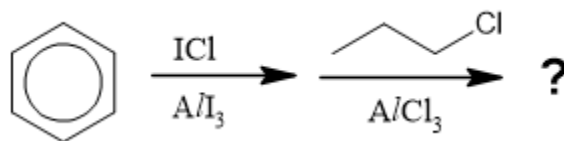


**Problem 16: A failed synthesis**

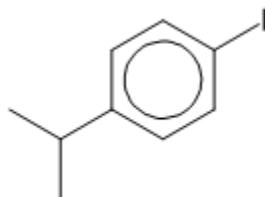
A student executed the following synthesis. He discovered that in both steps, monosubstitution occurred, and concluded that sterics were a major factor in controlling the product of the reaction.



What is the major product formed?

*Leave your answer as an organic structure.*

*Solution:*

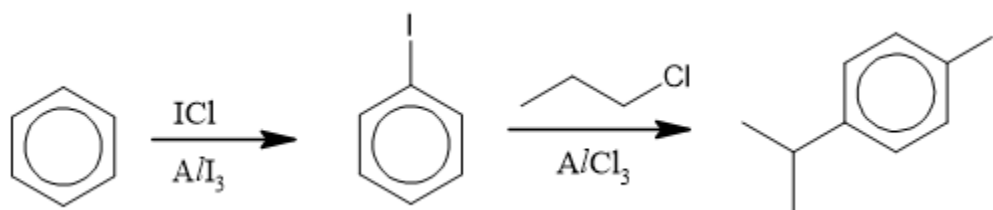


Sterics play the larger role in the second step, indicating that the para product was probably formed due to the large iodine substituent.

In the first step, the iodobenzene is formed because iodine is less electronegative and  $I^+$  is formed as the electrophile.

In the second step, the carbocation formed undergoes a rearrangement to give the more stable tertiary carbocation. It is then substituted at the para position due to steric hindrance.

The intermediates are shown below:



**Problem 12: Funny moments**

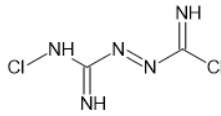
Which of the following pairs of compounds are likely **not soluble** in each other at room temperature?

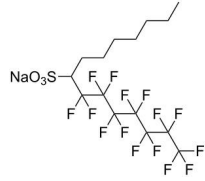
- 1)  $\text{IF}_5$  and benzene



- 2)  and 

- 3)  $\text{Li}_2\text{CO}_3$  and water

- 4)  and water

- 5) Supercritical  $\text{CO}_2$  and 

Present your answer as a single number comprising the digits of the pairs insoluble in each other, in increasing order. If your answer is  $a$ ,  $b$  and  $c$ , leave your answer as  $\overline{abc}$ .

*Leave your answer as a string of numbers.*

*Solution:*

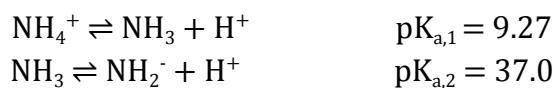
**134**

- 1)  $\text{IF}_5$  is polar. Benzene is nonpolar. They are likely not to be soluble in each other.
- 2)  $\text{MgCp}_2$  dissociates in ethers, thus being soluble. Unlike ferrocene,  $\text{MgCp}_2$  is relatively more unstable, due to the favorable bonding interactions arising from the electrons in the 3s orbital being promoted to the  $3p_{xy}$  orbital, and backbonding to the 3s orbital, leading to a lower degree of orbital overlap and therefore a fairly weak metal-ring bond.
- 3)  $\text{Li}_2\text{CO}_3$  has relatively high covalent character and is insoluble in water.
- 4) Chlorazodin is *too* strongly hydrogen bonded to be easily soluble in water.
- 5) The fluorocarbon is soluble in supercritical  $\text{CO}_2$  because (1) electrostatics minorly govern the solubility of alkanes in supercritical  $\text{CO}_2$ , and (2) the fluorocarbon given has very strong dispersion interactions given its huge electron cloud, given that the main interactions are dispersion forces.

**Problem 1: Ammonolysis**

Ammonolysis is the process of splitting  $\text{NH}_3$  into  $\text{NH}_2^-$  and  $\text{H}^+$ . Similarly to water, liquid ammonia also undergoes auto-ionization,  $2\text{NH}_3 \rightleftharpoons \text{NH}_2^- + \text{NH}_4^+$ .

Consider the first and second pKas of  $\text{NH}_4^+$ .



It is given that the rate of the forward reaction of the auto-ionization of liquid ammonia is  $k_1 = 1.9 \times 10^{-38}$ . Let the rate of the reverse reaction of the auto-ionization of liquid ammonia be  $k_{-1}$ .

Find the value of  $\log_{10}(k_{-1})$ .

*Leave your answer to 4 significant figures.*

*Solution:*

**-9.991**

We can write the equilibrium constant of the reaction as  $K = \frac{[NH_4^+][NH_2^-]}{[NH_3]^2}$ .

We also notice that  $\frac{K_{a,2}}{K_{a,1}} = \frac{[NH_2^-][H^+]}{[NH_3]} \cdot \frac{[NH_4^+]}{[NH_3][H^+]} = \frac{[NH_4^+][NH_2^-]}{[NH_3]^2} = K$ .

Hence, we can compute the value of  $K = \frac{10^{-37.0}}{10^{-9.27}} = 10^{-27.73}$ .

We know that  $K = \frac{k_1}{k_{-1}} \Rightarrow k_{-1} = \frac{k_1}{K} = \frac{1.9 \times 10^{-38}}{10^{-27.73}}$ .

Therefore, we can compute the answer as  $\lg(k_{-1}) = \lg\left(\frac{1.9 \times 10^{-38}}{10^{-27.73}}\right) = \mathbf{-9.991}$  (4 s.f.).

**Problem 17: BlueBlackPink**

All unknown compounds in this question have a common element, **X**.

Compound **A** is black. Upon heating compound **A** with oxygen gas at high temperatures, a pink substance **B** is formed. At lower temperatures, a red solid **C** is formed instead. On the addition of concentrated ammonia solution, a colourless solution is formed, and on standing, this solution turns blue, containing compound **D**. Upon addition of dilute sulfuric acid, then ethanol to compound **D**, a blue solid, compound **E** is formed.

What is the electronic configuration of element **X** in spdf notation?

Leave your answer without subscripts or spaces, in increasing principal quantum number. If your answer is neon, for example, leave your answer as 1s22s22p6. If your answer is xenon, for example, leave your answer as 1s22s22p63s23p63d104s24p64d105s25p6.

*Leave your answer as a string.*

*Solution:*

**1s22s22p63s23p63d104s1**

Firstly, we know that the element is most likely a transition metal, given the different colour it exhibits.

Next, we can guess that the element is copper, as there are many clues pointing to this in the question:

*On addition of concentrated ammonia solution, a colourless solution is formed, and on standing, this solution turns blue, containing compound **D**.*

This is characteristic of copper(I) oxide.  $\text{Cu}_2\text{O}$  dissolves in concentrated ammonia solution to form the colourless complex  $[\text{Cu}(\text{NH}_3)_2]^+$ , which is then oxidized to the blue copper tetraamine complex.

*Upon heating compound **A** with oxygen gas at high temperatures, a pink substance **B** is formed.*

This is a typical redox reaction.  $\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2 \text{Cu} + \text{SO}_2$ , and copper is the pink solid mentioned.

*At lower temperatures, a red solid **C** is formed instead.*

This is typical of  $\text{Cu}_2\text{O}$ .  $\text{Cu}_2\text{S}$  indeed undergoes a redox reaction to form  $\text{SO}_2$  and  $\text{Cu}_2\text{O}$ .

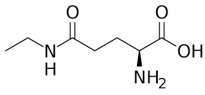
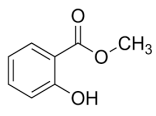
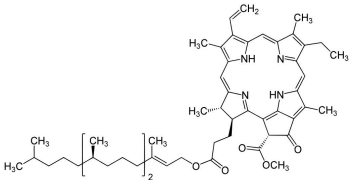
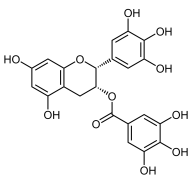
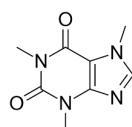
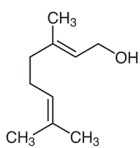
Now, the electronic configuration of Cu is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ , not  $3d^9 4s^1$ !

This gives the final answer of **1s22s22p63s23p63d104s1**.



**Problem 24: Bri'ish???**

Let us have a bit of fun! Match the following compounds to their tastes / effects in tea!

S/N	Compounds	Function / Effect
1		Gives tea its bitter taste
2		Makes you stay awake after drinking tea
3		Gives tea its sweet and umami taste, and promotes relaxation
4		Gives tea its dark colour
5		Gives tea its floral aroma
6		Gives tea its fruity aroma

Match the functions to the correct compound in each row. If the function in row 6 matches to the compound in row 1, function in row 5 matches to that in row 2, and etc., leave your answer as 654321.

*Leave your answer as a 6 digit number.*

*Solution:*

**364125**

Compound 1 is an amino acid, giving it the sweetness.

Compound 2 is methyl salicylate, giving it a fruity smell associated with esters.

Compound 3 is a pheophytin, a dark coloured pigment.

Compound 4 is a polyphenol, giving tea its bitter taste.

Compound 5 is caffeine, making you stay awake.

Compound 6 is geraniol, giving tea its floral smell.

**Problem 3: Chemicle****[5 points]**

Have you ever played Wordle? You probably have, but just in case you haven't, here's a brief overview of it!

**Overview of Wordle**

In Wordle, you have to guess a 5 letter word. After each guess, the color of the tiles will change to show how close your guess was to the word.

W E A R Y

A green letter **W** means that it is in the word and is in the correct spot.

P I L O T

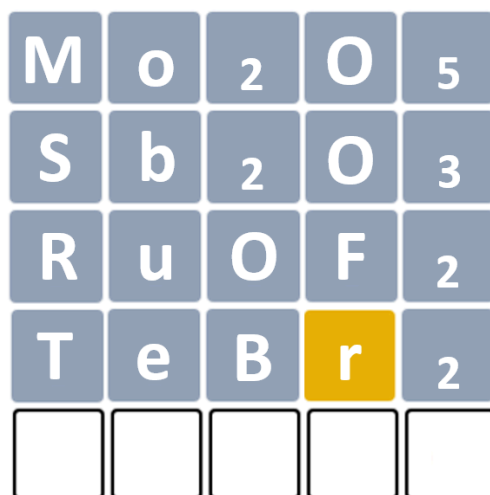
A yellow letter **L** means that it is in the word, but is in the wrong spot.

V A G U E

A gray letter **U** means that it is not in the word in any spot.

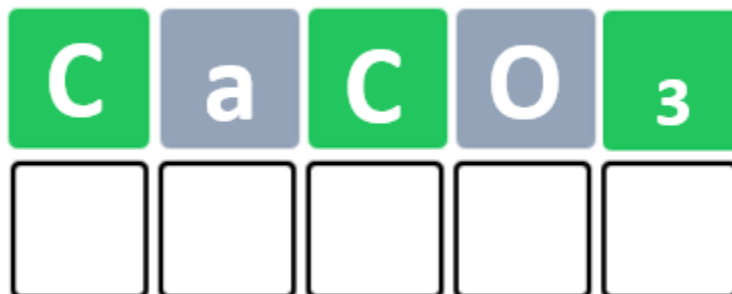
What if we play a chemistry version of it, or *chemicle*? 😊

In *chemicle* (which is an [actual game](#), by the way), you get to guess chemical formulae that are 5 characters long, for example,  $\text{NaBH}_4$ . Do note that it is case-sensitive, however. That is, if the answer is  $\text{AlCl}_3$ , and you choose  $\text{NaBH}_4$ , the lowercase 'a' will be marked as gray.



After seeing the above configuration, Tim exclaims "Aha!". Tim has narrowed down the possibilities to two compounds (Note that the answer must be a stable compound at room temperature that does not contain any radioactive elements).

- (a) If the two compounds are **ABCDE** and **FGHIJ** respectively, where **ABCDE** has a lower molar mass than **FGHIJ**, write down the two possible compounds in the form ABCDEFGHIJ. **[2 points]**



- (b) Now, given the above configuration, how many possible compounds can be a solution to the above *chemicle* puzzle, if the compounds must be stable at room temperature? Include radioactive compounds that have a half life of more than 1 day. **[2 points]**

Tim decided to spoil the solution to the puzzle above by giving a hint:

"The compound above can be synthesised by bubbling  $\text{Cl}_2$  gas into an acid, then heating it with aqueous  $\text{NaOH}$ . This reaction forms the compound above, and a separate compound **X**."

- (c) What is the unknown compound above, and what is compound **X**?  
If the unknown compound above is **ABCDE**, and the unknown compound is **FGHI** (may have less or more characters than shown), leave your answer in the form ABCDEFGHI. **[2 points]**

*Solution:*

This question, while seeming like a random chemical puzzle, is actually an exercise in inorganic chemistry and periodicity.

**(a)  $\text{ZrCl}_4\text{IrCl}_4$** 

Notice that the digits that can appear are likely 4 or 6. We also note that the anion is most likely Cl, given that F and Br are eliminated. We can also eliminate the chalcogens, as O and S are already eliminated.

Consider the ending digit to be 4.

Then, our cation must have a *r* in it, and the only elements with *r* (lowercase) in it are:

1. Cr
2. Zr
3. Ir
4. Pr
5. Er

Of these 5 elements, we can eliminate Cr, Pr and Er because they do not exhibit the +4 oxidation state commonly.  $\text{CrCl}_4$  is unstable, existing at elevated temperatures but reverting to  $\text{CrCl}_3$  and  $\text{Cl}_2$  at room temperature.  $\text{PrCl}_4$  is unknown as of the time of writing, and Pr does not readily exhibit the +4 oxidation state. Er also does not readily exhibit the +4 oxidation state.

So our only possible compounds are:  **$\text{ZrCl}_4$  and  $\text{IrCl}_4$** .

**(b) 5**

Now, it is clear that the answer is of the form  $\text{C}_5\text{Cl}_3$ . We now examine the possible compounds that exhibit a stable +3 oxidation state, that start with C. We start off by listing elements starting with C:

- |       |       |
|-------|-------|
| 1. Cr | 5. Ce |
| 2. Co | 6. Cf |
| 3. Cd | 7. Cm |
| 4. Cs | 8. Cn |

Of these, we can eliminate Co because  $\text{CoCl}_3$  is highly unstable, only stabilised at very low ( $-60^\circ\text{C}$ ) or very high ( $644^\circ\text{C}$ ) temperatures. Cd is also eliminated because it does not exhibit a stable +3 oxidation state (usually 0/+1/+2). Cs is also eliminated because it does not exhibit a stable +3 oxidation state (usually 0/+1). Cn is also eliminated because it is too unstable (longest half-life of about 30s, with  $^{285}\text{Cn}$ ).

$\text{CrCl}_3$  and  $\text{CeCl}_3$  are common compounds found in laboratories.  $\text{CfCl}_3$  and  $\text{CmCl}_3$  do exist, also they are radioactive, but with a half-life of hundreds of days. So we have 4 inorganic solutions.

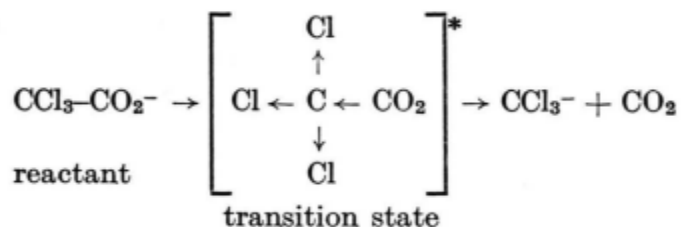
Interestingly, we note that an organic compound can also be a solution:  $\text{CHCl}_3$ .

Therefore, the final answer is **5 (4 inorganic, 1 organic)**.

### (c) $\text{CHCl}_3\text{CO}_2$

$\text{CHCl}_3$  can be synthesised by passing  $\text{Cl}_2$  gas through ethanoic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , to form trichloroacetic acid,  $\text{CCl}_3\text{CO}_2\text{H}$ . This undergoes alkaline solvolysis to form  $\text{CHCl}_3$  and  $\text{CO}_2$ .

In fact, the mechanism of the decomposition is as follows:



**Problem 23: Electrifying!**

In acidic solution, technetium undergoes the following half reactions:

Redox <b>unbalanced</b> half-equation	Cell potential / V
$\text{TcO}_4^- \rightarrow \text{TcO}_3$	+0.700
$\text{TcO}_4^- \rightarrow \text{TcO}_2$	+0.738
$\text{TcO}_4^- \rightarrow \text{TcO}_4^{2-}$	-0.569
$\text{TcO}_3 \rightarrow \text{Tc}$	+0.434
$\text{TcO}_4^{2-} \rightarrow \text{TcO}_2$	<b>(1)</b>
$\text{TcO}_2 \rightarrow \text{Tc}$	<b>(2)</b>

What are the cell potentials **(1)** and **(2)**? Concatenate your answers to both, in order, and include the sign (+ or -). For example, if the cell potential **(1)** is +0.420V and the cell potential **(2)** is -0.690V, leave your answer as +0.420-0.690.

*Leave your answer as a string. Each of the cell potentials should be in 3 s.f.*

*Solution:*

**+1.39+0.272**

Firstly, let's consider the cell potential of  $\text{TcO}_4^- \rightarrow \text{Tc}$ . Recall that electrode potentials are **not additive**.

Electrode potential =  $(+0.700 \times 1 + 0.434 \times 6) / 7 = +0.472 \text{ V}$ .

Next, we can directly compute **(1)**, using the data above from the +7 oxidation state to the +6 and +4 oxidation state .

Electrode potential =  $(+0.738 \times 3 - (-0.569) \times 1) / 2 = +1.39 \text{ V (3 s.f.)}$

Lastly, we have all the information we need to compute **(2)**.

Electrode potential =  $(+0.472 \times 7 - (+0.738) \times 3) / 4 = +0.273 \text{ V (3 s.f.)}$

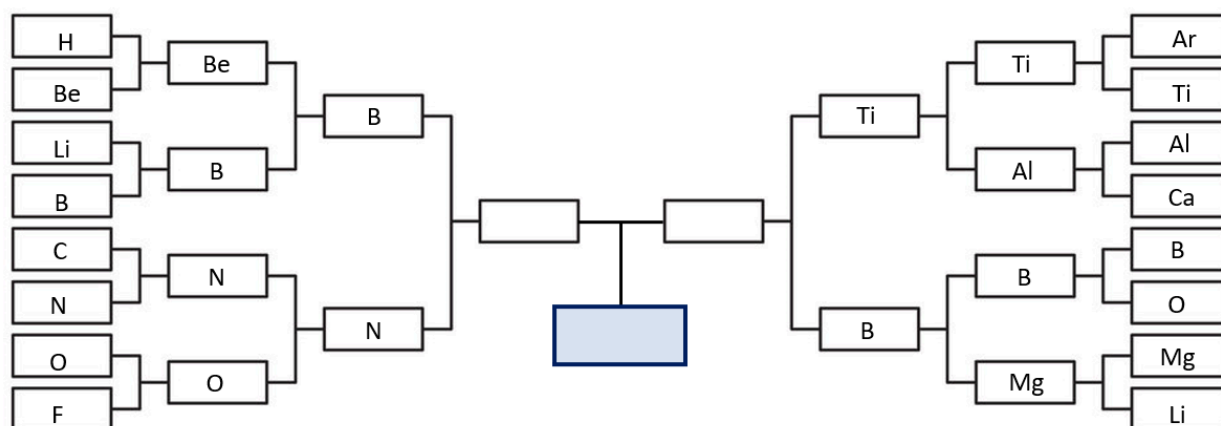


**Problem 1: Knockout!****[6 points]**

Chances are, you probably have seen an elimination tournament diagram before, knocking out teams one at a time. But what if we do that with elements? And what if we do not know the rules for elimination?

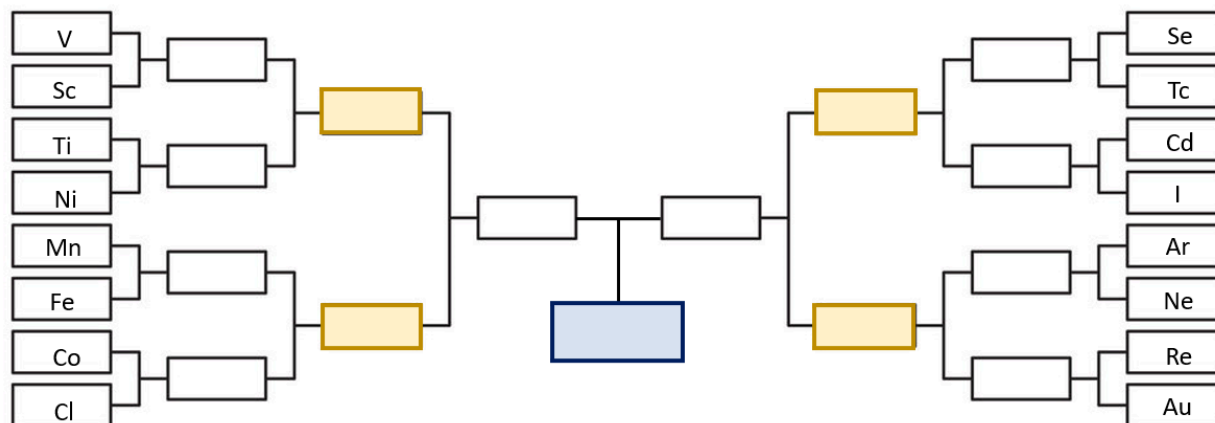
**[Note:** By default, if two elements *draw*, the one with a higher atomic number moves on. You may assume that in the first elimination tournament diagram below, none of the matches are a draw.]

Consider the tournament diagram below. Some of the winners are filled for you below.  
**[Note:** Some elements are repeated, so that you have some invariant point of references.]



- (a) By considering the possible rule set for *winning*, determine which element is the overall winner in the above tournament (i.e. is filled in the blue box). **[2 points]**

Now that we have established the rules of the tournament, let us consider a more complex tournament setup, with the same rules as **part (a)**.



- (b) Determine the answer to the following questions:

- (i) Which element wins the above tournament (i.e. is filled in the blue box)?
- (ii) Amongst the 4 elements filled in the yellow boxes, two move on to the final round, but two are eliminated. These two eliminated elements move on to a losers' bracket to vie for third place. Which element comes in third place?
- (iii) How many draws are there in total?

Then, based on your answers to **parts (i) to (iii)**, concatenate your answer into a string, keeping the capitalization. For example, if your answer for **part (i)** is He, **part (ii)** is U, and **part (iii)** is 9, then submit the answer HeU9 (note the preservation of the capitalization). **[3 points]**

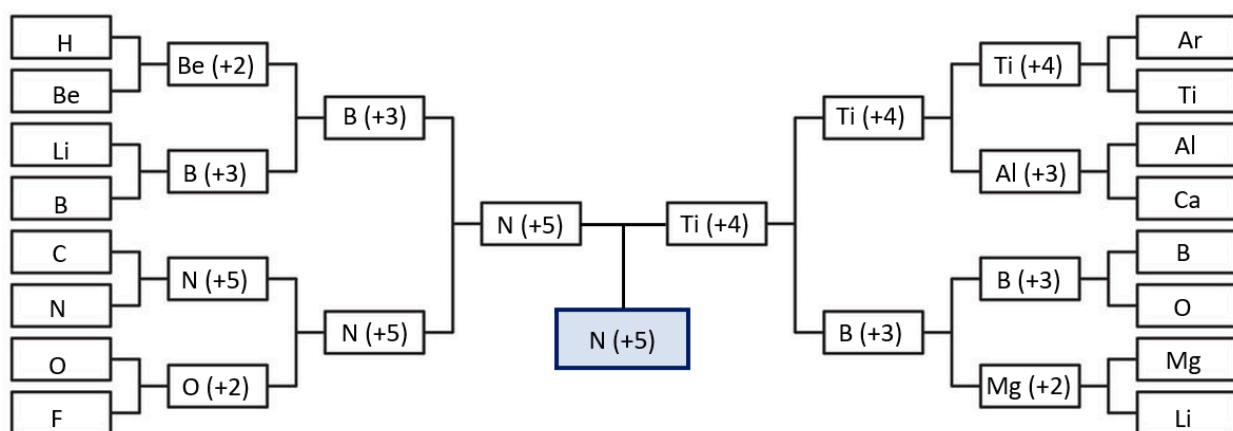
- (c) Now, suppose that we do the elimination rounds with all 118 elements in the periodic table. Which element will emerge as the overall winner? **[1 point]**

*Solution:***(a) N**

The elimination works via choosing the element with the highest **maximum** oxidation state as the winner. For example, between H and Be, H has a maximum oxidation state of +1 (e.g. HF), while Be has a maximum oxidation state of +2 (e.g.  $\text{BeCl}_2$ ). Accordingly, filling up the knockout table, we get the final answer to be nitrogen, N, with a maximum oxidation state of +5.

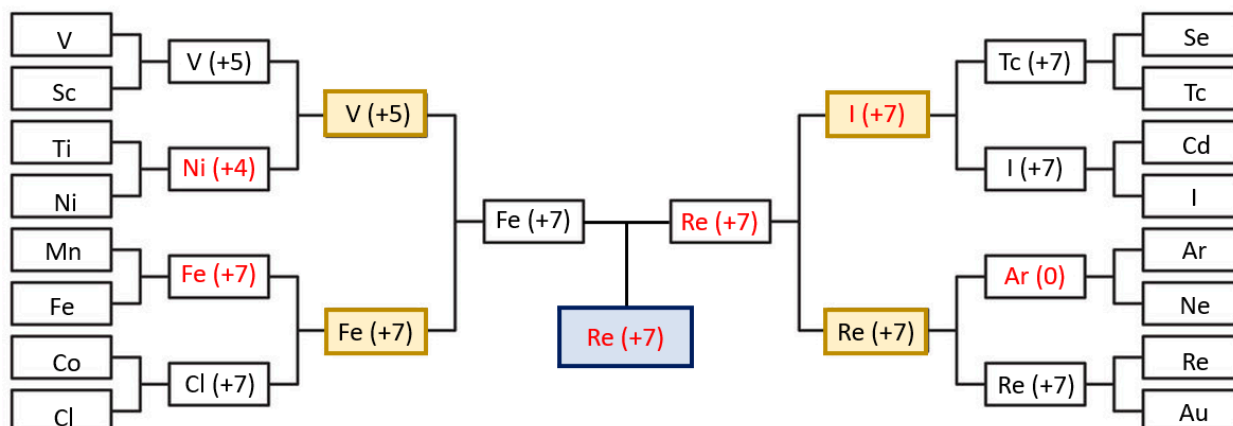
We can deduce the knockout rule as follows:

- Notice that amongst metals, those metals with more valence electrons tend to win.
- However, certain non-metals like F, despite having 7 valence electrons, lose to O with 6 valence electrons. What could possibly be the difference? F is highly electronegative, which could explain the trend, but this does not correlate to the rest of the data. Therefore, the trend must be related to the electronegativity of F, but not directly comparing electronegativity.
- Notice that in general, elements closer to the center on the periodic table tend to win elements on the left (B wins Li, N wins C, but O wins F). This is a very strong indication of it being the highest maximum oxidation number of the element, because most trends are not bitonic (strictly increasing then decreasing, or strictly decreasing then increasing).



**(b) ReI6**

The final knockout chart looks like this:



Note that the boxes with red colours are those with draws (i.e. identical highest oxidation states, and therefore the element with a higher atomic mass wins by default).

The winner is therefore rhenium, with a +7 oxidation state. Next, amongst the losers (which are V and I), I wins the losers' bracket with a +7 oxidation state, thereby coming in third.

Counting the number of red boxes, there are 6 draws in total.

Therefore, the final answer is **ReI6**.

**(c) Ir**

Out of all the elements, Ir exhibits the highest maximum oxidation state of +9, as in  $[\text{IrO}_4]^+$ . None of the other elements exhibit such a high maximum oxidation state.

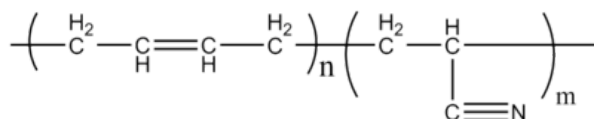
**Problem 19: Lab Safety**

A common personal protective equipment (PPE) in labs is a pair of gloves. However, not all gloves are made equal, and using the wrong type of glove can harm you more!

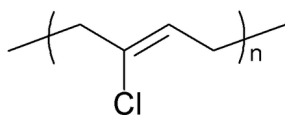
You have the following compounds:

- 1) 70% nitric acid
- 2) Dimethyl formamide
- 3) Furfural
- 4) Linoleic acid
- 5) Perchloroethylene
- 6) Phenol
- 7) Propylene oxide

There are two common types of gloves in the lab: nitrile gloves and neoprene gloves. Their structures are shown below:



Nitrile gloves



Neoprene gloves

For each of the gloves, indicate whether they will be effective against each of the 7 chemicals. If they are effective, type E, and N if they are not effective. Start with the 7 chemicals against nitrile, then neoprene.

A glove being effective against a chemical means that the glove does not weaken upon prolonged contact with the chemical.

For example, if you answer for nitrile is effective for everything, and your answer for neoprene is ineffective for everything, type EEEEEENNNNNN.

*Leave your answer as a 14 character string.*

*Solution:*

**NNNEENNNEEEENEN**

For nitrile gloves:

1) 70% nitric acid

Nitrile gloves fare poorly against concentrated nitric acid – the nitrile simply hydrolyses.

2) Dimethyl formamide

It is not effective - DMF is strongly hydrogen bonded to the nitrile groups of the gloves and therefore, as DMF solvates the nitrile group, it can cause the nitrile polymer chains in the glove material to swell, compromising structural integrity of the glove.

3) Furfural

It is not effective - furfural has an aldehyde group that can undergo the Knoevenagel condensation with nitriles, disrupting the polymer chain.

4) Linoleic acid

It is fairly effective against linoleic acid.

5) Perchloroethylene

It is also quite effective against perchloroethylene.

6) Phenol

It is not effective against phenol, because phenol reacts with the nitrile groups in the Pinner reaction, which can reduce the structural integrity of the glove, albeit at a slow rate. Combined with the hydrogen bonding mentioned in (2), this can wear out the glove quickly.

7) Propylene oxide

It is not effective against propylene oxide. Propylene oxide has a ring opening reaction.

For neoprene gloves:

1) 70% nitric acid

Neoprene gloves are quite effective against concentrated nitric acid.

2) Dimethyl formamide

Neoprene gloves are quite effective against DMF.

## 3) Furfural

Neoprene gloves are quite effective against furfural.

## 4) Linoleic acid

Neoprene gloves are quite effective against linoleic acid.

## 5) Perchloroethylene

It is not effective against perchloroethylene – the perchloroethylene interacts strongly with the polymer and causes it to swell, ruining the structural integrity of the polymer.

## 6) Phenol

It is effective against phenol.

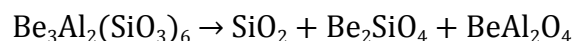
## 7) Propylene oxide

It is not effective against propylene oxide – it also undergoes a ring opening reaction.

## Problem 6: Liquefied Emeralds

In the popular MMORPG Minecraft server, WynnCraft, the main currency used are liquefied emeralds.

Emeralds are a variety of the mineral beryl, with the formula  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ . However, real emeralds are hard to liquefy. Instead, they decompose at fairly low temperatures. The **unbalanced** equation is shown below:



To determine the purity of 113.5 grams of emeralds, the emeralds were heated and fully decomposed. Next,  $\text{SiO}_2$  was fully dissolved in excess HF, forming  $\text{H}_2\text{SiF}_6$ . Assume that the other compounds formed do not react with HF.

The amount of  $\text{H}_2\text{SiF}_6$  was then determined by gravimetry. Excess  $\text{BaCl}_2$  was added to the solution of  $\text{H}_2\text{SiF}_6$ , forming  $\text{BaSiF}_6$ . After filtering and weighing with a high precision electronic balance, the mass of the precipitate was 252.8663 grams.

What is the percentage purity (by mass) of the emerald sample (in %)?

*Leave your answer to 2 d.p.*



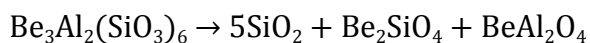
*Solution:*

**86.07%**

Number of moles of  $\text{BaSiF}_6 = 253.8663 \div (137.3 + 28.09 + 19.00 \times 6) = 0.908645 \text{ mol}$

This is equal to the number of moles of  $\text{H}_2\text{SiF}_6$ , and equivalently the number of moles of  $\text{SiO}_2$ , since  $\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$ .

Next, we need to determine the number of moles of  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ . We will start off by balancing the equation of the decomposition:



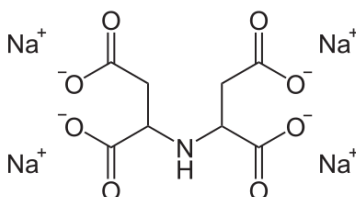
Hence, the number of moles of  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6 = 0.908645 \div 5 = 0.181729 \text{ mol}$

Mass of  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6 = 0.181729 \times (9.01 \times 3 + 26.98 \times 2 + (28.09 \times 3 + 16.00 \times 3) \times 6) = 97.684779 \text{ grams}$ .

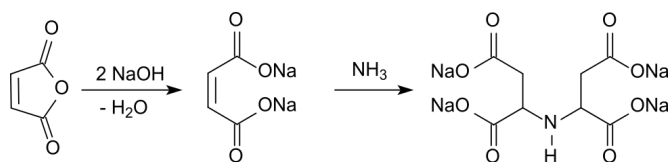
Percentage purity =  $97.684779 \div 113.5 \times 100\% = \mathbf{86.07\%}$ .

**Problem 22: Make-a-ligand**

The compound below is a common chelating agent for alkaline earth metals as a pentadentate ligand.



This ligand can be fairly easily synthesized:



In the synthesis above, how many stereoisomers of the final product will be formed? .

*Leave your answer as a number.*

*Solution:*

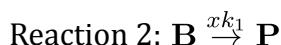
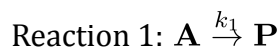
**3**

There are two chiral centres in the molecule, but the (R, S) and (S, R) products are identical as it is a meso compound. This leaves us with 3 stereoisomers.

**Problem 1: 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  $x$ .

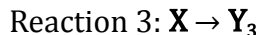
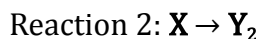
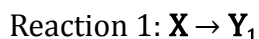


It is given that reaction 1 is a  $n^{\text{th}}$  order reaction, while reaction 2 is a  $(n-1)^{\text{th}}$  order reaction, where  $n \geq 1$ . The first half-life of reaction 1 is 1.802 times that of reaction 2, regardless of the value of  $x$ .

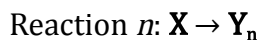
(a) What is the value of  $n$ ? **[3 points]**

*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, **Y<sub>1</sub>**, **Y<sub>2</sub>**, **Y<sub>3</sub>**, 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, find the value of  $\overline{abc}$ . **[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,

$$\frac{\frac{\ln 2}{xk_1}}{\frac{x}{2k_1}} = \frac{2 \ln 2}{x^2} \text{ for } n = 1, \text{ and } \frac{\frac{1}{x(xk_1)}}{\frac{\ln 2}{xk_1}} = \frac{1}{x \ln 2}, \text{ which are not constants with changing } x \text{ values.}$$

Now, consider how we can derive the half-life for a generic  $n^{\text{th}}$  order reaction, where  $n > 2$ . For an  $n^{\text{th}}$  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.

$$\begin{aligned} t_{1/2} &= \frac{1}{k(n-1)} \left( \left(\frac{1}{2}a\right)^{1-n} - a^{1-n} \right) \\ t_{1/2} &= \frac{a^{1-n}}{k(n-1)} \left( \frac{1}{2^{1-n}} - 1 \right) \Rightarrow \boxed{t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)a^{n-1}}} \end{aligned}$$

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:

$$\begin{aligned}\int_x^{[\mathbf{X}]} ([\mathbf{X}] - 1)d[\mathbf{X}] &= \int_0^t k dt \\ \frac{[\mathbf{X}]^2}{2} - [\mathbf{X}] - \frac{x^2}{2} + x &= kt\end{aligned}$$

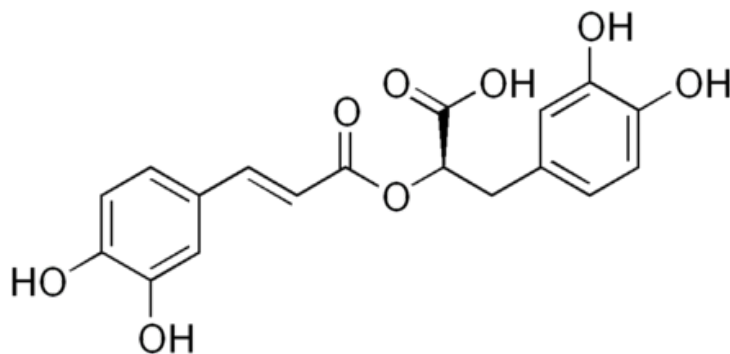
Noting that the half-life is when  $[\mathbf{X}] = x/2$ , we can determine that the half-life can be expressed as follows:

$$\begin{aligned}\frac{\left(\frac{x}{2}\right)^2}{2} - \frac{x}{2} - \frac{x^2}{2} + x &= kt_{1/2} \\ t_{1/2} &= \frac{1}{k} \left( \frac{x}{2} - \frac{3x^2}{8} \right)\end{aligned}$$

It is therefore easy to see that **a** = 2, **b** = 3 and **c** = 8. Hence,  $\overline{abc} = 238$ , which is the solution.

**Problem 4: Organic Chemistry**

Oregano contains many organic compounds. One such compound is rosmarinic acid, and its structure is shown below.



**Structure of rosmarinic acid**

A sample of rosmarinic acid was heated in an open test tube for a prolonged period with acidified  $\text{KMnO}_4$ , with vigorous stirring. How many **distinct organic products** are formed at the end of the reaction, assuming the reaction goes to completion?

*Leave your answer as an integer.*

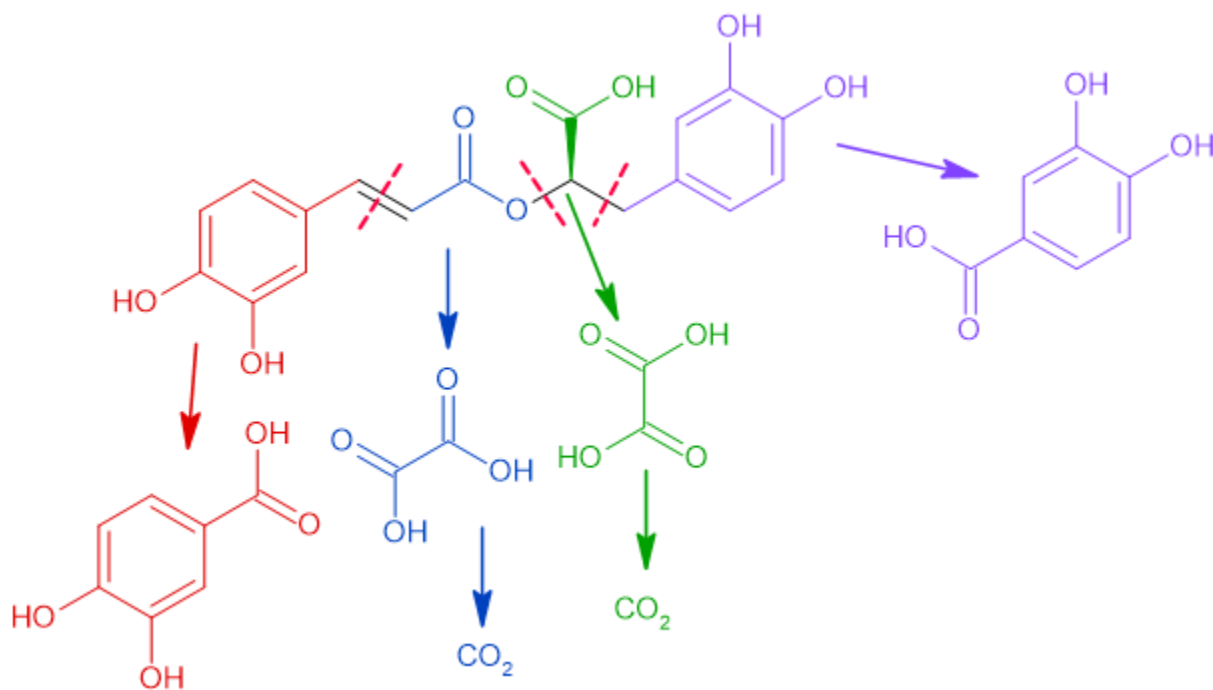
*Solution:*

1

We can see that  $\text{KMnO}_4$  will cleave the alkene, yielding the red and blue products below. Under prolonged heating in acidic conditions, the ester hydrolyses to yield ethanedioic acid, which undergoes further oxidation to give  $\text{CO}_2$  gas.

$\text{KMnO}_4$  also does side-chain oxidation on the purple phenyl ring, yielding the purple structure, which is **identical to the red structure**, and the remainder of the green structure is oxidised to ethanedioic acid, which also undergoes further oxidation to give  $\text{CO}_2$  gas.

Hence, only one unique product (the red / purple product) is formed.





**Problem 7: Phasing through the Floor**

The pressure-volume behaviour of nitrogen gas can be expressed through the following Van Der Waals equation, where  $P$  is in bar,  $V$  is in  $\text{dm}^3$ ,  $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T$  is in K, and the numbers are such that the equation is dimensionally constant:

$$P = \frac{RT}{V - 0.0387} + \frac{1.37}{V^2}$$

When considering the different phases of a substance, the liquid-vapour **critical point** is where phase boundaries vanish, and a liquid and its vapour can coexist.

The condition for the critical point to exist is for there to be a stationary point of inflection on the pressure-volume diagram. That is,

$$\frac{\partial P}{\partial V} = 0, \text{ and } \frac{\partial^2 P}{\partial V^2} = 0 .$$

Find the volume (in  $\text{cm}^3$ ) for which nitrogen has a critical point.

*Leave your answer to 1 d.p.*

*Solution:*

**116.1 cm<sup>3</sup>**

We simply differentiate with respect to  $V$ , and find the point where both are zeroes. This can be done manually fairly quickly, or can even be done with an online calculator (Wolfram Alpha, DerivativeCalculator, etc.).

$$\frac{\partial P}{\partial V} = 0 \Rightarrow RTV^3 = -2.74(V - 0.0387)^2$$

$$\frac{\partial^2 P}{\partial V^2} = 0 \Rightarrow 2RTV^4 = -8.22(V - 0.0387)^3$$

Dividing the equations,  $2V = 8.22/2.74(V - 0.0387)$

$$V = 3 \cdot 0.0387 = 0.1161 \text{ dm}^3 = \mathbf{116.1 \text{ cm}^3}$$

Problem x x% of total	Question	x.1	x.2	x.3	x.4	x.5	x.6	x.7	x.8	Total
	Points	3	3	3	3	5	2	5	3	27

## Problem x: Radiometric Dating

By Lim Dillion, Singapore

Potassium–argon dating is a radiometric dating method used in geochronology and archaeology. It is based on measurement of the product of the radioactive decay of an isotope of potassium (K) into argon (Ar).

This isotope of potassium is  $^{40}\text{K}$ , with a half-life of  $1.4 \times 10^5$  years, decaying to form  $^{40}\text{Ar}$ , which is stable and can be trapped within rocks. A sample of rock taken from the Jezero crater in Mars revealed that the ratio of potassium and argon are formed in the ratio:



$$\frac{\text{Number of potassium-40 atoms}}{\text{Number of argon-40 atoms}} = \frac{1}{9}$$

- 1) Write down the nuclear equation representing the decay, and identify the type of decay involved. A particle **Y** is emitted. What is the identity of this particle?

The age of the rock from the Jezero crater can in fact be determined by the ratio of isotopes present in the rock. The rock was pulverised in a mass spectrometer to obtain the data above, and scientists wanted to determine the age of the rock sample.

- 2) Assuming that before any radioactive decay occurred, the number of argon-40 atoms was  $D_0$ . Let the number of daughter nuclides ( $^{40}\text{Ar}$ ) at a time,  $t$ , be  $D$ . If the current number of parent nuclides ( $^{40}\text{K}$ ) was  $N_p$ , write an equation relating  $t$  to  $D$ ,  $D_0$ ,  $N_p$  and its half-life,  $t_{1/2}$ . This is commonly known as the age equation.
- 3) Assuming that there were no  $^{40}\text{Ar}$  in the rock at the beginning and none has escaped subsequently. Determine the age of the rock. Explain clearly, if your answer will be an overestimate or underestimate if some argon has escaped.

Another method of radiometric dating is using the isochron equation. The advantage of isochron dating as compared to simple radiometric dating techniques is that no assumptions are needed about the initial amount of the daughter nuclide in the radioactive decay sequence. A common system for isochron dating is using the  $^{87}\text{Sr}/^{86}\text{Sr}$  system. It is known that  $^{87}\text{Rb}$  undergoes a  $\beta$ -decay to form  $^{87}\text{Sr}$  with a half-life of  $4.8 \times 10^{10}$  years, while  $^{86}\text{Sr}$  is non-radiogenic and extremely stable.

- 4) Write down an equation relating the number of  $^{87}\text{Sr}$  atoms produced by decay, the number of  $^{87}\text{Sr}$  atoms present in the sample currently, and the initial number of  $^{87}\text{Sr}$  atoms in the sample.

Using a method similar to that of (2), express the current ratio of  $^{87}\text{Sr}/^{86}\text{Sr}$  atoms in terms of their initial ratios and an appropriate ratio of  $^{87}\text{Rb}$  atoms with another atom.

*[You can use  $\lambda$  to represent the rate constant of the decay for all subsequent parts.]*

By using the Taylor's expansion, it is known that for all  $x$  values,

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

It is known that for small  $x$  values, terms in  $x^2$  and higher can be ignored.

- 5) Hence, using the above approximation, suggest a possible linear graph which can be plotted from the data of the ratios of  $^{87}\text{Sr}/^{86}\text{Sr}$  atoms and the ratio of  $^{87}\text{Rb}/^{86}\text{Sr}$  at different points in time. What does the gradient of the graph represent, and what is its value? What does the y-intercept of the graph represent?

The following data is obtained for a sample of rock taken from the Sea of Tranquility on the Moon, containing both  $^{87}\text{Sr}$ ,  $^{86}\text{Sr}$  and  $^{87}\text{Rb}$  atoms.

Time / $\times 10^5$ years	5.0	10.0	15.0	20.0	25.0
$(^{87}\text{Sr}/^{86}\text{Sr}) \times 10^{-5}$	7.666	3.177	4.116	4.910	5.145
$^{87}\text{Rb}/^{86}\text{Sr}$	3.8	2.3	2.1	1.9	1.6

- 6) Hence, by performing a linear regression, determine the initial ratio of  $^{87}\text{Sr}/^{86}\text{Sr}$  atoms.

#### Information: Linear Regression

For a simple linear regression, if the data points can be seen to follow a linear trend:  $y = a + bx$ , then  $a$  and  $b$  can be determined by:

$$a = \frac{\sum y \sum x^2 - \sum x \sum xy}{n(\sum x^2) - (\sum x)^2}$$

$$b = \frac{n \sum xy - (\sum x)(\sum y)}{n \sum x^2 - (\sum x)^2}$$

Another method of isochron dating is  $^{235}\text{U}/^{238}\text{U}/^{207}\text{Pb}/^{206}\text{Pb}/^{204}\text{Pb}$  dating.  $^{204}\text{Pb}$  is also non-radiogenic and hence its amount is constant since the formation of the rock. The half-life for the decay of  $^{238}\text{U}$  to  $^{206}\text{Pb}$  is 4.47 billion years, while that of  $^{235}\text{U}$  to  $^{207}\text{Pb}$  is 0.707 billion years.

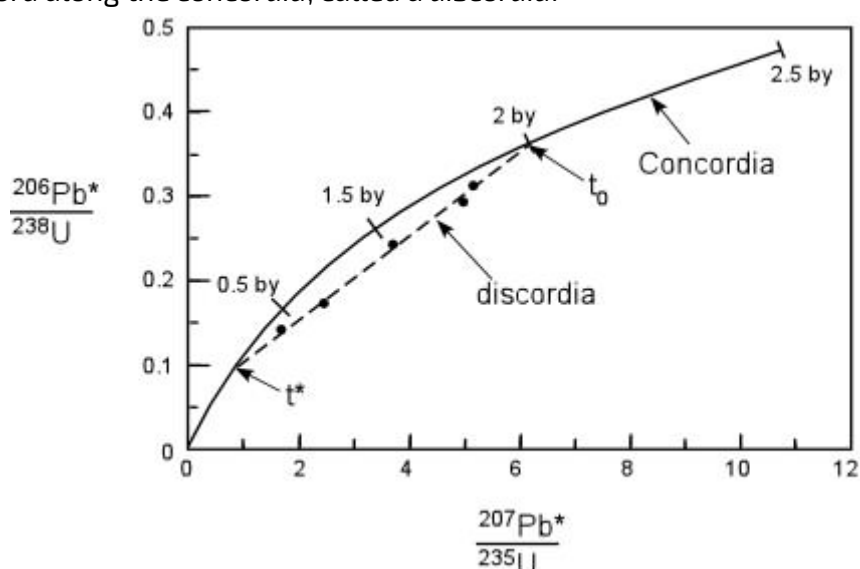
The following data was found in a sample of a volcanic rock:

	$N(^{238}\text{U}) / N(^{204}\text{Pb})$	$N(^{206}\text{U}) / N(^{204}\text{Pb})$	$N(^{235}\text{U}) / N(^{204}\text{Pb})$	$N(^{207}\text{U}) / N(^{204}\text{Pb})$
Sample A	1.943	10.142	0.479	17.498
Sample B	0.935	9.682	0.267	15.429

The benefit of uranium-lead dating is that since two equations can be obtained from the data above, the veracity of the age can be determined. If the age of the sample obtained from both samples are sufficiently similar, the age of the rock is said to be *concordant*. If the age of the sample obtained from both samples are different, the age of the rock is said to be *discordant*.

- 7) Write down two isochron equations, corresponding to the decay of  $^{238}\text{U}$  to  $^{206}\text{Pb}$  and  $^{235}\text{U}$  to  $^{207}\text{Pb}$  respectively. However, do not approximate  $e^x$  in your isochron equation. Consequently, use these two isochron equations to obtain two possible values of the age of the rock. Are these ages *concordant* or *discordant*?

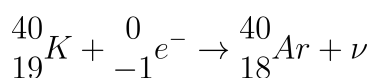
When plotting a graph of the ratio of  $^{238}\text{U}/^{206}\text{Pb}$  against  $^{235}\text{U}/^{207}\text{Pb}$ , concordant ages should form a curve, called a *concordia*. In practice, the ages are often *discordant*, leading to a separate chord along the *concordia*, called a *discordia*.



- 8) Give a possible reason why a *discordia* curve may be formed, and hence suggest possible interpretations of  $t_0$  and  $t^*$  in the diagram above.

## Problem x: Solution

- 1) Write down the nuclear equation representing the decay, and identify the type of decay involved. A particle **Y** is emitted. What is the identity of this particle?



This is an electron capture.

The particle **Y** is a neutrino.

**1 point for correct nuclear equation. (0.5 points for a correct  $\beta^{+}$  decay)**

**1 point for stating electron capture.**

**1 point for stating particle Y is a neutrino.**

- 2) Assuming that before any radioactive decay occurred, the number of argon-40 atoms was  $D_0$ . Let the number of daughter nuclides ( ${}^{40}\text{Ar}$ ) at a time,  $t$ , be  $D$ . If the current number of parent nuclides ( ${}^{40}\text{K}$ ) was  $N_p$ , write an equation relating  $t$  to  $D$ ,  $D_0$ ,  $N_p$  and its half-life,  $t_{1/2}$ . This is commonly known as the age equation.

Let  $N_0$  be the initial number of parent nuclides.

$$N_p = N_0 e^{-\frac{\ln 2}{t_{1/2}} t} \Rightarrow N_0 = N_p e^{\frac{\ln 2}{t_{1/2}} t}$$

Since parent nuclides all decay into daughter nuclides,

$$D - D_0 = N_0 - N_p = N_p (e^{\frac{\ln 2}{t_{1/2}} t} - 1)$$

Hence, rearranging the equation,

$$t = \frac{t_{1/2}}{\ln 2} \ln \left( 1 + \frac{D - D_0}{N_p} \right)$$

**1 point for identifying the first-order relationship between  $N_p$  and  $N_0$  and rearranging it to make  $N_0$  the subject.**

**1 point for writing  $D - D_0$  in terms of  $N_p$  only.**

**1 point for rearranging the equation to make  $t$  the subject of the equation.**

- 3) Assuming that there were no  ${}^{40}\text{Ar}$  in the rock at the beginning and none has escaped subsequently. Determine the age of the rock. Explain clearly if your answer will be an overestimate or underestimate if some argon has escaped.

Substituting in  $\frac{D}{N_p} = \frac{9}{1}$ ,  $t = 4.65 \times 10^5$  years.

Underestimate. Consider that  $t = \frac{t_{1/2}}{\ln 2} \ln \left( 1 + \frac{D - D_0}{N_p} \right)$  from (2). If some escape of argon occurred, the amount of argon-40 left would be lower than the true reading, and  $D$  above would be lower than the true reading. Hence, the ratio  $D/N_p$  would be smaller than the true value, and the age of the rock would thus be lower than the true age.

**1 point for the correct age of the rock.**

**1 point for stating underestimate.**

**0.5 points for stating that  $D$  is smaller than true reading.**

**0.5 points for justifying using the equation obtained earlier.**

- 4) Write down an equation relating the number of  $^{87}\text{Sr}$  atoms produced by decay, the number of  $^{87}\text{Sr}$  atoms present in the sample currently, and the initial number of  $^{87}\text{Sr}$  atoms in the sample. Using a method similar to that of (2), express the current ratio of  $^{87}\text{Sr}/^{86}\text{Sr}$  atoms in terms of their initial ratios and an appropriate ratio of  $^{87}\text{Rb}$  atoms with another atom. [You can use  $\lambda$  to represent the rate constant of the decay for all subsequent parts.]

It is known that  $^{87}\text{Sr}$  formed from decay must be from any  $^{87}\text{Sr}$  present -  $^{87}\text{Sr}$  present at the beginning. Hence, the following equation is obtained.

$^{87}\text{Sr}_{\text{decay}} = ^{87}\text{Sr}_t - ^{87}\text{Sr}_0$ , where  $^{87}\text{Sr}_{\text{decay}}$  is the number of  $^{87}\text{Sr}$  atoms formed from decay,  $^{87}\text{Sr}_t$  is the number of  $^{87}\text{Sr}$  atoms at a certain point in time,  $^{87}\text{Sr}_0$  is the number of  $^{87}\text{Sr}$  atoms initially present.

Making use of the fact that  $^{87}\text{Sr}_{\text{decay}} = ^{87}\text{Rb}(e^{\lambda t} - 1)$ , substitute this into the equation above and divide by  $^{86}\text{Sr}$ , which can be treated as a constant at all points in time due to it being non-radiogenic. Consequently, the following equation is obtained.

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_t = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_t (e^{\lambda t} - 1)$$

**1 point for writing down the  $^{87}\text{Sr}_{\text{decay}}$  equation. (0 points for improperly defined variables)**

**1 point for recognising the  $^{87}\text{Sr}_{\text{decay}}$  equation using (3).**

**1 point for the substitution and dividing it by  $^{86}\text{Sr}$  throughout as implied by the question.**

- 5) Hence, using the above approximation, suggest a possible linear graph which can be plotted from the data of the ratios of  $^{87}\text{Sr}/^{86}\text{Sr}$  atoms and the ratio of  $^{87}\text{Rb}/^{86}\text{Sr}$  at different points in time. What does the gradient of the graph represent, and what is its value? What does the y-intercept of the graph represent?

It is known that since  $t_{1/2}$  is very large,  $\lambda$  must be very small. Hence,  $e^{\lambda t} - 1$  can be approximated as  $\lambda t$ .

Hence, rewrite the equation obtained above.

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_t = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \left[t \cdot \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_t\right] \lambda$$

Plot the graph of  $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_t$  against  $\left[t \cdot \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_t\right]$ .

A straight-line curve will be obtained with the gradient  $= \lambda = 1.44 \times 10^{-11} \text{ yr}^{-1}$ , representing the rate constant of the decay, and y-intercept  $= \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0$ , representing the initial ratio of  $^{87}\text{Sr}$  to  $^{86}\text{Sr}$  in the sample.

**1 point for correct use of Taylor expansion to rewrite the equation into the linear law form. [0.5 points if the approximation is not used, as required by the question.]**

**0.5 points for each correct y- and x- variable to be plotted. (Total 1 point)**

**1 point for stating that gradient  $= \lambda$ , and its correct significance.**

**1 point for stating the correct significance of y-intercept.**

**1 point for calculating and stating the correct value of  $\lambda$ .**

- 6) Hence, by performing a linear regression or otherwise, determine the initial ratio of  $^{87}\text{Sr}/^{86}\text{Sr}$  atoms.

Since the product of time and  $^{87}\text{Sr}/^{86}\text{Sr}$  must be considered, simply calculate it, keeping in mind the powers associated with them.

Time / $\times 10^5$ years	5.0	10.0	15.0	20.0	25.0
$(^{87}\text{Sr}/^{86}\text{Sr}) \times 10^{-5}$	7.666	3.177	4.116	4.910	5.145
$^{87}\text{Rb}/^{86}\text{Sr}$	10.8	2.2	1.9	1.7	1.5
$(^{87}\text{Rb}/^{86}\text{Sr})(\text{Time}) / \times 10^5$ years	54	22	28.5	34	37.5

Now, the contestant could definitely perform a linear regression by hand – the formula is given, but an easier method would be to perform a linear regression by a calculator – most scientific calculators have this ability! [Do learn how to do it, it is especially useful for labs!]

From calculations, or by using the calculator, one obtains gradient =  $1.40 \times 10^{-11}$  (similar to the theoretical value) and y-intercept =  $1.24 \times 10^{-11}$ . Thus, the initial ratio of  $^{87}\text{Sr}/^{86}\text{Sr}$  atoms =  $1.24 \times 10^{-11}$ .

**1 point for correct calculation of  $(^{87}\text{Rb}/^{86}\text{Sr})(\text{Time})$ .**

**1 point for obtaining the y-intercept of the graph and stating that it is the initial ratio through linear regression.**

- 7) Write down two isochron equations, corresponding to the decay of  $^{238}\text{U}$  to  $^{206}\text{Pb}$  and  $^{235}\text{U}$  to  $^{207}\text{Pb}$  respectively. However, do not approximate  $e^x$  in your isochron equation. Consequently, use these two isochron equations to obtain two possible values of the age of the rock. Are these ages *concordant* or *discordant*?

$$\text{For } ^{238}\text{U to } ^{206}\text{Pb}, \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_t = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_0 + \left(\frac{^{238}\text{U}}{^{204}\text{Pb}}\right)_0 (e^{\lambda_{238}t} - 1)$$

$$\text{For } ^{235}\text{U to } ^{207}\text{Pb}, \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_t = \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_0 + \left(\frac{^{235}\text{U}}{^{204}\text{Pb}}\right)_0 (e^{\lambda_{235}t} - 1)$$

Hence, for  $^{238}\text{U}$  to  $^{206}\text{Pb}$ , letting  $a$  be the initial ratio of  $^{206}\text{Pb}$  to  $^{204}\text{Pb}$ ,

$$10.142 = a + 1.943(e^{(1.55 \times 10^{-10})t} - 1)$$

$$9.682 = a + 0.935(e^{(1.55 \times 10^{-10})t} - 1)$$

Solving simultaneously yields  $t = 2.424 \times 10^9$  years.

Similarly, for  $^{235}\text{U}$  to  $^{207}\text{Pb}$ , letting  $b$  be the initial ratio of  $^{207}\text{Pb}$  to  $^{204}\text{Pb}$ ,

$$17.498 = b + 0.479(e^{(9.804 \times 10^{-10})t} - 1)$$

$$15.429 = b + 0.267(e^{(9.804 \times 10^{-10})t} - 1)$$

Solving simultaneously yields  $t = 2.423 \times 10^9$  years.

These ages are *concordant* as within experimental limits, they are equal.

**1 point each for writing down each isochron equation. (Total 2 points)**

**1 point each for solving each set of simultaneous equations. (Total 2 points)**

**1 point for stating that the ages are concordant.**



- 8) Give a possible reason why a *discordia* curve may be formed, and hence suggest possible interpretations of  $t_0$  and  $t^*$  in the diagram above.

**Possible reasons:**

- Pb leakages due to events such as metamorphism could heat the crystal to the point where Pb will become mobile (or any other reasonable events)
- U leakages due to events such as metamorphism could heat the crystal to the point where U will become mobile (or any other reasonable events)

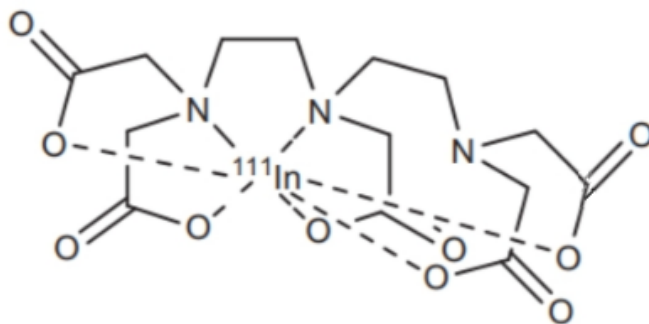
Hence,  $t^*$  represents the age of an event (such as metamorphism) that was responsible for the leakage of Pb/U, while  $t_0$  represents the date that the system became closed.

**1 point for a possible reason with appropriate justification. [0.5 points for stating either Pb or U leakage]**

**1 point for correct explanation of  $t^*$  and  $t_0$  each. (Total 2 points)**

## Problem 2: Radiopharmaceuticals

The structure below shows the structure of pentetate indium disodium, or  $^{111}\text{In}$ -DTPA (the cations are not shown for brevity). It is a mouse monoclonal antibody which is used for cancer diagnosis.



The  $^{111}\text{In}$  atom decays in the body through electron capture.

Electron capture is a process where an atom absorbs an electron and emits a neutrino (with a small mass and zero charge).

What is the oxidation state of the In atom in  $^{111}\text{In}$ -DTPA, and what is the oxidation state of the central atom in the decay product?

Denote an oxidation state of  $-x$  as  $0x$ , an oxidation state of  $+x$  as  $1x$  and an oxidation state of  $0$  as  $00$ . Your answer will be the two numbers concatenated.

For example, if the oxidation state of the In atom in  $^{111}\text{In}$ -DTPA is  $+1$ , and the oxidation state of the central atom in the decay product is  $-5$ , leave your answer as  $1105$ .

*Leave your answer a 4 digit number.*

*Solution:*

**1312**

Notice that there are 5 singly negatively charged ligands in  $^{111}\text{In-DTPA}$  (5  $\text{CO}_2^-$  ligands), and the nitrogen-containing ligands are all neutral.

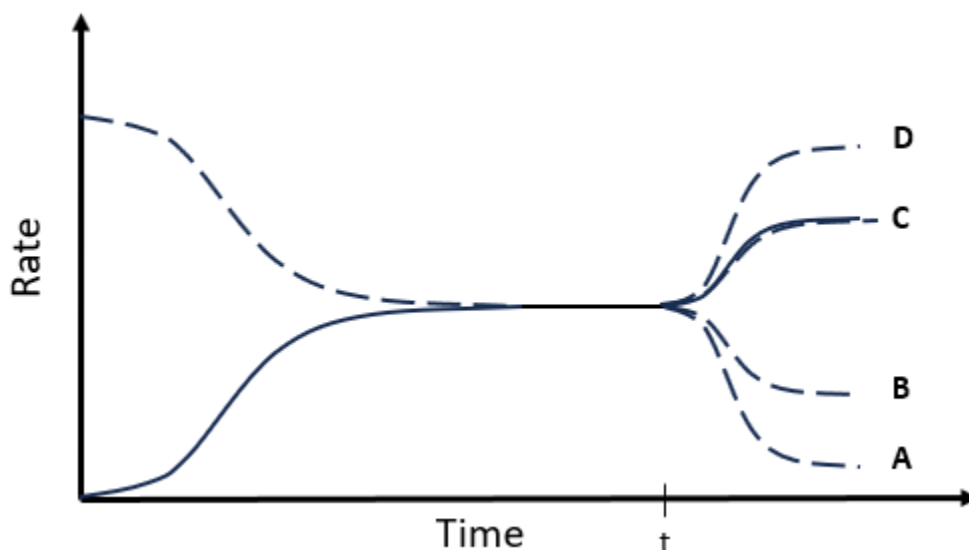
Since  $^{111}\text{In-DTPA}$  is a disodium salt, we can deduce that the oxidation state of the In atom is  $+5 - 2 = +3$ .

When the  $^{111}\text{In}$  atom decays via an electron capture mechanism, it becomes  $^{111}\text{Cd}$ . The oxidation state of  $^{111}\text{Cd}$  decreases by 1 to become +2.

Therefore, the answer is **1312**.

**Problem 13: Rates**

The rate of the gas phase isomerisation of  $\mathbf{A}(\text{g}) \rightleftharpoons \mathbf{B}(\text{g})$  was investigated. The rate-time graph was shown below. The dashed line shows the rate of the forward reaction, and the solid line the rate of the reverse reaction.



At time  $t$ , each of the following changes were made, and the rate of the reverse reaction is shown by the solid line.

- 1) A catalyst to produce **A** at a faster rate was added.
- 2) A catalyst to produce **B** at a faster rate was added.

Which of the dotted curves show how the rate of the forward reaction changes?

Present your answer as a single string comprising the answer to each part, in order. If your answer to part 1 is E, and your part to part 2 is F, leave your answer as EF.

*Leave your answer as a string of two letters.*

*Solution:*

**CC**

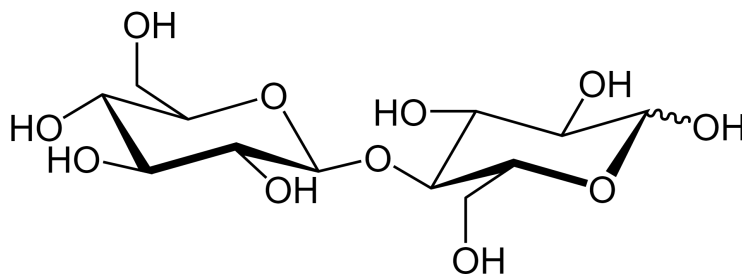
Catalysts increase the rate of the forward and reverse reactions by the same amount.

**Problem 14: Reduce Your Payments**

Source: <https://xkcd.com/1426/>

Paper cannot easily be reduced – so  $\text{NaBH}_4$  may not get rid of your debts.

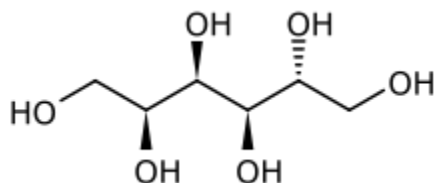
However, cellulose is a major component of paper, and upon treatment with exoglucanase, it forms smaller molecules like cellotriose and cellobiose. The structure of cellobiose is shown below:



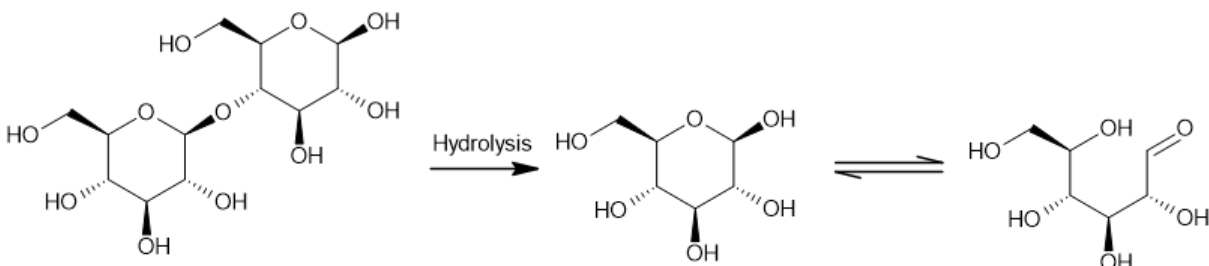
Upon treatment with an acid, then excess  $\text{NaBH}_4$ , what will the end product be? **Include stereochemistry.**

*Leave your answer as an organic structure.*

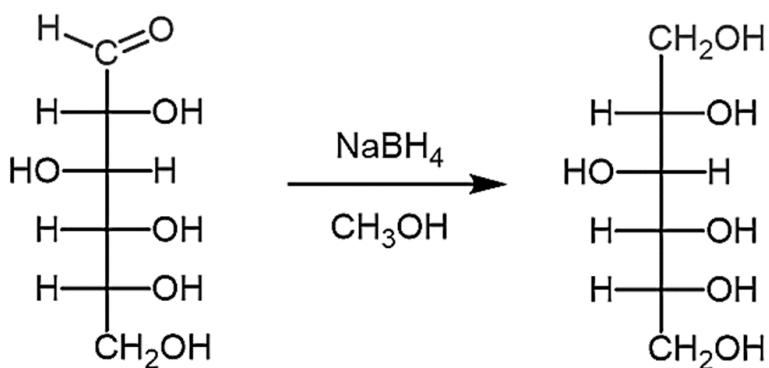
*Solution:*



In the hydrolysis, the 1,4-glycosidic linkages are hydrolysed to yield 2 glucose molecules:



Rewriting glucose into its fischer projection, we can write the reduction of D-glucose into D-sorbitol, which is our final product:



**Problem 11: Something doesn't add up...**

Compound **A** is an interesting compound with two anions, and  $\text{Ca}^{2+}$  as the cation. **A** has calcium constituting 85.1% by mass of the compound. One of the anions is the nitride ion,  $\text{N}^{3-}$ .

Let the mass of the heavier anion be  $a$ , and the lighter anion be  $b$ . What is the value of  $a/b$ ?

*Leave your answer to 5 significant figures.*



*Solution:*

**25538**

We can first start off by finding the molar mass of the compound. If calcium comprises 85.1% by mass of the compound, if the compound has one calcium atom, the molar mass is  $40.08 / 0.851 = 47.1$ , which is very low and hence unlikely (no two anions make sense).

We can construct a list of the possible molar masses for the sum of the two anions:

7.02, 14.04, 21.06, 28.08, ...

Recalling that the compound should be electrically neutral, going beyond 4 calcium atoms (+8 charge) is unlikely. When we try out common anions, we find that 3 and 4 calcium atoms do not make too much sense (e.g. 28.08 likely corresponds to either 2 nitride anions with total -6 charge).

If the compound has two calcium atoms, the molar mass is  $40.08 \times 2 / 0.851 = 94.20$ . This means the combined mass of the two anions is 14.0. This looks oddly reminiscent of the nitride anion... but what could the other anion be?  $\text{Ca}_2\text{N}$  is not charge balanced, with a missing -1 charge. Could the other anion be... an electron? Yes, it is! The compound is in fact, an electride,  $[\text{Ca}_2\text{N}]^+ \text{e}^-$ .

So now we know the two anions,  $\text{N}^{3-}$  and  $\text{e}^-$ . We get that the  $\text{N}^{3-}$  anion has a relative atomic mass of 14.01, and using  $1 \text{ amu} = 1.6605 \times 10^{-27} \text{ kg}$  from the data sheet, we know that the mass of  $\text{N}^{3-}$  is  $1.6605 \times 10^{-27} \times 14.01 = 2.3263605 \times 10^{-26} \text{ kg}$ .

We also know the mass of an electron to be  $9.1093 \times 10^{-31} \text{ kg}$ , also from the data sheet. Dividing their masses, we get  $(2.3263605 \times 10^{-26}) / (9.1093 \times 10^{-31}) = 25538.30152 = \mathbf{25538}$  (5 s.f.).