_{H_2}} [S] + \sqrt{K_N p_{N_2}} [S]$$

$$[S] = \frac{[S]_0}{1 + \sqrt{K_H p_{H_2}} + \sqrt{K_N p_{N_2}}}$$

$$[H_{ad}] = \sqrt{K_H p_{H_2}} [S] = \frac{\sqrt{K_H p_{H_2}} [S]_0}{1 + \sqrt{K_H p_{H_2}} + \sqrt{K_N p_{N_2}}}$$

$$\theta_H = \frac{[H_{ad}]}{[S]_0} = \frac{\sqrt{K_H p_{H_2}}}{1 + \sqrt{K_H p_{H_2}} + \sqrt{K_N p_{N_2}}}$$

$$[N_{ad}] = \sqrt{K_N p_{N_2}} [S] = \frac{\sqrt{K_N p_{N_2}} [S]_0}{1 + \sqrt{K_H p_{H_2}} + \sqrt{K_N p_{N_2}}}$$

$$\theta_N = \frac{[N_{ad}]}{[S]_0} = \frac{\sqrt{K_N p_{N_2}}}{1 + \sqrt{K_H p_{H_2}} + \sqrt{K_N p_{N_2}}}$$

$$v = k(\theta_H)^3 \theta_N = \frac{\sqrt{(K_H p_{H_2})^3 K_N p_{N_2}}}{(1 + \sqrt{K_H p_{H_2}} + \sqrt{K_N p_{N_2}})^4}$$

Let x be the ratio p_{N_2}/p_{H_2} .

$$v = k(\theta_H)^3 \theta_N = \frac{\sqrt{(K_H p_{H_2})^3 (2x K_H p_{H_2})}}{(1 + \sqrt{K_H p_{H_2}} + \sqrt{2x K_H p_{H_2}})^4} = \frac{(K_H p_{H_2})^2 \sqrt{2x}}{(1 + (1 + \sqrt{2x}) \sqrt{K_H p_{H_2}})^4}$$

$$v = \frac{9\sqrt{2x}}{(1 + (1 + \sqrt{2x})\sqrt{3})^4}$$

$$\frac{dv}{dx} = \frac{(1+(1+\sqrt{2x})\sqrt{3})^4 \left(\frac{9\sqrt{2}}{2\sqrt{x}}\right) - (9\sqrt{2x})4(1+(1+\sqrt{2x})\sqrt{3})^3 \left(\frac{\sqrt{2}}{2\sqrt{x}}\right)(\sqrt{3})}{(1+(1+\sqrt{2x})\sqrt{3})^8}$$

$$\frac{dv}{dx} = \frac{9((1+(1+\sqrt{2x})\sqrt{3}) - 4\sqrt{6x})}{\sqrt{2x}(1+(1+\sqrt{2x})\sqrt{3})^5}$$

At maximum,

$$(1 + (1 + \sqrt{2x})\sqrt{3}) - 4\sqrt{6x} = 0$$

$$3\sqrt{6x} = 1 + \sqrt{3}$$

$$x = 0.13822 = 0.138 \text{ (3 s.f.)}$$

Problem 33: Redox Galore**[6 points]**

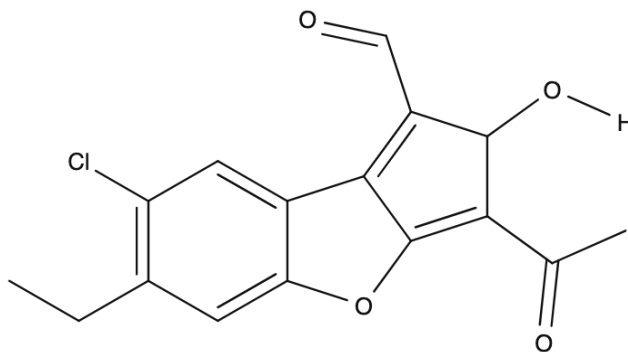
The most popular oxidants at a pre-tertiary level for organic chemistry are KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, while for the reductants LiAlH_4 , NaBH_4 and H_2 , Ni, Heat take the most fame. Most of the redox properties they possess are fairly straightforward: For example, KMnO_4 would almost always oxidise a primary alcohol to a carboxylic acid.

In the world of synthetic organic chemistry, chemists employ a wide repertoire of oxidants and reductants to create their desired molecule. A good redox reagent would fulfill the following qualifications (non-exhaustive):

1. Highly regioselective, chemoselective and stereoselective
2. Cost-effective
3. Minimal side products

Keqing is a newly-inducted pharmacist who currently happens to be in a chemistry laboratory full of all the reagents and apparatus she could ever want. Spoilt for choice, she conducts the following experiments below:

(a) This molecule is subject to a whole list of **oxidants** below.

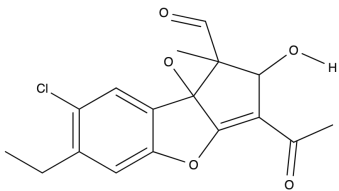
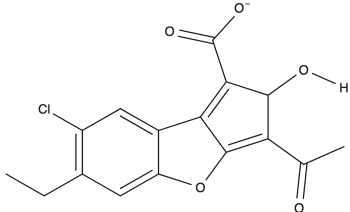
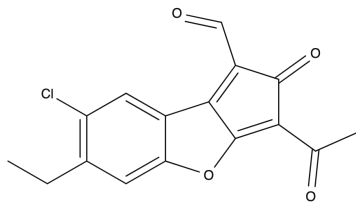
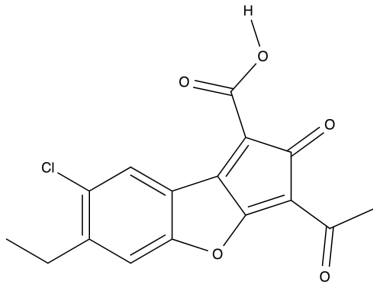
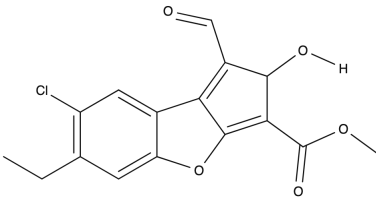
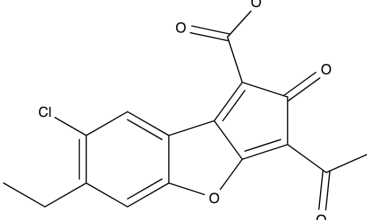


1. $\text{Na}_2\text{Cr}_2\text{O}_7$
2. Tollen's Reagent
3. Fehling's Reagent
4. MnO_2
5. CrO_3
6. PCC
7. mCPBA
8. IBX

Assign the end product after oxidation to each oxidizing reagent, by selecting a suitable number corresponding to a possible product found in the list below. **The same numbers can be used. [3 points]**

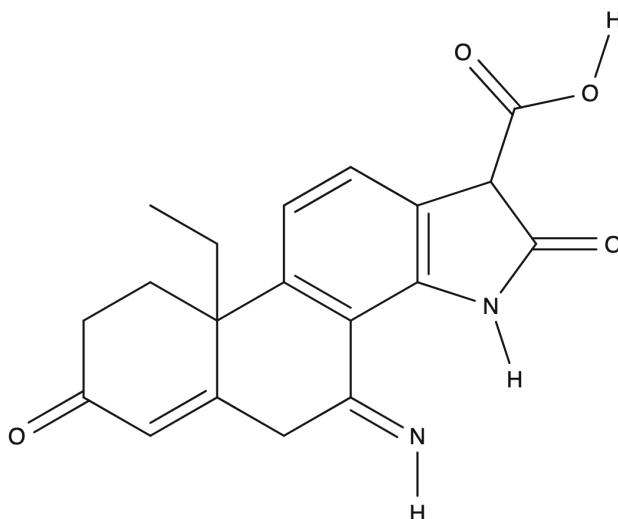
If you think the reagent assigned the number of x above converts the reactant to product assigned the number of y below, then input your answer as concatenated number \overline{xy} . **If you think none of the below products are correct, input as concatenated number $\overline{x0}$.**

Hence, for example, if you think reagent no. 1 converts the reactant to product no. 1 below, reagent no. 2 converts the reactant to **none** of the products below, and reagent no. 3 converts the reactant to product no. 5 below, then input in the answers with no spaces as such: **105**
Continue to do this for every reactant listed; you should have 8 digits in your part (a) answer.

<p>1.</p> 	<p>2.</p> 	<p>3.</p> 
<p>4.</p> 	<p>5.</p> 	<p>6.</p> 

Note: Part (b) is not linked to part (a).

(b) The following molecule below is subject to a whole list of **reductants** below.



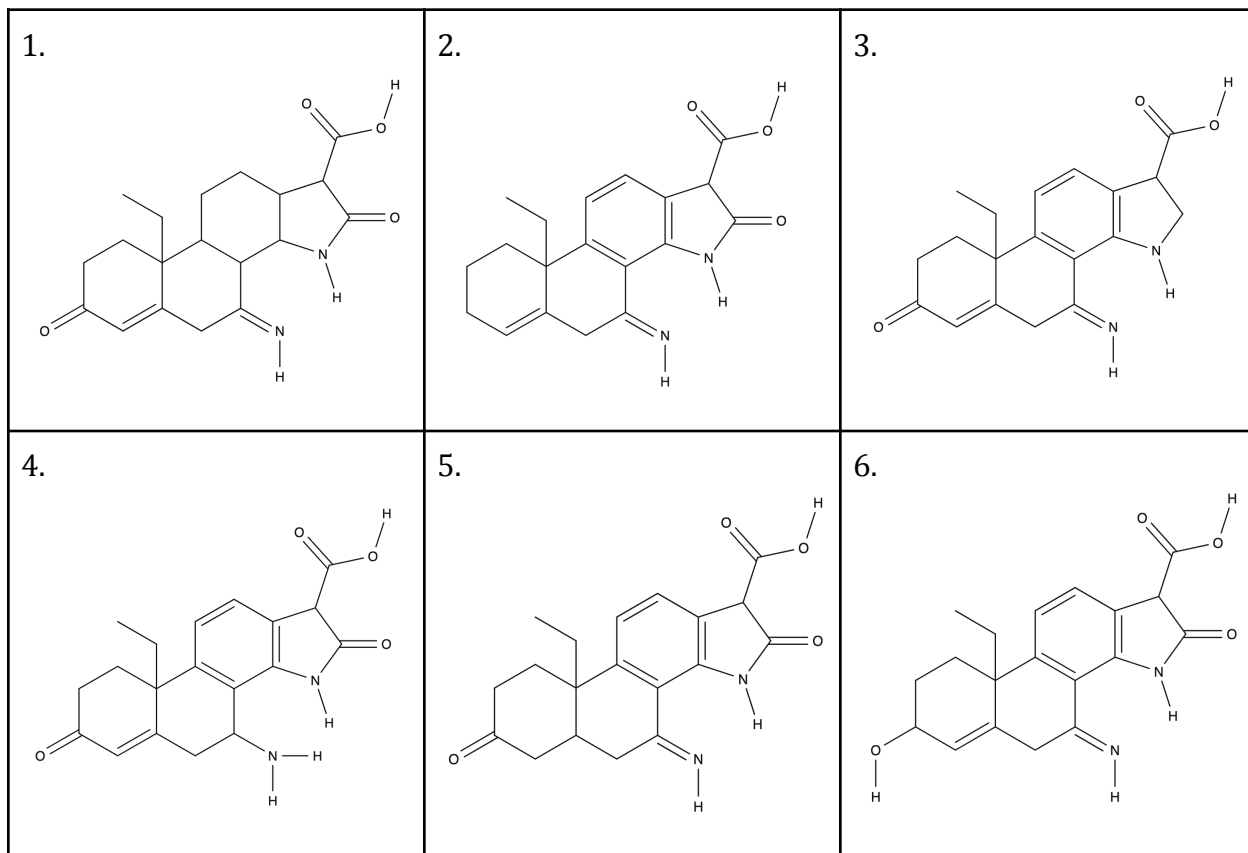
1. H₂, Lindlar Catalyst
2. LiBH₄
3. Na[(CN)BH₃]
4. BH₃
5. L-Selectride
6. NaBH₄, CeCl₃
7. DIBAH

Assign the end product after oxidation to each oxidizing reagent, by selecting a suitable number corresponding to a possible product found in the list below. **The same numbers can be used [3 points]**

*If you think the reagent assigned the number of x above converts the reactant to product assigned the number of y below, then input your answer as concatenated number \overline{xy} . **If you think none of the below products are correct, input as concatenated number $\overline{x0}$.***

*Hence, for example, if you think reagent no. 1 converts the reactant to product no. 1 below, reagent no. 2 converts the reactant to **none** of the products below, and reagent no. 3 converts the reactant to product no. 5 below, then input in the answers with no spaces as such: **105***

Continue to do this for every reactant listed; you should have 7 digits in your part (b) answer.



*Solution:***(a) 32234303**

For oxidants,

1. $\text{Na}_2\text{Cr}_2\text{O}_7$ oxidises secondary alcohols to ketones. Answer: 3
2. Tollen's Reagent oxidises aldehydes to carboxylic acids. Answer: 2
3. Fehling's Reagent oxidises aliphatic aldehydes to carboxylic acids. Answer: 2
4. MnO_2 oxidises allylic alcohols to the corresponding aldehydes or ketones. Answer: 3
5. CrO_3 is used in the Jones oxidation, oxidising primary alcohols to carboxylic acids and secondary alcohols into ketones. Answer: 4
6. PCC is more chemoselective than CrO_3 , oxidising primary alcohols to aldehydes preferentially instead of carboxylic acids. PCC oxidises secondary alcohols to ketones. Answer: 3
7. mCPBA (used in the Baeyer-Villiger oxidation) 'adds' an oxygen atom next to a carbonyl functional group. Aldehydes and ketones become esters. If there is a **lone** aliphatic alkene group, it is oxidised into an epoxy group. Answer: 0
8. IBX changes alcohols to aldehydes via the hypervalent twisting mechanism. Answer: 3

(b) 0040660

For reductants,

1. H_2 with Lindlar Catalyst (poisoned catalyst) only reduces alkynes to alkenes. Thus, nothing will happen to the product. Answer: 0
2. LiBH_4 is commonly used for the selective reduction of esters and lactones to the corresponding alcohols in the presence of carboxylic acids, tertiary amides, and nitriles. Thus, nothing will happen to the product. Answer: 0
3. $\text{Na}[\text{BH}_3(\text{CN})]$ converts imines to amines. Answer: 4
4. BH_3 reduces carboxylic acids selectively in the presence of esters. None of the products shown are correct. Answer: 0
5. L-selectride reduces ketones. Answer: 6
6. NaBH_4 and CeCl_3 (used in Luche reduction) selectively reduces 1,2-unsaturated ketones to allylic alcohols. Answer: 6
7. DIBAH, or DIBAL converts carboxylic acids and derivatives, and nitriles to aldehydes. None of the products shown are correct. Answer: 0

Problem 34: The Five Orange Pips**[5 points]**

“How often have I said to you that when you have eliminated the impossible, whatever remains, however improbable, must be the truth?”

~Sherlock Holmes, “The Sign of Four”

Sherlock Holmes has been invited to a conference of eminent chemists who have come to share their ideas. To his horror, while everyone was working on their demonstrations, all his cigars which he left in his luggage disappeared! Since he knows that cigars do not disappear on their own, and neither he nor Watson used the cigars, someone else must have stolen them. He rounds up all the chemists who were near the scene of the crime and questions them one by one. The following is Watson’s notes from the questioning.

Sherlock: “Catherine, where were you when the cigars were taken?”

Catherine: “I was heating a solid. 1g of solid produced 0.285 dm³ of a gas at r.t.p. and left 0.478g of residue. This solid, interestingly, is found in toothpaste.”

Sherlock: “And you, Peter?”

Peter: “I was running the electrolysis of a concentrated solution, containing a salt with relative formula mass 168.35. After running a 10A current for 30 minutes, I obtained two gases in a 1:1 ratio. At s.t.p., I obtained 0.188 g of one gas and 2.12 dm³ of the other. This process is very important industrially.”

Sherlock: “Interesting. Moving on, Emily?”

Emily: “Well, I was preparing a standard solution of a salt. I measured out 200 grams of the solid to add to 1 dm³ of water, but it appears I calculated wrongly and only have 0.857 molar concentration of it rather than the 1 molar I was aiming for. Out of the 200 grams, about 118 grams of it was the heaviest element in the salt. This salt is used in various pigments and paints.”

Sherlock: “I see. David? Where were you and what were you doing?”

David: “I investigated the reaction of an ubiquitous element with water. Adding 1g of the element at r.t.p. produced a gas that had volume 0.5232 dm³. This element has uses as a desiccant.”

Sherlock: "Hmm... that's unusual. Jonathan?"

Jonathan: "I was carrying out an organic reaction. I added aqueous bromine to 1g of a compound in the dark, and got 3.3031g of a product. During this reaction, 0.02377 mol of bromide ion was released. The reactant is sometimes used to weld metals."

Sherlock: "I see. Lastly, Norman?"

Norman: "I synthesised a gas and stored it in an ampoule. At s.t.p., the gas had a density of 1218 g m⁻³. This gas can be combined with other reagents to oxidise alkenes."

Sherlock: "Hmm. All very interesting alibis. However, one of you must be lying. You see, I was sitting in the room opposite the lab. Whenever I saw a shadow enter the lab, I removed an orange pip from the orange I was eating and placed it in this ash-tray. But look! There are only five orange pips. One of you six did not enter the lab to work, but went to my quarters to take my cigars. One of you must be lying, and it is none other than –"

Unfortunately, it seems that Watson has lost the rest of his notepad where he wrote down how Sherlock identified the thief. Can you help Watson identify the thief? Only the thief is lying, and the thief's lie is chemically impossible. (You may assume all reactions have 100% yield).

*Key in your answer in terms of the first initial of your accused thief. In other words, if you think the thief is Catherine, key in **C**; if the thief is Peter, key in **P**; if the thief is Emily, key in **E**; if the thief is David, key in **D**; if the thief is Jonathan, key in **J**; if the thief is Norman, key in **N**.*

EXTRA: Just for fun, try and identify who the suspects are! (This is not worth any points).

Solution:

E

It appears that Watson did not lose the pages, but they were kept secretly by Holmes to test Watson's (and the reader's) deductive skills. They are enclosed below.

Sherlock: "Emily."

Emily: "What? How dare you accuse me of such impunity, I- I-"

Sherlock: "Stop lying! I will work through everyone's alibis one by one and show why it can only be you. See, Catherine's experiment involved 0.0119 mol of gas and 0.522g of it: its molar mass is 44.0, so it is CO₂. We can obtain a molar mass of 84.2 for the solid and 40.3 for the residue. This nicely leads to MgCO₃ and MgO, which make sense."

Catherine: "That's exactly what I was doing. Magnesium carbonate is used as an abrasive in toothpaste, after all."

Sherlock: "Now, Peter. We can calculate the amount of electrons passed: 0.18656 mol. The amount of gas formed was 0.09335 mol, which is logical: a 2 is to 1 ratio. The molar mass of one of the gases is 2.014, so it must be H₂ gas. This means we are electrolysing a salt of a reactive metal. Indeed, the salt's mass corresponds to caesium chloride which would produce hydrogen and chlorine gases in exactly the ratios we need."

Peter: "Yes, I was demonstrating the industrial processes by which caesium hydroxide is made."

Sherlock: "As for you, David, I sure hope you followed basic safety protocol. Your reaction produced 0.0217 mol of gas, and if we try a 2:1 ratio of the element and the gas, we get its molar mass to be 22.99 – you were playing with sodium."

David: "Yes, and fret not, I had a fire extinguisher on hand. Sodium is indeed a dessicant."

Sherlock: "What about Jonathan? Well if we assume 1 bromide is released in the reaction, the compound has molar mass 42.070 g mol⁻¹ (close to propene) and the product has molar mass 138.96 g mol⁻¹. The increase in molar mass is 96.891, which is close to that of 1 Br, 1 O and 1H. Indeed, brominating propene in aqueous medium gives us C₃H₇BrO."

Jonathan: "Exactly right! You amaze me. And yes, propene is used to weld metals – the process is called oxy-fuel welding."

Sherlock: "Our last innocent suspect, Norman. Quite a simple deduction, really: what would have a molecular mass of 27.66 besides diborane, which is combined with hydrogen peroxide to hydroxylate alkenes!"

Norman: "Yes, that is correct! So that means..."

Sherlock: "And now, Emily. Your lies may have fooled a lesser mind – like Watson's, but not mine. Indeed, at first glance your alibi holds up: the molar mass of your salt is 233.37, and the heaviest element has mass of 137.68. Yes, it all seems to match up very well with barium sulfate, BaSO_4 , used in pigments and paints... how clever of you... except you forgot one minor detail."

Watson: "And what was that?"

Sherlock: "Barium sulfate is insoluble in water, so you could never have gotten such a high concentration of it, be it 1 molar or 0.857 molar."

Emily: "Yes, yes, I did it... I didn't pack any cigars for the conference. I'm really sorry, I shouldn't have done it, here they are, I haven't used any of them..."

Emily was dealt with by the relevant authorities. Sherlock got his cigars back, and everyone enjoyed an evening of interesting chemistry. Everyone involved left satisfied. Did you manage to guess the culprit?

Also, in Watson's archives, a page of the guestbook at the conference was found. It reads as follows:

Sherlock Holmes

John Watson

Catherine Housecroft

Peter Atkins

Emily (unknown surname)

David Klein

Jonathan Clayden

Norman Greenwood

Problem 35: Timmy And His Tungsten Toys**[6 points]**

Timmy's father is a chemist. After learning about electrolysis in chemistry class, Timmy decides to apply a thin layer of silver onto his father's prized tungsten cube, which is a perfect cube of side length 8.00 cm. He assembles an electrolysis setup with a silver fork as the anode and AgNO_3 (aq) as the electrolyte. He runs a current of 0.28 A in the circuit. 2 hours after Timmy starts his experiment, his father comes home and makes him dismantle the setup.

The entire cube is now uniformly coated with silver. The silver was deposited such that *the shortest distance between the top of the silver layer and the tungsten body was exactly the same for each face, edge and vertex*, so that the resulting cube has perfectly round edges and vertices.

- (a) Calculate the thickness of silver deposited onto the cube in micrometres. The density of silver is 10.49 g/cm^3 .

Leave your answer to 3 significant figures. [2 points]

Timmy's father gives him a brutal scolding and locks his cube and silver away. The next day, Timmy finds a perfect cylinder of tungsten of radius 3.00 cm and height 7.00 cm, and decides to repeat his experiment. This time, he uses a copper wire as the anode and CuSO_4 (aq) as the electrolyte. He runs a current of 0.62 A for 10 hours, and the tungsten cylinder is uniformly coated with copper in the same manner as before, with perfectly round edges.

- (b) Calculate the thickness of copper deposited onto the cylinder in micrometres. The density of copper is 8.96 g/cm^3 .

Leave your answer to 3 significant figures. [4 points]

Solution:

(a) 5.60 μm

The silver deposits itself as a:

- cuboid on each face of the cube,
- $\frac{1}{4}$ of a cylinder on each edge of the cube (since the faces meet at 90°),
- $\frac{1}{8}$ of a sphere on each vertex.

Let the thickness of the silver be d cm. Since there are 6 faces, 12 edges and 8 vertices,

$$\begin{aligned} V_{total} &= V_{faces} + V_{edges} + V_{vertices} \\ &= 6(8 \times 8 \times d) + 12\left(\frac{1}{4}\right)(\pi \times d^2 \times 8) + 8\left(\frac{1}{8}\right)\left(\frac{4}{3} \times \pi \times d^3\right) \\ &= \frac{4}{3}\pi d^3 + 24\pi d^2 + 384d \end{aligned}$$

And since $n = \frac{It}{F}$,

$$V_{total} = \frac{ItA_r}{F\rho} = \frac{0.28 \times 2 \times 3600 \times 107.9}{96485 \times 10.49} = 0.21492 \text{ cm}^3$$

Where ρ is the density and A_r is the relative atomic mass of silver.

By substituting the appropriate values, we obtain a cubic equation in d , which we solve to obtain the answer.

(b) 43.5 μm

The copper deposits itself as a:

- Hollow cylindrical shell on the curved vertical side
- Cylinder on each of the circular ends
- Outer 'half' of a torus on the 2 circular edges when combined (Imagine if you lay a torus flat, draw a line along its highest point, then cut vertically along that line. Take the outer part and divide it horizontally into 2. This "quarter" of a torus is how the copper deposits itself along the cylinder's circular edge. Every point on its curved surface is equidistant from the edge).

Let the thickness of copper be d cm.

$$\begin{aligned} V_{total} &= V_{curved} + V_{ends} + V_{edges} \\ &= [\pi(3+d)^2 \times 7 - \pi(3)^2 \times 7] + 2(\pi \times 3^2 \times d) + V_{edges} \\ &= 60\pi d - 7\pi d^2 + V_{edges} \end{aligned}$$

For V_{edges} , consider a circle $(x - 3)^2 + y^2 = d^2$. We take the semicircle bounded by $3 \leq x \leq 3 + d$ and rotate that 2π rad around the y -axis. By the washer method, the volume of revolution of this semicircle is:

$$\begin{aligned} V_{edges} &= \pi \int_{-d}^d \left(3 + \sqrt{d^2 - y^2} \right)^2 - 3^2 dy \\ &= \pi \int_{-d}^d 6\sqrt{d^2 - y^2} + d^2 - y^2 dy \\ &= \pi \int_{-d}^d d^2 - y^2 dy + 6\pi \int_{-d}^d \sqrt{d^2 - y^2} dy \\ &= \pi \left[d^2 y - \frac{1}{3} y^3 \right]_{-d}^d + 3\pi^2 d^2 \text{ (By substituting } y = d \sin \theta) \\ &= \frac{4}{3} \pi d^3 + 3\pi^2 d^2 \end{aligned}$$

Hence,

$$\begin{aligned} V_{total} &= \frac{4}{3} \pi d^3 + (3\pi^2 - 7\pi) d^2 + 60\pi d \\ &= \frac{1}{2} \times \frac{ItA_r}{F\rho} = \frac{0.62 \times 10 \times 3600 \times 63.55}{2 \times 96485 \times 8.96} = 0.82037 \text{ cm}^3 \end{aligned}$$

Note that one mole of electrons only reduces half a mole of $\text{Cu}^{2+}(\text{aq})$ to $\text{Cu}(\text{s})$.

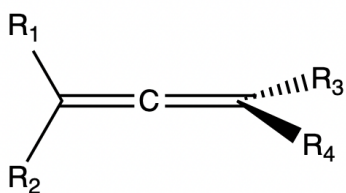
Substituting and solving the cubic in d yields the final answer.

Problem 36: What does DOPA do?**[8 points]**

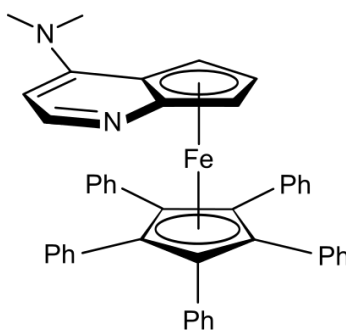
Take a moment to think about that. Maybe you haven't heard of the drug before, and searched it on Google. Or maybe you already knew that DOPA is a precursor to dopamine, and is used in the treatment of Parkinson's disease.

Well, not quite. *L-DOPA*, specifically, is used to treat Parkinson's disease, while its mirror image *D-DOPA* is biologically inactive at best and toxic at worst. This is the essence of why chirality matters to us; nature is inherently chiral, and to dissect its manifold mysteries we must inevitably confront ourselves with this topic.

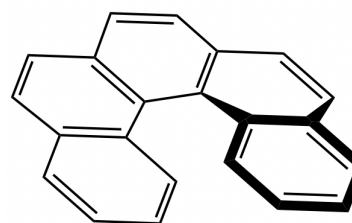
Chirality arising from chiral carbons belong to a specific subset of chirality called **point chirality**. Other chiral molecules with no chiral centres such as allene **1** exhibit **axial chirality**, where substituents are twisted into a non-planar conformation around an axis, resulting in the lack of a plane of symmetry. Further consider molecules displaying **planar chirality** such as ferrocene derivative **2**, where a chiral molecule is composed of two or more planar portions. Finally, some molecules derive their chirality from a curvature or deformation in 3D space, such as helicene **3**. There are myriad ways that symmetry can be broken, and chirality generated.



1



2

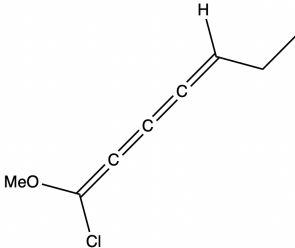
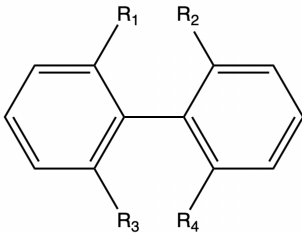
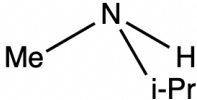
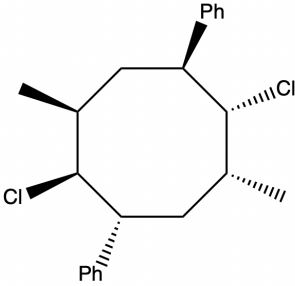
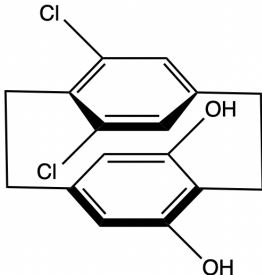
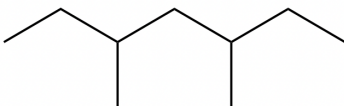

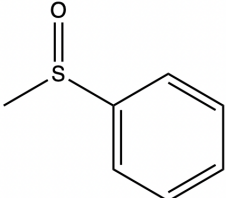
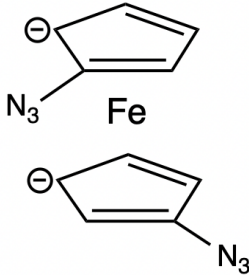
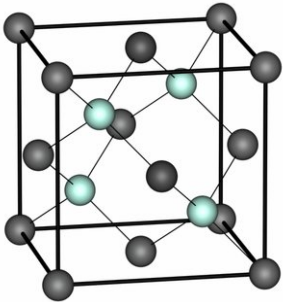


3

- (a) A series of chemical molecules and structures are shown below. Assign each of them a score based on Table 1. What is the total sum of the scores of all the molecules? **[3 points]**

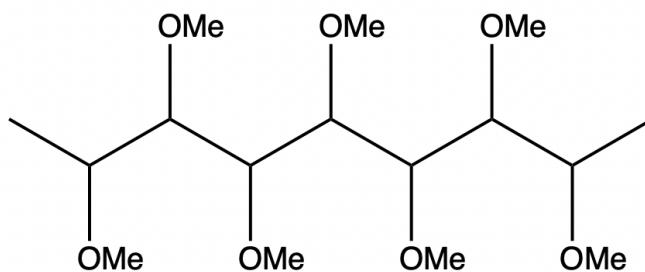
Classification	Score
Definitely achiral	0
May or may not be chiral	1
Definitely chiral	2

Table 1

<p>$W(bipy)_3$</p>		 <p>R = H, alkyl, aryl</p>
<p>  (At low temperatures) </p>		
		
<p>  N_3 Fe N_3 </p>	<p>DNA double helix</p>	

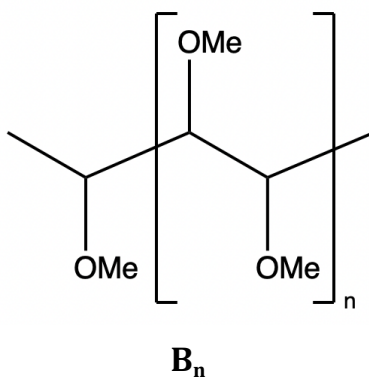
Chirality becomes a rapidly more complicated concept when multiple stereocenters are present, and additional considerations have to be made.

- (b) Deduce the number of **chiral** stereoisomers that the following molecule has.
[3 points]



- (c) Imagine that the molecule above is extended as follows below, to an arbitrary integer n . Let the molecule thus formed be called \mathbf{B}_n , where n is the number of repeating $-\text{CH}(\text{OMe})\text{CH}(\text{OMe})-$ units, as illustrated below. Let x_n be the number of **chiral** stereoisomers \mathbf{B}_n has.

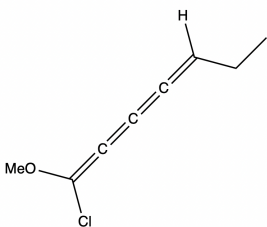
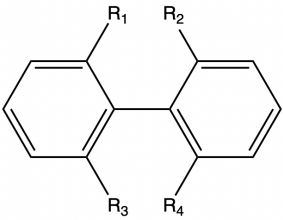
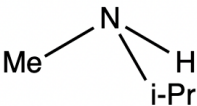
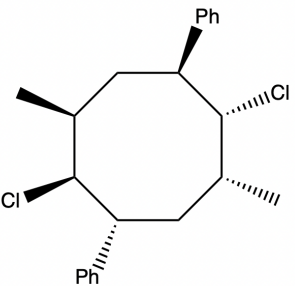
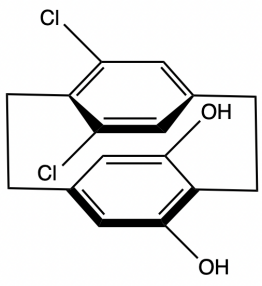
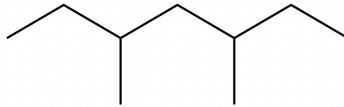
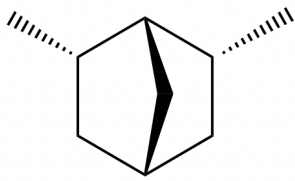
Find $\frac{x_{2023}}{x_{2022}}$. Give your answer to 0 decimal places. **[2 points]**

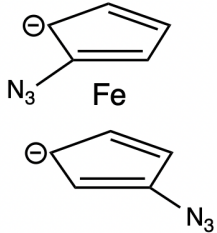
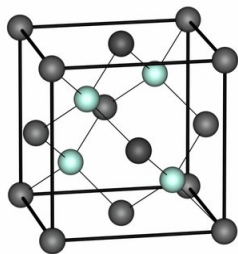


Solution:

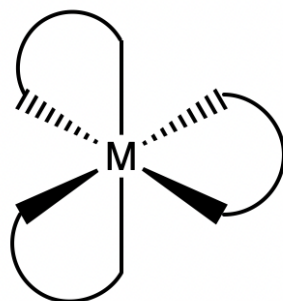
(a) 12

The scores of each compound are shown below, along with labels for convenience of reference in the explanation:

	A	B	C
1	W(bipy) ₃		 R = H, alkyl, aryl
	2	2	1
2	 (at low temperatures)		
	2	0	0
3			MeSOPh
	1	0	2

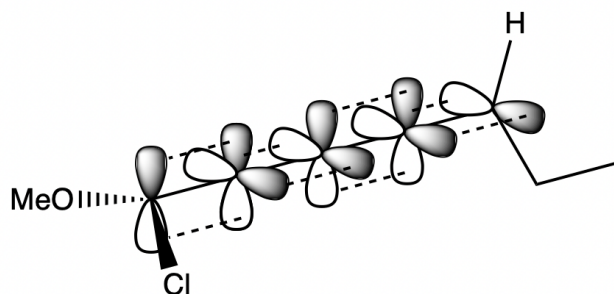
4		DNA double helix	
	0		

A1: Chiral. This is a recurring theme in transition metal complexes, where three bidentate ligands bond to a transition metal in a generalised scheme shown below. M stands for an arbitrary transition metal, while the three curved lines represent arbitrary bidentate ligands:

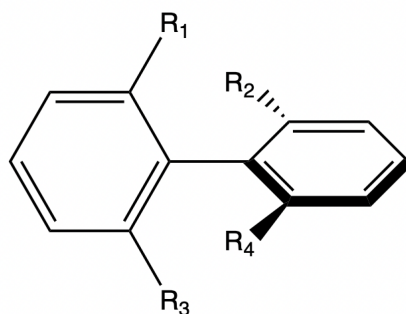


A prototypical example would be $\text{Co}(\text{en})_3$. A Google search will show you various ways to visualise this chirality, or if you happen to have a ball-and-stick modelling set, try to put the compound together. It is not possible to find a plane of symmetry in the molecule.

B1: Chiral. This is an extension of the axial chirality displayed by allenes. By visualising the orientation of the p orbitals, the non-planar geometry of the molecule becomes apparent:

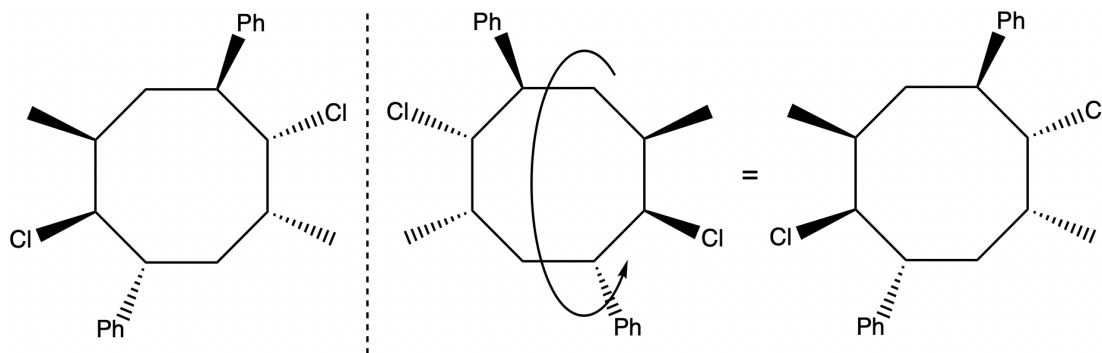


C1: May or may not be chiral. Such biaryl compounds have potential to exhibit axial chirality due to the perpendicular orientation of the aryl rings relative to each other, as visualised below. Whether they are chiral then depends on whether the groups on an aryl ring are identical or different.



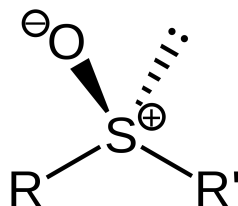
A2: Chiral. The nitrogen has four different groups oriented around it in a tetrahedral confirmation (don't forget the lone pair!), not dissimilar to a chiral carbon in this respect. At low temperatures, racemization does not occur, and we can consider it to be chiral.

B2: Chiral. This molecule possesses a *centre of inversion*, where every atom located at a certain distance and direction from the centre is the same as the atom located at the same distance but opposite direction. Despite not possessing a plane of symmetry, the mirror image of this molecule is superimposable onto the original, as visualised:

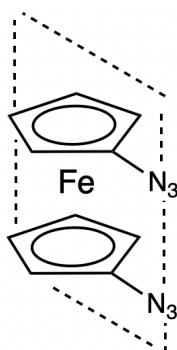


This is an example of when a lack of plane of symmetry does not lead to non-superimposable mirror images. The two concepts are not equivalent.

C2: Achiral. While the molecule may suggest some planar chirality of sorts, there is a plane of symmetry running perpendicular through both benzene rings, making it achiral.



A4: Achiral. This is a ferrocene azide explored for its potential applications in click chemistry (for which the 2022 Nobel Prize in Chemistry was awarded!). The lone pair is delocalised in the aromatic cyclopentadienyl, so the only symmetry-breaking element is the azide group. One can envision a prismatic orientation with the N_3 aligned with each other and the plane of symmetry shown below, or alternatively an antiprismatic orientation with N_3 groups aligned antiperiplanar.

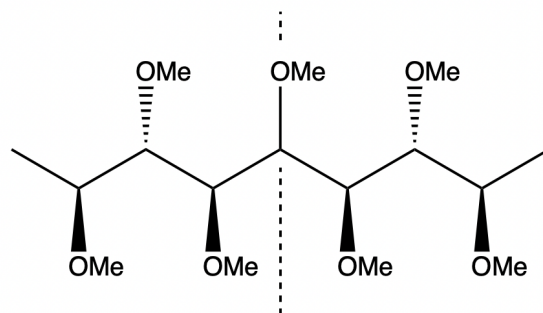


B4: Chiral. Given the chirality of nature at large, it shouldn't be surprising that the most fundamental part of life, our genome, is chiral. Specifically, DNA is *right-handed*, because when you form a thumbs up with your right hand, the individual strands twist upwards (along the vector of the thumb) in the direction shown by your fingers (which would be anticlockwise).

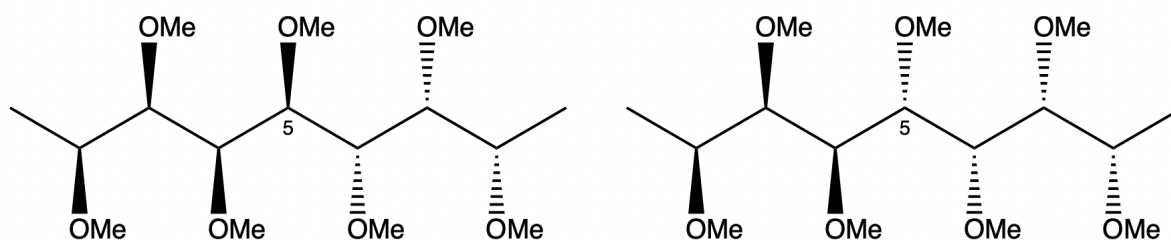
C4: Achiral. This is a particular unit cell representing a *diamond cubic structure*, which is actually just two face-centred cubic structures with one displaced by (0.25, 0.25, 0.25) of a unit cell relative to the other. There are many binary compounds that adopt this structure (especially of the group 14 elements), such as carbon-silicon alloys.

(b) 56

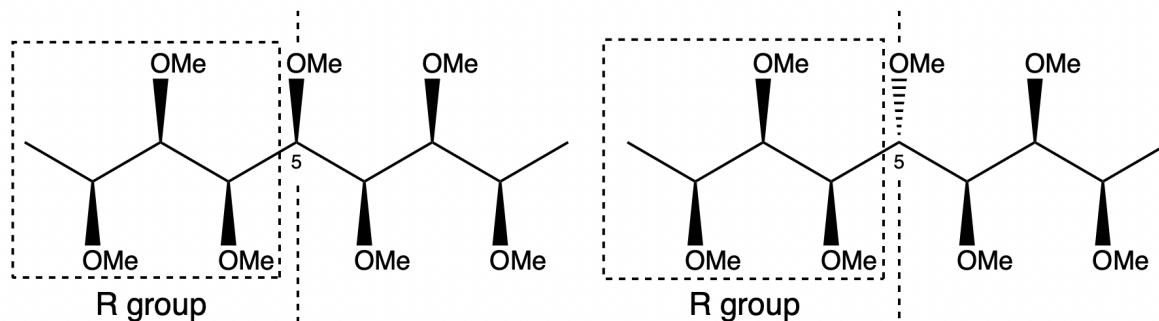
First, we must understand the question requirements. Chiral stereoisomers will exclude meso compounds, an example of which is shown below:



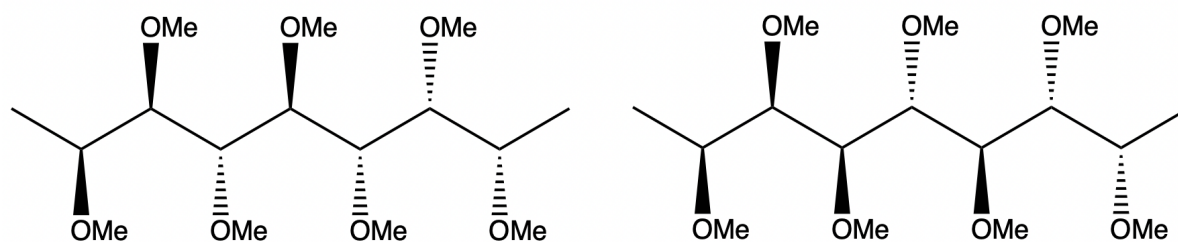
A starting point would be to ask ourselves how many chiral centres there are: The answer is 7, giving us a maximum of $2^7 = 128$ possible structures. In this explanation, I will make a distinction between structures and stereoisomers: A structure is a unique permutation of wedges and dashes that the $-OMe$ bonds can take up, taken as if the molecule has a fixed directionality as it is viewed. Thus, multiple structures could give the same stereoisomer, such as by rotating the molecule 180 degrees as shown below.



First, we consider the number of structures that are *meso compounds*. For the sake of classification, let us “tag” each structure by the portion of the molecule found to the left of the central C5 carbon, as enclosed in a dashed triangle below. We will call this the “R group”. As the C6-C9 portion of the molecule must be a mirror image of the R group chosen, Each unique R-group has only 2 structures that will give meso compounds, depending on whether the central C5 carbon is a wedge or dash. There are a total of $2^3 = 8$ R groups possible, i.e all possible permutations of 3 $-OMe$ groups. Thus, there are a total of $2^3 \times 2 = 16$ structures that are meso compounds.



We are left with $128 - 16 = 112$ structures that are not *meso*. Finally, we get down to determining the number of distinct stereoisomers that fall under this category. It turns out that each stereoisomer can be expressed by exactly two different structures, depending on which side we view the molecule from. An example is shown below. Essentially, the permutations of wedge/dashes are different, but the resultant molecule is the same.



Thus, there are $112 / 2 = 56$ chiral stereoisomers.

(c) 4

To solve this, it is necessary to obtain a rule for x_n in terms of n . This is, in fact, straightforward if you have completed part (b) successfully. Observe that B_n will have $2n+1$ chiral carbons. We obtain the maximum number of stereoisomers B_n can have: 2^{2n+1} .

In similar fashion as part (b), we find the number of *meso* structures first. Each R group of the central carbon in B_n will have n chiral centres, hence 2^n distinct R-groups are possible. It follows that there are $2 \times 2^n = 2^{n+1}$ of each type of structure, where we simply substitute the known constant in (b) with the algebraic expression in terms of n .

Thus, B_n has $2^{2n+1} - 2^{n+1}$ structures that are *not meso*, and $\frac{2^{2n+1} - 2^{n+1}}{2} = 2^{2n} - 2^n = 2^n(2^n - 1)$ stereoisomers. We may now write an algebraic expression for $\frac{x_{n+1}}{x_n}$:

$$\frac{x_{n+1}}{x_n} = \frac{2^{n+1}(2^{n+1}-1)}{2^n(2^n-1)} = \frac{2(2^{n+1}-1)}{2^n-1}$$

In the (likely) event that the calculator is unable to solve for $\frac{2(2^{2023}-1)}{2^{2022}-1}$, recognise that

$\lim_{n \rightarrow \infty} \frac{2(2^{n+1}-1)}{2^n-1} = 4$. As 2023 is a sufficiently large integer, $\frac{2(2^{2023}-1)}{2^{2022}-1} \simeq 2(2) = 4$. Thus the

answer is 4 (0 d.p.).

Problem 37: Error Functions**[6 points]**

When solving problems involving multiple equilibria, we often have to assume the concentration of certain species are negligible to simplify the question. However, if we are not careful with what species we omit, the results can be catastrophic, as we will investigate below using acid-base equilibria.

Let us consider solution N which is 0.0100M trisodium citrate (citric acid: $pK_{a1} = 3.13$, $pK_{a2} = 4.76$, $pK_{a3} = 6.39$).

(a) Find the pH of solution N.

Leave your answer to 2 decimal places. [3 points]

For the rest of this question, two functions are defined:

The *individual error* ($e(n)$) for omitting a species n is given by the difference between the true pH of the solution (to 2 d.p.) and the calculated pH of the solution assuming species n is negligible (to 2 d.p.).

The *error function* ($\text{erf}(X)$) for a certain solution X is given by the total *individual errors* for all species in the solution. Note that for an acidic equilibrium, we have to also consider the errors when omitting OH^- , while for a basic equilibrium, we have to consider the errors when omitting H^+ .

As an example, consider the equilibria involving a 0.0100M solution of oxalic acid ($pK_{a1} = 1.25$, $pK_{a2} = 4.14$). Let this solution be solution M and oxalic acid be given by H_2A .

True pH of the solution = 2.0587 = 2.06

Calculated pH when omitting $\text{H}_2\text{A} = 1.9969 = 2.00$

Hence, $e(\text{H}_2\text{A}) = 2.06 - 2.00 = 0.06$.

Carrying on similarly,

n	H_2A	HA^-	A^{2-}	OH^-
Calculated pH when omitting n	2.00	2.40	2.06	2.06
$e(n)$	0.06	0.34	0.00	0.00

Hence, $\text{erf}(M) = 0.06 + 0.34 + 0.00 + 0.00 = 0.40$.

(b) Calculate $\text{erf}(N)$. **[3 points]**

Solution:

(a) 9.19

Let citrate ion be B^{3-} (ie citric acid is H_3B).

$pK_{b1} = 7.61$, $pK_{b2} = 9.24$, $pK_{b3} = 10.87$

The following balance equations are relevant:

$$\text{MBE: } [B^{3-}]_0 = [H_3B] + [H_2B^-] + [HB^{2-}] + [B^{3-}] = 0.0100M$$

$$\begin{aligned} \text{CBE: } [H^+] + [Na^+] &= [H_2B^-] + 2[HB^{2-}] + 3[B^{3-}] + [OH^-] \\ [Na^+] &= 0.0300M \end{aligned}$$

From the MBE, we can derive expressions for the concentrations of each citrate-related species. I will demonstrate B^{3-} .

$$[H_3B] + [H_2B^-] + [HB^{2-}] + [B^{3-}] = 0.0100M$$

$$K_{b1} = \frac{[HB^{2-}][OH^-]}{[B^{3-}]} \Rightarrow [HB^{2-}] = \frac{K_{b1}[B^{3-}]}{[OH^-]}$$

Similar relationships allow us to rewrite the MBE:

$$\frac{K_{b1}K_{b2}K_{b3}[B^{3-}]}{[OH^-]^3} + \frac{K_{b1}K_{b2}[B^{3-}]}{[OH^-]^2} + \frac{K_{b1}[B^{3-}]}{[OH^-]} + [B^{3-}] = 0.0100M$$

$$[B^{3-}] = \frac{0.0100}{\frac{K_{b1}K_{b2}K_{b3}}{[OH^-]^3} + \frac{K_{b1}K_{b2}}{[OH^-]^2} + \frac{K_{b1}}{[OH^-]} + 1}$$

$$[B^{3-}] = \frac{0.0100[OH^-]^3}{K_{b1}K_{b2}K_{b3} + K_{b1}K_{b2}[OH^-] + K_{b1}[OH^-]^2 + [OH^-]^3}$$

Similarly, we can derive:

$$[HB^{2-}] = \frac{0.0100K_{b1}[OH^-]^2}{K_{b1}K_{b2}K_{b3} + K_{b1}K_{b2}[OH^-] + K_{b1}[OH^-]^2 + [OH^-]^3}$$

$$[H_2B^-] = \frac{0.0100K_{b1}K_{b2}[OH^-]}{K_{b1}K_{b2}K_{b3} + K_{b1}K_{b2}[OH^-] + K_{b1}[OH^-]^2 + [OH^-]^3}$$

$$[H_3B] = \frac{0.0100K_{b1}K_{b2}K_{b3}}{K_{b1}K_{b2}K_{b3} + K_{b1}K_{b2}[OH^-] + K_{b1}[OH^-]^2 + [OH^-]^3}$$

A quick substitution into the CBE gives us:

$$\frac{K_w}{[OH^-]} + 0.0300 = \frac{0.0100(K_{b1}K_{b2}[OH^-] + 2K_{b1}[OH^-]^2 + 3[OH^-]^3)}{K_{b1}K_{b2}K_{b3} + K_{b1}K_{b2}[OH^-] + K_{b1}[OH^-]^2 + [OH^-]^3} + [OH^-]$$

You can directly solve this for $[OH^-]$ using software like Desmos or a graphing calculator. This gives us the true pH of solution = 9.1947 = 9.19 (2 d.p.)

(b) 4.18

From the derivation in (a), it should be clear that any $K_{b1}K_{b2}K_{b3}$ term corresponds to H_3B , $K_{b1}K_{b2}[OH^-]$ corresponds to H_2B^- , $K_{b1}[OH^-]^2$ corresponds to HB^{2-} and $[OH^-]^3$ corresponds to B^{3-} . $\frac{K_w}{[OH^-]}$ terms correspond to H^+ . If we want to omit the species, we just need to remove all corresponding terms from the above equation and re-solve.

As an example, removing B^{3-} results in the following equation:

$$\frac{K_w}{[OH^-]} + 0.0300 = \frac{0.0100(K_{b1}K_{b2}[OH^-] + 2K_{b1}[OH^-]^2)}{K_{b1}K_{b2}K_{b3} + K_{b1}K_{b2}[OH^-] + K_{b1}[OH^-]^2} + [OH^-]$$

Solving this gives us pH = 12.00, so $e(B^{3-}) = 12.00 - 9.19 = 2.81$

Proceeding similarly gives us $e(n)$ for all the species.

n	H_3B	H_2B^-	HB^{2-}	B^{3-}	H^+
pH	9.19	9.19	7.82	12.00	9.19
$e(n)$	0.00	0.00	1.37	2.81	0.00

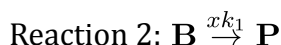
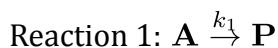
Hence, $\text{erf}(N) = 0.00 + 0.00 + 1.37 + 2.81 + 0.00 = 4.18$

We can clearly see that some terms are much more significant than others, and this speaks to the importance of judicious assumptions in solving equilibria, in this case whittling a quintic down to a quadratic.

Problem 38: To infinity and beyond!**[5 points]**

Two meteorites have crash landed, and scientists are examining the compounds within these meteorites, which, interestingly, exhibit interesting kinetics of decomposition.

The first meteorite contains compounds **A** and **B**, which both undergo the following reactions to become product **P**. The initial concentration of **A** and **B** respectively is x .

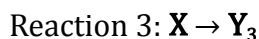
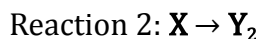
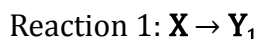


It is given that reaction 1 is a n^{th} order reaction, while reaction 2 is a $(n-1)^{\text{th}}$ order reaction, where $n \geq 1$. The first half-life of reaction 1 is 1.802 times that of reaction 2, regardless of the value of x .

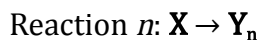
(a) What is the value of n ? **[3 points]**

Leave your answer to the nearest whole number.

The second meteorite contains a special compound **X**, which decomposes in the following interesting manner. It produces an infinite number of products, **Y₁**, **Y₂**, **Y₃**, and so on at the same time. All reactions have the rate constant k . This is what is commonly known as a *parallel reaction*.



...



...

In this very special decomposition, reaction 1 is a zeroth-order reaction, reaction 2 is a first-order reaction, reaction 3 is a second-order reaction, and so on. Reaction n will thus be a $(n-1)^{\text{th}}$ order reaction. Let the initial concentration of **X** be x , where $0 < x < 1 \text{ mol dm}^{-3}$.

(b) Given that the half life can be written in the form $t_{1/2} = \frac{1}{k} \left(\frac{x}{a} - \frac{bx^2}{c} \right)$, where **b** and **c** are coprime (have no common factors other than 1), find the value of the concatenated number \overline{abc} . **[2 points]**

Leave your answer as a whole number.

Solution:

(a) 11

Firstly, let us consider the cases of $n = 1$ and $n = 2$.

For a zeroth-, first- and second-order reaction, we know that the half-lives respectively are $a/(2k)$, $(\ln 2)/k$ and $1/(ka)$ respectively, where a is the initial concentration of **A**. By dividing the half-lives pairwise, it is clear that none of these are the solutions. That is,

$$\frac{\frac{\ln 2}{xk_1}}{\frac{x}{2k_1}} = \frac{2 \ln 2}{x^2} \quad \text{for } n = 1, \quad \text{and} \quad \frac{\frac{1}{xk_1}}{\frac{\ln 2}{xk_1}} = \frac{1}{x \ln 2}, \quad \text{which are not constants with changing } x \text{ values.}$$

Now, consider how we can derive the half-life for a generic n^{th} order reaction, where $n > 2$. For an n^{th} order reaction, rate = $k[\mathbf{A}]^n$, where **A** is the starting product. In this derivation, denote a as the initial concentration of **A**.

We then formulate the following differential equations that can be solved by separation:

$$\begin{aligned} \frac{d[\mathbf{A}]}{dt} &= -k[\mathbf{A}]^n \Rightarrow \int_a^{[\mathbf{A}]} [\mathbf{A}]^{-n} d[\mathbf{A}] = - \int_0^t k dt \\ &-\frac{1}{n+1}([\mathbf{A}]^{1-n} - a^{1-n}) = -kt \end{aligned}$$

Now, if $[\mathbf{A}] = a/2$, then t is the half-life of the reaction.

$$t_{1/2} = \frac{1}{k(n-1)} \left(\left(\frac{1}{2}a\right)^{1-n} - a^{1-n} \right)$$

$$t_{1/2} = \frac{a^{1-n}}{k(n-1)} \left(\frac{1}{2^{1-n}} - 1 \right) \Rightarrow \boxed{t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)a^{n-1}}}$$

Of course, the boxed equation can easily be found online, or can be derived quickly.

Now, let us consider the ratio of the half-life of reaction 1, say t_1 and that of reaction 2, say t_2 . We can formulate the relationship as follows by direct substitution into the relationship above:

$$\frac{t_1}{t_2} = \frac{\frac{2^{n-1}-1}{k_1(n-1)x^{n-1}}}{\frac{2^{n-2}-1}{xk_1(n-2)x^{n-2}}}$$

We can rewrite it as a non-nested fraction, yielding:

$$\frac{t_1}{t_2} = \frac{(2^{n-1}-1)(xk_1(n-2)x^{n-2})}{(2^{n-2}-1)(k_1(n-1)x^{n-1})}$$

A lot of the unknown terms, including x and k_1 , cancel out nicely, leaving us with the following equation in terms of n only:

$$\frac{t_1}{t_2} = \frac{(2^{n-1}-1)(n-2)}{(2^{n-2}-1)(n-1)} = 1.802$$

Quickly plugging this into a graphing calculator (like Desmos, Wolfram Alpha) will yield the solution $n = 11.013$. To the nearest integer, this yields the answer **$n = 11$** .

(b) 238

For a parallel reaction, we can write the rate of disappearance of **X** as follows:

$$\frac{d[\mathbf{X}]}{dt} = -(k + k[\mathbf{X}] + k[\mathbf{X}]^2 + k[\mathbf{X}]^3 + \dots)$$

We note that the right side looks like an infinite geometric series. Since x is between 0 and 1, this infinite geometric series converges.

We can therefore rewrite the differential equation as follows:

$$\frac{d[\mathbf{X}]}{dt} = -\frac{k}{1-[\mathbf{X}]} = \frac{k}{[\mathbf{X}]-1}$$

This differential equation is easy to solve by separation:

$$\int_x^{[\mathbf{X}]} ([\mathbf{X}] - 1)d[\mathbf{X}] = \int_0^t k dt$$

$$\frac{[\mathbf{X}]^2}{2} - [\mathbf{X}] - \frac{x^2}{2} + x = kt$$

Noting that the half-life is when $[\mathbf{X}] = x/2$, we can determine that the half-life can be expressed as follows:

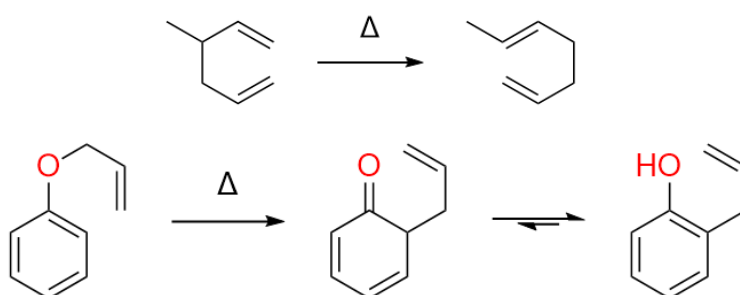
$$\frac{\left(\frac{x}{2}\right)^2}{2} - \frac{x}{2} - \frac{x^2}{2} + x = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k} \left(\frac{x}{2} - \frac{3x^2}{8} \right)$$

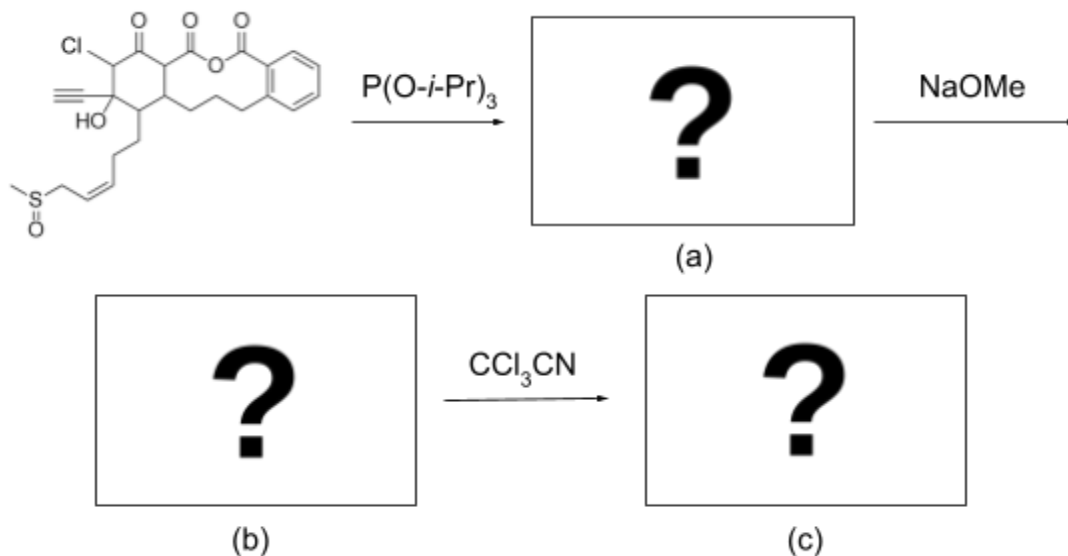
It is therefore easy to see that **a** = 2, **b** = 3 and **c** = 8. Hence, $\overline{abc} = 238$, which is the solution.

Problem 39: Where Did It Go?**[8 points]**

At a pre-tertiary level, organic chemical reactions taught generally involve the direct reaction of the functional group and the reagent, without affecting the rest of the carbon skeleton. Rearrangement reactions are a diverse class of organic chemical reactions that involve the restructuring of the carbon skeleton to form the structural isomer of the original molecule. Most of the time, a substituent moves from one atom to another atom on the same molecule, and rearrangement reactions are usually intramolecular. Examples of rearrangement reactions include the Cope rearrangement and Claisen rearrangement (shown below).



The strange-looking reactant below undergoes 3 distinct rearrangement reactions according to the scheme below to eventually yield an even stranger-looking product.⁹



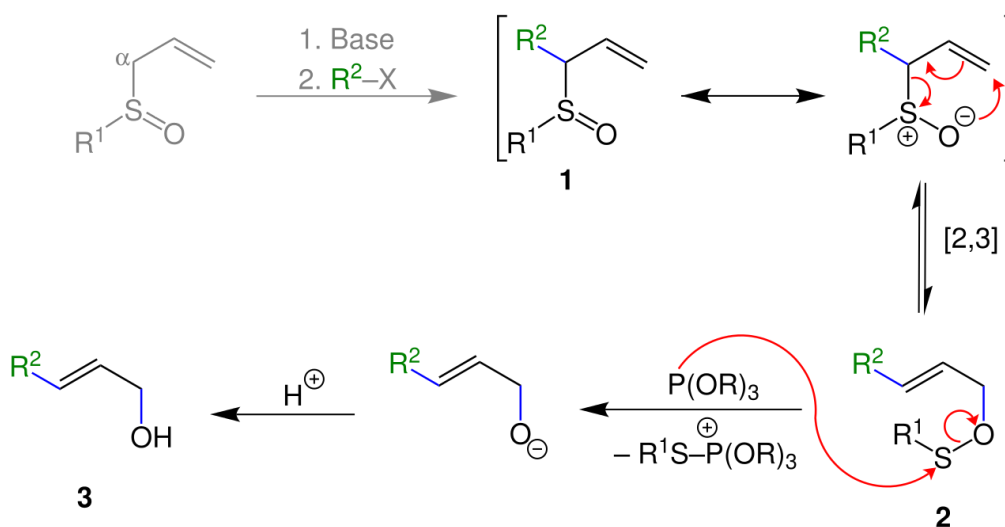
Deduce the structural intermediates (a) **[2 points]**, (b) **[3 points]**, as well as the final product (c) **[3 points]**.

⁹ Erratum: The correct structure of the molecule has since been updated. We extend our thanks to the groups that informed us of the error.

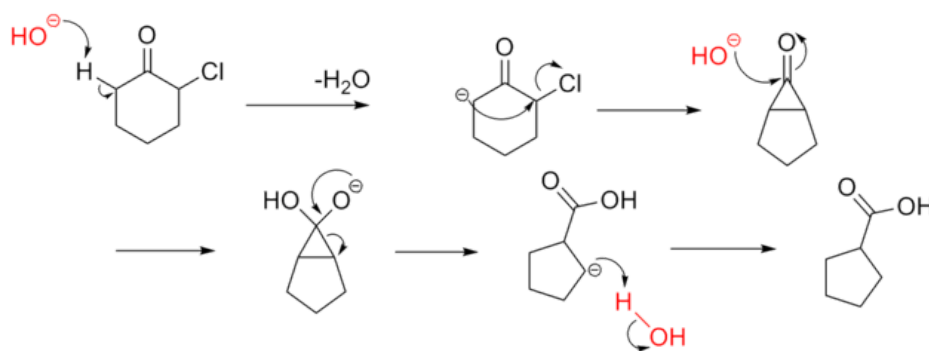
Each reagent corresponds to a well-established named rearrangement reaction, and the sequence is below:

- (a) Evans-Mislow Rearrangement
- (b) Favorskii Rearrangement
- (c) Overman Rearrangement

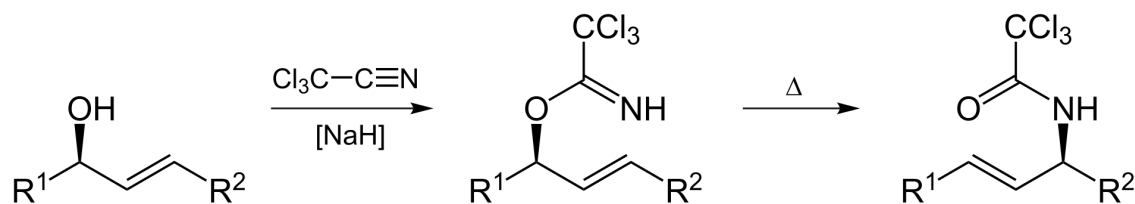
Mechanism of Evans-Mislow Rearrangement



Favorskii Rearrangement



Overman Rearrangement



Problem 40: Mendeleev's Mistake

[6 points]

In constructing the periodic table, Mendeleev astutely left several gaps for elements which he believed fit in the table but had not yet been discovered. For example, he predicted the properties of scandium, gallium and germanium (which he then called *eka-boron*, *eka-aluminium* and *eka-silicon*) to significant success. However, it may be lesser known that Mendeleev also predicted incorrectly that there would be two noble gas elements lighter than hydrogen, which he denoted by symbols x and y : x lied in a period above hydrogen ("period zero") while y lied in the same period as hydrogen but to its left (Mendeleev had denoted the noble gases to be in the next period, e.g. He to be in the same period as Li, Be, B, etc, which is different from our current convention.)

Series	Zero Group	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII			
0	x											
1	y	Hydrogen H=1.008										
2	Helium He=4.0	Lithium Li=7.03	Beryllium Be=9.1	Boron B=11.0	Carbon C=12.0	Nitrogen N=14.04	Oxygen O=16.00	Fluorine F=19.0				
3	Neon Ne=19.9	Sodium Na=23.05	Magnesium Mg=24.1	Aluminium Al=27.0	Silicon Si=28.4	Phosphorus P=31.0	Sulphur S=32.06	Chlorine Cl=35.46				
4	Argon Ar=38	Potassium K=39.1	Calcium Ca=40.1	Scandium Sc=44.1	Titanium Ti=48.1	Vanadium V=51.4	Chromium Cr=52.1	Manganese Mn=55.0	Iron Fe=55.9	Cobalt Co=59	Nickel Ni=59	(Cu)
5		Copper Cu=63.6	Zinc Zn=65.4	Gallium Ga=70.0	Germanium Ge=72.3	Arsenic As=75.0	Selenium Se=79	Bromine Br=79.95				
6	Krypton Kr=81.8	Rubidium Rb=85.4	Strontium Sr=87.6	Yttrium Y=89.0	Zirconium Zr=90.6	Niobium Nb=94.0	Molybdenum Mo=96.0		Ruthenium Ru=101.7	Rhodium Rh=103.0	Palladium Pd=106.5	(Ag)
7		Silver Ag=107.9	Cadmium Cd=112.4	Indium In=114.0	Tin Sn=119.0	Antimony Sb=120.0	Tellurium Te=127	Iodine I=127				
8	Xenon Xe=128	Cesium Cs=132.9	Barium Ba=137.4	Lanthanum La=139	Cerium Ce=140				(—)			
9												
10				Ytterbium Yb=173		Tantalum Ta=183	Tungsten W=184		Osmium Os=191	Iridium Ir=193	Platinum Pt=194.9	(Au)
11		Gold Au=197.2	Mercury Hg=200.0	Thallium Tl=204.1	Lead Pb=206.9	Bismuth Bi=208						
12			Radium Rd=224		Thorium Th=232		Uranium U=239					

Figure 1: Mendeleev's 1904 periodic table, which shows elements x and y .

Mendeleev's element x , also referred to as "Newtonium", was proposed as the constituent of the aether which served as a medium for transmission of light. In many aspects, this conjecture was founded: the aether was predicted to be inert, like noble gases, and was as hard to detect as the noble gases had been. Mendeleev suggested that newtonium had one-millionth the mass of hydrogen and was lost in atomic decay.

- (a) Consider the decay of carbon-14 to nitrogen-14. Determine the number of newtonium particles that would have been lost, if all the change in mass is due to newtonium particles.

Give your answer to the nearest whole number. [2 points]

Binding energy per nucleon of $^{14}\text{C} = 7.520 \text{ MeV}$

Binding energy per nucleon of $^{14}\text{N} = 7.476 \text{ MeV}$.

Rest mass of a proton = $1.672622 \times 10^{-27} \text{ kg}$

Rest mass of a neutron = $1.674927 \times 10^{-27} \text{ kg}$

Element y was also referred to as “coronium”. It was so named because Mendeleev suggested that it explained a then-unexplained line in the Sun’s coronal spectrum with wavelength 530.3 nm. Later studies show that the line actually originates from a highly ionised form of iron, Fe^{13+} . Studies of Fe^{13+} show that the line at 530.3nm is the only one in the visible range, with the other lines lying in the extreme ultraviolet range or beyond.

- (b) Determine the energy of the $n = 2$ energy level in Fe^{13+} . The 14th ionisation energy of iron is $37840 \text{ kJ mol}^{-1}$.

Give your answer to 3 significant figures in units of electronvolts. [2 points]

Mendeleev also attempted to predict the mass of coronium using periodic trends, in particular the mass ratio between each element and the element directly below it. Although Mendeleev considered the trend all the way until F, meaning he used the values from the H:Li ratio all the way to the F:Cl ratio, the trend holds best from H to Be. Mendeleev deduced that the mass ratios followed an **exponential** trend.

- (c) Calculate the proposed relative atomic mass of coronium using the relevant ratios. Use the values in Mendeleev’s periodic table.

Give your answer to 3 significant figures. [2 points]

Solution:

(a) 722

Binding energy of $^{14}\text{C} = 14(7.520) = 105.28 \text{ MeV} = 1.68448 \times 10^{-11} \text{ J}$

Mass defect of $^{14}\text{C} = 1.68448 \times 10^{-11} / (2.9979 \times 10^8)^2 = 1.87427 \times 10^{-28} \text{ kg}$

Mass of $^{14}\text{C} = 6(1.672622 \times 10^{-27}) + 8(1.674927 \times 10^{-27}) - 1.87427 \times 10^{-28} = 2.32477 \times 10^{-26} \text{ kg}$

Binding energy of $^{14}\text{N} = 14(7.476) = 104.664 \text{ MeV} = 1.67462 \times 10^{-11} \text{ J}$

Mass defect of $^{14}\text{N} = 1.67462 \times 10^{-11} / (2.9979 \times 10^8)^2 = 1.86330 \times 10^{-28} \text{ kg}$

Mass of $^{14}\text{N} = 7(1.672622 \times 10^{-27}) + 7(1.674927 \times 10^{-27}) - 1.86330 \times 10^{-28} = 2.32465 \times 10^{-26} \text{ kg}$

Mass change in reaction = $2.32477 \times 10^{-26} - 2.32465 \times 10^{-26} = 1.2084 \times 10^{-30} \text{ kg}$

Mass of a newtonium particle = $10^{-6}(1.008)(1.6605 \times 10^{-27}) = 1.6737 \times 10^{-33} \text{ kg}$

No of newtonium = $1.2084 \times 10^{-30} / 1.6737 \times 10^{-33} = 721.96 = 722$ (nearest whole no)

(b) -390 eV

Energy of transition = $\frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34})(2.9979 \times 10^8)}{530.3 \times 10^{-9}} = 3.7459 \times 10^{-19} \text{ J} = 2.3412 \text{ eV}$

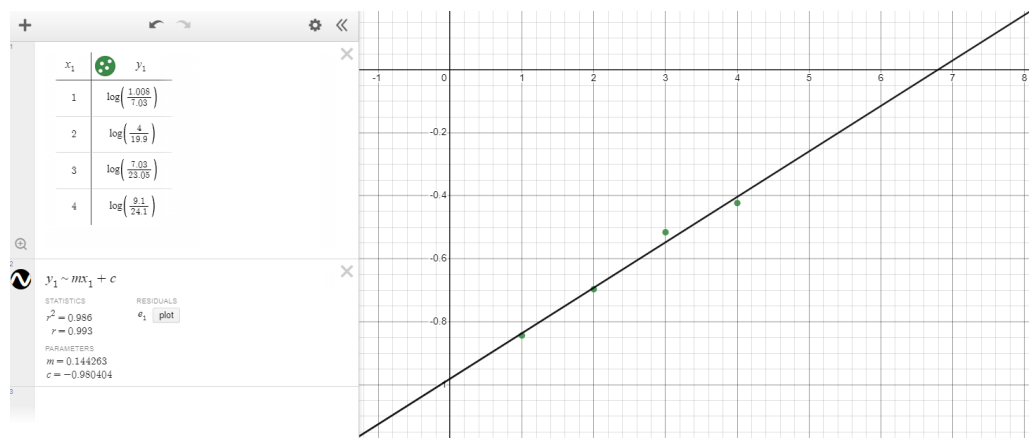
Ionisation energy = $\frac{37840 \times 10^3}{6.0221 \times 10^{23}} = 6.2835 \times 10^{-17} \text{ J} = 392.72 \text{ eV}$

Energy of lowest level = -392.72 eV

Energy required = $-392.72 + 2.3412 = -390.38 \text{ eV} = -390 \text{ eV}$ (3 s.f.)

(c) 0.418

We can calculate the respective ratios and run a linear regression of $\log(\text{ratio})$ against atomic number. You can do this in any suitable graphing calculator.



The y-intercept of this graph is -0.980404 , so the proposed ratio $y/\text{He} = 0.10462$
 $\Rightarrow M_r$ of $y = 0.10462(4.0) = 0.418$ (3 s.f.)