Singapore Chemistry League 2024

Core Problems and Solutions

Problem Setters

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List of Errata

All errata present in the competition duration (as at 100824, from 0900h to 1300h) have been rectified and highlighted in red in the subsequent solutions.

Any dispute of scores owing to the misattribution of points caused by the following errors have been addressed accordingly.

Core 3(b)	During the competition duration, teams who inputted the correct final answer “55.10” did not receive the allocated points. This has since been addressed.
Core 7(b)	This question will be voided (?)
Core 13(b)	Final answer was initially “ReI6”. This is inaccurate as there are actually 7 draws instead of 6 in the knockout tournament. The correct final answer should be “ReI7”.
Core 16	
Core 25(b)	Final answer was initially only “CH3N”. However, “H3CN” has been raised as an alternative answer as the order writing of elements in the cation was not specified. “H3CN” will also be accepted as a possible final answer.
Core 27(a)	Final answer was initially “173”. This is in units of m^3, which is incorrect as the problem states to leave the final answer in units of dm^3. The correct final answer should be “173000”.
Core 31(a)	Final answer was initially only “14778”. However, “6850728” has been raised as an alternative answer, as it is another PubChem CID number of CaO. “6850728” will also be accepted as a possible final answer.

The Organising Team takes full responsibility for the above errors.

Problem 1: Very Stable Compound

[6 points]

In a phenomenal feat of chemical synthesis paralleled only by the courage exhibited, Benz et. al from LMU Munich[1] synthesised C_2N_{16}, simultaneously proving that spectrometers are not the only things in the lab made of steel:

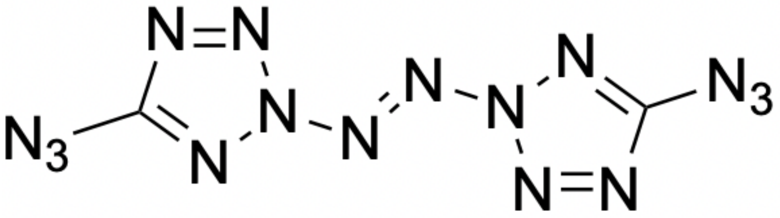

Figure 1: Structure of C_2N_{16}

(a) What is the percentage by mass of nitrogen in C_2N_{16}? Omit the percentage symbol in your answer. **[2 points]**
Leave your answer to 5 significant figures.

(b) What types of bonding does C_2N_{16} have? **[2 points]**

A) Instantaneous dipole-induced dipole interactions
B) Permanent dipole-permanent dipole interactions
C) Ionic bonds
D) Covalent bonds
E) Hydrogen bonds

Leave your answer as a string of capital letters in ascending alphabetical order. For example, if you believe A, B and D are correct, leave your answer as ABD.

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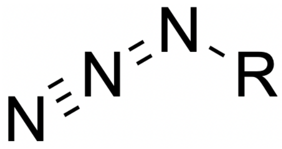
[1] Benz, Maximilian, et al. "Synthesis and Characterization of Binary, Highly Endothermic, and Extremely Sensitive 2,2′-Azobis(5-Azidotetrazole)." *Journal of the American Chemical Society*, vol. 144, no. 14, Apr. 2022, pp. 6143–47.

A re-inspection of Figure 1 will expose the fact that the problem setter was too lazy to draw out the $-N_3$ groups! Incidentally, this is called an azide group, and appears quite widely in organic compounds.

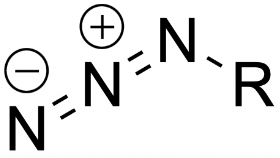
(c) Which of the following are acceptable Lewis structures for an azide group? R represents the rest of the molecule, which is irrelevant here. **[2 points]**

Leave your answer as a string of ***capital letters*** *in ascending alphabetical order. For example, if you believe A, B and D are correct, leave your answer as ABD.*

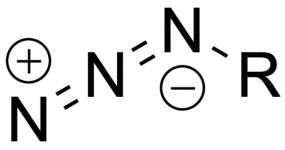
A



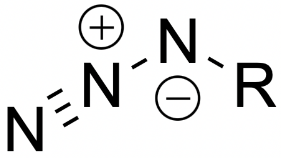
B



C



D



Solution:

(a) 90.322

$$\% \text{ by mass of nitrogen} = \frac{Number\ of\ N\ in\ one\ molecule\ of\ C_2N_{16} \times molar\ mass\ of\ N}{Molar\ mass\ of\ C_2N_{16}} \times 100\%$$

$$= \frac{16(14.01)}{16(14.01) + 2(12.01)} \times 100\%$$

$$= 90.322\% \text{ (5 s.f.)}$$

(b) AD

A) Practically any molecule will possess id-id interactions.

B) C_2N_{16} is centrosymmetric and does not have a net dipole moment, despite the existence of atoms of different electronegativity. The local dipole moments cancel out.

C) C_2N_{16} is a neutral molecule and would not hence have ionic interactions.

D) C—N bonds exist within the molecule.

E) Although N is present, the molecule lacks any H.

(c) BD

A) The central N is pentavalent and exceeds the full octet. N is unable to expand octet due to being in period 2[2] and lacking d orbitals, so this is impossible.

B) All N have a full octet - in your thought process, you can consider the charges to represent electrons added or removed from the valence electrons of that specific N. As a case in point, the positively charged N has a total valence electron count of 5 (from N) + 4 (from bonds) − 1 (due to charge) = 8.

C) The negatively charged N has 9 valence electrons.

D) All N have a full octet.

Problem prepared by: Lin Bohan

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[2] In reality the situation is a little more complicated, but this is a handy explanation nonetheless. The really fundamental reason is simply because N is too small to accommodate more than 8 valence electrons.

Problem 2: The Big Bang Theory

[6 points]

The vast majority of elements existing in the universe today came from nuclear fusion processes initiated within the picoseconds following the Big Bang. Quarks and other subatomic particles combined to form hydrogen, which then formed helium, neon, silicon and ever-heavier elements until an island of nuclear stability is reached at iron.

After ^{1}H, one of the earliest isotopes formed would have been ^{2}H, or D for deuterium.

(a) Which of the following statements are correct? **[2 points]**
Leave your answer as a string of ***capital letters*** *in ascending alphabetical order. For example, if you believe A, B and D are correct, leave your answer as ABD.*

A) D has the same physical properties as H but different chemical properties.
B) The nuclide notation for D would be $^{2}_{2}H$.
C) The mass of a D nucleus is almost, but not exactly twice of a H nucleus.
D) H is more abundant in nature than D.
E) The addition of one more proton to a deuterium nucleus would produce tritium, ^{3}H.

(b) The following is one of many fusion reactions that occur during stellar nucleosynthesis. What is the integer X? **[2 points]**

$$^{16}_{8}O + ^{16}_{8}O \rightarrow ^{X}_{14}Si + 2\ ^{1}_{1}H$$

Stars are not the only entities capable of nuclear fusion and fission. Modern technological breakthroughs have enabled humanity to achieve the holy grail of ancient alchemy - the transmutation of elements. Much of the heavy elements in Period 7 were created entirely synthetically.

One such element, Z, was discovered in the 20th century, and was produced by the following reaction:

$$A + B \rightarrow Z + {}^{1}_{0}n$$

Where A and B are two distinct elements. The following clues are given:

- Element A has no stable isotopes.
- Elements A and B differ in proton number by 55.
- Element B is a common catalyst used in steam reforming, the industrial process that generates H_2 gas. It can also be used in organic reactions, frequently for the cleavage of C—S bonds.

(c) What is the proton number of element Z? **[2 points]**

Solution:

(a) CD

A) D has the same physical properties as H but different chemical properties.

It is the exact opposite: isotopes have different physical properties but the same chemical properties.

B) The nuclide notation for D would be ${}^{2}_{2}H$.

It should be ${}^{2}_{1}H$, as the number on the bottom represents the proton number, which is still one.

C) The mass of a D nucleus is almost, but not exactly twice of a H nucleus.

Protons and neutrons slightly differ in mass, even though they are very close.

D) H is more abundant in nature than D.

The natural abundance of deuterium is 1 per approximately 6600 hydrogen atoms.

E) The addition of one more proton to a deuterium nucleus would produce tritium, ^{3}H.

This would be achieved by addition of a neutron to form the even heavier isotope of H, but not a proton. Adding a proton to deuterium would result in ^{3}He being formed instead.

(b) 30

$${}^{16}_{8}O + {}^{16}_{8}O \rightarrow {}^{30}_{14}Si + 2\ {}^{1}_{1}H$$

This is a straightforward matter of balancing the total nucleon number (or the total number of protons and neutrons) on both sides of the equation. So we form the equation $16 \times 2 = X + 2 \times 1$, giving $X = 32 - 2 = 30$.

(c) 111

B is Ni, which is indeed used as a catalyst in steam reforming, and is also used as an organic reducing agent in the form of Raney Ni. From there, we can obtain the identity of A, which has atomic number $28 + 55 = 83$. Contrary to popular belief, it indeed does not have any stable isotopes, although ^{209}Bi is exceptionally stable with a half-life of 2.01×10^{19} yr. Balancing proton numbers, we arrive at element Z, which turns out to be roentgenium.

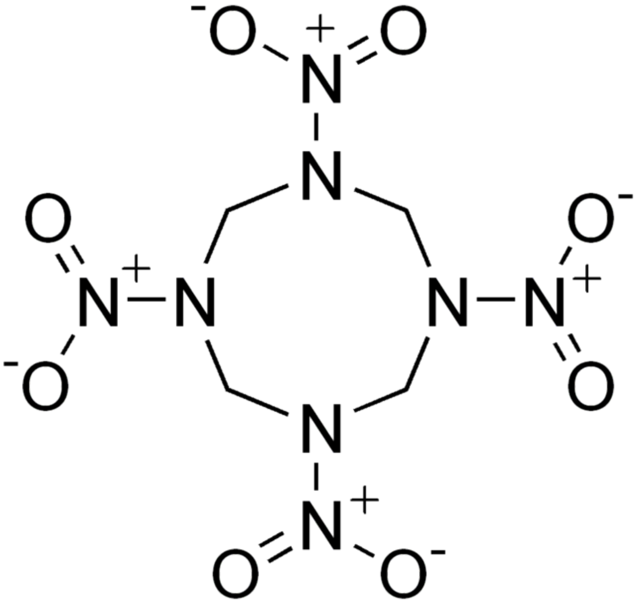
$$_{83}Bi \ + \ _{28}Ni \ \rightarrow \ _{111}Rg \ + \ _{0}^{1}n$$

Problem prepared by: Lin Bohan

Problem 3: TNT?

[4 points]

1,3,5,7-tetranitro-1,3,5,7-tetrazocane, more commonly known as HMX, is a powerful and relatively insensitive nitroamine high explosive. The structure of HMX is shown below.



The following equation represents the thermal decomposition of HMX ($C_4H_8N_8O_8$):

$$C_4H_8N_8O_8(s) \rightarrow 4\,N_2(g) + 4\,CO(g) + 4\,H_2O(g)$$

(a) Determine the magnitude of the standard enthalpy change of decomposition of HMX using the bond energies data given in the table below. **[2 points]**
Leave your answer to 4 significant figures, in units of kJ mol^{-1}.

	C≡O	N=O	C−H	C−N	N−N	N≡N	O−H
Bond energy / kJ mol^{-1}	1072	469	410	305	160	944	460

(b) Determine the heat produced when 10.00 g of HMX undergoes thermal decomposition. **[2 points]**
Leave your answer to 4 significant figures, in units of kJ.

Solution:

(a) 1632

$$\begin{aligned}\Delta H^{\ominus} &= (8\,\mathrm{BDE(C{-}H)} + 8\,\mathrm{BDE(N{=}O)} + 4\,\mathrm{BDE(N{-}N)} + 8\,\mathrm{BDE(C{-}N)}) \\ &\quad - (4\,\mathrm{BDE(N{\equiv}N)} + 4\,\mathrm{BDE(C{\equiv}O)} + 8\,\mathrm{BDE(O{-}H)}) \\ &= (8(410) + 8(469) + 4(160) + 8(305)) - (4(944) + 4(1072) + 8(460)) \\ &= -\,1632\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

At first glance the presence of a dative bond between the N and O in the nitro ($-NO_2$) group may be a bit confusing, but what is crucial to recognise is the presence of resonance forms which effectively makes the two N—O bonds equivalent, with bond strength between a single and double bond. Hence we can use the data for the $N{=}O$ bond in our calculations.

(b) 55.10

$$\begin{aligned}\text{Heat released, } q &= \frac{1632 \times 10.00}{4(12.01) + 8(1.008) + 8(14.01) + 8(16.00)} \\ &= 55.10\ \mathrm{kJ}\end{aligned}$$

Problem prepared by: Ranen Yong

Problem 4: Ice And Fire

[4 points]

Methane clathrate, or "fire-ice”, is a marine sediment that can be harvested from the ocean floor. While its appearance looks remarkably similar to that of normal ice, it gets its name from its combustible nature, due to its stored methane content:

(Image from https://geology.usgs.gov/connections/mms/joint_projects/methane.htm)

Under the high pressures and low temperatures at the bottom of the ocean, methane gas can get into gaps within the lattice structure of hydrogen-bonded water, forming solid ice with methane gas trapped inside.

(a) Methane clathrate has a molecular formula of $4CH_4 \cdot 23H_2O$. Find the percentage by mass of methane in methane clathrate. **[2 points]**
Leave your answer to 3 significant figures, omitting the % sign.

(b) It is given that the density of methane clathrate is 0.9 g cm^{-3}.
A 10 cm^3 piece of methane clathrate is harvested from the ocean floor. What volume of methane could be extracted from it, when it is brought back to the ocean surface (at 20 °C, 1 atm)? **[2 points]**
Leave your answer to 3 significant figures, in units of cm^3.

Solution:

(a) 13.4

M_r(Methane clathrate) = 4[12.01 + 4(1.008)] + 23[2(1.008) + 16.00]
= 478.536

$M_r(CH_4)$ = 12.01 + 4(1.008)
= 16.042

$\Rightarrow$ Percentage by mass of $CH_4 = \frac{4(16.042)}{478.536} \times 100\%$
$\approx 13.409\%$
= 13.4% (3 s.f.)

(b) 1810

Mass of methane clathrate formed = 0.9 × 10
= 9.0 g

Given composition of methane clathrate is about 13.409% CH_4 by mass,

Mass of CH_4 = 9.0 × 13.409%
= 1.20681 g

Amount of $CH_4 = \frac{1.20681}{12.01+4(1.008)}$
= 0.075228 mol (5 s.f.)

From pV = nRT,

Volume of CH_4 extractable $= \frac{(0.075228)(8.3145)(273.15+20)}{101325}$
= 0.00181 m^3 (3 s.f.)
= 1810 cm^3

Problem prepared by: George Zhou

Problem 5: Back And Forth

[5 points]

Beakers P and Q are placed side by side. Initially, P contains 100 cm^3 of 1.00 M Na^+ solution, while Q contains the same volume of 1.00 M K^+ solution .

10.0 cm^3 of P's contents are pipetted into Q, which is then stirred. Then, 10.0 cm^3 of Q's contents are pipetted back into P, which is then stirred. This constitutes one 'cycle' of mixing.

(a) What is the concentration of Na^+ in P after **four** cycles, in mol dm^{-3} ? **[2 points]**
Leave your answer to 3 significant figures.

(b) How many cycles of mixing will it take, minimally, for the concentrations of Na^+ and K^+ in P to be within 0.0100 M of each other? **[3 points]**

Solution:

(a) 0.724
(b) 23

For this question, it is easier to work with amounts than concentrations. There are two things to note:

- The total amount of Na^+ and K^+ in each beaker always adds up to 0.1 mol. When $\frac{1}{10}$th of P (0.01 mol) is transferred to Q, P now has 0.09 mol of ions while Q has 0.11 mol. When $\frac{1}{11}$th of Q (also 0.01 mol) is transferred back to P, both P and Q have 0.1 mol of ions.
- The Na^+ : K^+ proportions are mirrored. If there is n mol of sodium in P, then there is n mol of potassium in Q, and vice versa. This is because, after every cycle, a) the volume of each beaker is constant at 100 cm^3, and b) the total amount of sodium and potassium present is constant at 0.1 mol each.

Suppose P contains n mol of Na^+ and $\left(\frac{1}{10} - n\right)$ mol of K^+. Q must have n mol of K^+ and $\left(\frac{1}{10} - n\right)$ mol of Na^+.

P	Moles of Na^+	n	$\frac{1}{10}n$ mol of Na^+ and $\frac{1}{100} - \frac{1}{10}n$ mol of K^+ transferred from P to Q.	$\frac{9}{10}n$	$\frac{1}{110} - \frac{9}{110}n$ mol of Na^+ and $\frac{1}{1100} + \frac{9}{110}n$ mol of K^+ transferred from Q to P.	$\frac{1}{110} + \frac{9}{11}n$
	Moles of K^+	$0.1 - n$		$\frac{9}{100} - \frac{9}{10}n$		$\frac{1}{11} - \frac{9}{11}n$
Q	Moles of Na^+	$0.1 - n$		$\frac{1}{10} - \frac{9}{10}n$		$\frac{1}{11} - \frac{9}{11}n$
	Moles of K^+	n		$\frac{1}{100} + \frac{9}{10}n$		$\frac{1}{110} + \frac{9}{11}n$

Therefore we have the recursive relationship $n_{k+1} = \frac{1}{110} + \frac{9}{11}n_k$, where n_k is the amount (in moles) of sodium in P after k cycles. Since by definition $n_0 = \frac{1}{10}$, we can derive the general formula for n_k:

$$n_k = \frac{1}{110}\left[1 + \frac{9}{11} + \left(\frac{9}{11}\right)^2 + \ \dots \ + \left(\frac{9}{11}\right)^{k-1}\right] + \left(\frac{9}{11}\right)^k\left(\frac{1}{10}\right)$$

$$= \frac{1}{20}\left[1 + \left(\frac{9}{11}\right)^k\right] \text{(Using the formula for sum of a GP)}$$

So after 4 cycles, [Na$^+$] in P $= \frac{1}{0.1}n_4 = \frac{1}{0.1} \times \frac{1}{20}\left[1 + \left(\frac{9}{11}\right)^4\right] =$ **0.724** M (3 s.f.)

For (b), we just need to find the smallest value of k for which $[\text{Na}^+] - [\text{K}^+] < 0.01$ mol dm^{-3} in beaker P.

$$[\text{Na}^+] = \frac{1}{0.1} \times \frac{1}{20}\left[1 + \left(\frac{9}{11}\right)^k\right] = \frac{1}{2}\left[1 + \left(\frac{9}{11}\right)^k\right]$$

$$[\text{K}^+] = \frac{1}{0.1} \times \left\{0.1 - \frac{1}{20}\left[1 + \left(\frac{9}{11}\right)^k\right]\right\} = 1 - \frac{1}{2}\left[1 + \left(\frac{9}{11}\right)^k\right]$$

$$[\text{Na}^+] - [\text{K}^+] = \frac{1}{2}\left[1 + \left(\frac{9}{11}\right)^k\right] - 1 + \frac{1}{2}\left[1 + \left(\frac{9}{11}\right)^k\right] = \left(\frac{9}{11}\right)^k$$

$$\left(\frac{9}{11}\right)^k < 0.01$$

$$k > \frac{\ln(0.01)}{\ln(\frac{9}{11})} = 22.94$$

$$k = \mathbf{23}$$

Problem prepared by: Wang Jiahua

Problem 6: Hypothermia

[5 points]

It's winter in London, and Bobo wishes to find a way to use chemistry to warm his hands.

Bobo has two metal powders to experiment with. He has iron powder, which can produce heat via an oxidation reaction with atmospheric O_2 (g), and aluminium powder, which can produce heat via a metal-alkali reaction with NaOH (aq). He prepares a calorimeter for each setup to find out which reaction can produce the most heat given the same total mass of reactants.

In the oxidative setup, he uses 5.0 g of iron powder. He also adds 5.0 g of vermiculite, a catalyst which, like a sponge, holds an excess amount of water to allow both reactions to occur at a sufficiently high rate.

In the metal-alkali setup, he uses aluminium powder, calcium oxide powder, and sodium carbonate powder mixed in stoichiometric ratios adding up to 5.0 g total. He also adds the same 5.0 g of vermiculite. The alkali is generated in situ when the calcium oxide powder reacts with the excess water in the vermiculite to form calcium hydroxide, which then reacts with the sodium carbonate to form sodium hydroxide.

(a) What is the amount of aluminium powder used in the metal-alkali setup?
Leave your answer to 3 significant figures, in units of moles. **[3 points]**

Assume that the enthalpy changes of the two exothermic reactions are as follows:

	Equation	**ΔH° / kJ mol^{-1}**
Oxidative setup	$4Fe\ (s) + 3O_2\ (g) \rightarrow 2Fe_2O_3\ (s)$	−1650
Metal-alkali setup	$2Al\ (s) + 2NaOH\ (aq) + 2H_2O\ (l) \rightarrow 2NaAlO_2\ (aq) + 3H_2\ (g)$	−850

(b) In theory, assuming both reactions go to completion, which setup will produce the greater amount of heat?
Input your answer as the atomic symbol of the metal element involved (Fe ***or*** *Al). The answer is case-sensitive.* **[2 points]**

Solution:

(a) 0.0463

In the metal-alkali setup,
The reactions to generate NaOH is as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$$

I mol of CaO reacts completely with 1 mol of Na_2CO_3 to form 2 mol of NaOH.
2 mol of NaOH reacts completely with 2 mol of Al.
Therefore, stoichiometric ratios of CaO : Na_2CO_3 : Al required in one unit of complete reaction is 1:1:2.

M_r of CaO $= 40.08 + 16.00 = 56.08$
M_r of $Na_2CO_3 = 2(22.99) + 12.01 + 3(16.00) = 105.99$

Amount of CaO used $= \frac{5.0}{1(56.08)+1(105.99)+2(26.98)} = 0.023145$ mol
Amount of Al used $= 0.023145 \times 2 = 0.046290$ mol $= 0.0463$ mol (3 s.f.)

(b) Fe

In the oxidative setup,
Amount of Fe $= \frac{5.0}{55.85} = 0.089526$ mol (5 s.f.)
Amount of heat produced $= 0.089526 \div 4 \times 1650 = 36.929$ kJ (5 s.f.)

In the metal-alkali setup,
Amount of heat produced $= 0.023145 \times 850 = 19.673$ kJ (5 s.f.)

In theory, the oxidative setup could produce about twice the amount of heat produced by the acid-alkali setup. In fact, we find that the oxidative reaction is also safer and more practical, as the acid-alkali setup could produce almost 1700 cm^3 of flammable H_2 gas.

Hence we input the answer Fe.

Problem prepared by: George Zhou

Problem 7: Chemicle

[6 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 colour of the tiles will change to show how close your guess was to the word.

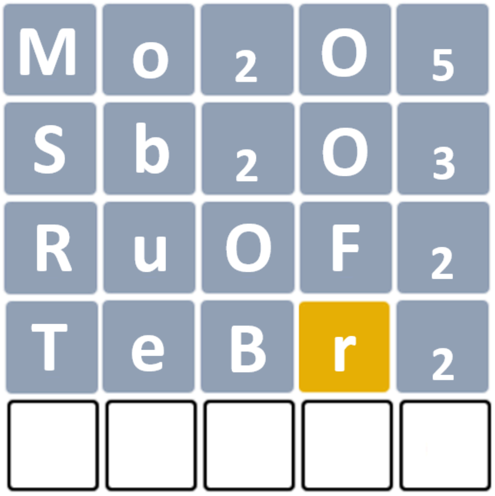
A green letter **W** means that it is in the word and is in the correct spot.

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

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

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

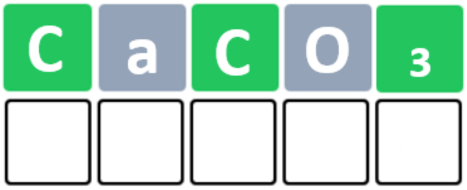
In *chemicle* (which is an actual game, by the way), you get to guess chemical formulae that are 5 characters long, for example, $NaBH_4$. Do note that it is case-sensitive, however. That is, if the answer is $AlCl_3$, and you choose $NaBH_4$, the lowercase 'a' will be marked as grey.



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).

[Note that the answer may not correspond to Chemicle's actual accepted list.]

(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 $\overline{ABCDEFGHIJ}$. **[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 Cl_2 gas into an acid, then heating it with aqueous 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 $\overline{ABCDEFGHI}$. **[2 points]**

Solution:

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

(a) ZrCl4IrCl4

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. $CrCl_4$ is unstable, existing at elevated temperatures but reverting to $CrCl_3$ and Cl_2 at room temperature. $PrCl_4$ 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: **$ZrCl_4$ and $IrCl_4$**.

(b) 5

Now, it is clear that the answer is of the form C_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
2. Co
3. Cd
4. Cs
5. Ce
6. Cf
7. Cm
8. Cn

Of these, we can eliminate Co because $CoCl_3$ is highly unstable, only stabilised at very low (−60 °C) or very high (644 °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}Cn).

$CrCl_3$ and $CeCl_3$ are common compounds found in laboratories. $CfCl_3$ and $CmCl_3$ do exist, also they are radioactive, but with a half-life of hundreds of days. So we have 4 inorganic solutions.

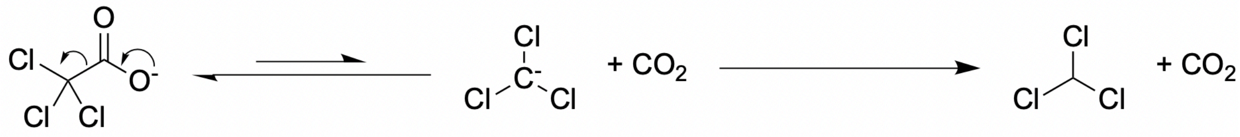
Interestingly, we note that an organic compound can also be a solution: $CHCl_3$.

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

(c) CHCl3CO2

$CHCl_3$ can be synthesised by passing Cl_2 gas through ethanoic acid, CH_3CO_2H, to form trichloroacetic acid, CCl_3CO_2H. This undergoes alkaline solvolysis via haloform reaction to form $CHCl_3$ and CO_2.

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



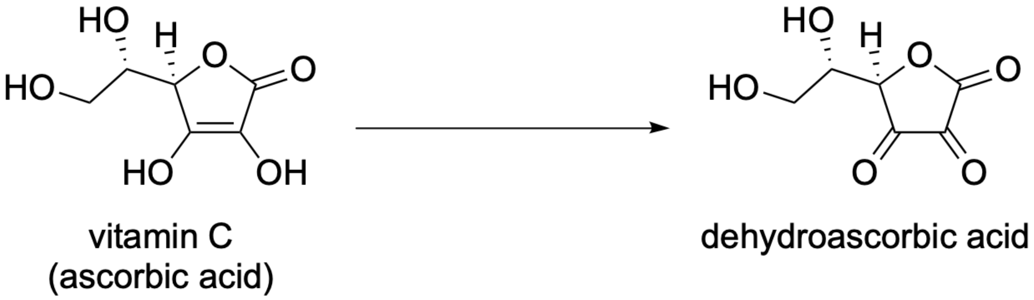
* A more complicated mechanism involving ortho-acid formation has recently been proposed, but is not presented here for the sake of simplicity.

Problem prepared by: Lim Dillion

Problem 8: The T in Vitamin C Stands For Titration

[5 points]

Cheng Zhi wants to measure the amount of vitamin C present in the juice of each orange. Vitamin C is a reducing agent, hence it is classified as an antioxidant. It is oxidised to dehydroascorbic acid.



In order to determine the amount of vitamin C, he sets up the following experiment:

1. Juice one orange and filter the extract.
2. Pipette 25.0 cm^3 of the orange juice into a 250 cm^3 conical flask.
3. Add 2 cm^3 of saturated KI (aq) solution and 10 cm^3 of 2 mol dm^{-3} H_2SO_4 (aq) using a measuring cylinder.
4. Titrate the mixture against 0.00100 mol dm^{-3} KIO_3 (aq) solution.
5. Once the mixture starts to remain pale yellow for longer periods upon addition of the KIO_3 solution, add 10 drops of 1% starch solution.
6. Continue titrating against KIO_3 (aq) until a pale blue colour persists in the mixture.

When KI and KIO_3 are added together in acidic medium, a comproportionation reaction occurs.

At the end of the experiment, an average titre value of 26.75 cm^3 was obtained.

(a) Calculate the amount of iodine formed in the experiment.
Leave your answer to 3 significant figures, in units of moles. **[2 points]**

(b) Calculate the average mass of vitamin C in the juice of each orange, given that the average volume of juice obtained from one orange is 100 cm^3.
Leave your answer to 3 significant figures, in units of grams. **[3 points]**

Solution:

(a) 0.0000803

Upon addition of iodate(V) ions, it reacts with iodide ions to form iodine, which is reduced by ascorbic acid. Once all the ascorbic acid is consumed, the small amount of excess iodine produced forms a dark-blue starch-iodine complex.

Firstly, looking at the comproportionation of iodide and iodate(V),

$$5\,I^- + IO_3{}^- + 6\,H^+ \longrightarrow 3\,I_2 + 3\,H_2O$$

Therefore,

$$\begin{aligned} n(I_2) = 3n(KIO_3) &= 3\left(\frac{26.75}{1000} \times 0.00100\right) \\ &= 0.000\,080\,25 \text{ mol} \end{aligned}$$

(b) 0.0565

Dehydroascorbic acid has two protons less than ascorbic acid:

$C_6H_8O_6$ (ascorbic acid) → $C_6H_6O_6$ (dehydroascorbic acid) + $2H^+$ + $2e^-$
$I_2 + 2e^- \rightarrow 2I^-$

Overall: **ascorbic acid + $2I^-$ → dehydroascorbic acid + $2H^+$ + I_2**

Hence,

$$n(I_2) = n(\text{ascorbic acid}) = 0.000\,080\,25 \text{ mol}$$

Considering that only 25.0 cm^3 of 100 cm^3 of juice was used,

$$\begin{aligned} M_r(C_6H_8O_6) &= 176.124 \\ m(C_6H_8O_6) &= 0.00008025 \times \frac{100}{25.0} \times 176.124 \\ &= 0.0565 \text{ g} \quad (3 \text{ s.f.}) \end{aligned}$$

Problem prepared by: Timothy Chek

Problem 9: My Favourite Elements

[4 points]

Five chemists, Anna, Ben, Cathy, David and Eddie each work in a different field of chemistry (organic, inorganic, analytical, physical and biological chemistry, not in any order) in five different laboratories. Their labs are located in the same building and arranged in a row from left to right. Each chemist also has a **unique** favourite element in either period 2 or 3.

1) Anna is the physical chemist and her favourite element is a metalloid.
2) Eddie, who is not the analytical chemist, occupies the rightmost lab.
3) The inorganic chemist's favourite element is a metal and a key component of psychiatric medications.
4) A chemist whose favourite element is in group 14 works in the lab between Ben's and the inorganic chemist's.
5) Eddie's favourite element is in period 3.
6) David does not work in inorganic chemistry.
7) The physical chemist's lab is to the right of the analytical chemist's, with one other lab separating them.
8) A compound containing only David's and his neighbour's favourite elements is a gas at r.t.p, and has a tetrahedral structure.
9) The organic chemist's favourite element is carbon (surprise, surprise) and their lab is not adjacent to Eddie's.
10) The chemist whose favourite element is in period 3 and known for its many differently coloured allotropes uses a lab adjacent to Cathy's.
11) Of the favourite elements, two are in the same group and two are consecutive in the same period.

List the five chemists' favourite elements in a row according to which lab they occupy, from left to right. Note that "left" and "right" in the question refer to **your** left and right.

Leave your answer as a concatenated string of five element symbols. The answer is case-sensitive. For example, if the chemist in the first lab has sodium as their favourite, the chemist in the second lab has magnesium as their favourite, and so on (the first five period 2 elements), input "NaMgAlSiP".

Solution:

FCSiLiP

From clue 1, Anna's favourite element could be boron or silicon. Clue 4 mentions a group 14 element as a favourite, so let's assume Anna's favourite is **silicon** (we'll come back to this later).

From clue 3, the inorganic chemist must have **lithium** as his favourite — lithium salts such as Li_2CO_3 are commonly prescribed for bipolar disorder and manic episodes[3].

From clues 3 and 5, Eddie cannot be the inorganic chemist since his favourite element (lithium) would be in period 2.

From clues 4 and 6, Cathy must work in inorganic chemistry (because Anna, Ben, David and Eddie all do not).

From clue 4, Ben, Anna and Cathy must be together (in that order, or reverse). From clue 7, these three must occupy the middle three labs (so Anna's lab is in the middle), and the analytical chemist (who must be David) must occupy the first.

From clue 9, Ben is the organic chemist (leaving Eddie as the biological chemist). From clue 8, because Ben's favourite is **carbon**, David's favourite must be **fluorine** (CF_4 is a gas at r.t.p, CCl_4 is a liquid, and H is in period 1 so the gas cannot be CH_4). Ben must also occupy the second lab from the left (so Cathy's lab is the second from the right).

Finally, from clue 10, Eddie's favourite element must be **phosphorus**. Phosphorus can exist as white, red, black and violet phosphorus under standard conditions, all with different molecular structures.

Clue 11 confirms this: carbon and silicon are both in group 14, while silicon and phosphorus are consecutive elements in period 3.

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[3] https://www.mayoclinic.org/drugs-supplements/lithium-oral-route/description/drg-20064603

Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
David	Ben	Anna	Cathy	Eddie
Analytical	Organic	Physical	Inorganic	Biological
F	**C**	**Si**	**Li**	**P**

Hence we input **FCSiLiP.**

Note: Assuming Anna's favourite is boron instead, David must occupy the lab in between Ben's and Cathy's, who in turn must be the inorganic chemist (clue 6). From clue 7, Anna must occupy the lab beside Eddie, and David must be the analytical chemist. However, clue 8 means that Ben's favourite must be fluorine and David's favourite carbon (since his favourite is in group 14), which is a contradiction since David isn't the organic chemist. Furthermore, David's lab is adjacent to Cathy's but silicon (which is in group 14 and period 3) is *not* known for having many coloured allotropes. Hence Anna's favourite cannot be boron!

Problem prepared by: Wang Jiahua

Problem 10: Thermite Heist

[3 points]

In *Breaking Bad*, Walter White and Jesse Pinkman steal a barrel of methylamine required for their synthesis of a certain crystalline drug. To break into the warehouse, they disable the metal lock with thermite.

Thermite is a pyrotechnic mixture of Iron (III) oxide and Aluminium powder. When ignited, an extremely exothermic redox reaction occurs.

$$Fe_2O_3\ (s) + 2\ Al\ (s) \rightarrow Al_2O_3\ (s) + 2\ Fe\ (s)$$

The products melt due to the large amount of heat produced.

Suppose 600 g of perfectly stoichiometric thermite powder is ignited at 25 °C, and all the products reach the same final temperature. 30% of the heat produced is lost to the surroundings. Using **only** the information below, what temperature (in °C) will the products reach?

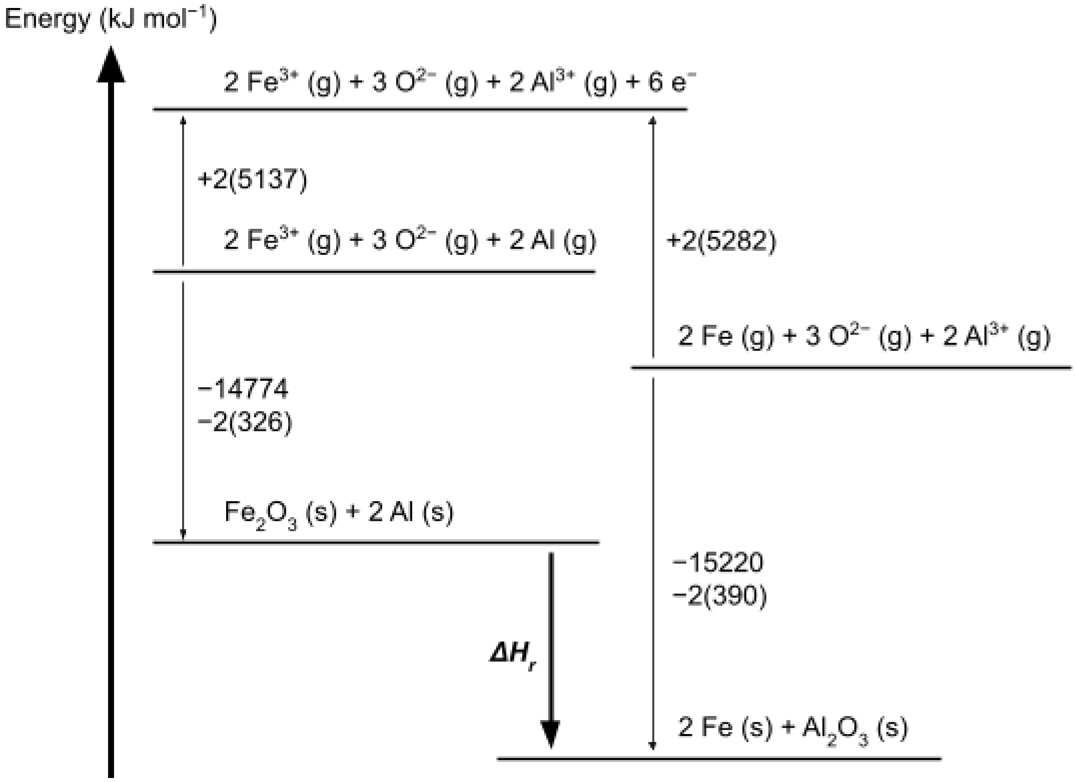
Lattice energy of Fe_2O_3	**−14774 kJ mol^{-1}**	Lattice energy of Al_2O_3	**−15220 kJ mol^{-1}**
Σ of first 3 ionisation energies of Fe	**5282 kJ mol^{-1}**	Σ of first 3 ionisation energies of Al	**5137 kJ mol^{-1}**
ΔH_{atom} (Fe)	**390 kJ mol^{-1}**	ΔH_{atom} (Al)	**326 kJ mol^{-1}**
Specific heat capacity of Fe (s)	**25.1 J mol^{-1} K^{-1}**	Specific heat capacity of Al_2O_3 (s)	**90.7 J mol^{-1} K^{-1}**
Melting point of Fe	**1538 °C**	Melting point of Al_2O_3	**2051 °C**
ΔH_{fus} (Fe)	**13.8 kJ mol^{-1}**	ΔH_{fus} (Al_2O_3)	**111.5 kJ mol^{-1}**
Specific heat capacity of Fe (l)	**50.2 J mol^{-1} K^{-1}**	Specific heat capacity of Al_2O_3 (l)	**170.3 J mol^{-1} K^{-1}**

Leave your answer to 3 significant figures. Assume the values for enthalpy change and specific heat capacity to be constant.

Solution:

2620

Using the information, the following energy level diagram can be constructed:



$\Delta H_r = 14774 + 2(326) + 2(5137) - 2(5282) - 15220 - 2(390) =- 864$ kJ mol^{-1}

Moles of reaction $= \frac{600}{159.7+2(26.98)} = 2.8082$ mol, so 5.6164 mol of Fe (s) and 2.8082 mol of Al_2O_3 (s) are produced.

Heat absorbed by products = 864 kJ mol^{-1} × 2.8082 mol × 0.7 = 1698.4 kJ

Energy needed to heat 5.6164 mol of Fe (s) from 25 °C to 1538 °C = (0.0251)(5.6164)(1538 − 25) = 213.29 kJ
Energy needed to melt 5.6164 mol of Fe (s) at 1538 °C = (13.8)(5.6164) = 77.506 kJ
Energy needed to heat 5.6164 mol of Fe (l) from 1538 °C to 2051 °C = (0.0502)(5.6164)(2051 − 1538) = 144.64 kJ

Energy needed to heat 2.8082 mol of Al_2O_3 (s) from 25 °C to 2051 °C = $(0.0907)(2.8082)(2051 - 25) = 516.03$ kJ
Energy needed to melt 2.8082 mol of Al_2O_3 (s) at 2051 °C = $(111.5)(2.8082) = 313.11$ kJ

Energy left = $1698.4 - 213.29 - 77.506 - 144.64 - 516.03 - 313.11 = 433.8$ kJ

Let temperature change above 2051 °C be ΔT.

$$(5.6164)(0.0502)\Delta T + (2.8082)(0.1703)\Delta T = 433.8$$

$$\Delta T = 570.65\ °\mathrm{C}$$

Hence final temperature reached is 2051 + 570.65 = **2620 °C** (3 s.f.).

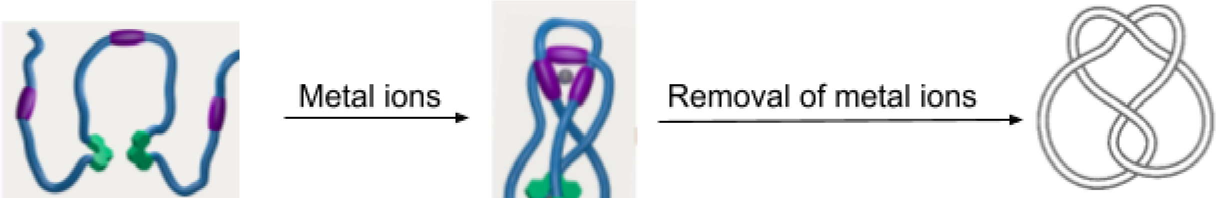
Note that this figure is independent of the amount of thermite powder to start with.

Problem prepared by: Wang Jiahua

Problem 11: Do Knot Attempt This At Home

[5 points]

The synthesis of a molecular knot has recently been accomplished by a team of chemists using some transition metal cations:

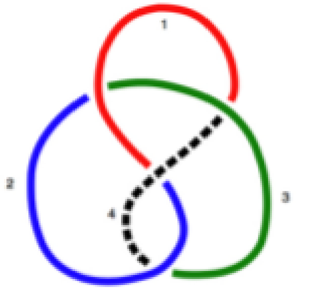


Structure **X**

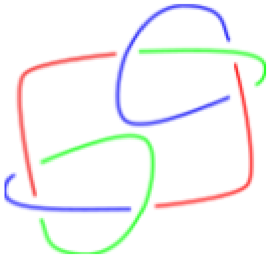
For knots to be transformed from one to another without breakage of the string, the knots must have the same knot invariants (i.e. a quantity defined for each knot which is the same for equivalent ones). One type of knot invariant is tricolorability. A knot is tricolorable if and only if each arc of the knot diagram can be coloured one of three colours subject to the following rule:

1. At least 2 colours must be used AND
2. At each crossing (can be an over or undercrossing), 3 overlapping strands are either all the same colour or all different colours

An arc is a section of the string that goes from one undercrossing to the next. Some examples of tricolorability is shown:



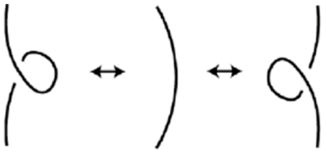
Non-tricolorable knot with 4 arcs



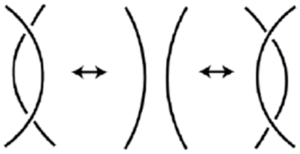
Tricolorable knot with 6 arcs

The unknotting number is also a knot invariance, and refers to the smallest number of crossings that have to be swapped (i.e. the string segment at the bottom of the crossing is passed through the one on top, changing their position in the crossing whilst keeping the rest of the knot the same), for a knot to be changed to an unknot. The unknot refers to the most basic form of a knot, which is a circle.

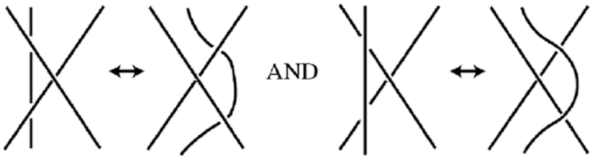
Note that all knotting movements that occur without breakage of the string can be classified into 3 Reidemeister moves, which preserve knot invariance:



Type I



Type II



Type III

(a) Is structure **X** is tricolorable? **[2 points]**

(b) Do structure **X** and the unknot have the same tricolorability? **[1 point]**

(c) State the unknotting number of structure **X**. **[2 points]**

For parts (a) and (b), leave your answer as "T" for true or "F" for false. The answer is case-sensitive.

Solution:

(a) F

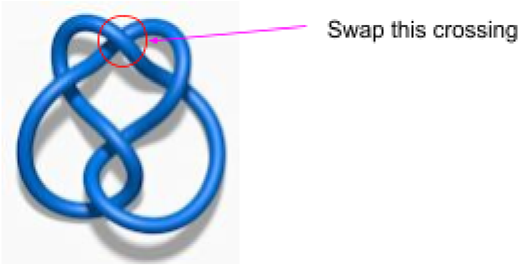
No matter how one attempts to colour the knot, it is impossible to fulfil the 2 criteria of tricolorability. This is a 5_2 knot, also known as a three-twist knot.

(b) T

The unknot is also not tricolorable.

(c) 1

We swap the circled crossing and it will then become obvious that we can perform a series of Reidenmaster moves to get to the unknot:



Source: Leigh, D.A., Schaufelberger, F., Pirvu, L. et al. Tying different knots in a molecular strand. Nature 584, 562–568 (2020). https://doi.org/10.1038/s41586-020-2614-0

Problem prepared by: Chua Ming Xiu

Problem 12: Suspicious pHs I

[7 points]

Let us start off with some easy problems.

(a) Find the pH value of HCl with a concentration of:

(i) 1 mol dm^{-3}
(ii) 0.1 mol dm^{-3}
(iii) 0.01 mol dm^{-3}

If your answer to parts (i), (ii) and (iii) are a, b and c respectively (to the nearest integer), then leave your answer as the concatenated number $\overline{abc}$. **[2 points]**

Now, let us consider the pH of 10^{-8} mol dm^{-3} HCl. Suspicious, isn't it? If you use the method above, you would probably get an *extremely* wrong-looking pH value.

The reason for this is because of the autoionisation of water, and it is significant when we have such dilute acids. So how do we solve it?

We follow a process known as constructing the mass-charge balances.

<u>Charge balance:</u> Write down a list of all the cations and anions present in the solution. Let us say the cations are A^+ and B^{2+} while the anion is C^{3-}.

Then, because we cannot have unbalanced charges, we have $[A^+] + 2[B^{2+}] = 3[C^{3-}]$.

<u>Mass balance:</u> Mass balances follow directly from the principle of atom conservation. To illustrate this idea, suppose we have a solution of H_3PO_4, formed by dissolving 1 mol of H_3PO_4 into 1 dm^3 of water (obviously, the concentration is 1 mol dm^{-3}). Then, it is clear that the sum of the concentration of all phosphate species must also add up to 1 mol dm^{-3}, because phosphate cannot simply disappear or appear in the system!

That is, 1 mol dm^{-3} = $[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$.

Convince yourself that the equations above are correct before moving on.

Now, construct the mass-charge balances for a 10^{-8} mol dm^{-3} HCl solution. When we calculate the pH of a 10^{-8} mol dm^{-3} HCl solution at 25 °C, solving the equations exactly, we will get a cubic equation in $[H^+]$. Let the equation be $a[H^+]^3 + b[H^+]^2 + c[H^+] + d = 0$.

(b) Denote $K_a(HCl) = x$, K_w at 25 °C $= y$, and the initial concentration of HCl, 10^{-8} mol $dm^{-3} = z$.

Here are some possible coefficients for the variables *a* to *d*:

A) 1
B) 2
C) x
D) y
E) z
F) xy
G) yz
H) xz
I) $x + yz$
J) $y + xz$
K) $z + xy$
L) xyz

You will notice that all the coefficients here are positive. If you think that the coefficient should be negative, insert a M before the option (e.g. if you think the coefficient should be $-x$, then choose MC).

If your answer for *a*, *b*, *c*, *d* are *A*, *B*, *C*, *–D* respectively, then input the answer as *ABCMD*. **[3 points]**

Now, it is known that the K_a of HCl is 1.3×10^6.

(c) Using your answer from **part (b)**, solve the equation to get the pH of 10^{-8} mol dm^{-3} HCl at 25 °C. **[2 points]**
Leave your answer to 3 decimal places.

Solution:

(a) 012

(i) 0
(ii) 1
(iii) 2

This is fairly straightforward. By definition, pH = – lg [H^+], and since HCl is a strong acid, we can assume that it dissociates completely in water. Therefore,

(i) –lg(1) = 0
(ii) –lg(0.1) = 1
(iii) –lg(0.01) = 2

Combining these, we get **012** as the final answer.

(b) ACMJMF

We will set up the mass-charge balances:
Mass balance (1): $[HCl] + [Cl^-] = 10^{-8}$ mol dm^{-3}
Charge balance (2): $[H^+] = [Cl^-] + [OH^-]$

We also have our **K_a equation (3)**: $[HCl] \times K_a = [H^+][Cl^-]$
Lastly, we also have our **K_w equation (4)**: $K_w = [H^+][OH^-]$

Let us now solve these equations.

- First, rearrange equation (1) using equation (3):

$$\frac{[H^+][Cl^-]}{K_a} + [Cl^-] = 10^{-8} \Longrightarrow [Cl^-]\left(\frac{[H^+]}{K_a} + 1\right) = 10^{-8}$$

  So, rearranging the equation, we get:

$$[Cl^-] = \frac{10^{-8}}{\frac{[H^+]}{K_a} + 1} = \frac{10^{-8}}{\frac{[H^+]+K_a}{K_a}} = \frac{10^{-8}K_a}{[H^+] + K_a}$$

- Then, substitute equation (2) using the equation above:

$$[H^+] = \frac{10^{-8}K_a}{[H^+] + K_a} + [OH^-]$$

- Also, from equation 4: $[OH^-] = K_w/[H^+]$, and substituting this into the equation above, we get:

$$[H^+] = \frac{10^{-8}K_a}{[H^+]+K_a} + \frac{K_w}{[H^+]}$$

Now, solve the equation above, then:

$$[H^+] = \frac{cK_a}{[H^+]+K_a} + \frac{K_w}{[H^+]}$$

$$[H^+] = \frac{cK_a[H^+] + K_w([H^+]+K_a)}{[H^+]([H^+]+K_a)}$$

$$[H^+]^2([H^+]+K_a) = cK_a[H^+] + K_w([H^+]+K_a)$$

$$[H^+]^3 + [H^+]^2K_a = cK_a[H^+] + [H^+]K_w + K_aK_w$$

$$[H^+]^3 + [H^+]^2K_a - [H^+](cK_a + K_w) - K_aK_w = 0$$

If we denote K_a(HCl) = x, K_w at 25 °C = y, and the initial concentration of HCl, 10^{-8} mol dm^{-3} = z.

Putting in the coefficients, we get:

- $a = 1$ (A)
- $b = x$ (C)
- $c = -y - xz$ (MJ)
- $d = -xy$ (MF)

So, the answer is **ACMJMF**.

(c) 6.978

Solving the cubic equation with any method of your choice (this was done with Wolfram Alpha and Desmos), it gives a result of $[H^+] \approx 1.051\times10^{-7}$ (or 1.052, but it does not affect the final answer).

Using pH = $-\lg[H^+]$, we get a 3 decimal place result of **6.978**.

Problem prepared by: Lim Dillion

Problem 13: Knockout!

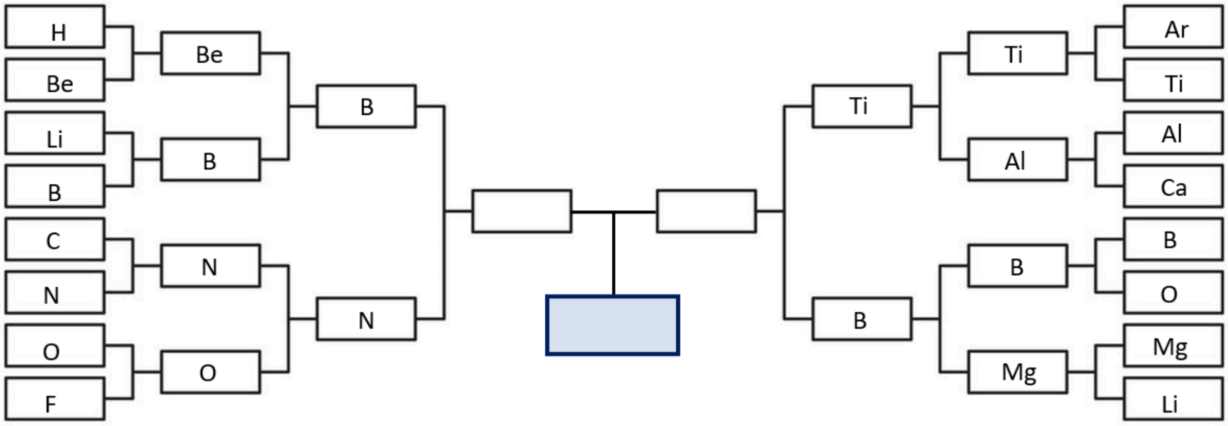
[7 points]

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.]

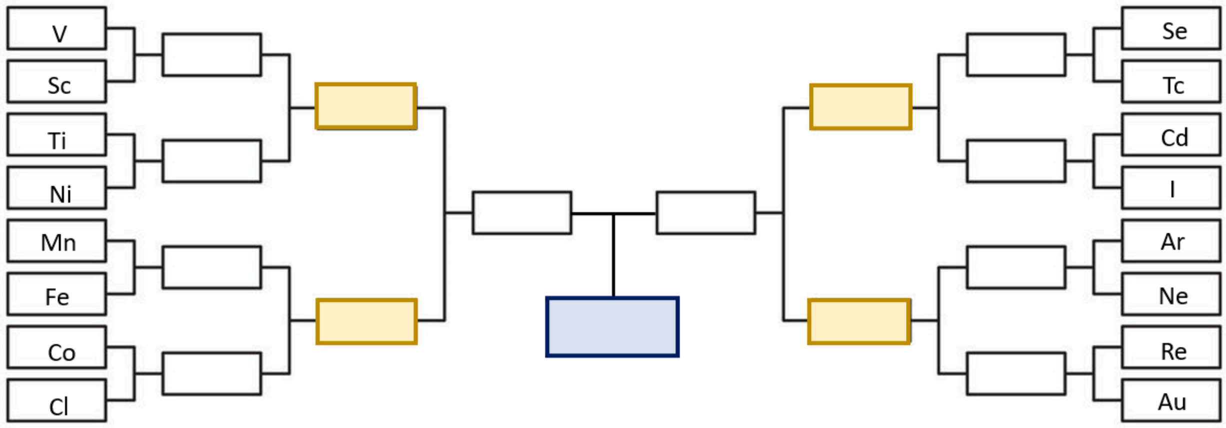
Consider the tournament diagram below. Some of the winners are filled for you below.

[**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]**
Leave your answer as an element symbol. The answer is case-sensitive.

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?

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". Again, the answer is case-sensitive. **[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? **[2 points]**

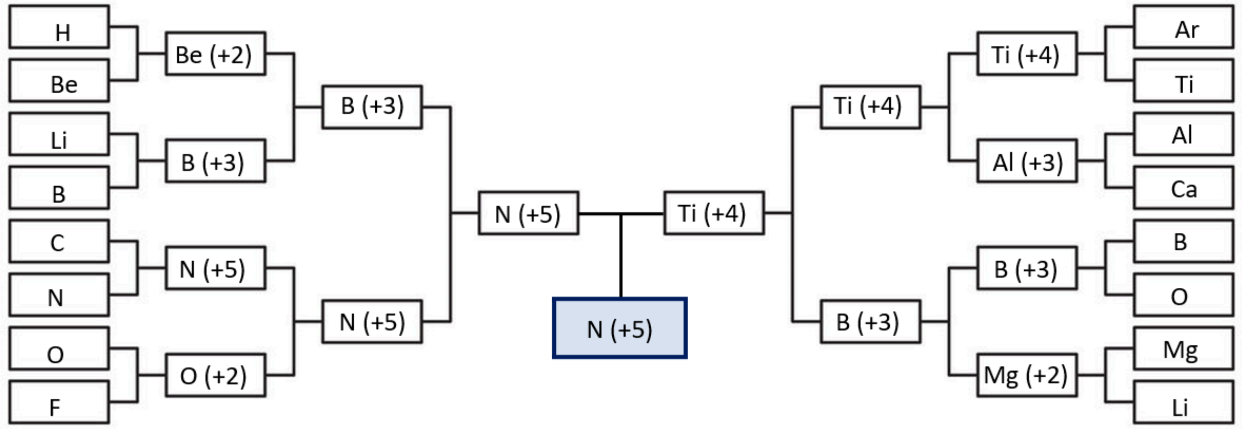
Solution:

(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. $BeCl_2$). Accordingly, filling up the knockout table, we get the final answer to be nitrogen, N, with a maximum oxidation state of +5.

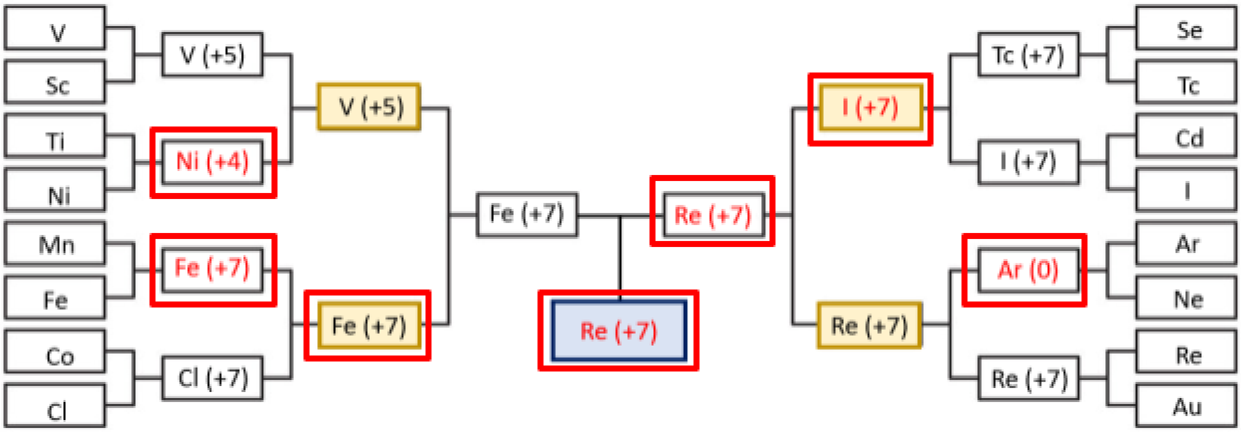
We can deduce the knockout rule as follows:

- 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 centre 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) ReI7

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 7 draws in total (not 6).

Therefore, the final answer is **ReI7**.

(c) Ir

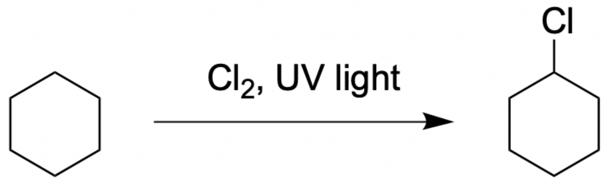
Out of all the elements, Ir exhibits the highest maximum oxidation state of +9, as in $[IrO_4]^+$. None of the other elements exhibit such a high maximum oxidation state.

Problem prepared by: Lim Dillion

Problem 14: Counting Stars

[6 points]

In high school-level considerations of the free-radical substitution reaction, we typically only consider mono-substituted products, as follows:



However, the sad reality is that what we obtain is a complete jumble of isomers which don't give you the product you want. Consider the 6-substituted products of the above reaction (i.e. products with the formula $C_6H_6Cl_6$).

(a) Determine the number of unique possible products, **ignoring** any stereochemistry. **[2 points]**

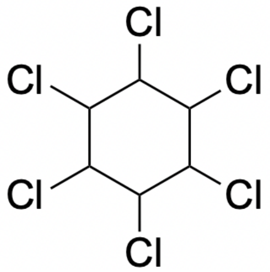
(b) Determine the number of unique possible products, **including** the stereochemistry. **[4 points]**

Solution:

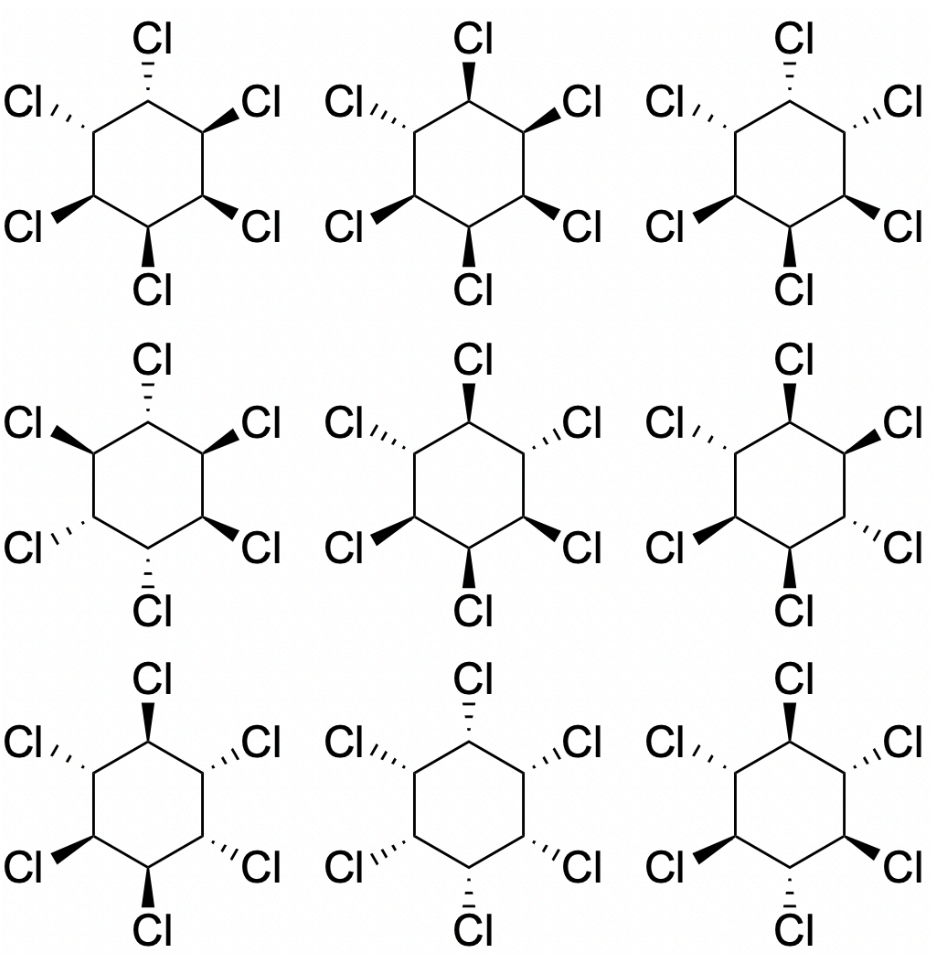
- **(a) 18**
- **(b) 90**

The key to this question is to ensure you are systematic with the entire procedure. As suggested by the question parts, we can take an approach where we determine the number of regioisomers, before determining the stereoisomers for each such possible structure. It would be prudent to use the answer to part (a) as a way to check if your working is correct, before proceeding with part (b).

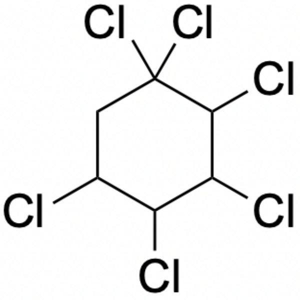
First, let us consider the easiest category, which is the 1,2,3,4,5,6-isomers, with one chlorine on each carbon.

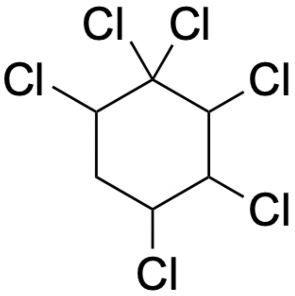
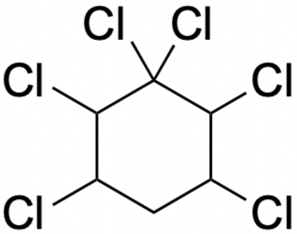


You can use a tool like MarvinSketch (free demo of isomer counting at https://plugins.calculators.cxn.io/stereoisomers/) to determine the total number of stereoisomers. Or draw them out yourself. Either way, you can determine that there are 9 stereoisomers for this configuration.

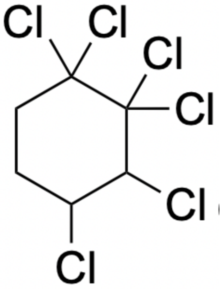
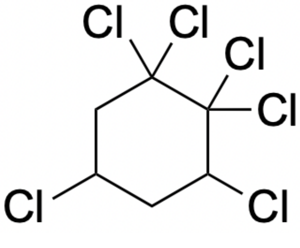


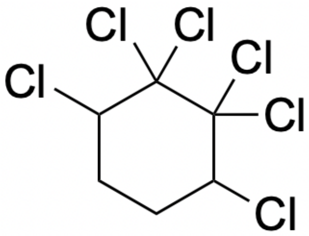
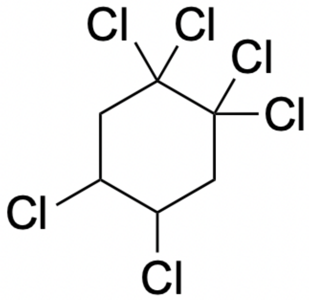
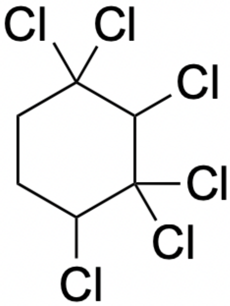
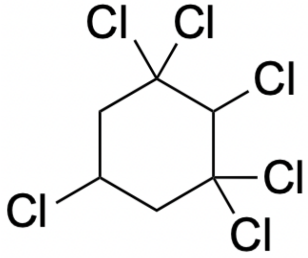
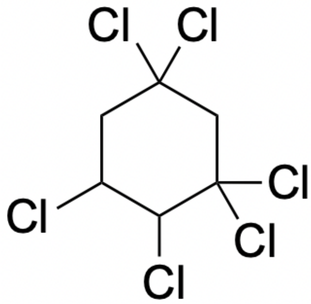
Next, what if there are 2 Cls on one carbon?

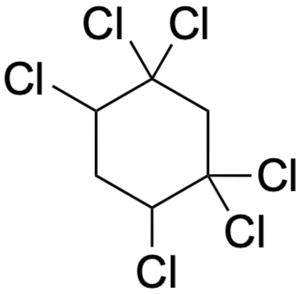
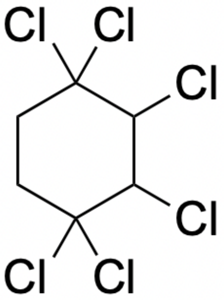
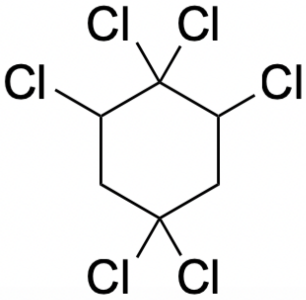
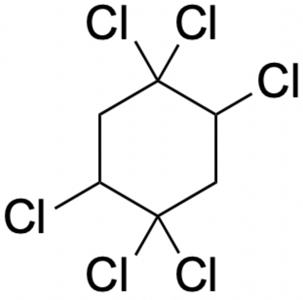
Isomer	No of Stereoisomers
 1,1,2,3,4,5-hexachlorocyclohexane	16

 1,1,2,3,4,6-hexachlorocyclohexane	16
 1,1,2,3,5,6-hexachlorocyclohexane	10

Or 2 Cls on 2 carbons?

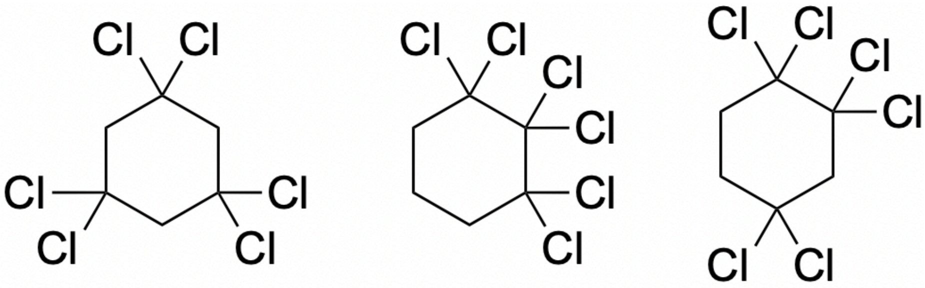
Isomer	No of Stereoisomers
 1,1,2,2,3,4-hexachlorocyclohexane	4
 1,1,2,2,3,5-hexachlorocyclohexane	4

 1,1,2,2,3,6-hexachlorocyclohexane	3
 1,1,2,2,4,5-hexachlorocyclohexane	3
 1,1,2,3,3,4-hexachlorocyclohexane	4
 1,1,2,3,3,5-hexachlorocyclohexane	2
 1,1,3,3,4,5-hexachlorocyclohexane	4

 1,1,2,4,5,5-hexachlorocyclohexane	3
 1,1,2,3,4,4-hexachlorocyclohexane	3
 1,1,2,4,4,6-hexachlorocyclohexane	3
 1,1,2,4,4,5-hexachlorocyclohexane	3

And 2 Cls on 3 carbons. There is no chirality for these isomers (1,1,2,2,3,3-hexachlorocyclohexane, 1,1,2,2,4,4-hexachlorocyclohexane, 1,1,3,3,5,5-hexachlorocyclohexane)

.



Lastly, we just need to do a final tally to discover that there are a total of $9 + 42 + 36 + 3 = 90$ isomers.

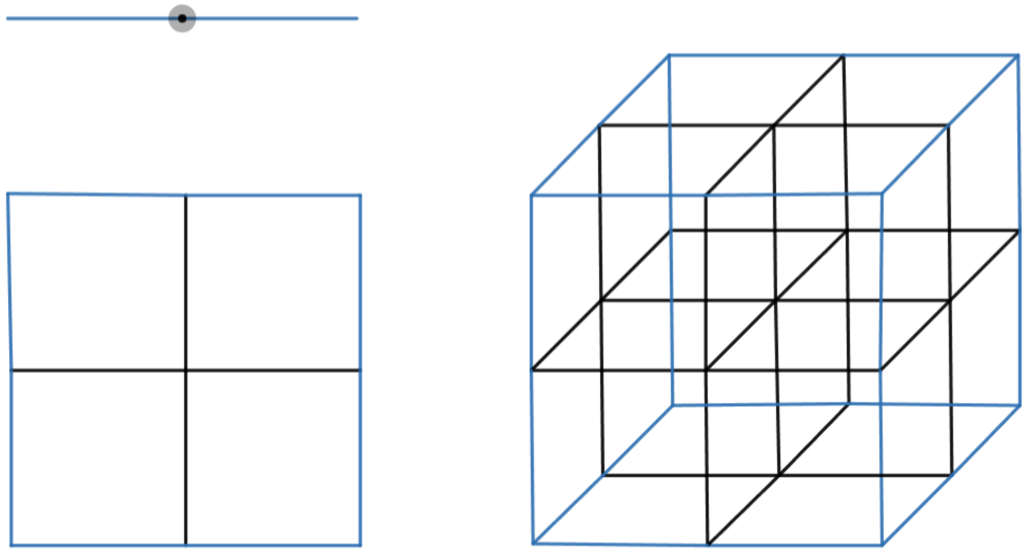
Problem prepared by: Brennan Ting

Problem 15: Extradimensional Chemistry

[9 points]

We live in a 3D world[citation needed]. In this problem, we will consider crystal structures in different dimensions. For your information:

- **Vertex**: A 'point' or 'corner' of a unit cell.
- **Edge**: A line connecting two vertices.
- **Face**: A closed surface bounded by a series of edges.



(a) Two 1D unit cells connected to each other. (b) Four 2D unit cells connected to each other. (c) Eight 3D unit cells connected to each other.

(a) Extrapolate the values for the fourth dimension. **[3 points]**

Hint: The number of faces of a 4D cube is not easy to visualise. Use the Euler characteristic for a 4D cube, $V - E + F = 8$.

No. dimensions	No. vertices of each unit cell (V)	No. edges of each unit cell (E)	No. faces of each unit cell (F)
1	2	1	NA
2	4	4	1
3	8	12	6
4			

Give your answer as $\overline{VEF}$.

(b) Extrapolate the values for the fourth dimension. **[2 points]**

No. dimensions	No. of unit cells that share a vertex (V_s)	No. of unit cells that share an edge (E_s)	No. of unit cells that share a face (F_s)
1	2	NA	NA
2	4	2	NA
3	8	4	2
4			

Give your answer as $\overline{V_sE_sF_s}$.

(c) The following is an excerpt from a newspaper in 20XX.

The Nobel Prize in Chemistry in 20XX is awarded to Seeklik V. Ametree and Ex R. Dee for "the discovery of novel 4D crystal structures". Ametree and Dee used 4D-zinc atoms (A_r = 65.38, r = 138 pm) and 4D-copper atoms (A_r = 63.55, r = 128 pm) to create an alloy with a face-centred unit cell. 4D-zinc takes the corners and 4D-copper takes the faces in the unit cell. This new foray into 4D crystal structures presents an exciting opportunity for the future!

Our thoughts and prayers go to the team's crystallographers, who are currently hospitalised after analysing the XRD spectrum of the crystal.

Calculate the density of the 4D alloy. Give your answer in g cm^{-4}. **[4 points]**
Leave your answer in decimal form to 4 significant figures.

Solution:

(a) 163224

The number of vertices follows a simple power-of-two relation. An n+1-dimensional unit (e.g. cube) is formed by two copies of the n-dimensional unit (e.g. square) with each pair of vertices connected by edges, hence the total number of vertices is **16**. The total number of edges $E_{n+1} = 2E_n + V_n$. Hence, the number of edges is **32**. Using the Euler characteristic, the number of faces is **24**.

(b) 1684

Each number simply follows a simple power-of-two relation.

(c) 370400000

The dimensions of the unit cell will still be constrained by the face diagonal, which will be

$$D = 2\times(138\,pm + 128\,pm) = 532\,pm.$$

$$a = \frac{532\,pm}{\sqrt{2}} = 376.18\,pm$$

There is $\frac{16}{16} = 1$ zinc atom and $\frac{24}{4} = 6$ copper atoms in each unit cell.

$$\rho = \frac{65.38\,g\,mol^{-1} + 6\times63.55\,g\,mol^{-1}}{(376.18\,pm)^4} \times \left(\frac{1\,pm}{10^{-10}\,cm}\right)^4 \times \left(\frac{1}{6.022\times10^{23}\,mol^{-1}}\right)$$

$$= 370400000\,gcm^{-4}(4\text{ s.f.})$$

Problem prepared by: Leemen Chan

Problem 16: Feelin' Rusty

[4 points]

Rusting in marine environments is caused by the oxidation of Iron metal, due to the presence of oxygen gas and seawater, which acts as an electrolyte.

Rusting is a surprisingly complex process. However, it includes the formation of green Iron (II) hydroxide, $Fe(OH)_2$, as described below. With enough oxygen, it will oxidise further to reddish-brown Iron (III) hydroxide, $Fe(OH)_3$.

$$2\ Fe\ (s) + O_2\ (g) + 2\ H_2O\ (l) \rightarrow 2\ Fe(OH)_2\ (s)$$

Given the following information and conditions, calculate the change in gibbs free energy (ΔG_r) for the above reaction in kJ mol^{-1}.

$$O_2\ (g) + 2\ H_2O\ (l) + 4\ e^- \rightleftharpoons 4\ OH^-\ (aq) \qquad E^\circ = +\ 0.40\ V$$

$$Fe^{2+}\ (aq) + 2\ e^- \rightleftharpoons Fe\ (s) \qquad E^\circ = -\ 0.44\ V$$

- Seawater has a density of 1.03 g cm^{-3}, contains 1.5 μg of dissolved Fe^{2+} per kg of seawater, and has a pH of 8.10.
- K_{sp} of $Fe(OH)_2 = 4.87 \times 10^{-17}$ mol^3 dm^{-9}.
- Air has a pressure of 1.00 bar and contains 21.0 % oxygen by volume.
- The temperature is 25 °C.

Leave your answer to 3 significant figures. Include a '-' sign for negative answers.

Solution:

-507

There are 2 separate steps here:

1. The redox reaction between Fe (s) and O_2 (g) to form Fe^{2+} (aq) and OH^- (aq) in aqueous solution.

$$2\ Fe\ (s) + O_2\ (g) + 2\ H_2O\ (l) \rightarrow 2\ Fe^{2+}\ (aq) + 4\ OH^-\ (aq) \qquad (\Delta G_1)$$

2. The precipitation of sparingly soluble $Fe(OH)_2$.

$$2\ Fe^{2+}\ (aq) + 4\ OH^-\ (aq) \rightarrow 2\ Fe(OH)_2\ (s) \qquad (\Delta G_2)$$

By Hess' Law, $\Delta G_r = \Delta G_1 + \Delta G_2$.

Given a pH of 8.10, $[OH^-] = 10^{-(14-8.10)} = 1.2589 \times 10^{-6}$ M. 1 kg of seawater with a volume of $\frac{1}{1.03} = 0.97087$ dm^3 will contain $\frac{1.5\times10^{-6}}{55.85} = 2.6858 \times 10^{-8}$ mol of Fe^{2+}. Hence $[Fe^{2+}] = \frac{2.6858\times10^{-8}}{0.97087} = 2.7663 \times 10^{-8}$ M. And since the mole fraction of oxygen in air is equal to its percentage by volume, the partial pressure of oxygen $p_{O_2} = 0.210$ bar.

We need to use the Nernst equation to determine E_{cell} since the concentrations are not standard.

$$E°_{cell} = 0.40 - (-0.44) = 0.84\ \text{V} \qquad\qquad z = 4$$

$$E_{cell} = E°_{cell} - \frac{RT}{nF}\ln\left(\frac{[Fe^{2+}]^2\ [OH^-]^4}{p_{O_2}}\right) = 0.84 - \frac{(8.3145)(25+273.15)}{(4)(96485)}\ \ln\left(\frac{(2.7663\times10^{-8})^2\ (1.2589\times10^{-6})^4}{0.210}\right)$$
$$= 1.4026\ \text{V}$$

Hence $\Delta G_1 =- nFE_{cell} =- (4)(96485)(1.4026) =- 541.32$ kJ mol^{-1}.

For the precipitation step, the value of the equilibrium constant $K = \frac{1}{K_{sp}^{\ 2}} = 4.2164 \times 10^{32}$ (due to the coefficient of 2 and the fact that the ions are precipitating, not dissolving), while the value of $Q = \frac{1}{[Fe^{2+}]^2\ [OH^-]^4}$ $= \frac{1}{(2.7663\times10^{-8})^2\ (1.2589\times10^{-6})^4} = 5.2028 \times 10^{38}$.

Hence $\Delta G_2 = \Delta G°_2 + RT\ln Q = \ - RT\ln K + RT\ln Q = RT\ln\frac{Q}{K}$
$= (8.3145)(298.15)\ln\frac{5.2028\times10^{38}}{4.2164\times10^{32}} = 34.769$ kJ mol^{-1}.

Therefore $\Delta G_r = - 541.32 + 34.769 = -$**507** kJ mol^{-1} (3 s.f.)

Problem prepared by: Wang Jiahua

Problem 17: A Murder In Three Acts

[7 points]

Of all the poisons known to man, cyanide may be the one that has garnered the greatest infamy in popular culture, but it is hardly the only one. Let us put on our detective hats, and elucidate the name of another poison that has found brief fame in an assortment of novels.

Firstly, here is the percentage by mass of each element in the molecule. The molecular mass is also given, to 0 d.p.

C	H	N	O
75.42%	6.63%	8.38%	9.57%
Molecular mass			334g

(a) What is the molecular formula of this poison?
Leave your answer in the format $C_aH_bN_cO_d$*, where a, b, c and d are integers. For example, if you believe the molecular formula is* CH_2O_3*, leave your answer as C1H2N0O3.* **[2 points]**

The poison has been investigated for its toxicity in mice populations, and the results are summarised below. The median lethal dose (LD_{50}) is the dosage required to kill half of a sample population on average.

Route	**LD_{50} (mg/kg)**
Intraperitoneal	0.99
Intravenous	0.42
Parenteral	1.03
Oral	2.1
Subcutaneous	0.48

(b) Which of the following statements are correct? **[3 points]**

A) The poison is more effective when introduced intravenously rather than orally.
B) A human will require a greater mass of the poison to attain a lethal dose compared to a mouse, assuming a similar LD_{50}.
C) If 0.0127 mg of the poison is introduced via intraperitoneal injection into a healthy mouse of mass 15 g, the mouse statistically has more than 50% probability of dying.
D) The unit of LD_{50} is kg.

Leave your answer as a concatenated string of ***capital letters*** *in ascending alphabetical order. For example, if you believe A, B and D are correct, leave your answer as ABD.*

A quick google search of the molecular formula should render the identity of the compound abundantly clear. It was the subject of intense synthetic investigation for many decades, due to its pharmacological properties and fascinating hexacyclic structure.

One particular synthesis used a very creative transformation called a Cope rearrangement — specifically a cationic aza-Cope rearrangement.

(c) Which year was this synthesis towards (−)-strychnine published? **[2 points]**
Hint: It can be found on Synarchive, a handy resource for students of synthetic chemistry!

Solution:

(a) C21H22N2O2

This can be done by dividing by the atomic mass of each element, from which the simplest stoichiometric ratio can be obtained. As the total molecular mass is 334.41g, we know that the molecular formula is the same as the empirical formula.

	C	H	N	O
% by mass	75.42	6.63	8.38	9.57
A_r	12.01	1.008	14.01	16.00
Ratios	6.28	6.58	0.598	0.599
Simplest ratio	21	22	2	2

(b) AB

A) The poison is more effective when introduced intravenously rather than orally.

True. A lower LD_{50} indicates introduction by that route is more effective as a small mass of poison is needed to attain a lethal dose.

B) A human will require a greater mass of the poison to attain a lethal dose compared to a mouse, assuming a similar LD_{50}.

True. LD_{50} is given in terms of mg/kg, and varies with the mass of the organism. A human is heavier than a mouse (if not, something is very wrong) and will hence need a larger dosage for the poison to be lethal.

C) If 0.0127mg of the poison is introduced via intraperitoneal injection into a healthy mouse of mass 15g, the mouse statistically has more than 50% probability of dying.

False. The dosage as expressed in mg/kg $\frac{0.0127}{15/1000} = 0.847$ mg/kg. This is lower than the LD_{50} and is not sufficient for a reliable lethal dose.

D) The unit of LD_{50} is kg.

False. LD_{50} is expressed in mg/kg, for which the SI unit of both is the kilogram. Hence LD_{50} is a dimensionless quantity with no units.

(c) 1993

The compound is in fact strychnine, which interestingly was featured in both Agatha Christie's *The Sign of Four* and Stephen King's *Mr. Mercedes*.

A quick Google Scholar search using "strychnine Cope rearrangement" would have vested the answer — Larry E. Overman completed the synthesis in 1993. He made the unnatural (+) enantiomer in 1995, but this is not the answer we seek!

Problem prepared by: Lin Bohan

Problem 18: Connections

[4 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 chemical compound.

Rust	VX2	ξ	Pound
Stone	Marina Bay	Mothball	Steel
Shifting	Plastic	Sonnet	Candle
Sirius	^{14}C	Tar	Bit

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

Give your answer in the form of the ***CAS Registry Number*** *of the compound, omitting any dashes. For example, if you believe the compound is titanium tetrachloride, which has a CAS Registry Number of 7550-45-0, input 7550450.*

Solution:

7631869

The wall is labelled for ease of reference.

	A	B	C	D
1	Rust	VX2	ξ	Pound
2	Stone	Marina Bay	Mothball	Steel
3	Shifting	Plastic	Sonnet	Candle
4	Sirius	^{14}C	Tar	Bit

The groupings are as follows:

____ sands:

- Marina Bay (Marina Bay Sands)
- Shifting (shifting sands [phrase]; to describe something that changes constantly yet unpredictably)
- Tar (tar sands)
- Pound (pound sand [idiom]; ie, do something purposeless)

Binary:

- Sirius (binary star)
- Bit (binary digit)
- Steel (binary alloy)
- VX2 (binary VX, an extremely toxic nerve agent)

Insoluble in water:

- Plastic (polymer)
- Candle (wax)
- Mothball (naphthalene)
- Rust (Fe_2O_3)

Relating to the number 14:

- Stone (1 stone = 14 pounds)
- ^{14}C
- Sonnet (14-line poem)
- ξ (xi, 14th letter of the Greek alphabet)

The clue "relating to the number 14" could refer to Si, the element whose atomic number is 14. We are looking for a certain water-insoluble silicon-containing binary compound found in sand. This is silicon dioxide, SiO_2, whose CAS Registry Number is 7631-86-9. The answer is therefore **7631869**.

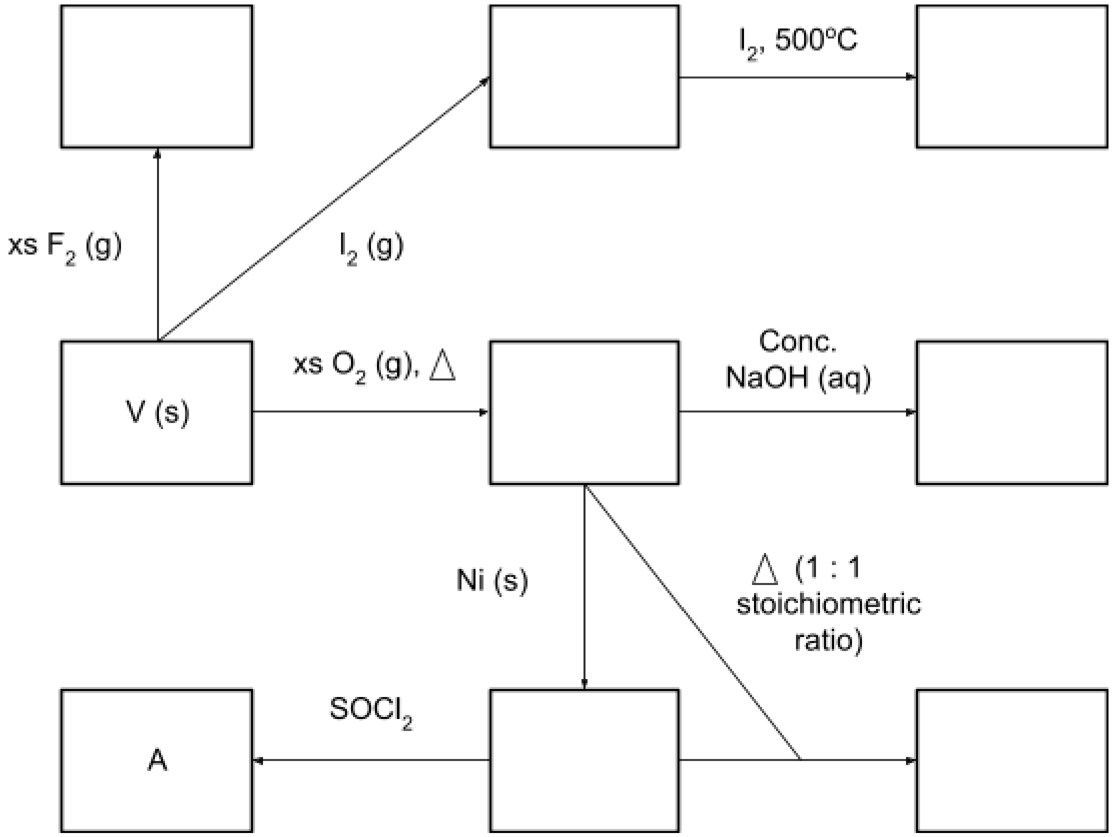
Problem prepared by: Lie Huan Yew

Problem 19: V Is For…

[6 points]

Vanadis, the Norse goddess of love and beauty, lends her name to the element vanadium, which has been noted for its staggering array of coloured compounds.

In the scheme below, vanadium metal is reacted with a variety of reagents to form neutral, vanadium-containing compounds.



In addition, some additional clues are given:

1. The compound formed by reacting V with $I_2(g)$ possesses a CdI_2 unit cell structure.
2. Relevant reduction potentials are given:

Half-cell	**E^θ / V**
$VO_4^{3-}/HV_2O_5^-$	+2.19
$HV_2O_5^-/V_2O_3$	+0.542
V_2O_3/VO	−0.486
VO/V	−0.820
Ni^{2+}/Ni	−0.257

(a) Suggest the oxidation state of vanadium in compound A. If it is positive, omit the + sign. **[3 points]**

Hint: You are not expected to be familiar with the reaction. Look at the oxidation states of the other compounds, and their positions in what seems suspiciously similar to the 3x3 grids used in IQ tests...

As it turns out, A is a vanadium chloride which is used in the synthesis of a vanadium coordination compound, the simplified reaction of which is shown below. *a, b, c* and *d* are integral coefficients in the balanced equation, in their simplest ratios.

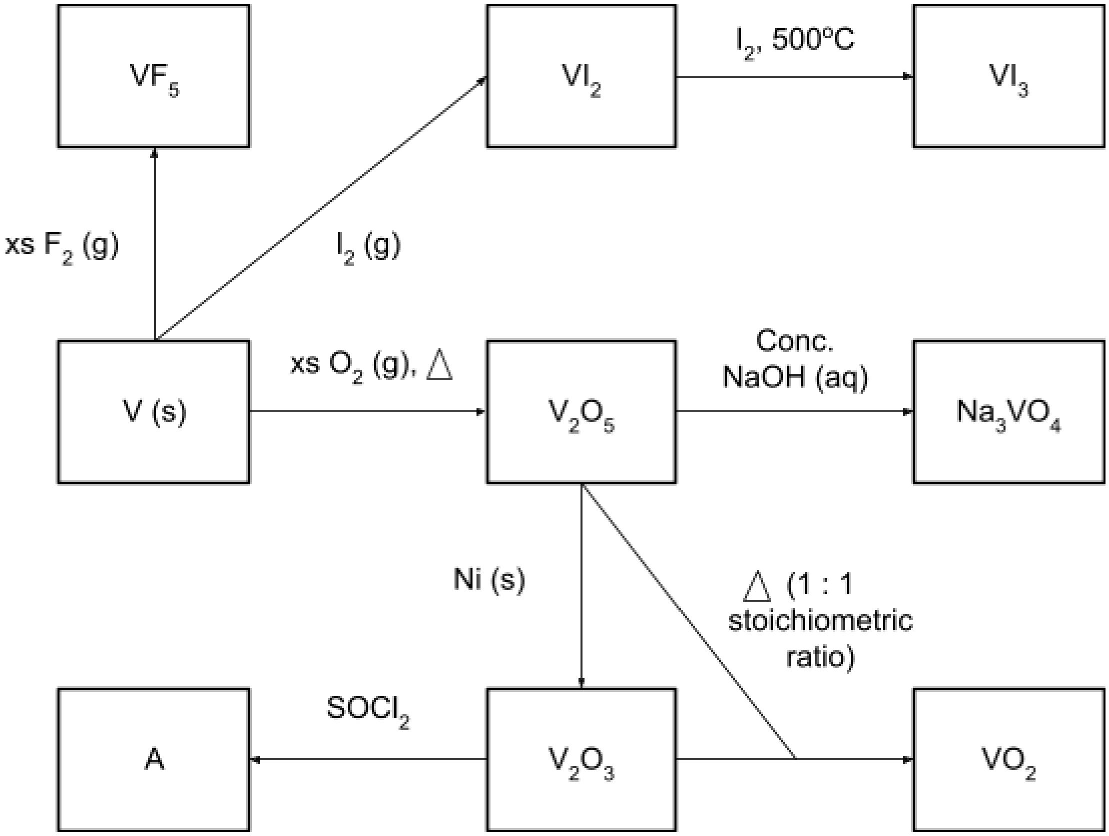
$$\boldsymbol{a}\,\mathrm{Na} + \boldsymbol{b}\,\mathrm{VCl_x} + \boldsymbol{c}\,\mathrm{CO} \rightarrow \boldsymbol{d}\,\mathrm{Na[V(CO)_6]} + \boldsymbol{e}\,\mathrm{NaCl}$$

(b) Give the concatenated number $\overline{abcde}$. **[3 points]**

Solution:

(a) 3

The completed reaction scheme is shown below:



The first key concept is that O and F are extremely electronegative, and have a tendency to bring out the maximum oxidation state of the elements that it reacts with, especially when reacted in excess. V is in group V (pun intended) and can attain a maximum oxidation state of +5. Hence the respective fluoride and oxide formed are VF_5 and V_2O_5.

As for the reaction of V with I_2 (g), it is given that the unknown compound has a CdI_2 unit cell structure - the exact unit cell is unimportant, and the critical piece of information is that the stoichiometry is given - we should expect it to have the same stoichiometry as CdI_2. Hence we may reasonably suggest VI_2 as the product. Upon further reaction with I_2 under more forcing conditions we should expect VI_3 to form - I_2 is not as oxidising as F_2 and cannot bring out the +4/+5 OS of V.

V_2O_5 is amphoteric and can react with excess base to form a vanadate anion - this is quite similar to the reaction of Al_2O_3! In any case, one does not even need to propose the exact structure to complete part (a) - it is more important to realize that this is not a redox reaction, and that V would hence still bear a +5 oxidation state.

The reaction of V_2O_5 with Ni is a classical redox reaction. The Ni half-equation is:

$$\text{Ni (s)} \rightarrow \text{Ni}^{2+} \text{(aq)} + e^- \qquad E = +0.257 \text{ V}$$

Thus, any V half-equation that has $E > -0.257$ V will proceed, as the overall reaction has $E > 0$ and is spontaneous. Hence, V can be reduced to the +3 oxidation state, corresponding to V_2O_3.

Finally, V_2O_5 and V_2O_3 react in a 1:1 ratio to form a single vanadium-containing compound. This is a comproportionation reaction of a +3 and +5 species, which would lead to a +4 species.

If we were to plot the oxidation states of the compounds in their respective positions in a 3x3 grid, an interesting pattern emerges:

+5	+2	+3
0	+5	+5
?	+3	+4

The oxidation states in each row add up to 10! Thus, the unknown compound A has an oxidation state of 3.

(b) 41613

Since A has oxidation state +3, its chloride would have the structure VCl_3. The equation is thus:

$$a\,\text{Na} + b\,\text{VCl}_3\; c\,\text{CO} \rightarrow d\,\text{Na}[\text{V(CO)}_6] + e\,\text{NaCl}$$

It is useful at this point to write the oxidation states of the species undergoing redox reactions, which are Na and V.

$$a\,\overset{0}{\text{Na}} + b\,\overset{+3}{\text{V}}\text{Cl}_3 + c\,\text{CO} \rightarrow d\,\overset{+1}{\text{Na}}[\overset{-1}{\text{V}}(\text{CO})_6] + e\,\overset{+1}{\text{Na}}\text{Cl}$$

The $\text{Na}[\text{V(CO)}_6]$ species takes a little more work. We separate it into the Na^+ cation and $[\text{V(CO)}_6]^-$ complex anion. To find the oxidation state of V, we need to know the charge on CO, carbon monoxide. This turns out to be a neutral ligand, so for the overall charge to be −1, V has to be in a −1 oxidation state (all that stuff about metals only forming positive oxidation states are lies)!

The oxidation state of Na increases by 1 and that of V decreases by 4. For redox balance, the ratio of Na : VCl_3 has to be 4 : 1. Let's say we substitute those values in first:

$$4\,\text{Na} + \text{VCl}_3 + c\,\text{CO} \rightarrow d\,\text{Na}[\text{V(CO)}_6] + e\,\text{NaCl}$$

The only V-containing species on the right hand side is $\text{Na}[\text{V(CO)}_6]$, so d = 1 as well. That then gives e = 3 so that all the Na is accounted for, and c = 6 as 6 CO ligands enter the V transition metal complex. Thus the balanced equation is:

$$4\,\text{Na} + \text{VCl}_3 + 6\,\text{CO} \rightarrow \text{Na}[\text{V(CO)}_6] + 3\,\text{NaCl}$$

$\overline{abcde}$ is 41613.

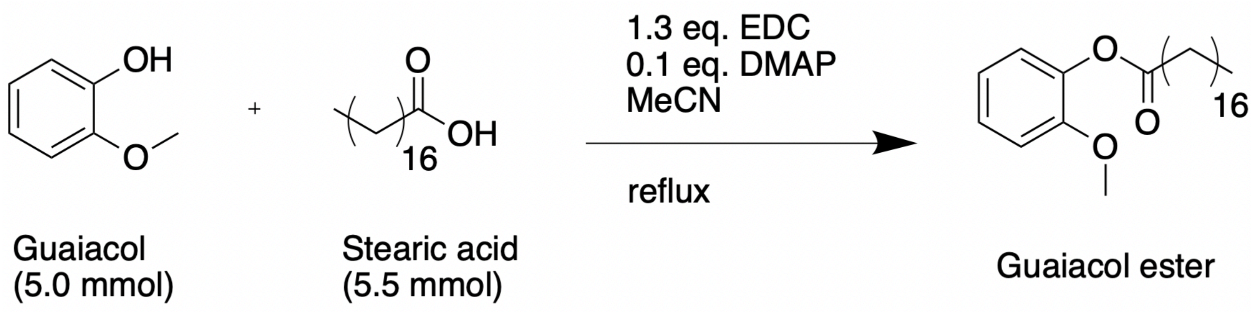
Problem prepared by: Lin Bohan

Problem 20: The Pain Of Real Synthesis

[6 points]

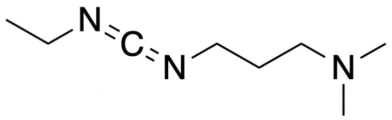
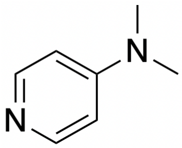
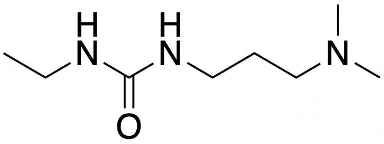
One of the oft-overlooked dimensions of an organic reaction is the workup. Today, let us put on our gloves, lab coats and goggles, and step into the shoes of a synthetic chemist working at the bench.

The Steglich esterification is often used in coupling carboxylic acids to alcohols to form esters. An example reaction scheme is as follows:



Eq. refers to equivalents of the limiting reagent, in this case guaiacol. A look at the mechanism[4] should also be useful.

The structure of certain chemical species are given below:

EDC	DMAP	Urea byproduct
		

(a) When the reaction has proceeded to completion, how many chemical species, including the solvent, are present in the reaction mixture? Assume no reaction intermediates survive. **[2 points]**

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[4] For instance, https://synarchive.com/named-reactions/steglich-esterification

The fundamental tenet of organic workups is solubility. In an aqueous workup, chemical species are partitioned between an organic phase and an aqueous phase, and one layer is retained depending on which layer the desired product dissolves in, while the other layer is discarded.

The Steglich esterification is performed in the stoichiometries as detailed above, followed by aqueous workup as follows:

1. To the reaction mixture is added 2 x 20 mL of 1.0 M HCl (aq). Aqueous layer is collected and discarded after each washing.
2. To the reaction mixture is added 20 mL of 10% $NaHCO_3$ (aq). Aqueous layer is collected and discarded.
3. Reaction mixture washed with 2 x 20 mL brine.
4. MgSO4 is added until a snow-globe effect is observed and filtered under gravity filtration.

At which point a solution of the desired ester product should have been obtained.

(b) Following washing with HCl, how many chemical species have been removed from the reaction mixture? **[2 points]**

(c) What may be the purpose of washing the mixture with brine? Choose ONE option. **[2 points]**

A) To create a pH neutral environment by the use of neutral NaCl.
B) To allow NaCl to dissolve in the organic layer, hence facilitating the removal of solvent in later steps.
C) To purify the guaiacol ester product.
D) To remove trace amounts of water that have dissolved in the organic layer.

Leave your answer as a capital letter corresponding to the correct option.

Solution:

(a) 6

The species that are present are:

1. **MeCN:** As the solvent, this would of course be present.
2. **Stearic acid:** It was present in excess, and hence not all of it would have reacted with guaiacol. Strictly speaking it is present as an acid-EDC adduct, but we have assumed no intermediates survive.
3. **Guaiacol ester** product
4. **DMAP:** It plays the role of a catalyst here, and would be expected to be regenerated.
5. **EDC:** Similarly, it was present in excess to the stearic acid and not all of it would have reacted.
6. **Urea:** This is the byproduct generated from the reaction of stearic acid with EDC, after the initial adduct has dissociated.

(b) 3

1.0 M HCl (aq) serves a dual purpose of protonation of any basic species present, and also allowing water-soluble species to dissolve in the aqueous layer. An analysis of the above species will reveal that DMAP (being a pyridine), EDC and urea are all basic species which are protonated and subsequently washed away.

(c) D

Brine is commonly used for the purpose of drawing water present in the organic layer into the aqueous layer, hence ensuring the isolated product is completely dry.

Problem prepared by: Lin Bohan

Problem 21: Two Lead Compounds

[4 points]

A large beaker with 5.00 dm^3 of water initially contains 3.43×10^{-5} M lead (II) ions, 9.11×10^{-5} M oxalate ions, and an unknown concentration of iodide ions. It is maintained at room temperature and water evaporates slowly. Assume the solution remains homogenous and no complexes form.

K_{sp} of $PbC_2O_4 = 8.50 \times 10^{-9}$ $mol^2\ dm^{-6}$
K_{sp} of $PbI_2 = 9.80 \times 10^{-9}$ $mol^3\ dm^{-9}$

(a) After x cm^3 of water evaporates, a white precipitate just starts to appear.
Find the value of x. **[2 points]**
Leave your answer to 3 significant figures.

(b) After a **further** 973 cm^3 of water evaporates, a yellow precipitate just starts to appear.
Find the initial concentration of iodide in mol dm^{-3}. **[2 points]**
Leave your answer to 3 significant figures in decimal form.

Solution:

(a) 1970

Suppose that y dm^3 of solution remains after evaporation.

Hence, final $[Pb^{2+}] = \frac{5}{y}\left(3.430 \times 10^{-5}\right)$ and final $[C_2O_4^{2-}] = \frac{5}{y}\left(9.110 \times 10^{-5}\right)$ M.

When the white precipitate of PbC_2O_4 (s) just starts to form, the solution will be saturated with PbC_2O_4 and its ionic product = $K_{sp} = [Pb^{2+}][C_2O_4^{2-}]$.

$$8.50 \times 10^{-9} = \frac{25}{y^2}\left(3.430 \times 10^{-5}\right)\left(9.110 \times 10^{-5}\right)$$

$$y = \sqrt{\frac{25\left(3.430\times10^{-5}\right)\left(9.110\times10^{-5}\right)}{8.50\times10^{-9}}} = 3.0316 \text{ dm}^3$$

Therefore $x = 1000(5 - y) = 1000(5 - 3.0316) = 1968.4 \approx$ **1970 cm^3**.

(b) 0.00600

Let the initial concentration of iodide be z mol dm^{-3}.

After an additional 973 cm^3 of water evaporates, the amount left is $3.0316 - 0.973 = 2.0586$ dm^3, so at this instant $[I^-] = \frac{5}{2.0586}z = 2.4289z$.

To find $[Pb^{2+}]$, we must assume PbC_2O_4 did *not* precipitate. At this instant,

$$[Pb^{2+}] = \frac{5}{2.0586}\left(3.430 \times 10^{-5}\right) = 8.3311 \times 10^{-5} \text{ mol dm}^{-3}$$
$$[C_2O_4^{2-}] = \frac{5}{2.0586}\left(9.110 \times 10^{-5}\right) = 2.2127 \times 10^{-4} \text{ mol dm}^{-3}$$

Since some amount of PbC_2O_4 did indeed precipitate, at this instant, equilibrium is achieved and $K_{sp} = [Pb^{2+}][C_2O_4^{2-}]$:

Concentrations	Pb^{2+} (aq)	+	$C_2O_4^{2-}$ (aq)	⇌	PbC_2O_4 (s)
Initial	8.3311×10^{-5}		2.2127×10^{-4}		
Change	$-p$		$-p$		
Equilibrium	$8.3311 \times 10^{-5} - p$		$2.2127 \times 10^{-4} - p$		

$$K_{sp} = 8.50 \times 10^{-9} = \left(8.3311 \times 10^{-5} - p\right)\left(2.2127 \times 10^{-4} - p\right)$$
$$p = 3.7146 \times 10^{-5}\ \mathrm{M}$$
$$[Pb^{2+}] = 8.3311 \times 10^{-5} - 3.7146 \times 10^{-5} = 4.6165 \times 10^{-5}\ \mathrm{M}$$

And since the solution is now also saturated with PbI_2,

$$[Pb^{2+}][I^-]^2 = K_{sp}$$
$$\left(4.6165 \times 10^{-5}\right)(2.4289z)^2 = 9.80 \times 10^{-9}$$

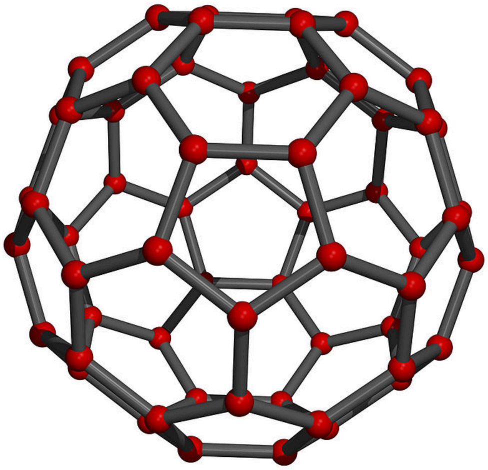
Therefore $z = 0.0059986 \approx$ **0.00600 mol dm^{-3}**.

Problem prepared by: Wang Jiahua

Problem 22: Ball Games

[5 points]

Buckminsterfullerene (C_{60}) looks like a ball[5]:



(a) Using the degree of unsaturation and then calculating the number of double bonds, deduce the number of rings in buckminsterfullerene. **[2 points]**

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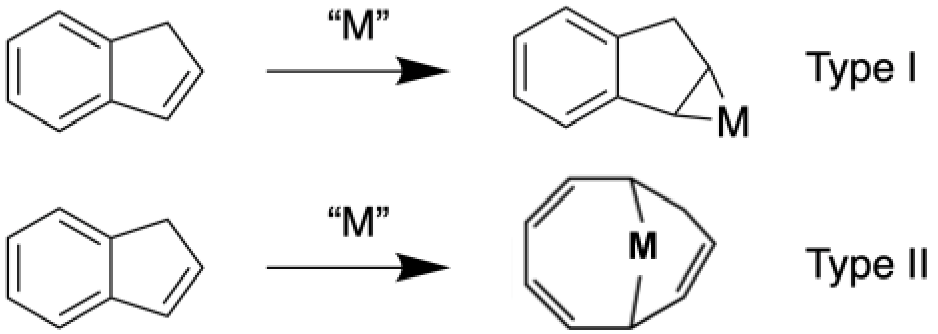
[5] Image source: https://fineartamerica.com/featured/buckminsterfullerene-molecule-friedrich-saurer.htm

Buckminsterfullerene can undergo addition reactions with transition metals. Type I reactions involve a direct addition onto a double bond, while type II reactions involve breakage of a single bond.

Some **examples** of Type I and Type II reactions are shown below:



(b) How many isomers are formed when 1 molar equivalent of a metal "M" reacts with buckminsterfullerene? **[3 points]**

Solution:

(a) 31

Degree of unsaturation $= [2(60) + 2\,]/2 = 61$

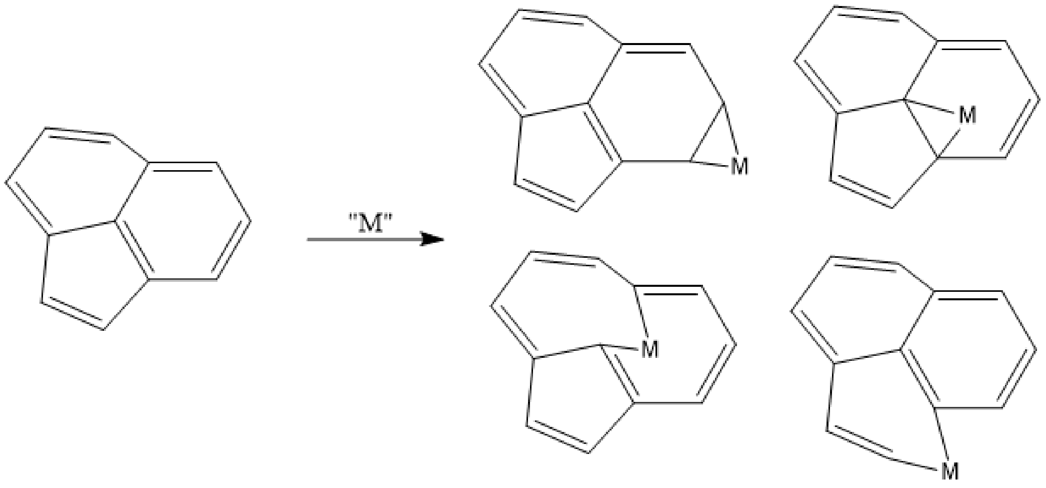
There are 30 double bonds in buckyball. Hence, if we were to calculate the theoretical number of rings (as stated in the question prompt) by subtracting the number of double bonds from the degree of unsaturation, we find that the number of rings $= 61 - 30 = \mathbf{31}$.

This is actually an incorrect number because the degree of unsaturation actually predicts the number of single bonds to be cleaved to turn buckyball into a non-cyclic alkane. For the first cleavage, cleaving buckyball at any single bond leads to the destruction of 2 rings instead of 1 (this is apparently because a sphere with an infinitesimally small hole is homeomorphic to a plane). So DOU actually underestimates the number of rings, which should be 32.

However, even though the correct number of rings is 32, the answer we are looking for, which requires us to calculate the value based on degree of unsaturation and number of double bonds, is 31.

(b) 4

A fragment of buckyball is used to represent the whole structure:



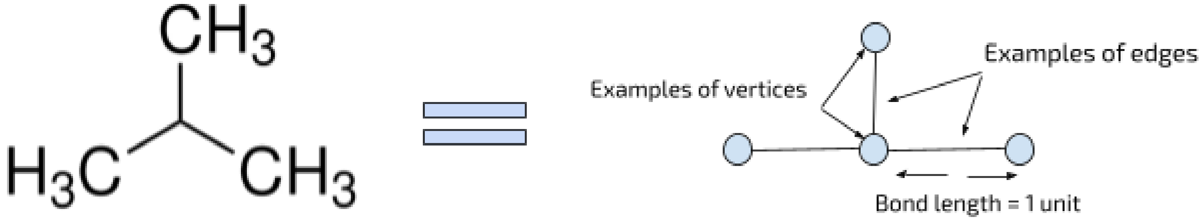
No stereoisomers are formed because the metal cannot react with buckyball from the inside of the sphere, only from the outside.

Problem prepared by: Chua Ming Xiu

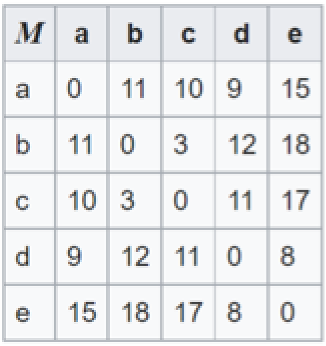
Problem 23: Graphs

[5 points]

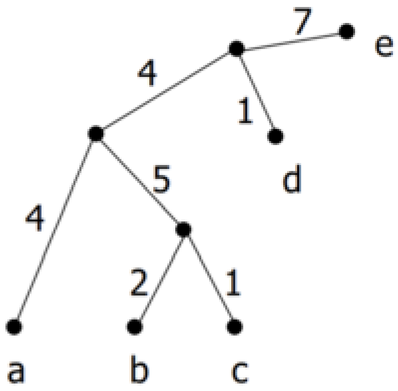
A graph refers to a set of geometrically related objects. Alkanes can be expressed as graphs by assuming that the hydrogen atoms are non-existent, and that all C—C bond lengths are unitary. The graphical representation of 2-methylpropane is shown below:



For an alkane with n number of carbon atoms, the distance matrix (**D**) refers to an $n \times n$ matrix representing all pairwise distances between the labelled atoms. The labelling of atoms is arbitrary, but you have to stick to the same order of atoms throughout all matrices. An example of a distance matrix is given below[6]:



M	a	b	c	d	e
a	0	11	10	9	15
b	11	0	3	12	18
c	10	3	0	11	17
d	9	12	11	0	8
e	15	18	17	8	0



The adjacency matrix (**A**) is another $n \times n$ Boolean matrix (i.e.values are only either 0 or 1). If two carbon atoms are adjacent to each other, the matrix term takes a value of 1; otherwise, the value is 0.

Lastly, the valency matrix (**v**) is a $1 \times n$ matrix containing terms which represent the number of single bonds to an adjacent carbon atom which each carbon atom possesses.

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[6] Source: IvanMontoya, CC BY-SA 4.0 <https://creativecommons.org/licenses/by-sa/4.0>, via Wikimedia Commons

The molecular topological index (MTI) of an alkane can be calculated using the following formula. It takes an integer value.

MTI = sum of horizontal components of matrix *M*,

$$M = v \times (D + A)$$

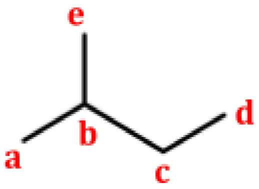
Calculate the MTI of 2-methylbutane.

Hint: search up how matrix multiplication works if you have forgotten.

Solution:

68

This question can be solved by labelling each carbon in 2-methylbutane with a letter from a to e. Without loss of generality, let the labelling be as such.



Taking reference from the matrix filling convention in the preamble, the 3 matrices will hence be as follows. Let A be the valency matrix (**v**), B be the distance matrix (**D**) and C be the adjacency matrix (**A**).

$$A = \begin{bmatrix} 1 & 3 & 2 & 1 & 1 \end{bmatrix}, \quad B = \begin{bmatrix} 0 & 1 & 2 & 3 & 2 \\ 1 & 0 & 1 & 2 & 1 \\ 2 & 1 & 0 & 1 & 2 \\ 3 & 2 & 1 & 0 & 3 \\ 2 & 1 & 2 & 3 & 0 \end{bmatrix}, \quad C = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{bmatrix}$$

$\mathbf{M} = \mathbf{v} \times (\mathbf{D} + \mathbf{A}) = \mathbf{A} \times (\mathbf{B} + \mathbf{C}) = [15\ 10\ 12\ 16\ 15]$

$\Rightarrow \text{MTI} = 15 + 10 + 12 + 16 + 15 = 68$

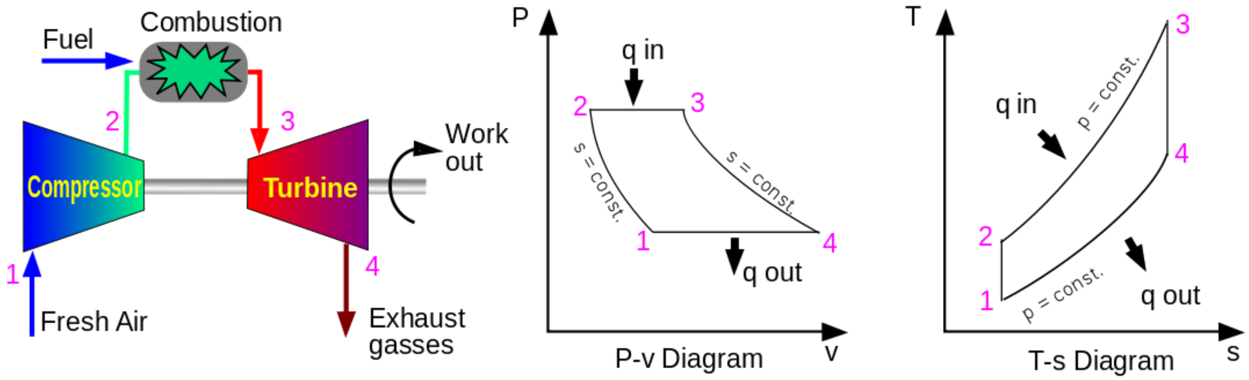
Note that surprisingly, the MTI remains unchanged no matter how the carbon atoms are labelled initially, as long as the matrix filling convention is consistent for all 3 matrices.

Problem prepared by: Chua Ming Xiu

Problem 24: Above All

[6 points]

Jet engines are multi-purpose devices as they can suck, squeeze, bang and blow. The thermodynamic cycle of jet engines is known as a Brayton cycle:



Assuming that air taken into the combustion chamber can be modelled by an ideal gas, the behaviour of air in the isentropic stages ($\Delta S = 0$) of the Brayton cycle are given by the following equation:

$$PV^{\gamma} = c$$

Where γ and c are constants. For air, γ = 1.40. Using ideal gas relations, one can derive a relation $\frac{T_2}{T_1} = (\frac{p_2}{p_1})^{k}$, in which k is a constant. Note: this equation is very important for the subsequent parts.

(a) Find the value of k. **[3 points]**

Leave your answer to 3 significant figures.

A jet engine manufacturer, Watt and Pritney, released a new engine with the following specifications:

Verified specifications (at cruising altitude)	
Maximum temperature of engine	2273 K
Maximum pressure of air compressed	15.6 bar
Pressure of air taken into engine	0.3 bar
Temperature of air taken into engine	223 K

(b) Calculate the thermodynamic efficiency, in percent, of the jet engine. **[3 points]**
Leave your answer to 3 significant figures. Omit the % sign.

Solution:

(a) 0.286

Given that, $P(\frac{nRT}{p})^{\gamma} = c, T^{\gamma} = \frac{c}{(nR)^{\gamma}(p^{1-\gamma})}$. By substituting T_1 and T_2,

$(\frac{T_1}{T_2})^{\gamma} = \frac{c}{p_2^{1-\gamma}(nR)^{\gamma}} \times \frac{p_1^{1-\gamma}(nR)^{\gamma}}{c} = (\frac{p_1}{p_2})^{1-\gamma}$.

Hence, it is obvious through algebraic manipulation that $\frac{T_1}{T_1} = (\frac{p_1}{p_2})^{\frac{1-\gamma}{\gamma}}$.

k = 0.4/1.4 = 0.286 (3 s.f.)

(b) 67.7

Net work is given by work done - work required. Work is done in the isentropic expansion (bang) stage while work is given in the isentropic compression stage (squeeze). For both stages, W = $C_p\Delta T$. Heat is given during the isobaric stage (blow), hence $Q_{in} = C_p\Delta T$.

Efficiency = $\frac{C_p[(T_4-T_1)-(T_3-T_2)]}{C_p(T_3-T_2)} = 1 - \frac{T_4-T_1}{T_3-T_2}$

T_3 is the maximum temperature of the engine, 2273K. T_1 is given to be 223K,

To find T_2, as 1→ 2 is an isentropic stage, $T_2 = T_1(\frac{p_2}{p_1})^{k} = 223(52)^{0.286} = 690.4K$ (4 sig. fig)

As 3 → 4 is also isentropic, $T_4 = T_3(\frac{1}{52})^{k} = 734.2K$ (4 s.f.)

Hence, efficiency = $1 - \frac{734.2-223}{2273-690.4} = 67.7\%$

Problem prepared by: Chua Ming Xiu

Problem 25: An Alternate Universe

[7 points]

The four quantum numbers n, l, m_l and m_s describe the movement of each electron in any atom. The restrictions on these numbers also determine the arrangement of elements in the different blocks of the periodic table.

- $n = 1, 2, 3, 4...$ is the principal quantum number, describing the principal electron shell containing the specified electron. It determines the element's period.
- l is the orbital angular momentum quantum number, describing the type of subshell. It is an integer between 0 and $n - 1$ inclusive. 0 corresponds to the s subshell, 1 corresponds to the p subshell, 2 corresponds to the d subshell, and so on.
- m_l is the magnetic quantum number, describing the projection of the orbital's angular momentum along a given axis.
  It is an integer between $-l$ and l inclusive. The number of values m_l takes determines the number of orbitals in that subshell.
- m_s is the electron spin quantum number, describing the direction of electron spin.
  It can take values of $\frac{1}{2}$ or $-\frac{1}{2}$ for upward and downward spin respectively.

For example, to describe the single 3s electron of sodium in its ground state, $n = 3$, $l = 0$, $m_l = 0$, and $m_s = \frac{1}{2}$.

In an alternate universe, the rules for n, l, and m_s stay the same. However, m_l is now an integer between 0 and l inclusive. Assume the Aufbau principle still applies, and that the order and atomic symbols of elements in the alternate universe is identical to our actual universe. For example, the element with atomic number 10 is still neon, Ne.

(a) What are the chemical symbols of the first **four** noble gases found in this alternate universe? **[3 points]**
Input four concatenated chemical symbols. The answer is case-sensitive. If your answer is H, He, Li and Be, input "HHeLiBe".

(b) An ionic compound containing only hydrogen, carbon and nitrogen has been synthesised. If carbon is only present in the cation, and nitrogen only present in the anion, what is the **simplest** chemical formula possible for this compound?

[2 points]

Input your answer as you would an ordinary ionic compound, with numbers as ordinary characters and brackets when necessary. I.e. if your answer is $(HC_2)_3N_4$*, input "(HC2)3N4".*

(c) A neutral covalent compound with the formula $B_7H_kC_2N$ has been synthesised. It contains 1 double bond but not a ring.

What is the value of k? **[2 points]**

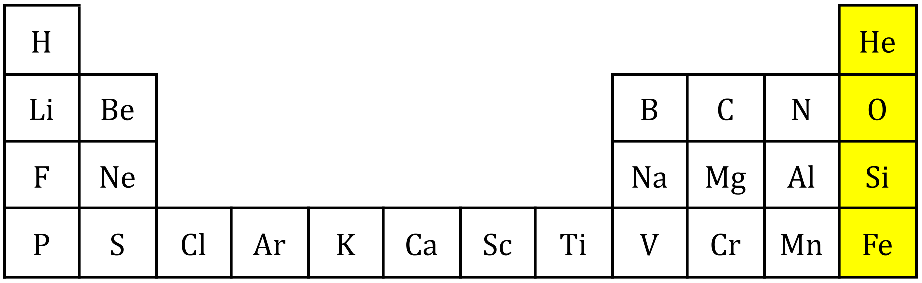
Solution:

(a) HeOSiFe

Using the rules given, we can find the number of each type of orbital in every electronic shell:

n	l	Subshell	m_l	Values of m_l	Orbitals	Atomic numbers
1	0	s	0	1	1s	1, 2
2	0	s	0	1	2s	3, 4
	1	p	0, 1	2	2p, 2p	5, 6, 7, 8
3	0	s	0	1	3s	9, 10
	1	p	0, 1	2	3p, 3p	11, 12, 13, 14
	2	d	0, 1, 2	3	3d, 3d, 3d	17, 18, 19, 20, 21, 22
4	0	s	0	1	4s	15, 16
	1	p	0, 1	2	4p, 4p	23, 24, 25, 26
... and so on						

Hence we can draw the first 4 periods of the periodic table:

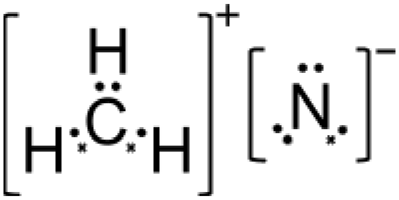


H											He
Li	Be							B	C	N	O
F	Ne							Na	Mg	Al	Si
P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe

(b) CH3N or H3CN

Carbon has 4 valence electrons. In period 2, a filled valence shell has 6 electrons, so it requires 2 more. It can form 2 covalent bonds with 2 hydrogen atoms. A 3rd dative covalent bond to a proton produces a CH_3^+ cation.

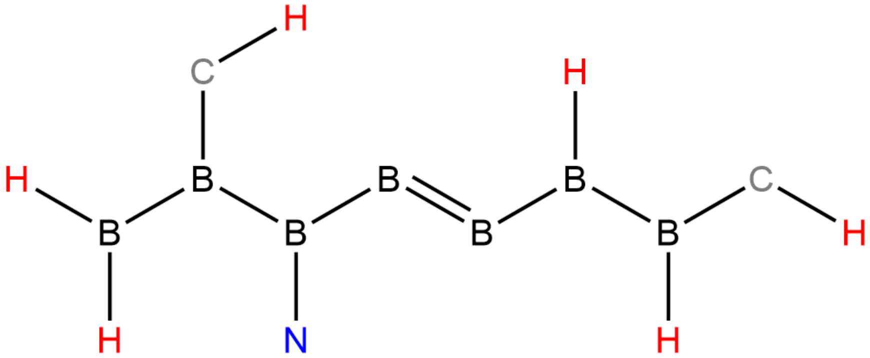
Meanwhile, nitrogen has 5 valence electrons. Gaining one more electron forms a stable N^- anion.



(c) 6

Boron can form 3 covalent bonds to another atom (3 single bonds or 1 single + 1 double bond). Carbon can form 2 covalent bonds to another atom (2 single bonds or 1 double bond). Hydrogen and nitrogen can form only 1 covalent bond to another atom.

Hence, a possible molecule with the formula $B_7H_kC_2N$ is the following:



Therefore $k = 6$. Any isomer will deliver the same result.

Problem prepared by: Wang Jiahua

Problem 26: Disappearing Solid

[5 points]

Jorge has 200 cm^3 of 0.1000 M $Pb(NO_3)_2$ solution. He adds 0.0800 M KCl solution slowly, stirring such that the mixture is always perfectly homogeneous.

After some KCl solution is added, a precipitate of $PbCl_2$ ($K_{sp} = 1.70 \times 10^{-5}$ mol^3 dm^{-9}) forms. As Jorge continues to add KCl, the mass of precipitate increases and then falls. Eventually, all the $PbCl_2$ re-dissolves. Equilibrium is maintained throughout this process.

Assume that no complexes of Pb^{2+} (eg. $[PbCl_4]^{2-}$) form throughout, so all lead is present either as Pb^{2+}(aq) or $PbCl_2$(s) .

What is the maximum mass of solid $PbCl_2$ present at any time during this process, in grams?

Leave your answer to 4 significant figures.

Solution:

3.152

Assume first that $PbCl_2$ is completely soluble in water, and that x cm^3 of KCl solution has been added to the $Pb(NO_3)_2$ solution. At this point,

$$[Pb^{2+}] = 0.1 \times \frac{200}{x+200} = \frac{20}{x+200}$$
$$[Cl^{-}] = 0.08 \times \frac{x}{x+200} = \frac{0.08x}{x+200}$$

But since $PbCl_2$ is sparingly soluble, for some range of x, y mol Pb^{2+} and $2y$ mol Cl^- will precipitate to form y mol $PbCl_2(s)$ (where $y > 0$).

$$Pb^{2+}\,(aq) + 2\,Cl^-\,(aq) \rightleftharpoons PbCl_2\,(s)$$

As $PbCl_2$ precipitates, equilibrium is reached where the ionic product of $PbCl_2$, $[Pb^{2+}][Cl^-]^2 = K_{sp}$. Since K_{sp} requires us to work with concentrations (in M),

$$\text{Loss in } [Pb^{2+}] = \frac{y}{\frac{x}{1000}+0.2} = \frac{1000y}{x+200}$$
$$\text{Loss in } [Cl^{-}] = 2 \times \frac{1000y}{x+200} = \frac{2000y}{x+200}$$

Now we can do up an ICE table:

Concentrations	**$Pb^{2+}(aq)$**	**+**	**$2\,Cl^-(aq)$**	**$\rightleftharpoons$**	**$PbCl_2\,(s)$**
Initial	$\frac{20}{x+200}$		$\frac{0.08x}{x+200}$		
Change	$-\frac{1000y}{x+200}$		$-\frac{2000y}{x+200}$		
Equilibrium	$\frac{20-1000y}{x+200}$		$\frac{0.08x-2000y}{x+200}$		

Hence,

$$K_{sp} = [Pb^{2+}]_{eq}[Cl^{-}]_{eq}^{\ 2} = \frac{(20-1000y)(0.08x-2000y)^2}{(x+200)^3}$$
$$(20 - 1000y)(0.08x - 2000y)^2 = K_{sp}(x + 200)^3 \qquad (1)$$

Because we want the mass of $PbCl_2$ to be maximum, y has to be maximum. We need to differentiate (1) implicitly with respect to x.

$$(20 - 1000y)(2)(0.08x - 2000y)(0.08 - 2000\frac{dy}{dx}) + (0.08x - 2000y)^2(- 1000\frac{dy}{dx}) = 3K_{sp}(x + 200)^2$$

$$\text{Because } \frac{dy}{dx} = 0,$$

$$2(20 - 1000y)(0.08x - 2000y)(0.08) = 3K_{sp}(x + 200)^2$$

$$(20 - 1000y)(0.08x - 2000y) = \frac{75}{4}K_{sp}(x + 200)^2$$

$$(20 - 1000y)(0.08x - 2000y)^2 = \frac{75}{4}K_{sp}(x + 200)^2(0.08x - 2000y) \qquad (2)$$

Now we can substitute (2) into (1):

$$\frac{75}{4}K_{sp}(x + 200)^2(0.08x - 2000y) = K_{sp}(x + 200)^3$$

$$75(0.08x - 2000y) = 4(x + 200)$$

$$6x - 150000y = 4x + 800$$

$$y = \frac{x}{75000} - \frac{2}{375} \qquad (3)$$

This tells us that the maximum value of y lies on the intersection of (1) and (3). Substituting (3) into (1) yields

$$\left(\frac{76}{3} - \frac{1}{75}x\right)\left(\frac{32}{3} + \frac{4}{75}x\right)^2 = \left(1.7 \times 10^{-5}\right)(x + 200)^3$$

$$x = 1250.0337$$

$$y = 0.01133378$$

So the maximum mass of $PbCl_2$ that can precipitate is:

$0.01133378 \times 278.1 =$ **3.152** g (4 s.f.)

Problem prepared by: Wang Jiahua

Problem 27: Smooth Operator

[11 points]

Ferrari driver Carlos Sainz won the 2023 Singapore Grand Prix[7].

The fuel used by modern Formula 1 cars is actually similar to ordinary petrol one can purchase at a gas station. However, even ordinary petrol is a complex blend of different hydrocarbons and additives such as octane boosters, corrosion inhibitors, stabilisers and lubricants that improve the performance of an engine.

For simplicity, suppose the fuel supplied to F1 cars has the exact composition as described below, with a density of 752 kg m^{-3} in its liquid form.

Name	Structure	w/w%	$\Delta H_c^\ominus$ / kJ mol^{-1}
ethanol	CH_2CH_3OH	10.0	−1367
n-heptane	$CH_3(CH_2)_5CH_3$	4.9	−4817
isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	76.5	−5461
toluene	$C_6H_5CH_3$	5.0	−3910
MTBE	$(CH_3)_3COCH_3$	3.6	−3368

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[7] Image source: Smith, D. (2023, September 19). 2023 Singapore grand prix: 7 talking points: GRR. Goodwood. https://www.goodwood.com/grr/race/modern/2023-singapore-grand-prix--7-talking-points/

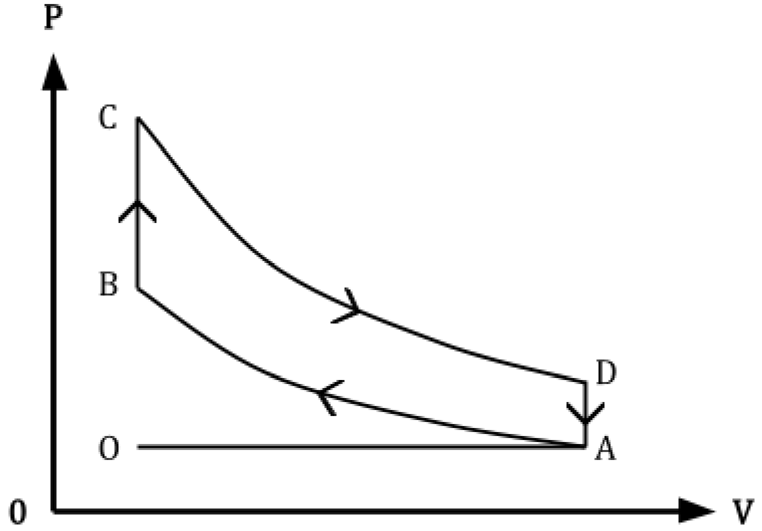
(a) As of 2024, the Singapore Grand Prix comprises 62 laps of the 4.940 km-long Marina Bay street circuit. Suppose that the average fuel efficiency of an F1 car is 2.15 km l^{-1}, and that the fuel undergoes complete combustion.
What is the total volume of CO_2, in dm^3 and measured at r. t. p, produced by a single car during the race? **[3 points]**
Leave your answer to 3 significant figures.

(b) Calculate the energy released, in kJ, when 1 kg of fuel undergoes complete combustion. **[2 points]**
Leave your answer to 3 significant figures.

(Note: the following parts are separate from (a) and (b).)

Of course, in reality, not all of this energy is converted to useful work. Still, modern F1 cars achieve a high thermal efficiency in excess of 50% through a hybrid power system that recovers energy from exhaust gases and braking. However, the bulk of the F1 car's power is still supplied by its 1.6 litre turbocharged V6 engine.

An idealised spark ignition piston engine follows the Otto cycle. In a 4-stroke engine, after the fuel-air mixture enters a cylinder (OA), it is rapidly compressed by the piston (AB) and ignited by the spark plug (BC) when the piston momentarily reaches the top. The power stroke causes rapid expansion (CD), after which the exhaust gases are cooled (DA) and ejected (AO). AB and CD are adiabatic processes, while BC and DA are isovolumetric.



The Otto cycle on a P-V diagram.

Consider an ideal F1 engine with a displacement of 1.6 litres, running on an ideal gas.

Gas enters each cylinder at a pressure of 3.5 bar and temperature of 300 K. Compression increases its temperature to 945 K. The constant volume molar heat capacity ($C_{V,m}$) of the gas is 20.8 J mol^{-1} K^{-1}.

(c) Calculate the compression ratio of this engine. **[2 points]**
Leave your answer to 3 significant figures.

During ignition, 1.65 kJ of heat is delivered to the gas in **each** cylinder. **Assume the amount of gas remains constant during ignition.** The 6 cylinders are timed such that each fires every 2 revolutions of the crankshaft[8]. After expansion and cooling, the gas is ejected at the same pressure and temperature as when it entered the engine.

(d) An F1 engine can rev up to 15000 rpm. Calculate the maximum theoretical horsepower produced, measured at the crankshaft, given that 1 hp = 746 W.
Assume that all work done by the gas is translated into rotation in the crankshaft, and that none is lost due to friction. **[4 points]**
Leave your answer to 3 significant figures.

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[8] To visualise how the cylinders in a V6 engine are synchronised, you can watch the following video: https://youtu.be/RDOJijSiIvg?si=C8atpEx33EaJmnc4&t=80

Solution:

(a) 173000 (not 173)

Total mass of fuel used $= \frac{4.940\times62}{2.15} \times \frac{1}{1000} \times 752 = 107.13$ kg

Fraction by mass of carbon in the fuel

$= \Sigma(\%\ by\ mass\ of\ substituent\ in\ fuel)(\%\ by\ mass\ of\ carbon\ in\ substituent)$

$= (0.100)\frac{24.02}{46.068} + (0.049)\frac{84.07}{100.198} + (0.765)\frac{96.08}{114.224} + (0.050)\frac{84.07}{92.134} + (0.036)\frac{60.05}{88.146}$

$= 0.80689$

$$n_C = \frac{107.13\times1000\times0.80689}{12.01} = 7197.5\ \text{mol} = n_{CO_2}$$

Hence $V_{CO_2} = \frac{nRT}{P} = \frac{7197.5\times8.3145\times293.15}{1.01325\times10^5} = 173.14\ \text{m}^3 \approx$ **173000 dm³**

Note: while this may seem like a lot of CO_2, over the course of a single season, the F1 cars themselves only contribute to less than 1 % of the sport's total carbon emissions. The bulk of emissions arise from the immense logistics of hosting more than 20 races over 5 continents. F1 has pledged to be carbon neutral by 2030, but whether the sport can achieve that is still up for debate.

(b) 45400

$$\Delta H = \frac{100}{46.068}(1367) + \frac{49}{100.198}(4817) + \frac{765}{114.224}(5461) + \frac{50}{92.134}(3910) + \frac{36}{88.146}(3368)$$

$$= 45395\ \text{kJ} \approx \mathbf{45400\ kJ}$$

(c) 17.6

In the Otto cycle, the compression (AB) and expansion (CD) process are adiabatic. Hence, we can use the relation

$$T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1}$$

Which can be rewritten as $\left(\frac{V_A}{V_B}\right)^{\gamma-1} = \frac{T_B}{T_A}$

The compression ratio $r = \frac{Maximum\ volume\ of\ cylinder}{Minimum\ volume\ of\ cylinder} = \frac{V_A}{V_B}$, and the heat capacity ratio $\gamma = \frac{C_{P,m}}{C_{V,m}} = \frac{C_{V,m}+R}{C_{V,m}} = \frac{20.8+8.3145}{20.8} = 1.40$ since the gas is ideal. Hence,

$$r = \left(\frac{T_B}{T_A}\right)^{\frac{1}{\gamma-1}} = \left(\frac{945}{300}\right)^{\frac{1}{1.40-1}} = 17.611 \approx \mathbf{17.6}$$

(d) 1130

Although the 6 cylinders do not fire together, we can still consider them as a single system of volume 1.6 dm^3.

$$\text{Amount of gas in the system} = n = \frac{p_A V_A}{RT_A} = \frac{(3.5\times10^5)(1.6\times10^{-3})}{(8.3145)(300)} = 0.22451\ \text{mol}$$

$$\text{Heat supplied during process BC} = Q_{BC} = nC_{V,m}\Delta T_{BC}$$

$$\Delta T_{BC} = \frac{Q_{BC}}{nC_{V,m}} = \frac{6\times1650}{(0.22451)(20.8)} = 2120.0\ \text{K}$$

$$T_C = 2120.0 + 945 = 3065.0\ \text{K}$$

$$T_D = T_C\left(\frac{V_C}{V_D}\right)^{\gamma-1} = T_C\left(\frac{1}{r}\right)^{\gamma-1} = (3065.0)\left(\frac{1}{17.611}\right)^{1.40-1} = 973.01\ \text{K}$$

Work is only done by the gas during the adiabatic processes AB and CD. $W_{by\ gas} = \int_{V_i}^{V_f} p\ \mathrm{d}V$,

and if we use the relationship $pV^\gamma = p_iV_i^\gamma = p_fV_f^\gamma$ = constant,

$$W_{adiabatic} = \left(p_iV_i^\gamma\right)\int_{V_i}^{V_f}\frac{1}{V^\gamma}\,dV = \left(p_iV_i^\gamma\right)\left[\frac{1}{1-\gamma}V^{1-\gamma}\right]_{V_i}^{V_f} = \frac{1}{1-\gamma}\left(p_fV_f - p_iV_i\right)$$

$$= \frac{nR}{1-\gamma}\left(T_f - T_i\right) = -nC_{V,m}\Delta T$$

$$\text{Hence } W_{net} = W_{CD} + W_{AB} = -nC_{V,m}\left(T_D - T_C\right) - nC_{V,m}\left(T_B - T_A\right)$$

$$= nC_{V,m}\left[\left(T_C - T_B\right) - \left(T_D - T_A\right)\right]$$

$$= (0.22451)(20.8)[(3065.0 - 945) - (973.01 - 300)]$$

$$= 6757.2\ \text{J}$$

If each cylinder fires once every 2 revolutions, then W_{net} will be produced by the engine $\frac{15000}{2} = 7500$ times every 60 seconds. Hence, the theoretical maximum power in hp is

$$6757.2 \times \frac{7500}{60} \times \frac{1}{746} = 1132.2 \approx \mathbf{1130\ hp}$$

That is a LOT of power from a tiny 1.6 litre engine.

Problem prepared by: Wang Jiahua

Problem 28: Out Of The Woods

[5 points]

"Two paper aeroplanes flying, flying, flying, and I remember thinking, are we out of the woods yet?"

— Taylor Swift, "Out Of The Woods"

Taylor Swift is preparing for her global world tour, the Eras Tour. Of course, she is preparing to fly around the world on her private jet during the tour. After all, if she's already responsible for 8000 metric tons of emissions, one more flight can't hurt[9]. Taylor plans to power her private jet using a heat engine of 1 mol of monatomic ideal gas, but since she's unique, she will design her own cycle.

Since Taylor likes regular polygons, she chooses to make her heat engine a perfect square on a p-V diagram (units are in bar and dm^3 respectively). The cycle starts with 1 mol of ideal gas at 1.00 bar and 25 °C (A on the graph). On the graph, the cycle has dimensions of 5 by 5 as shown in Figure 1. Note that Figure 1 is not to scale.

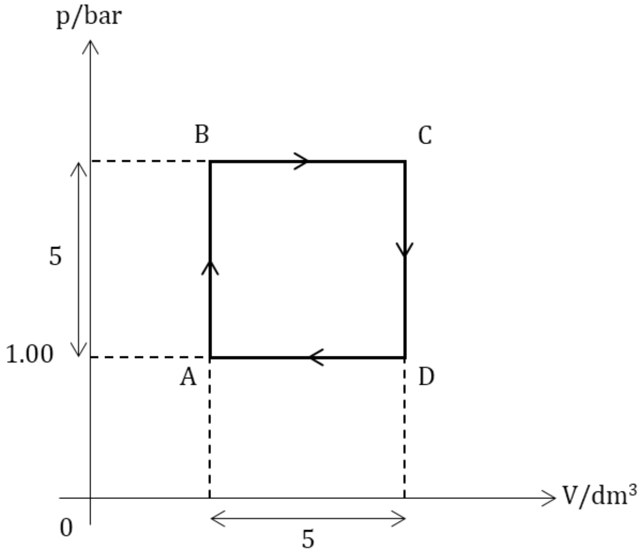

Figure 1: So it's gonna be forever, or it's gonna go down in flames.

(a) Find the efficiency of Taylor's heat engine in %. **[3 points]**

Give your answer in 3 significant figures, without the %. For instance, if the calculated answer is 0.69 = 69.0 %, key in 69.0.

---

[9] The SChL team does not endorse such environmentally destructive behaviour.

"Remember when we couldn't take the heat? I walked out, I said I'm setting you free."
— Taylor Swift, "Out Of The Woods"

Taylor finds her plane too hot to handle, so she decides to also design a refrigeration cycle to cool her plane. Taylor's refrigerator is also a perfect square but on a T-S diagram (units are in K and J K^{-1} respectively). The cycle also starts with 1 mol of monatomic ideal gas at 1.00 bar and 25 °C (E on the graph). The cycle is shown in Figure 2, which again is not to scale.

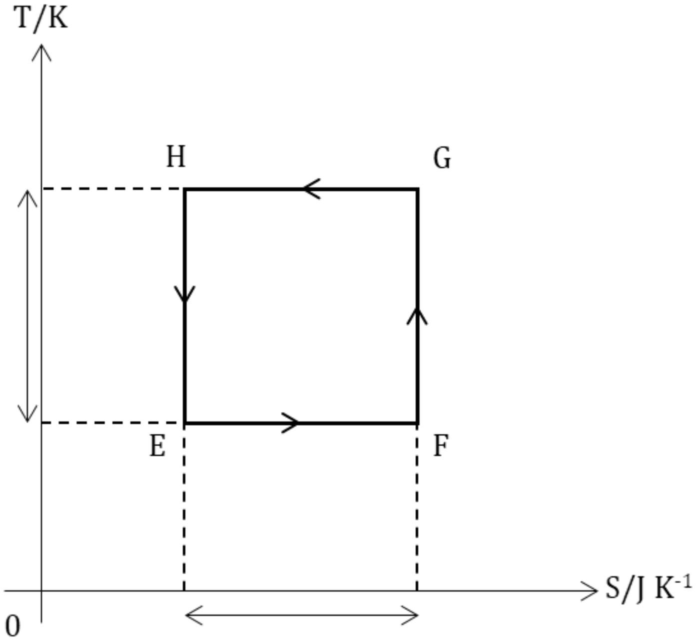

Figure 2: The players gonna play, play, play, play, play.

(b) Taylor is feeling 22, so she wants her cycle to have a coefficient of performance of 22. Calculate the side length of the cycle on the graph that would give her such a coefficient. **[2 points]**
Leave your answer to 3 significant figures.

Solution:

(a) 9.58

To calculate efficiency of a heat engine, we need to find the heat input and the net work done.

Note that net work done is easy to calculate: it is the area under the p-V graph. We will convert to SI units for convenience.

$$w_{net} = \left(5\times10^{5}\right)\left(5\times10^{-3}\right) = 2500J$$

Heat is input into the system in the two heating steps (A→B and B→C).

To proceed to calculate heat input, we first need the volume of the system at A.

$$V_A = \frac{nRT_A}{p_A} = \frac{1(8.3145)(298.15)}{10^5} = 0.0247897\, m^3 = 24.7897\, dm^3$$

For convenience, I will calculate the two steps in one go as a process from A→C, but you can also do them separately for clarity.

$$T_C = \frac{p_C V_c}{nR} = \frac{(6.00\times10^5)(29.7897\times10^{-3})}{1(8.3145)} = 2149.72K$$

$$\Delta U = nC_{v,m}\Delta T = 1\left(\frac{3}{2}\right)(8.3145)(2149.72 - 298.15) = 23092.3\, J$$

$$w = - p\Delta V = - \left(6.00\times10^{5}\right)\left(5.00\times10^{-3}\right) = - 3000J$$

$$q_{input} = \Delta U - w = 23092.3 - (- 3000) = 26092.3J$$

$$\eta = \frac{w_{net}}{q_{input}} = \frac{2500}{26092.3} = 0.095814 = 9.5814\% = 9.58\% \text{ (3 s.f.)}$$

Hence the answer to key in is 9.58. Turns out this cycle is really inefficient, but when you're a multi-millionaire, it probably doesn't matter.

(b) 13.6

Note that this refrigerator is actually a Carnot cycle working in reverse. Hence, we should be able to derive an expression for COP similar to the carnot efficiency that is in terms of the hot and cold temperatures only.

Also, note that the cycle involves an isothermal expansion from E to F, an isentropic adiabatic compression from F to G, then an isothermal compression from G to H, and lastly an isentropic adiabatic expansion from H to E. The two isentropic processes conveniently involve no heat transfer.

$$\frac{|q_{G\to H}|}{|q_{E\to F}|} = \frac{T_H}{T_C}$$

$$q_{net} = - |q_{G\to H}| + |q_{E\to F}|$$

$$w_{net} = -q_{net} = \left|q_{G\rightarrow H}\right| - \left|q_{E\rightarrow F}\right|$$

$$COP = \frac{\left|q_{E\rightarrow F}\right|}{\left|q_{G\rightarrow H}\right| - \left|q_{E\rightarrow F}\right|} = \frac{T_C}{T_H - T_C}$$

$\frac{298.15}{x} = 22$ where x is the side length

$$x = 13.552 = 13.6 \text{ (3 s.f.)}$$

Problem prepared by: Brennan Ting

Problem 29: To And Fro

[6 points]

Jorge is investigating the kinetics of a certain reversible reaction:

$$A\ (g) \rightleftharpoons 2\ B\ (g)$$

$$\text{Forward rate} = k_f[A]$$

$$\text{Backward rate} = k_b[B]^x$$

Where $k_f = 3.3108 \times 10^{-4}\ \text{s}^{-1}$ at 800 K.

To determine the order of the backward reaction x and its rate constant k_b, Jorge injects 3.28 mol of gas B into a 25.0 dm^3 container that contains a large excess of gas C. C is unreactive towards B but reacts very quickly with A, forming inert products.

The container is heated and maintained at 800 K. The concentrations of B at two different times t after it enters the container are shown below.

t / s	[B] / mol dm^{-3}
240	0.09121
540	0.05790

(a) Find the numerical value of k_b at 800 K in standard form. **[3 points]**

Leave your answer to 5 significant figures, in the form $\overline{xEy}$*, where* y *is the exponent of 10. For example, if your answer is* 1.2345×10^{-6}*, input "1.2345E-6".*

Jorge empties the container and injects 7.43 mol of A into it, maintaining it at 800 K as before. He observes that the system approaches equilibrium after some time.

(b) How long, in seconds, will it take for the concentration of B to reach 99.5 % of its value at equilibrium? **[3 points]**

Leave your answer to 3 significant figures. If you need to use k_b*, use the value you found in part (a).*

Solution:

(a) 7.5741E-4

If C is in excess and reacts quickly with A, no A will be formed essentially and the forward reaction will not take place. This means any changes to [B] will only be due to the backward reaction, 2 B → A.

For this reaction, rate $= k_b[B]^x = -\frac{1}{2}\frac{d[B]}{dt}$. The coefficient of $\frac{1}{2}$ is because the rate of reaction is 2 times the rate of disappearance of B.

Since the values of t provided are not half-lifes, we cannot use the half-life method to find x and k_b. We must find the integrated rate laws for the common values of x (0, 1, 2) and check against t and [B], to determine the value of x for which k_b is constant. The initial concentration of B, $[B]_0 = \frac{3.28}{25.0} = 0.1312$ M.

x	Integrated rate law[10]	1st value of k_b (from $t = 0$ to $t = 240$)	2nd value of k_b (from $t = 0$ to $t = 540$)	Is k_b approximately constant?
0	$[B]_t = [B]_0 - 2k_bt$	$\frac{0.1312-0.09121}{2\times240}$ $= 8.33125 \times 10^{-5}$	$\frac{0.1312-0.05790}{2\times540}$ $= 6.78704 \times 10^{-5}$	No
1	$\ln[B]_t = \ln[B]_0 - 2k_bt$	$\frac{1}{2\times240}\left(\ln\frac{0.1312}{0.09121}\right)$ $= 7.57413 \times 10^{-4}$	$\frac{1}{2\times540}\left(\ln\frac{0.1312}{0.05790}\right)$ $= 7.57412 \times 10^{-4}$	Yes
2	$\frac{1}{[B]_t} = \frac{1}{[B]_0} + 2k_bt$	$\frac{1}{2\times240}\left(\frac{1}{0.09121} - \frac{1}{0.1312}\right)$ $= 6.96200 \times 10^{-3}$	$\frac{1}{2\times540}\left(\frac{1}{0.05790} - \frac{1}{0.1312}\right)$ $= 8.93445 \times 10^{-3}$	No

Hence, the backward reaction must be first order with respect to B.

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[10] How these are derived can be found here: https://chem.libretexts.org/Bookshelves/General_Chemistry/Chemistry_1e_(OpenSTAX)/12%3A_Kinetics/12.4%3A_Integrated_Rate_Laws

The third value of $k_b = \frac{1}{2\times300}\left(\ln\frac{0.09121}{0.05790}\right) = 7.57412 \times 10^{-4}$ can be calculated using $t = 240$ to $t = 540$. Hence the value of k_b to 5 s.f. is 7.5741×10^{-4}, and we input **7.5741E-4.** (Since it is overall first order, the units must also be s^{-1}.)

(b) 4870

Both the forward and backward reactions are occuring now, so the net rate of appearance of [B] will depend on both [B] and [A].

Let the initial concentration of A be C M (what this value is doesn't actually matter). After t seconds, suppose y M of A has reacted. Now [A] = $(C - y)$ M and [B] = $2y$ M.

$$\text{Rate of appearance of B} = 2k_f[A]$$
$$\text{Rate of disappearance of B} = k_b[B]$$
$$\textbf{Net}\text{ rate of appearance of B} = \frac{d[B]}{dt} = 2k_f[A] - k_b[B] = 2k_f(C - y) - 2k_b y$$

Since $[B] = 2y$,

$$\frac{dy}{dt} = k_f(C - y) - k_b y$$

Integrating,

$$\frac{1}{k_fC - k_fy - k_by}\,dy = dt$$
$$-\int_0^t \frac{-(k_f + k_b)}{k_fC - (k_f + k_b)y}\,dy = \int_0^t k_f + k_b\,dt$$
$$-\left[\ln\left|k_fC - (k_f + k_b)y\right|\right]_0^t = (k_f + k_b)t$$
$$\ln(k_fC) - \ln\left(k_fC - (k_f + k_b)y_t\right) = (k_f + k_b)t$$
$$\ln\left(\frac{k_fC}{k_fC - (k_f + k_b)y_t}\right) = (k_f + k_b)t$$

At equilibrium, $\frac{dy}{dt} = 0$, so $k_f(C - y) = k_b y \Rightarrow y_{eq} = \frac{k_fC}{k_f + k_b}$. When [B] is 99.5% its value at equilibrium, $y = \frac{0.995k_fC}{k_f + k_b}$. Substituting this above,

$$\ln\left(\frac{k_f C}{k_f C-(k_f+k_b)\frac{0.995k_f C}{k_f+k_b}}\right)=\ln\left(\frac{1}{1-0.995}\right)=\ln(200)=(k_f+k_b)t$$

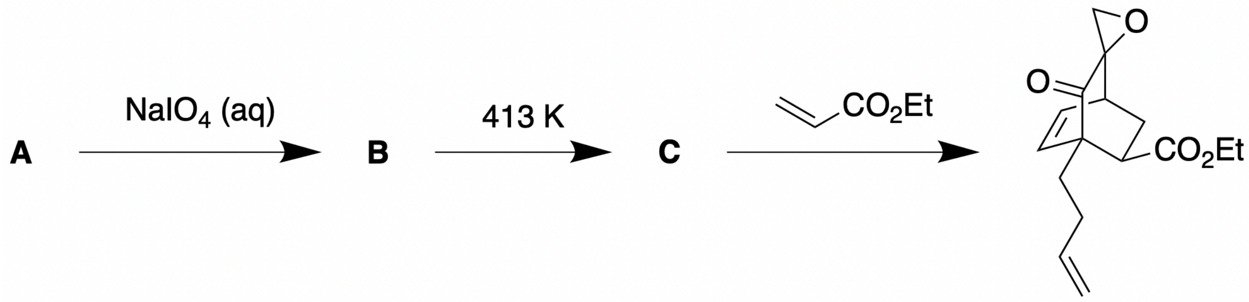
$$\text{Hence } t=\frac{\ln(200)}{7.5741\times10^{-4}+3.3108\times10^{-4}}\approx \mathbf{4870\ s}\ (3\text{ s.f.}).$$

Problem prepared by: Wang Jiahua

Problem 30: It Is Periodic

[5 points]

Periodate is the conjugate base of periodic acid, and is known to oxidatively cleave alkenes via the Malaprade reaction. However, a lesser known use of sodium periodate is in the generation of epoxides. The following reaction scheme shows the usage of $NaIO_4$ in a total synthesis:

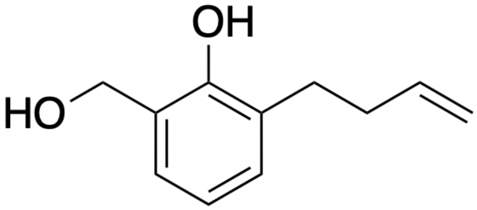


Structure **A** is a diol, but it is **not** a vicinal or geminal diol. Addition of EtO_2CCHCH_2 directly to the reaction mixture containing compound **A** and $NaIO_4$ yielded a mixture of compound **B** and the final product. The molar mass of compound **B** is 352 g mol^{-1}.

Give the structure of compound **A**.

Solution:

Compound **A**:

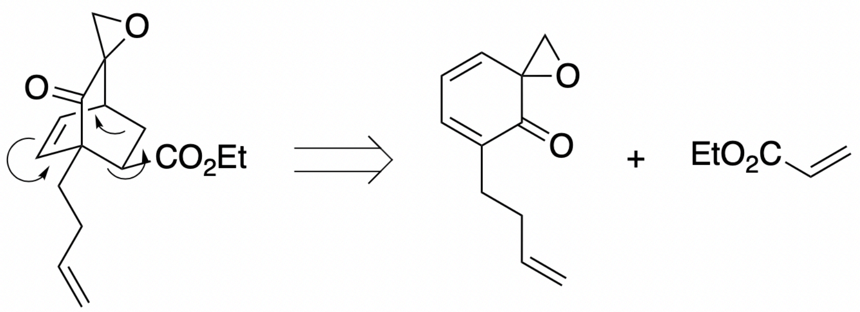


One easy point of entry into this question is through careful examination of the final product:

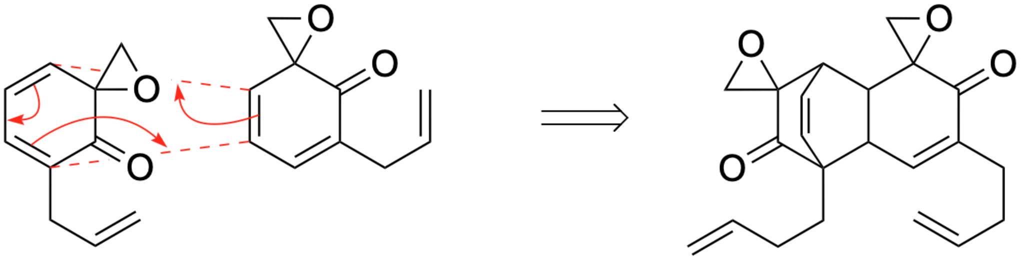
1. An epoxide is present in the final product, but there seems to not have been any reactions known to generate an epoxide in the reaction scheme.
2. The carbon skeleton of the final product is a bridged bicyclic alkene.

Given information (2), and by noticing that the reagent in the final step contains an alkene bonded to an electron-withdrawing group, we can deduce that the last step involves a classic Diels-Alder reaction.

As such, we can easily perform a retro Diels-Alder reaction to deduce the structure of compound **C**:



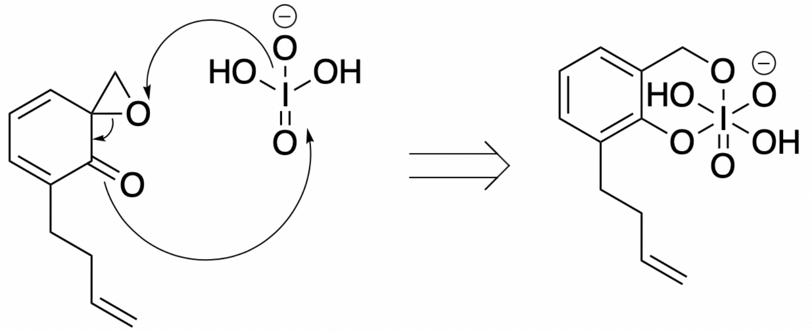
Now, notice that the molecular formula of compound **C** is $C_{11}H_{12}O_2$ which has a molar mass of 176 g mol^{-1} - which is exactly equal to half the molar mass of compound **B**! Given that the conversion for **B** to **C** requires heating, and that $EtO_2CCH_2CH_2$ can react with compound **A** albeit producing the final product at a poor yield, we can easily conclude that the side reaction which produces **B** instead of the final produce involves **dimerization** of compound **C**. Given the structure of compound **C** contains a diene, we can easily deduce that compound **B** is formed through the Diels-Alder reaction of 2 equivalents of compound **C**:



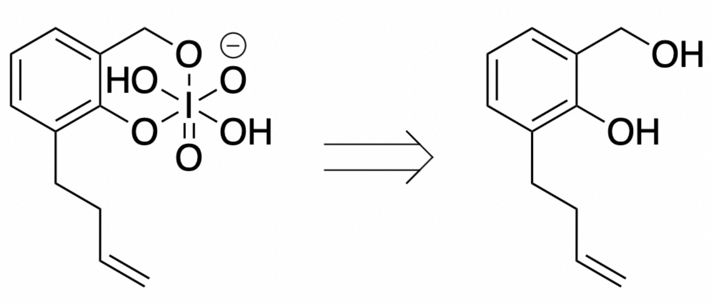
The molecular formula of compound **B** is $C_{22}H_{24}O_4$, which fits the given molar mass of 352 mol^{-1}.

The reaction scheme in reality looks something like this: **2A → 2C → B → 2C → final product**

To deduce the conversion from **A** to **B**, we can first deduce the structure of the IO_4-containing intermediate by easily working backwards from **C**:



We can now easily deduce the structure of compound **A**:



Reference: Singh, Vishwakarma & Bhalerao, Pravin & Sahu, Bharat & Shaikh, Mohammad. (2013). Molecular complexity from aromatics. Cycloaddition of spiroepoxycyclohexa-2,4-dienones and intramolecular Diels-Alder reaction: A stereoselective entry into tetracyclic core of atisane diterpenoids. Tetrahedron. 69. 137-146. 10.1016/j.tet.2012.10.051.

Problem prepared by: Chua Ming Xiu

Problem 31: Electrides

[7 points]

Electrides are ionic compounds which have electrons as the anion. They are often used as powerful reducing agents. Electride **X** can be directly synthesised by sintering a mixture of compound **A**, binary oxide $\mathbf{M}_m\text{O}_n$, and metal **M** under high heat in a vacuum. It is known that compound **A** contains metal **M**.

(a) $\mathbf{M}_m\text{O}_n$ is an oxide of metal **M** which contains 71.47 % of metal **M** by mass. State the PubChem CID number of $\mathbf{M}_m\text{O}_n$. **[2 points]**

Compound **A** (M_r = 158.0) is a ternary oxide that rarely occurs in nature. Compound **A** reacts rapidly with water to form the metastable hydrate $\mathbf{M}_m\text{O}_n \cdot \mathbf{N}_p\mathbf{O}_q \cdot 10\text{H}_2\text{O}$.

Pepperius Peppa Pig was given a procedure by George Pig, who wanted her to help separate the elements **M** and **N** in electride **X** with a few provided reagents.

Hence, she crushed the hydrate $\mathbf{M}_m\text{O}_n \cdot \mathbf{N}_p\mathbf{O}_q \cdot 10\text{H}_2\text{O}$ into a fine powder and dissolved it in excess HCl (aq), after which an unknown sodium salt **C** was added. Then, she filtered the mixture to obtain a precipitate **B** and a solution (filtrate) containing **D**.

Next, to verify the identity of salt **C**, Peppa added a sample of salt **C** to a solution of binary chloride **F** which contains 34.05 % Cl by mass, and a white precipitate formed. The white precipitate was found to be insoluble in excess strong acids. She then filtered the mixture to obtain a solution containing cations of metal **M**.

Subsequently, Peppa evaporated the solution containing **D** to dryness before treating it with a compound of molar mass 8.0 g mol^{-1}. This produced substance **E**, a substance commonly used in organic synthesis.

(b) State the chemical formula of compound **A**. **[3 points]**

Arrange the elements in compound ***A*** *in order of decreasing atomic number. For example, if the compound is $K_2Cr_2O_7$, input "Cr2K2O7".*

It is known that electride **X** is a ternary compound given by the formula $[\mathbf{M}_x\mathbf{N}_y\mathbf{O}_z]^{4+}\,(\text{e}^-)_4$, where x, y and z are whole numbers and $x + y = 52$.

(c) Given that 274.14 g of **X** contains 0.1 mol of the substance, determine the value of $x + y + z$. **[2 points]**

Solution:

(a) 14778 (or 6850728)

Let the M_r of metal **M** be M. Since $\omega(\mathbf{M}) = 0.7147$, $\omega(\mathrm{O}) = 0.2853$. Then,

$$0.2853 = \frac{16.00n}{16.00n + mM}$$

$$mM = 40.08n.$$

It becomes obvious that when $n = m = 1$, metal **M** corresponds to Ca. Hence, $\mathbf{M}_m\mathrm{O}_n$ is calcium oxide. The PubChem CID number of CaO is 14778 (or 6850728), and we hence arrive at the answer.

(b) CaAl2O4

Let us start with the information provided in the second paragraph of this question-part.

Let the formula of compound **F** be $\mathbf{P}_a\mathrm{Cl}_b$. Let the M_r of element **P** be P. Since $\omega(\mathrm{Cl}) = 0.3405$,

$$0.3405 = \frac{35.45b}{aP + 35.45b}$$

$$aP = 68.662b.$$

After some guess-and-check, it becomes obvious that element **P** is Ba (when $a = 1$ and $b = 2$). Hence, compound **F** is $BaCl_2$. Since the white precipitate was found to be insoluble in excess strong acids, the white precipitate is $BaSO_4$ (and not $BaSO_3$). It immediately follows that compound **C** is Na_2SO_4, and that precipitate **B** is $CaSO_4$. Hence, we can confirm that compound **D** only contains element **N** and not **M**.

The only salt with a molar mass of 8.0 g mol^{-1} is lithium hydride, LiH. Given the clue that compound **E** is commonly used in organic synthesis, it can be deduced that compound **E** is lithium aluminium hydride, $LiAlH_4$. It follows that compound **D** is $Al_2(SO_4)_3$, and that element **N** is Al. Hence, oxide $\mathbf{N}_p\mathbf{O}_q$ is Al_2O_3.

Some guess-and-check with its M_r value would lead to the final conclusion that compound **A** is $CaAl_2O_4$, and we hence arrive at the answer.

(c) 116

Since 274.14 g of **X** contains 0.1 mol of the substance, $M_r(\mathbf{X}) = 2741.4\ \mathrm{g\ mol^{-1}}$.

Since we know that compound **X** is **neutral**, we can hence set up the following set of simultaneous equations:

$$40.08x + 26.98y + 16.00z = 2741.4,$$
$$x + y = 52,$$
$$2x + 3y - 2z = 4.$$

Solving the simultaneous equations yields $x = 24$, $y = 28$ and $z = 64$. Hence, compound **X** is $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$, and $x + y + z = 116$.

Problem prepared by: Ranen Yong

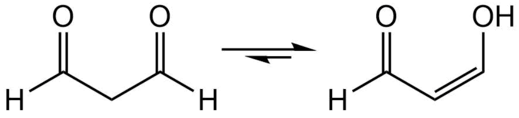
Problem 32: Proton MRT

[8 points]

Proton tunnelling is an important effect, albeit less well-known than its counterpart, electron tunnelling. This is simply because protons are over a thousand times heavier than electrons, making them much less likely to tunnel. Proton tunnelling involves the disappearance of a proton at one site and its reappearance at an adjacent site, separated by a potential barrier. It is associated heavily with hydrogen bonds, since a hydrogen atom sans its electron is simply a proton.

One area in which this phenomenon occurs is during DNA replication. The base pairs of DNA are held together by hydrogen bonds uniquely defined by a set of nitrogenous bases. Proton tunnelling is believed to alter the hydrogen bond configuration during DNA replication, possibly serving as the basis for mutations in cells.

β-dicarbonyls are some of the molecules for which proton tunnelling can occur. The structure of a β-dicarbonyl, malondialdehyde, is shown below. β-dicarbonyls with an α hydrogen atom can undergo keto-enol tautomerism. This includes malondialdehyde, which tautomerizes to hydroxyacrolein:

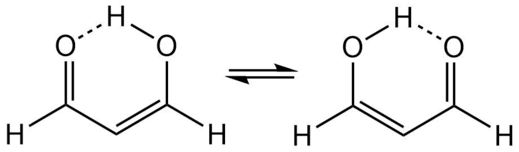


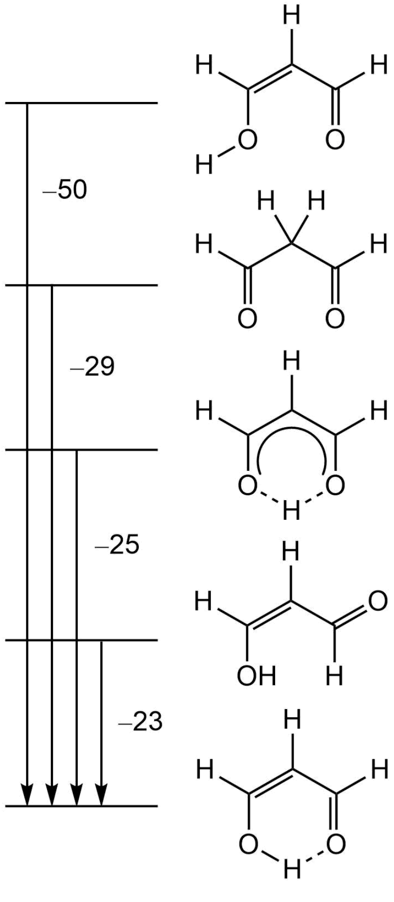
(a) In an aqueous solution, malondialdehyde is a weak acid, much like ethanoic acid. Determine if the following statements are true or false. **[2 points]**

1. The aldehyde proton can dissociate in water to give H^+ ions.
2. The monoanion of malondialdehyde is stable due to a conjugated π-electron system.
3. Intermolecular hydrogen bonds formed between hydroxyacrolein molecules stabilise the monoanion of malondialdehyde.
4. Malondialdehyde is a dibasic acid.
5. Hydroxyacrolein predominantly exists as the *cis* isomer in organic solvents.

If the statement is true, indicate T. If the statement is false, indicate F. Leave your answer as a concatenated string of ***five capital letters****. For example, if your answers are true, true, true, true, false, leave your answer as TTTTF.*

In malondialdehyde, proton tunnelling takes place when the proton in the −OH group of its tautomer delocalises across the two oxygen atoms. It is therefore of our interest to understand the interconversion between the two most stable tautomers of malondialdehyde, its enol *Z* forms.





relative energies of tautomers
wrt. malondialdehyde / kJ mol^{-1}

The relative energy levels of the tautomers of malondialdehyde are shown on the left. These values have been experimentally verified.

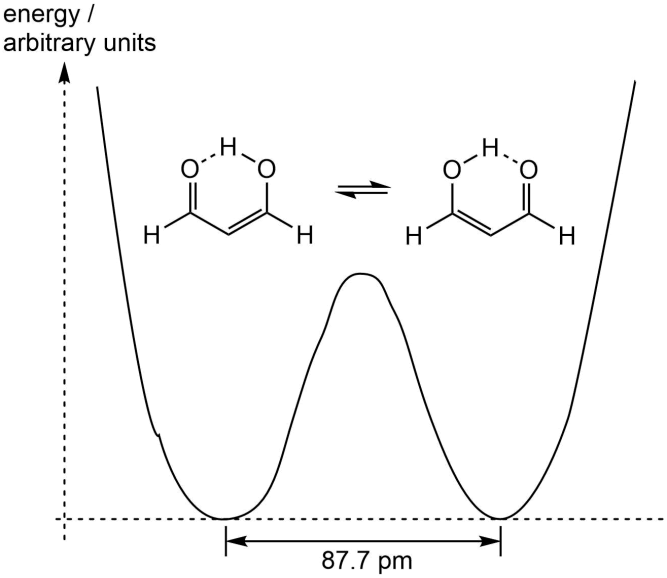
Calculations with various models have been conducted and the resulting data is listed below. The transition state is the energy barrier of the interconversion.

Energy level of TS / hartree	−266.00124
Energy level of enol *Z* form / hartree	−266.01472

Note: 1 hartree = 2625.5 kJ mol^{-1}.

(b) Calculate the difference between the calculated activation energy and actual activation energy in kJ mol^{-1}. **[2 points]**
Leave your answer to 3 significant figures.

To quantitatively describe the proton tunnelling effect in malondialdehyde, we can employ a diagram depicting its potential energy well. Each well represents the enol *Z* form.



The proton oscillates between the two wells with a frequency of 7.11×10^{10} Hz. It has a mass of 1.6726×10^{-27} kg.

(c) Calculate the theoretical mean speed of the proton in m s^{-1} as it moves from one well to the other. **[2 points]**
Leave your answer to 3 significant figures.

(d) Estimate the minimum uncertainty in the speed of the proton in m s^{-1}, to *one significant figure*. Compare this value to your answer in part (c) and select an appropriate conclusion below. **[2 points]**

A) Proton tunnelling can be described in classical terms as it is not a quantum phenomenon.
B) Proton tunnelling cannot be described in classical terms as it is a quantum phenomenon.

Leave your answer as a string of digits followed by a capitalised letter. For instance, if you believe the uncertainty is 100 m s^{-1}, and that the first conclusion is correct, input '100A'.

Hint 1: Heisenberg's uncertainty principle may be useful.

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Hint 2: The uncertainty in position is half the interminimal distance.

Solution:

(a) FTFFT

1. The aldehyde proton can dissociate in water to give H^+ ions.

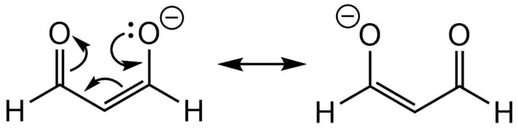
The acidic proton in the enol form of malondialdehyde is the hydroxyl proton, as its abstraction leads to the most stable conjugate base. The aldehydic proton cannot be abstracted by H_2O. Statement 1 is **false**.

2. The monoanion of malondialdehyde is stable due to a conjugated π-electron system.

The longer forward arrow informs us that malondialdehyde preferentially exists as its enol form, because it is more stable. The conjugated π-electron system in the enol can disperse the negative charge on the monoanion across two oxygen atoms, stabilising the monoanion. Statement 2 is therefore **true**.

3. Intermolecular hydrogen bonds formed between hydroxyacrolein molecules stabilise the monoanion of malondialdehyde.

The diagram to the right reveals the lack of H atoms that can form hydrogen bonds in the monoanion of malondialdehyde. Statement 3 is **false**.

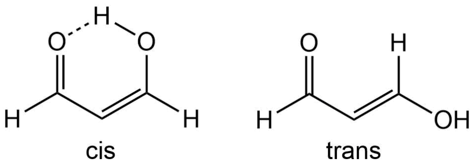


4. Malondialdehyde is a dibasic acid.

Similarly, only one hydroxyl group is present in the enol form; the formation of a second one using the remaining α hydrogen atom will form an allene instead, which is much more unstable since there is no conjugation. Only one proton can be dissociated per molecule of malondialdehyde, hence it is monobasic. Statement 4 is **false**.

5. Hydroxyacrolein predominantly exists as the cis isomer in organic solvents.

Organic solvents are nonpolar, thus there is no hydrogen bonding between hydroxyacrolein and the organic solvent molecules unlike in water. Hydroxyacrolein will adopt the cis structure as it can undergo intramolecular hydrogen bonding making it more stable. Statement 5 is **true**.



(b) 10.4

Based on our knowledge, we expect that the electrons in the conjugated π-electron system move from the hydroxyl group to the aldehyde group as the proton tunnels to the aldehydic oxygen atom. We therefore expect the transition state to be the structure in the centre of the energy level diagram, and the actual activation energy is +25 kJ mol^{-1}.

The calculated activation energy can also be calculated easily:

calculated E_a = [−266.00124 − (−266.01472)] × 2625.5
= 35.392 kJ mol^{-1} (5 s.f.)

difference = 35.392 − 25
= 10.4 kJ mol^{-1} (3 s.f.)

(As expected, the actual activation energy, or energy barrier, is lower than expected, suggesting a quantum tunnelling effect takes place.)

(c) 6.24

The speed can be easily calculated knowing the interminimal distance and period of oscillation.

speed = $87.7 \times 10^{-12} \times 7.11 \times 10^{10}$
= 6.24 m s^{-1} (3 s.f.)

(d) 700B

The uncertainty in momentum is the product of the proton's mass and uncertainty in velocity: $\Delta p = m\Delta v$

The minimum uncertainty will satisfy the equality $\Delta x \Delta p = \frac{h}{4\pi}$. Therefore, $\Delta x(m\Delta v) = \frac{h}{4\pi}$.
The uncertainty in position is $\Delta x = 0.5 \times 87.7 \times 10^{-12} = 43.85 \times 10^{-12}$ m

$$\Delta v = \frac{h}{4\pi m\Delta x} = \frac{6.6261 \times 10^{-34}}{4\pi \times 1.6726 \times 10^{-27} \times 43.85 \times 10^{-12}} = 700 \text{ m s}^{-1} \text{ (1 s.f.)}$$

Comparing 700 to 6.24 in part (c), we see that the notion of the proton's speed is senseless in classical terms. The second conclusion is therefore correct, and we input 700B.

Problem prepared by: Lie Huan Yew

Problem 33: Thermochromism

[4 points]

Thermochromism is an interesting property of some compounds. When the thermochromic substance experiences a change in temperature, a reversible change in colour can be observed. This can be used in a variety of useful products, such as thermal printing paper, erasable ink and liquid crystal displays.

Compound **A** is a ternary thermochromic compound with a mass percentage of element **X** of 59.573 %. Element **X** is a silvery metal with a low melting point. Upon heating to 500 °C, compound **A** turns from yellow to orange-red reversibly.

When 1.000 g of compound **A** is dissolved in water, a yellow solution is obtained. Addition of excess 2 M H_2SO_4 causes the solution to turn orange-red as well. When an aqueous solution of hydroxylammonium sulfate ($[NH_3OH]_2SO_4$) is added, effervescence is observed and the solution turns grey.

A set-up consisting of two lead rods connected to a 9.00 V power source is prepared. Upon inserting the rods into the grey solution, a white precipitate sloughs off the rod connected to the positive terminal, while the rod connected to the negative terminal develops a grey coating. This is carried out for 24 hours, until the rod connected to the negative terminal experiences no change in size, and the solution is entirely colourless. The total mass of white precipitate and increase in mass of the graphite rod is 1.767 g.

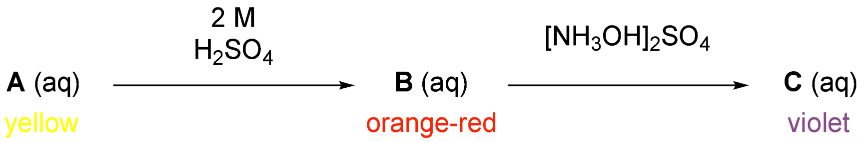
After the mixture is filtered off, the remaining solution is made neutral by addition of 13.6 cm^3 of 2 M NaOH solution, then boiled down completely to dryness. A white residue of 1.90 g remains.

Determine the chemical formula of **A**.

Solution:

Rb_2CrO_4

We can take an educated guess from the colours in the third paragraph to identify that Cr is one of the elements present in **A**.



A contains the yellow chromate ion, which forms the orange-red dichromate ion in acidic pH. Reduction using hydroxylammonium sulfate gives Cr(III) in the form of violet $[Cr(OH_2)_6]^{3+}$.

(One may incorrectly guess other elements wrongly, such as V, but trial-and-error on later parts will eventually reveal Cr. The point is to narrow down your search.)

From the electrolysis setup, we note that a grey metal **M** is formed on the cathode (connected to the negative terminal), whereas on the anode a white precipitate is formed. This cannot be a sulfate of an oxidised form of **M**, as **M** in an oxidised form was previously acidified with H_2SO_4 to give an orange-red solution, before it was reduced with hydroxylammonium sulfate, making it soluble. Thus, the white precipitate has to come from the Pb anode itself being oxidised, where $PbSO_4$ formed is indeed white.

Letting **M** be in the +n oxidation state in the grey solution before the electrolysis, we can write the following reactions happening at each electrode:

Cathode: $M^{n+} + n\,e^{-} \rightarrow M$

Anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^{-}$

Overall: $2M^{n+} + nPb + nSO_4^{2-} \rightarrow 2M + nPbSO_4$

The molar ratio of $PbSO_4$: **M** = n : 2, where n is a positive integer.

Hence, expressing in terms of amount of **M** produced, n(**M**),

$$M_r\left(PbSO_4\right) \cdot n\left(PbSO_4\right) + M_r(M) \cdot n(M) = 1.767$$

$$303.27\left[\frac{n}{2} \cdot n(M)\right] + M_r(M) \cdot n(M) = 1.767$$

$$\Rightarrow n(M) = \frac{1.767}{\frac{303.27n}{2} + M_r(M)} = \frac{1.767}{151.635n + M_r(M)}$$

From our earlier deduction, Cr is not a low boiling point metal, hence **X** is not Cr. Since the solution becomes clear after the electrolysis, **M** must be Cr, while **X** must be present as a colourless ion.

Substituting $M_r(M)$ with that of Cr, and $n = 3$,

$$n(Cr) = \frac{1.767}{(151.635)(3) + 52.00} = 0.0034859\ mol\ (5\ s.f.)$$

Let the chemical formula of A be **X**$(CrO_4)_y$.

Looking at the last paragraph, we need to figure out what is left in the solution after the electrolysis. **X** ions will be present, as well as any sulfate ions from H_2SO_4 and hydroxylammonium sulfate. The hydroxylammonium ions will decompose under heat to give a mixture of gaseous products (e.g. N_2, N_2O, NH_3) that will be expelled. The excess H_2SO_4 was neutralised by NaOH, giving Na_2SO_4. Therefore, we have a mixture of **X** sulfate and Na_2SO_4.

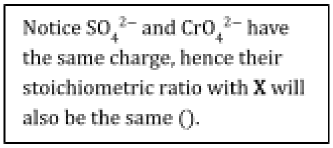
$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + H_2O$$

$$n\left(Na_2SO_4\right) = \frac{1}{2} n\left(H_2SO_4\right) = \frac{1}{2}\left(\frac{13.6}{1000}\right) = 0.00680\ mol$$

$$1.90 = m\left(Na_2SO_4\right) + m\left(X\left(SO_4\right)_y\right)$$

$$= n\left(Na_2SO_4\right) \cdot M_r\left(Na_2SO_4\right) + n(X) \cdot M_r\left(X\left(SO_4\right)_y\right)$$

$$= 0.00680\ (142.05) + n(X) M_r(X) + y \cdot n(X) M_r\left(SO_4\right)$$



Notice SO_4^{2-} and CrO_4^{2-} have the same charge, hence their stoichiometric ratio with **X** will also be the same ().

Since $n(X) = \frac{n(Cr)}{y}$,

$$1.90 = 0.96594 + \frac{n(Cr)}{y}M_r(X) + y\cdot\frac{n(Cr)}{y}(96.07)$$

$$1.90 = 0.96594 + \frac{0.0034859}{y}M_r(X) + (0.0034859)(96.07)$$

$$\frac{0.0034859}{y}M_r(X) = 0.59917\ (5\ s.f.)$$

$$\Rightarrow M_r(X) = \frac{0.59917}{0.0034859}y = 171.88y$$

Now, we guess values of y:

y	$M_r(X)$	**X**
0.5	85.94	Rb
1	171.88	Yb (173.0)
1.5	257.82	Fm

The only possible answer here is y = 0.5, hence **X** is Rb.

Alternatively, we can use the mass percentage and amount of **A** to determine the identity of X:

$$M_r(X) = \frac{m(X)}{\frac{n(Cr)}{y}} = \frac{y(0.59573)}{0.0034859} = 170.89y\ (5\ s.f.)$$

which gets us the same answer.

Hence, **A** is Rb_2CrO_4.

Problem prepared by: Timothy Chek

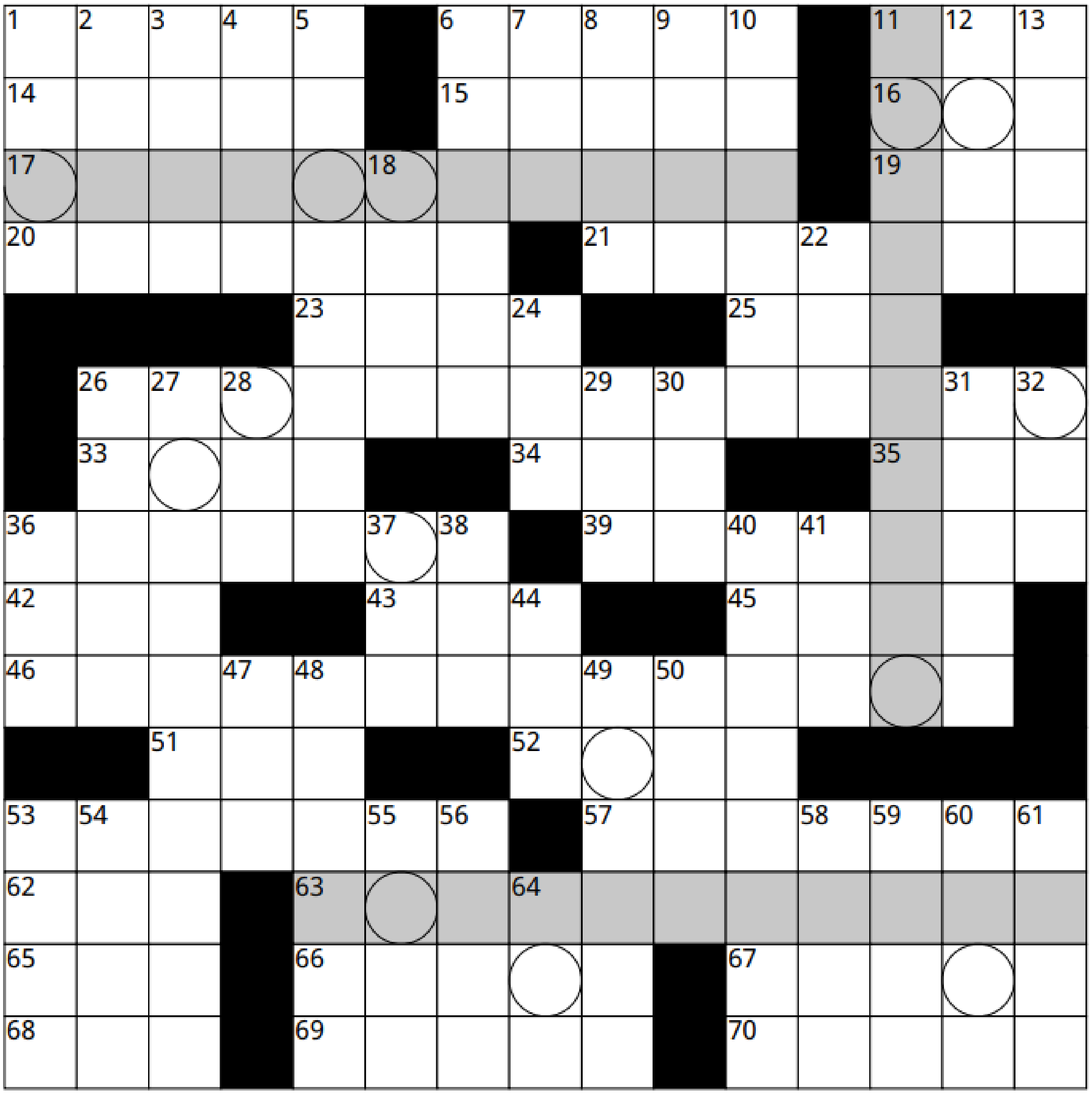
Problem 34: Crossword

[5 points]

American crosswords take place on a 15 x 15 grid. The classic rules state that they must have a plane of reflection along the diagonal axis, and no clues are to be shorter than three letters.

The three highlighted clues relate to the theme of this puzzle, and each also contains an element. The circled letters, when read in order, provide three other elements.

Multiply all six atomic numbers together and submit the product.



ACROSS

1. Popular British "cake"
6. Short for those short on sleep
11. Surprisingly has 19 forms, though we only see 1 in daily life
14. "It's _____ to you now"
15. The oxidizer in gunpowder
16. Only for parts of the electromagnetic spectrum above visible light
17. One crazy about jewels... or a clue to 46 Across
19. Lode load
20. Species name of pernicious Singaporean vector
21. Mathematics professor at NUS (sorry ok this was the last clue I made)
23. Racing track at Sentosa
25. Dot follower
26. EDTA, for example
33. What the property of being different in different directions and methoxybenzene have in common at the start
34. Skill in demand for many a business (abbr.)
35. Nest egg letters (in America at least)
36. Figure of terror for many admin workers (like me!)
39. Drug: Manidipine hydrochloride
42. Smartphone manufacturer based in Taipei
43. That one named reaction that uses oxone
45. Integral half r cross dr
46. An electronic theory applied to 5d elements... or a hint to the highlighted clues
51. Food whose circumference and diameter are related by the homophonic value
52. Intermediate in acidic halogenation of ketones
53. Drug: Pegfilgrastim
57. A delicious alcoholic drink
62. Part of it is the URL
63. Commanded an airship... or a clue to 46 Across
65. Start of the week, some claim (and they are wrong!)
66. Unit measuring the concentration of solute particles
67. Make corrections and revisions
68. Surprised acronym
69. Annoyances in a backyard garden
70. Agree with

DOWN

1. Actress Pinkett Smith
2. I would never tell _____

3. Symbol of a nation
4. Like conc. sulfuric acid
5. Space outside plant cell membranes
6. Colour after which element 49 is named
7. Compound: Nickel monohydride
8. Science is part of this quartet
9. A way to measure antioxidant ability
10. Ruling family of 15-17th Century Florence
11. Alternative Thatcher nickname... or a clue to 46 Across
12. Part of TLC?
13. Protected by safety goggles, always!
18. We know them as the supermarket, but they do much more
22. Not
24. Greek goddess of the dawn
26. _____ cuisine
27. Installation of functional groups onto free silanol moieties in a HPLC column
28. Twelve, to Julius Caesar
29. Mens ___ (criminal intent)
30. Golden, in France
31. Dobereiner's contribution to the development of the periodic table
32. Ether suffix?
36. Relaxed exclamation
37. First three letters of element to the right of 38 Down
38. First three letters of element to the left of 37 Down
40. Drug: Penicillin V (old name: V-_______)
41. Period of time
44. Mineral suffix
47. Compete (for)
48. Colour of sodium vapour lamps
49. Heavenly beings
50. Shape of tRNA
53. Opposite of homo
54. Benzene or cyclopentadienyl are examples, in short
55. Compound: Germanium selenide
56. Acronym describing how a drug interacts with the body
58. How-to presentation
59. Welsh boy name
60. Dryer detritus
61. Ring closure method
64. General enemy of Superman

Solution:

594060480

1 J	2 A	3 F	4 F	5 A	■	6 I	7 N	8 S	9 O	10 M	■	11 I	12 C	13 E
14 A	L	L	U	P	■	15 N	I	T	R	E	■	16 R	A	Y
17 D	I	A	M	O	18 N	D	H	E	A	D	■	19 O	R	E
20 A	E	G	Y	P	T	I	■	21 M	C	I	22 N	N	E	S
■	■	■	■	23 L	U	G	24 E	■	■	25 C	O	M	■	■
■	26 H	27 E	28 X	A	C	O	O	29 R	30 D	I	N	A	31 T	32 E
■	33 A	N	I	S	■	■	34 S	E	O	■	■	35 I	R	A
36 A	U	D	I	T	37 O	38 R	■	39 A	R	40 T	41 E	D	I	L
42 H	T	C	■	■	43 S	H	44 I	■	■	45 A	R	E	A	■
46 H	E	A	47 V	48 Y	M	E	T	49 A	50 L	B	A	N	D	■
■	■	51 P	I	E	■	■	52 E	N	O	L	■	■	■	■
53 L	54 A	P	E	L	55 G	56 A	■	57 G	O	O	58 D	59 A	60 L	61 E
62 U	R	I	■	63 L	E	D	64 Z	E	P	P	E	L	I	N
65 M	O	N	■	66 O	S	M	O	L	■	67 E	M	E	N	D
68 O	M	G	■	69 W	E	E	D	S	■	70 N	O	D	T	O

Note: 67 Across can also be “AMEND”. This does not affect the final answer.

The elements are Diamond/Carbon (6), Iron (26), Led/Lead (82), Radon (86), Xenon (54) and Neon (10). Their product is hence **594060480**.

Problem prepared by: Leemen Chan

Problem 35: Life’s Unstable Machines

[9 points]

“In the context of life, if you focus on the individual entity, [...] you are missing the essence of what defines life — its dynamic nature…”

— Addy Pross

In 1967, molecular biologist Sol Spiegelman added a small sample of RNA to a solution containing its building blocks, in the presence of an enzyme. Miraculously, the RNA molecules begin to duplicate, forming copies of itself and growing in number like a living bacterial colony. This early experiment showed us that nucleic acids, such as RNA, lie at the heart of a molecular self-replicating system.

Each RNA molecule is made up of a very specific sequence of building blocks, or monomers. Spiegelman’s observation of the exponentially growing RNA is what we now know as RNA replication.

With the help of an enzyme, an existing strand of RNA is used as a template. A free monomer collides with the template and becomes the starting point of the new strand. The second free monomer collides with the template and bonds with the first monomer, the third free monomer bonds with the second, and so on until a new complementary strand with the same number of monomers as the template RNA is formed. From just one starting RNA sequence, we now have two.

Assume the RNA replication reaction has the rate equation $rate = k[RNA][X]$, where k is the rate constant of the reaction in $\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$, and X represents the RNA monomer.

For an RNA with n monomers, the replication reaction of the RNA may be simplified as:

$$RNA + nX \rightarrow 2RNA$$

We start off with a mixture of $[\text{RNA}]_0 = 0.001$ M and $[\text{X}]_0 = 1.0$ M. Assume all RNA in the mixture, whether present at the start or formed later, is 10 monomers long.

We also assume that all RNA will not revert to its monomers (i.e. the backward reaction does not occur).

(For our frustrated Biology takers frowning at the screen and passionately exhorting the need for bio precision with your teammates: here we let the symbol X represent any of the U, A, C, G ribonucleotide triphosphates, and [X] be the total concentration of free U, A, C, G rNTPs. We also let [RNA] be the total concentration of RNA of any nucleotide sequence. Now back to the problem.)

(a) What is the theoretical maximum value of [RNA]? **[2 points]**
Leave your answer to 3 significant figures.

(b) The reaction is found to have a rate constant k = 0.149 $\text{mol}^{-1}\ \text{dm}^{3}\ \text{s}^{-1}$. Find the time taken, in seconds, for [RNA] to reach half of its theoretical maximum. **[4 points]**
Leave your answer to 3 significant figures.

(c) Determine whether there is a point in the reaction when the rate of increase of [RNA] is maximum. If there is, find the maximum rate of increase in $\text{mol dm}^{-1}\ \text{s}^{-1}$. If there is not (i.e. the rate keeps increasing), enter your answer as '000'. **[3 points]**
Leave your answer to 3 significant figures.

Solution:

(a) 0.101

Note that in this problem, even though $[\text{RNA}]_0 << [\text{X}]_0$, we do not consider it a limiting reactant because it is continually generated via the reaction. Counter-intuitively, it is [X] which limits the maximum yield.

As each RNA produced is 10 units of X long, $n = 10$. The equation we have is

$$RNA + 10X \rightarrow 2RNA$$

10 units of X is used to produce one unit of RNA. Hence 1.0 M of X can be used to produce $\frac{1}{10}(1.0) = 0.1$ M of new RNA, given the reaction goes to completion.

The theoretical maximum is the sum of [new RNA] and [initial RNA]:

$[\text{RNA}]_{\text{max}} = 0.1 + [\text{RNA}]_0 = \frac{1}{10}[\text{X}]_0 + [\text{RNA}]_0 = 0.1 + 0.001 = \underline{0.101}$ M

Alternatively, some teams may find success using a mass balance equation (which is essential in solving the next part):

$$[\text{RNA}] + \frac{1}{10}[\text{X}] = [\text{RNA}]_0 + \frac{1}{10}[\text{X}]_0$$

where [RNA] and [X] denotes concentrations of RNA and X at any point in time. We need to multiply [X] by $\frac{1}{10}$ to maintain equality because [X] is used up 10 times as much as [RNA] is formed per unit time.

Theoretical maximum [RNA] is achieved when the reaction goes to completion, when [X] = 0.
Substituting,
$[\text{RNA}]_{\text{max}} + 0 = [\text{RNA}]_0 + \frac{1}{10}[\text{X}]_0 \Rightarrow [\text{RNA}]_{\text{max}} = 0.101$ M

(b) 30.6

We know that in our case, $rate = \frac{d[RNA]}{dt}$[11].
Given the rate equation $rate = k[RNA][X]$,

$$\Rightarrow \frac{d[RNA]}{dt} = k[\text{RNA}][\text{X}]$$

---

[11] One net unit of RNA is produced per unit of reaction, hence the rate of RNA formation equals the rate of reaction.

In order to calculate [RNA] at a specific time we perform integration on this equation. However, we first have to express [X] in terms of [RNA]. This is quickly found using a mass balance equation from (a):

$$\frac{1}{10}[\mathrm{X}] = [\mathrm{RNA}]_0 + \frac{1}{10}[\mathrm{X}]_0 - [\mathrm{RNA}] \Rightarrow [\mathrm{X}] = 10[\mathrm{RNA}]_0 + [\mathrm{X}]_0 - 10[\mathrm{RNA}]$$

Substituting [X] in rate equation,

$$\frac{d[RNA]}{dt} = k[\mathrm{RNA}](10[\mathrm{RNA}]_0 + [\mathrm{X}]_0 - 10[\mathrm{RNA}])$$

To simplify our working, we let $\mathrm{C} = 10[\mathrm{RNA}]_0 + [\mathrm{X}]_0$, as it is constant:

$$\Rightarrow \frac{d[RNA]}{dt} = k[RNA](C - 10[RNA])$$

We can start integrating :)

$$\frac{1}{[RNA](C-10[RNA])}d[RNA] = kdt \Rightarrow \int_{[RNA]_0}^{[RNA]_t} \frac{1}{[RNA](C-10[RNA])}d[RNA] = \int_0^t kdt$$

To solve the integral on the LHS we split it into partial fractions, before integrating as normal:

$$\frac{1}{[RNA](C-10[RNA])} \equiv \frac{1}{C[RNA]} + \frac{10}{C(C-10[RNA])}$$

$$\int_{[RNA]_0}^{[RNA]_t} \frac{1}{C[RNA]} + \frac{10}{C(C-10[RNA])}d[RNA] = \int_0^t kdt$$

Moving the common denominator C to the other side,

$$\int_{[RNA]_0}^{[RNA]_t} \frac{1}{[RNA]} + \frac{10}{C-10[RNA]}d[RNA] = C\int_0^t kdt$$

$$\Rightarrow [ln|[RNA]| - ln|C - 10[RNA]||]_{[RNA]_0}^{[RNA]_t} = Ckt$$

Given that $[\mathrm{RNA}] > 0$, and that
$\mathrm{C} - 10[\mathrm{RNA}] = 10[\mathrm{RNA}]_0 + [\mathrm{X}]_0 - 10[\mathrm{RNA}] = [\mathrm{X}]$ (by mass balance), and $[\mathrm{X}] > 0$,[12] we have shown that $[\mathrm{RNA}] > 0$ and $\mathrm{C} - 10[\mathrm{RNA}] > 0$, so we can remove the absolutes.

$$[ln[RNA] - ln(C - 10[RNA])]_{[RNA]_0}^{[RNA]_t} = Ckt$$

Using ln identity,

$$[ln\frac{[RNA]}{C-10[RNA]}]_{[RNA]_0}^{[RNA]_t} = Ckt$$

---

[12] Even though we use [X]=0 to solve for $[\mathrm{RNA}]_{\mathrm{max}}$ in part (a), [X] cannot fall to 0 in practice because as [X] decreases, its rate of decrease also becomes slower and slower - the value of [X] forms an asymptote that tends towards zero and does not reach it. This will make sense with mathgic.

$$ln\frac{[RNA]_t}{C-10[RNA]_t} - ln\frac{[RNA]_0}{C-10[RNA]_0} = Ckt$$

Note that $C - 10[RNA]_0 = 10[RNA]_0 + [X]_0 - 10[RNA]_0 = [X]_0$,

$$ln\frac{[RNA]_t}{C-10[RNA]_t} - ln\frac{[RNA]_0}{[X]_0} = Ckt$$

$$ln\frac{\frac{[RNA]_t}{C-10[RNA]_t}}{\frac{[RNA]_0}{[X]_0}} = Ckt$$

$$\Rightarrow \frac{[RNA]_t}{C-10[RNA]_t} = \frac{[RNA]_0}{[X]_0}e^{Ckt}$$

$$\frac{C-10[RNA]_t}{[RNA]_t} = \frac{1}{\frac{[RNA]_0}{[X]_0}e^{Ckt}} = \frac{[X]_0}{[RNA]_0}e^{-Ckt}$$

$$\frac{C}{[RNA]_t} - 10 = \frac{[X]_0}{[RNA]_0}e^{-Ckt}$$

$$\frac{C}{[RNA]_t} = \frac{[X]_0}{[RNA]_0}e^{-Ckt} + 10$$

$$\frac{[RNA]_t}{C} = \frac{1}{\frac{[X]_0}{[RNA]_0}e^{-Ckt}+10}$$

$$\Rightarrow [RNA]_t = \frac{C}{\frac{[X]_0}{[RNA]_0}e^{-Ckt}+10}$$

We finished integrating and our favourite part now is subbing in the values. Recall $C = 10[RNA]_0 + [X]_0$. When $[RNA]_t = \frac{1}{2}[RNA]_{max}$,

$$\frac{1}{2}(0.101) = \frac{10(0.001)+1.0}{\frac{1.0}{0.001}e^{-[10(0.001)+1.0](0.149)t}+10} \Rightarrow 0.0505 = \frac{1.01}{1000e^{-1.01(0.149)t}+10}$$

$$1000e^{-1.01(0.149)t} + 10 = \frac{1.01}{0.0505}$$

$$e^{-1.01(0.149)t} = \frac{\frac{1.01}{0.0505}-10}{1000} = 0.01$$

$$-1.01(0.149)t = ln0.01$$

$\Rightarrow t = -\frac{ln0.01}{1.01(0.149)}$ = 30.601 (5 s.f.) = 30.6s (3 s.f.)

Note that it is also possible to solve this by integrating with respect to [X], by starting with $rate = -\frac{1}{10}\frac{d[X]}{dt}$. Note the negative sign and $\frac{1}{10}$ coefficient, which indicates that for every 1 unit of X consumed, the reaction progresses $\frac{1}{10}$ units.

(c) 0.00380

We can start with the rate of change of [RNA] equation from (b),

$$Rate\ of\ change\ of\ [RNA] = k[RNA](C - 10[RNA])$$

and differentiate to find the maximum using the 2nd derivative test.

Differentiating both sides w.r.t. [RNA],

$$\frac{d(Rate\ of\ change\ of\ [RNA])}{d[RNA]} = \frac{d}{d[RNA]}k[RNA](C - 10[RNA])$$

$$= \frac{d}{d[RNA]}(\mathrm{C}k[\mathrm{RNA}] - 10k[\mathrm{RNA}]^2)$$

$$= \mathrm{C}k - 20k[\mathrm{RNA}]$$

At maximum rate of change of [RNA], $\frac{d(Rate\ of\ change\ of\ [RNA])}{d[RNA]} = 0$

$$\mathrm{C}k - 20k[\mathrm{RNA}] = 0 \ \Rightarrow [\mathrm{RNA}] = \frac{1}{20}C$$

Hence maximum rate of increase of [RNA] occurs when $[\mathrm{RNA}] = \frac{1}{20}C$.

Sub $[\mathrm{RNA}] = \frac{1}{20}C$ into the rate of change equation,

$$Max.\ rate\ of\ increase\ of\ [RNA] = k(\frac{1}{20}C)[C - 10(\frac{1}{20}C)] = \frac{1}{40}kC^2$$

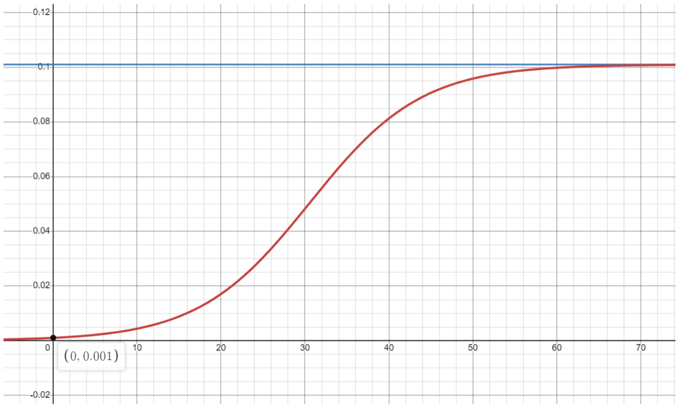
Recall $\mathrm{C} = 10[\mathrm{RNA}]_0 + [\mathrm{X}]_0$,

$$\Rightarrow Max.\ rate\ of\ increase\ of\ [RNA] = \frac{1}{40}(0.149)[10(0.001) + 1.0]^2$$

$$= 0.00380\ \mathrm{mol\ dm^{-3}\ s^{-1}}\ (3\ \mathrm{s.f.})$$

Note that unlike most reactions, the maximum rate does not occur at the start, but rather in the middle of the reaction, when $[\mathrm{RNA}] = \frac{1}{20}C = \frac{1}{2}([RNA]_0 + \frac{1}{10}[X]_0)$ and $[\mathrm{RNA}]_0$ is depleted by exactly half. This is unique to an autocatalytic reaction, showing that biological replication reactions are autocatalytic in nature. The product speeds up the reaction for its own formation up to a certain point.

It also helps to check this part by plotting the expression for $[\mathrm{RNA}]_t$ from (b) into a graphing calculator like Desmos (we are not sponsored by Desmos). The signature S-shape of the autocatalytic reaction becomes clear (y-axis [RNA]/mol $\mathrm{dm^{-3}}$, x-axis t/s).



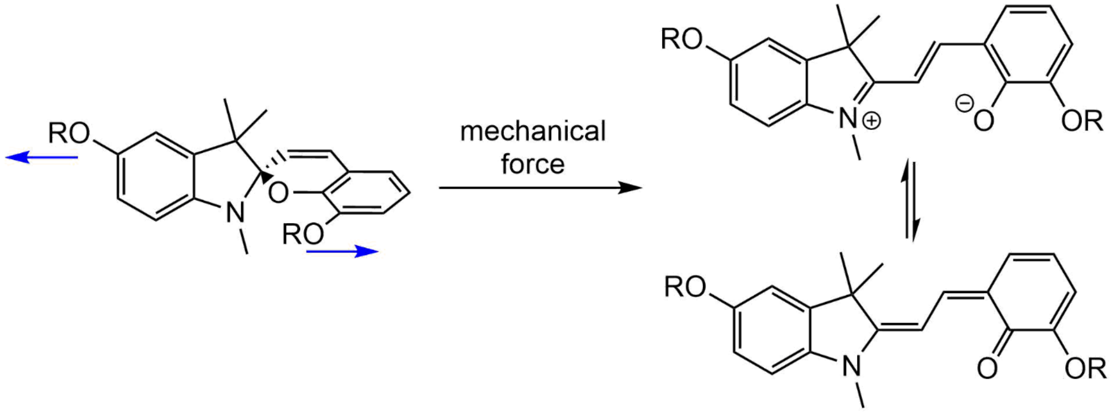
Problem prepared by: George Zhou

Problem 36: Pull it!

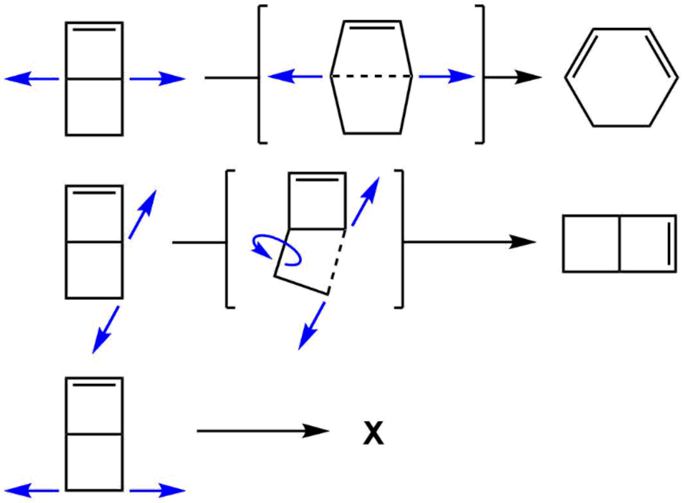
[6 points]

It is known that chemical reactions require energy to proceed, often provided through heat, light (in photochemistry), and electricity (in electrochemistry). Energy can also be provided through force as in mechanochemistry. In mechanochemical reactions, the mechanically reactive site is known as the mechanophore.

An example of such a reaction is shown below. When a force is applied to stretch the polymer chain containing the spiropyran, an electrocyclic ring-opening reaction takes place. The colourless polymer then turns violet.

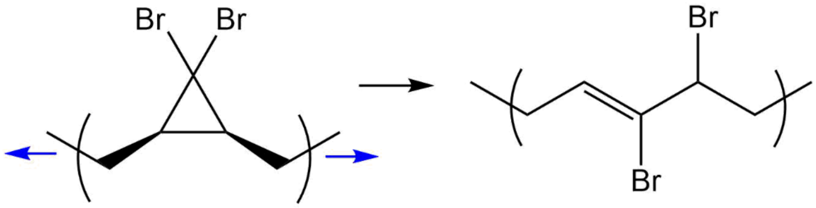


Mechanophore **A** has been designed to show how chemoselectivity can be achieved with mechanical force. Changing the positions at which the polymer chains are attached allows different bonds to be activated which form different products, as demonstrated below.



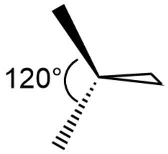
(a) Predict the structure of X. **[2 points]**

Another polymer has the following repeating unit that can rearrange under mechanical force.

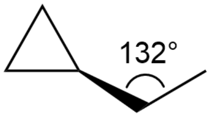


You are also given the following additional information:

bond	bond length / pm
C–C	151
C=C	134



The bond angle between the two substituents in a cyclopropane ring is 120°.



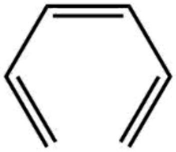
Perpendicular to the cyclopropane ring, this bond angle is 132°.

(b) Calculate the <u>percentage increase</u> in length of the polymer when it is stretched. You may assume that all the mechanophores react. **[4 points]**
Leave your answer to 4 significant figures, omitting the % sign.

Hint: Do not assume <u>all</u> C–C–C bond angles are 120°.

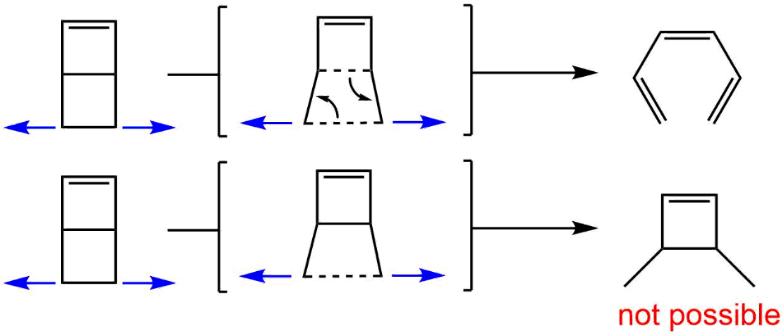
Solution:

(a)



From the two examples given, we make two observations:

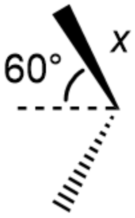
1. The degree of unsaturation (DOU) of the molecule is unchanged;
2. The number of hydrogen atoms bonded to each carbon atom is unchanged.



We know that the bond between the two carbon atoms being pulled apart will break, and it is tempting to leave the answer as the cyclobutene, but this is not possible as the DOU decreases from 3 to 2, and the number of H atoms bonded to each of these C atoms increases from 2 to 3. To satisfy observation #2, we know these two C atoms must be terminal alkenes. Therefore, the central C—C bond, also the weakest bond in this mechanophore, must break, and we are left with (*Z*)-1,3,5-hexatriene.

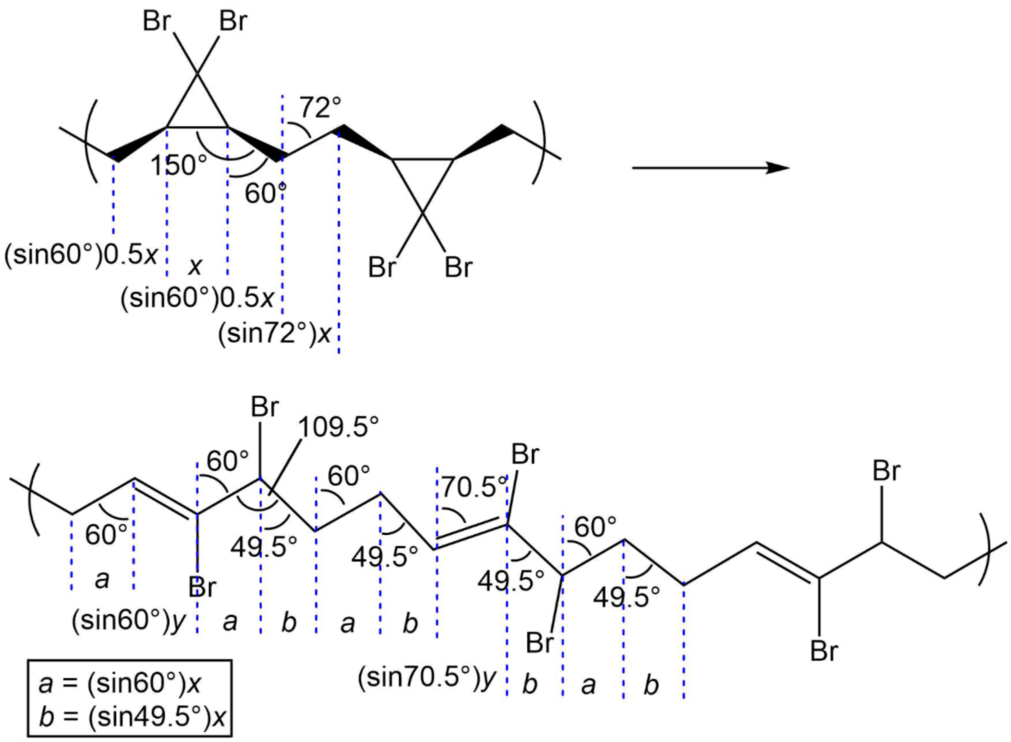
(b) 43.96

Let the C—C bond length be x, and C=C bond length be y.



As we are measuring the polymer's length along the cyclopropane plane, we need to first determine the length of the C—C wedge bond. We can do this with simple trigonometry: the length of the wedge bond = $x \cos 60° = 0.5x$.

Since all mechanophores react, the percentage increase in length of the polymer is the percentage increase in length of each repeating unit. Once we draw out some repeating units, the lengths can easily be calculated.



initial $= (2 \times 0.5 \sin 60° + 1 + \sin 72°)x$

final $= 0.5[4a + 4b + (\sin 60° + \sin 70.5°)y]$

$= 2(\sin 60° + \sin 49.5°)x + 0.5(\sin 60° + \sin 70.5°)y$

The percentage increase in length is therefore:

% increase $= \frac{final - initial}{initial} \times 100\%$

$$= \left(\frac{2(\sin 60° + \sin 49.5°)x + 0.5(\sin 60° + \sin 70.5°)y}{(2 \times 0.5 \sin 60° + 1 + \sin 72°)x} - 1\right) \times 100\%$$

$$= \left(\frac{2(\sin 60° + \sin 49.5°) \times 151 + 0.5(\sin 60° + \sin 70.5°) \times 134}{(\sin 60° + 1 + \sin 72°) \times 151} - 1\right) \times 100\%$$

$= 43.96\ \%$ (4 s.f.)

Drawing multiple repeating units and labelling all angles is key to solving this question systematically.

Problem prepared by: Lie Huan Yew

Problem 37: Chloe's Conundrum

[9 points]

Chloe, a chemistry student, is given four unknown compounds **W**, **X**, **Y** and **Z** that each contain an unknown element **A**. The compounds are further labelled with the percentage mass of **A** in each compound.

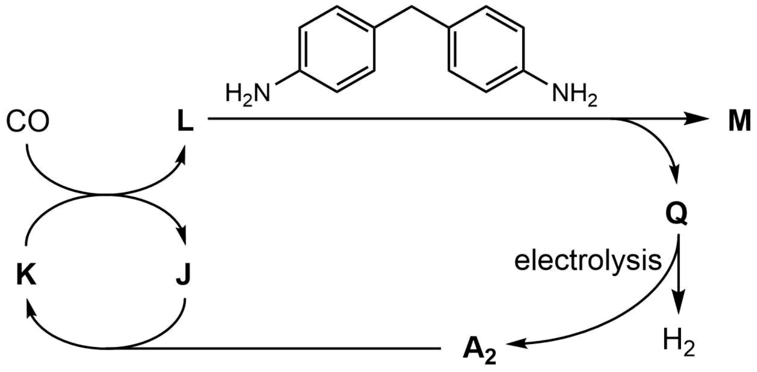
Tasked with identifying element **A**, Chloe discovers that **X**, **Y** and **Z** compounds are gaseous at 200 °C. She transfers each gas into an evacuated flask until the pressure inside reaches 1 atm before recording the mass of the gas. The procedure is repeated with nitrogen gas, and the results are tabulated below:

Gas	Mass of gas / g	% mass
X	2.815	52.50
Y	4.340	85.13
Z	2.488	89.09
N_2	0.584	0

Compound **W** is one of the most important binary compounds in the world. Chloe learns that the crystals contain 39.34% by mass of another element, **V** (which is not vanadium).

(a) Determine the proton number of the likely identity of element **V**. **[2 points]**

Chloe's professor, impressed with her acuity, passes her the following incomplete scheme. He adds: "I'm investigating a compound, **J**, that contains element **A**. I believe it can be used as an effective storage medium for A_2, which is toxic."



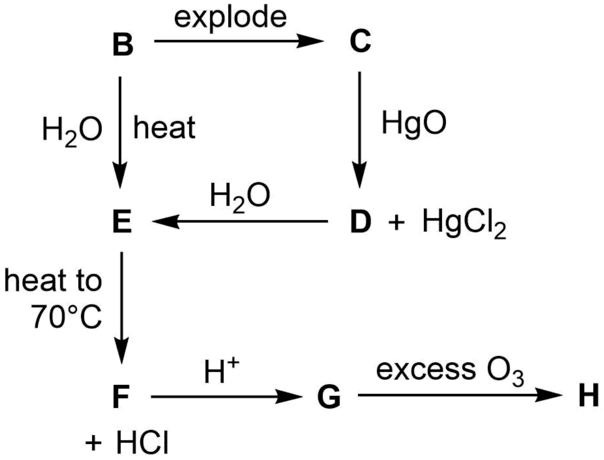
He also provides the following additional information:

- ^{1}H NMR of **J** reveals two peaks: a quartet of integral 8H and a triplet of integral 12H
- The percentage mass of **A** in **J** is 21.394 %; after storing **A$_2$**, the value increases by 23.555 % in **K**.
- **J** reacts with **A$_2$** in a 1 : 1 ratio to give **K**.

(b) Identify substances **J** and **M**. **[4 points]**

Leave your answer as the sum of the two CAS Registry Numbers, omitting any dashes.

Chloe has graduated, and discovers a short poem and scheme in her professor's drawer:



In a reaction scheme, chlorine's gleam,
Forms compounds in a calculated dream.
With every step, its presence clear,
In products formed, it does appear.

The following table contains the possible identities of the seven unknowns in the scheme:

(1) Cl_2	(2) ClO_2	(3) HClO	(4) $HClO_2$
(5) Cl_2O	(6) Cl_2O_4	(7) NCl_3	(8) $HClO_3$
(9) Cl_2O_6	(10) Cl_2O_7	(11) NOCl	(12) $HClO_4$

(c) Identify the seven unknowns **B** to **H**. **[3 points]**

Leave your answer as a string of concatenated numbers corresponding to the respective compounds in the table. For instance, if you think the answers to ***B***, ***C****, and* ***D*** *are Cl_2O_6 (9), Cl_2O_7 (10) and NOCl (11) respectively, input 91011.*

Solution:

(a) 11

Since the temperature and pressure of the evacuated flask are constant, the number of moles of each gas is equal.

$n(N_2) = \frac{0.584}{2 \times 14.01} = 0.02084226$ mol (7 s.f.)

The mass of **A** per mole of each compound $= \frac{mass\ of\ A\ in\ gas}{n(gas)} = \frac{mass\ of\ gas \times \%\ mass\ of\ A}{0.02084226}$

Gas	mass of gas / g	% mass	mass of **A** per mole / g mol^{-1}	divide by 35.45
X	2.815	52.50	70.91	2.00
Y	4.340	85.13	177.27	5.00
Z	2.488	89.09	106.35	3.00

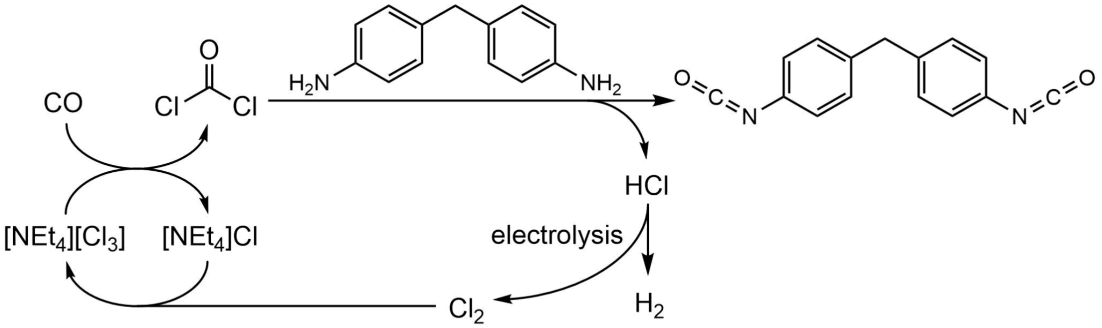
With some guess and check, we notice the largest common multiple of the three answers is 35.45, corresponding to the relative atomic mass of chlorine.

Compound **W** contains $100 - 39.34 = 60.66\%$ of chlorine. The number of moles of Cl in 100g of **W** is $\frac{60.66}{35.45} = 1.7111$ mol (5 s.f.). Assuming **V** and Cl are in a 1 : 1 ratio, the molar mass of **V** is $\frac{39.34}{1.7111} = 22.99$ (4 s.f.), which corresponds to sodium. Its proton number is 11.

(The identities of **X**, **Y**, and **Z** are S_2Cl_2, PCl_5, and $CHCl_3$ respectively.)

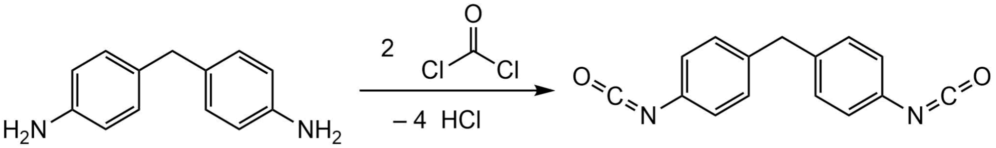
(b) 158036

The completed reaction scheme is shown below:



We can solve for **J** and **M** separately. This answer will solve for **M** first.

The conversion from **K** to **J** releases a Cl_2 molecule, thus CO is chlorinated by **K** to give phosgene, $COCl_2$. Phosgene reacts with primary amines to yield isocyanates, R—N=C=O (this can be verified with a quick Google search). 4,4'-methylenedianiline has two —NH_2 groups, and thus reacts with two molecules of phosgene to give methylene diphenyl diisocyanate (MDI), and HCl as the side product.



M is thus MDI, which has a CAS Registry Number of 101-68-8.

To solve for **J**, let the total mass of Cl per mole of **J** be *x*, and the total molar mass of **J** be *y*. We can set up a system of simultaneous equations from the percentage masses given:

% mass of Cl in **J** = $\frac{x}{y} = 0.21394$

% mass of Cl in **K** = $\frac{x + 2(35.45)}{y + 2(35.45)} = 0.21394 + 0.23555 = 0.44949$

Solving, we get $x = 35.45$, $y = 165.70$. This implies that **J** contains one Cl atom.

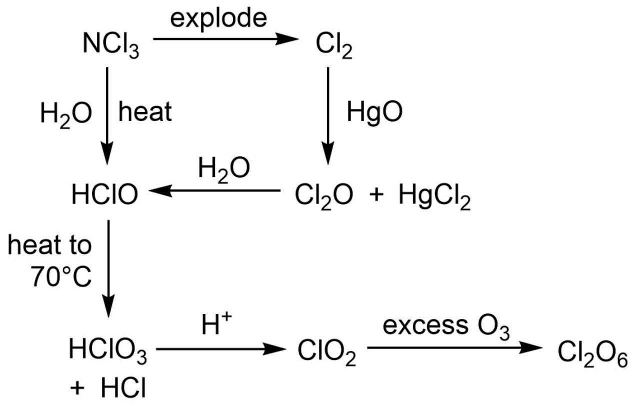
We are given that ^{1}H NMR of **J** gives a quartet of integral 8H and a triplet of integral 12H, which suggests there are likely four chemically equivalent —CH_2CH_3 groups in **J**. The molar mass of any remaining atoms in **J** is 165.70 − 35.45 − 4(2×12.01 + 5×1.008) = 14.01, corresponding to nitrogen.

J is hence $[N(CH_2CH_3)_4]Cl$, which has a CAS Registry Number of 56-34-8.

The final sum is hence 101688 + 56348 = 158036.

(c) 7153829

The completed scheme is shown below:



(1) Cl_2	(2) ClO_2	(3) HClO	(4) $HClO_2$
(5) Cl_2O	(6) Cl_2O_4	(7) NCl_3	(8) $HClO_3$
(9) Cl_2O_6	(10) Cl_2O_7	(11) NOCl	(12) $HClO_4$

The reactants used in the scheme are rather generic, so we can start investigating from the (rather odd) first reaction, where **B** explodes to yield **C**. This is likely a decomposition reaction of the unstable compound **B**, thus **C** is Cl_2 gas.

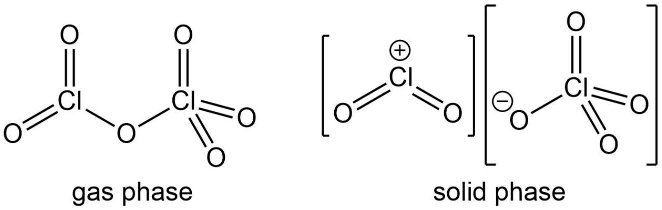
In the reaction of Cl_2 with HgO, we find the oxidation state of Hg is unchanged (+2), whereas that for Cl has reduced (0 to −1). Since **D** also contains chlorine, Cl_2 has likely undergone disproportionation to a chlorine oxide. Quick verification online shows that **D** is chlorine monoxide, Cl_2O.

Cl_2O is highly soluble in water as it exists in an equilibrium with HClO, with the equilibrium position favouring the formation of HClO. **E** is hence hypochlorous acid, HClO.

On careful heating, HClO can disproportionate (decompose?) to give $HClO_3$ and HCl. Some Cl_2 and O_2 may be produced in this reaction, but this may be minimised with the appropriate reaction conditions. **F** is hence chloric acid, $HClO_3$.

$HClO_3$ and HCl can react on the addition of concentrated acid to give ClO_2. The reaction of ClO_2 with water is $6\ ClO_2 + 3\ H_2O \rightarrow 5\ HClO_3 + HCl$, and excess acid can shift the equilibrium to the left. **G** is hence chlorine dioxide, ClO_2.

Ozone is an extremely powerful oxidising agent, and will oxidise ClO_2 further. We may first guess that ClO_3 is formed via the reaction $ClO_2 + O_3 \rightarrow ClO_3 + O_2$. Since the central Cl atom in ClO_3 contains one unpaired electron, it is unstable and dimerises to form dichlorine hexoxide, Cl_2O_6, the identity of **H**. Its structure is depicted below:



Of the remaining compounds, $HClO_2$ is unstable and disproportionates in aqueous solution to yield $HClO_3$ and HClO: $2\ HClO_2 \rightarrow HClO_3 + HClO$. Cl_2O_7 can explode to give Cl_2, but it dissolves in water to give perchloric acid, $HClO_4$, as the former is produced from the latter's dehydration: $2\ HClO_4 + P_4O_{10} \rightarrow Cl_2O_7 + H_2P_4O_{11}$. Cl_2O_4 is unstable and decomposes to give Cl_2 and Cl_2O_6 at room temperature, so it does not fit the first reaction. Nitrosyl chloride, NOCl, is stable. This leaves the identity of **B** as NCl_3.

Problem prepared by: Lie Huan Yew

Problem 38: Frozen Planet

[9 points]

*Note: Bolded labels, such as **A** or **B**, correspond to the defined substance, and as such, for example, **B** is not necessarily boron.*

After finishing *Interstellar* on his 16h flight to the UK, Bobo is amazed by its masterful storytelling and compelling cinematography. However, being a chemistry student, the part of the movie he finds the most intriguing was the crew's arrival on Dr Mann's planet.

The idea of a planet having raw materials for life is fascinating, and looking outside the plane window, Bobo thinks about Earth and what it was like in its first billion years. Much like Dr Mann's planet, the atmosphere of prebiotic Earth would be oxygen-poor. Instead of the current atmosphere which "oxidises", prebiotic Earth "reduces" due to the large proportion of reducing gases. Major atmospheric components include:

$$H_2, NH_3, CH_4, CO \text{ and } CO_2.$$

Dr Mann's findings that "the ammonia gives way to crystalline hydrocarbons" is just promising enough to the crew and just historically accurate enough for Bobo. In the warm temperatures of early Earth, two of the above gases can react to form toxic, weakly acidic **A** (gas at r.t.p.) as one of its products. Incidentally, industrial synthesis of gas **A** with a platinum catalyst can proceed via the same reaction. Another two of the above gases (which may or may not be different from the gases that form **A**) also react in an equimolar ratio to form organic **B** (gas at r.t.p.).

Gases **A** and **B** dissolve in liquid ammonia, reacting with each other in solution and then with NH_3 to form organic compound **C**, which finally reacts with water to form uncharged organic compound **D**.

(a) Suggest the structure of organic compound **D**. **[3 points]**
Give its uncharged form.

This is one way organics could have come about on Dr Mann's planet and on Earth. With that said, the temperature of the planet is another hurdle to whether the reactions can occur. The reaction forming gas **A**, for instance, takes place favourably only at high temperatures. This makes it difficult to happen on Dr Mann's frozen planet, but possible in Earth's more hospitable atmosphere.

(b) It is given that the reaction forming gas **A** has $\Delta S^{\emptyset} = +215.1\ \text{J mol}^{-1}\ \text{K}^{-1}$. Using the data below, calculate the $\Delta G^{\emptyset}$ of the reaction forming gas **A** in kJ mol^{-1}. Not all the information will be required. **[2 points]**
Leave your answer to 3 significant figures.
Leave a sign in front of the number only if your answer is negative. (I.e. if your answer is positive, do not include "+".)

The reaction will not occur easily on Dr Mann's planet… unless its clouds carry lightning. When lightning storms strike, a bolt of lightning can raise the surrounding air temperature significantly.

(c) Bobo estimates a bolt of lightning momentarily increases the air temperature to 5000K. Using the data below, calculate the ΔG of the reaction forming gas **A**, at the same pressure, in kJ mol^{-1}. Assume that ΔH and ΔS of the reaction change with temperature. **[4 points]**
Leave your answer to 3 significant figures.
Leave a sign in front of the number only if your answer is negative. (I.e. if your answer is positive, do not include "+".)

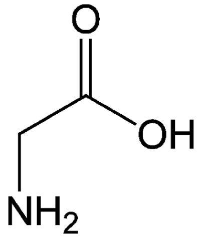
Bond	Energy (298.15 K) / kJ mol^{-1}	Bond	Energy (298.15 K) / kJ mol^{-1}
Homonuclear		O−O	150
H−H	436	C−H	410
N≡N	944	C−N	305
O=O	496	C=N	610
C≡O	1077	C≡N	890
Heteronuclear		C−O	360
C−C	350	C=O	740
C=C	610	C=O (CO_2)	805
C≡C	840	N−H	390
N−N	160	O−H	460
N=N	410		

Type of gas molecule	Constant volume molar heat capacity ($C_{v,m}$) from 100K to 1000K	Constant volume molar heat capacity ($C_{v,m}$) above 1000K
Monoatomic	$\frac{3}{2}R$	$\frac{3}{2}R$
Diatomic	$\frac{5}{2}R$	$\frac{7}{2}R$
Polyatomic linear	$\frac{5}{2}R$	$(3N - \frac{5}{2})R$
Polyatomic non-linear	3R	$(3N - 3)R$

Where *N* is the number of atoms in the molecule.

Solution:

(a)



The question can be solved by making educated guesses and testing different cases. The most helpful entry point is identifying **A** and **B**. It is known that both of these compounds can each be formed by reacting 2 of the five given gases H_2, NH_3, CH_4, CO and CO_2.

A is a toxic, weakly acidic gas. As most simple, toxic molecules are inorganic, it is reasonable to assume that **A** is inorganic, given the limited range of molecules that can be formed. It also contains a labile proton, hence one of its reactants must have hydrogen, i.e. H_2, NH_3 or CH_4. It is unlikely for H_2 to react with NH_3 and CH_4 as the latter are both fully reduced. H_2 could also react with CO and CO_2, yet the products would not be both weakly acidic and toxic.

B is an organic molecule. This is a more explicit hint as it means that one of its reactants must contain carbon, i.e. CH_4, CO or CO_2, as well as hydrogen. A place to start would be trying to "reduce" CO or CO_2 by reacting it with H_2 or NH_3.

With some thinking, we could find **A** by reacting NH_3 and CH_4, in the following reaction:

$$NH_3 + CH_4 \rightarrow HCN + 3H_2$$

A is **HCN**, which may come to mind at the mention of a toxic gas. It is also weakly acidic, being able to dissociate into H^+ and CN^-. The reaction is used industrially in the BMA or Degussa process, which uses a platinum catalyst at 1400°C.

We find **B** by reacting H_2 with CO, in the following reaction:

$$H_2 + CO \rightarrow CH_2O$$

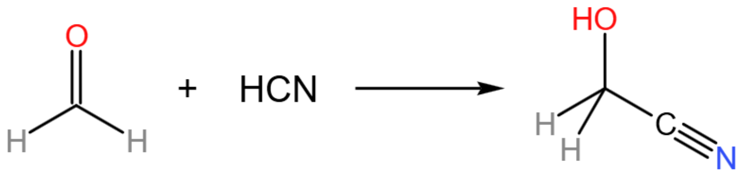
B is **CH_2O** or methanal, the smallest aldehyde. Trying out other pairs of reactants may also yield organic products, however they do not react in an equimolar ratio:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$
$$3H_2 + CO_2 \rightarrow CH_3OH + H_2O$$
$$2NH_3 + CO_2 \rightarrow CO(NH_2)_2 \text{ (urea)} + H_2O$$

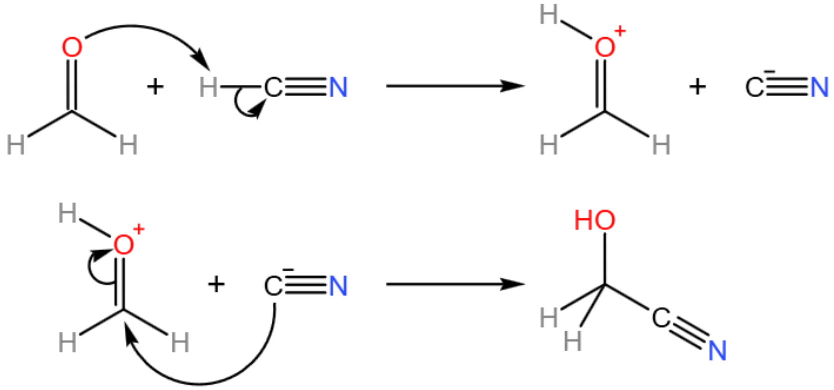
Note H_2 and CO_2 can also react in a 1:1 ratio to form HCOOH or methanoic acid, but it would not be **B** as HCOOH is a liquid at r.t.p. (boiling point = 100.8°C).

$$H_2 + CO_2 \rightarrow HCOOH$$

In solving for **C**, we consider reacting HCN (**A**) with CH_2O (**B**). This is an organic reaction and the mechanism is nucleophilic addition. The following reaction happens

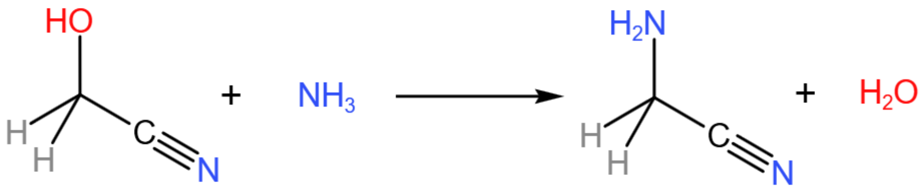


via the mechanism

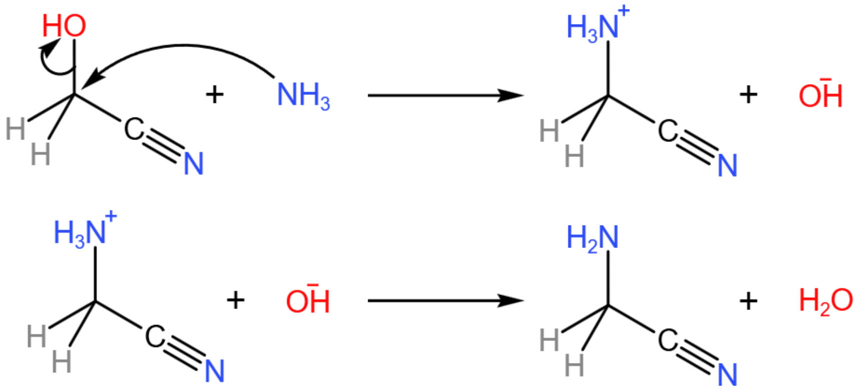


The CN^- is electron-rich and acts as a nucleophile, attacking the electron-deficient carbonyl carbon to form a cyanohydrin.

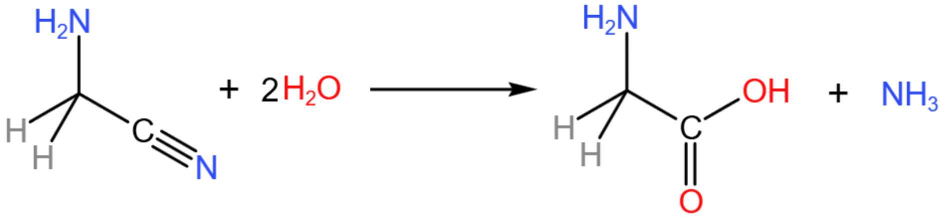
C is then found by reacting this intermediate with NH_3. The most likely role of NH_3 is a nucleophile, attacking the CH_2 carbon in a nucleophilic substitution reaction. The result is that NH_3 will substitute either the −OH or the −CN group. If the NH_3 substitutes the −CN, an alkanolamine is formed; this does not react with water to give new products. Hence, the NH_3 should substitute the −OH group



via the mechanism



This forms the aminonitrile **C**. The nitrile group remains and this is important because nitriles can react with water via hydrolysis to form carboxylic acids.



C **D**

Hence **D** has the above structure.

D is an amino acid, specifically glycine, the smallest amino acid. Detailed in the question is a well-known procedure known as the Strecker amino acid synthesis. In the presence of NH_3, a cyanide anion reacts with an aldehyde to form an aminonitrile, which is then hydrolysed into an amino acid. It is likely that this is the same pathway by which the first amino acids formed on Earth. This was tested by chemist Stanley Miller in his eponymous Miller-Urey experiment in 1953, which simulated the atmospheric conditions present on early Earth. It was found that a mixture of these gases in the presence of an electric spark could produce more complex molecules like amino acids (Miller, 1955)[13].

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[13] Miller, S. L. (1955). Production of Some Organic Compounds under Possible Primitive Earth Conditions. *Journal of the American Chemical Society, 77*(9), 2351-2361. doi: 10.1021/ja01614a001. Extracted from http://image.sciencenet.cn/olddata/kexue.com.cn/upload/blog/file/2008/9/200892213144963834.pdf

(b) 138

Recall the reaction to form HCN (**A**) is

$$NH_3 + CH_4 \rightarrow HCN + 3H_2$$

To find $\Delta G^{\varnothing}$ of this reaction, we need $\Delta H_r^{\varnothing}$ and $\Delta S_r^{\varnothing}$, which is $+215.1$ J mol^{-1} K^{-1}.

$\Delta H_r^{\varnothing}$ can be found using data from the table, through the formula

$$\Delta H_r^{\varnothing} = \sum BE(bonds\ broken) - \sum BE(bonds\ formed)$$

$$\begin{aligned}\Delta H_r^{\varnothing} &= [3\mathrm{BE(N{-}H)} + 4\mathrm{BE(C{-}H)}] - [\mathrm{BE(C{-}H)} + \mathrm{BE(C{\equiv}N)} + 3\mathrm{BE(H{-}H)}]\\ &= [3(390) + 4(410)] - [(410) + (890) + 3(436)]\\ &= +202\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Using the equation

$$\Delta G_r^{\varnothing} = \Delta H_r^{\varnothing} - T\Delta S_r^{\varnothing}$$

$$\Rightarrow \Delta G_r^{\varnothing} = 202 - (298.15)\left(\frac{+215.1}{1000}\right) = +137.87\ \mathrm{kJ\ mol^{-1}}\ (5\ \mathrm{s.f.}) = +138\ \mathrm{kJ\ mol^{-1}}\ (3\ \mathrm{s.f.})$$

(c) −1070

It is given that ΔH and ΔS change with temperature. If information of ΔH and ΔS at one temperature is known, ΔH and ΔS of the same reaction at another temperature **under constant pressure** can be found using the following two equations:

$$\Delta H_r^{\varnothing}(T_2) = \Delta H_r^{\varnothing}(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\varnothing}\, dT \quad \text{(Kirchhoff's Law)}$$

$$\Delta S_r^{\varnothing}(T_2) = \Delta S_r^{\varnothing}(T_1) + \int_{T_1}^{T_2} \frac{1}{T}\Delta_r C_p^{\varnothing}\, dT$$

where $\Delta_r C_p^{\varnothing} = \sum C_{p,m}(products) - \sum C_{p,m}(reactants)$.

$\Delta H_r^{\varnothing}(T_2)$ and $\Delta H_r^{\varnothing}(T_1)$ refer to the standard enthalpy change of reaction at temperatures T_2 and T_1 respectively and similarly for $\Delta S_r^{\varnothing}(T_2)$ and $\Delta S_r^{\varnothing}(T_1)$.[14] $C_{p,m}$ is the **constant pressure** molar heat capacity. A derivation of the equations is included at the end of the solution.

---

[14] Note that a reaction under standard conditions reflects that pressure is kept constant. Though the convention is to refer to standard conditions as 298.15K, 1 bar, temperature is not strictly part of its definition, hence we can have reactions under standard conditions at various temperatures, as long as pressure is constant at 1 bar.

Note however that we are only given data on **constant volume** molar heat capacity, $C_{v,m}$ of various gases. The **constant pressure** molar heat capacity can be calculated using

$$C_{p,m} = C_{v,m} + R$$

As we want to find how ΔH and ΔS change as temperature increases from 298.15K to 5000K, we need to find $\Delta_r C_p^{\emptyset}$ at both 298.15K and 5000K. It is assumed in the problem that $C_{v,m}$ and $C_{p,m}$ values remain constant in the ranges 100K < T < 1000K and T > 1000K.

Also note $C_{v,m}$ varies depending on the geometry of the gas molecule. We record down the geometries of our reactant and product molecules in the reaction, and their corresponding $C_{v,m}$ and $C_{p,m}$ values.

$$NH_3 + CH_4 \rightarrow HCN + 3H_2$$

Molecule	Type of molecule	$C_{v,m}$ from 100K - 1000K	$C_{p,m}$ from 100K - 1000K	$C_{v,m}$ above 1000K	$C_{p,m}$ above 1000K
NH_3	Polyatomic non-linear	**3R**	3R + R = **4R**	$(3N - 3)$R =(3(4) − 3)R = **9R**	9R + R = **10R**
CH_4	Polyatomic non-linear	**3R**	3R + R = **4R**	$(3N - 3)$R =(3(5) − 3)R = **12R**	12R + R = **13R**
HCN	Polyatomic linear	$\frac{5}{2}$**R**	$\frac{5}{2}$R + R = $\frac{7}{2}$**R**	$(3N - \frac{5}{2})$R =$(3(3) - \frac{5}{2})$R = $\frac{13}{2}$**R**	$\frac{13}{2}$R + R = $\frac{15}{2}$**R**
H_2	Diatomic	$\frac{5}{2}$**R**	$\frac{5}{2}$R + R = $\frac{7}{2}$**R**	$\frac{7}{2}$**R**	$\frac{7}{2}$R +R = $\frac{9}{2}$**R**

Let $C_{p,m}(298.15\ K)$ and $C_{p,m}(5000\ K)$ refer to the constant pressure molar heat capacities at 298.15 K and 5000 K respectively,

$$\begin{aligned}\text{Hence } \Delta_r C_p^{\emptyset}(298.15\ K) &= \sum C_{p,m}(298.15\ K)(products) - \sum C_{p,m}(298.15\ K)(reactants)\\ &= [C_{p,m}(\mathrm{HCN}) + 3C_{p,m}(\mathrm{H_2})] - [C_{p,m}(\mathrm{NH_3}) + C_{p,m}(\mathrm{CH_4})]\\ &= [\tfrac{7}{2}\mathrm{R} + 3(\tfrac{7}{2}\mathrm{R})] - (4\mathrm{R} + 4\mathrm{R})\\ &= 6\mathrm{R}\ \mathrm{Jmol^{-1}K^{-1}}\end{aligned}$$

and $\Delta_r C_p^{\varnothing}(5000\,K) = \sum C_{p,m}(5000\,K)(products) - \sum C_{p,m}(5000\,K)(reactants)$

$$= [C_{p,m}(\mathrm{HCN}) + 3C_{p,m}(\mathrm{H_2})] - [C_{p,m}(\mathrm{NH_3}) + C_{p,m}(\mathrm{CH_4})]$$

$$= [\tfrac{15}{2}\mathrm{R} + 3(\tfrac{9}{2}\mathrm{R})] - (10\mathrm{R} + 13\mathrm{R})$$

$$= -2\mathrm{R}\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

As we know ΔH and ΔS at 298.15 K,

Sub $T_2 = 5000$ K, $T_1 = 298.15$ K, $\Delta_r C_p^{\varnothing}(298.15\,K) = 6\mathrm{R}$, and $\Delta_r C_p^{\varnothing}(5000\,K) = -2\mathrm{R}$,

$$\Delta H_r^{\varnothing}(5000\,K) = \Delta H_r^{\varnothing}(298.15\,K) + \int_{T_1}^{T_2} \Delta_r C_p^{\varnothing}\,dT$$

$$= \Delta H_r^{\varnothing}(298.15\,K) + \int_{T_1}^{1000} \Delta_r C_p^{\varnothing}(298.15\,K)dT + \int_{1000}^{T_2} \Delta_r C_p^{\varnothing}(5000\,K)dT$$

$$= (+\ 202) + \Delta_r C_p^{\varnothing}(298.15\,K)(1000 - T_1) + \Delta_r C_p^{\varnothing}(5000\,K)(T_2 - 1000)$$

$$= (+\ 202) + (\tfrac{6R}{1000})(1000 - 298.15) + (-\tfrac{2R}{1000})(5000 - 1000)$$

$$= +170.50\ \mathrm{kJ\ mol^{-1}}\ (5\ \mathrm{s.f.})$$

$$\Delta S_r^{\varnothing}(5000\,K) = \Delta S_r^{\varnothing}(298\,K) + \int_{T_1}^{T_2} \tfrac{1}{T}\Delta_r C_p^{\varnothing}\,dT$$

$$= \Delta S_r^{\varnothing}(298\,K) + \int_{T_1}^{1000} \tfrac{1}{T}\Delta_r C_p^{\varnothing}(298.15\,K)\,dT + \int_{1000}^{T_2} \tfrac{1}{T}\Delta_r C_p^{\varnothing}(5000\,K)dT$$

$$= (+215.1) + \Delta_r C_p^{\varnothing}(298.15\,K)ln\tfrac{1000}{T_1} + \Delta_r C_p^{\varnothing}(5000\,K)ln\tfrac{T_2}{1000}$$

$$= (+215.1) + (6R)ln\tfrac{1000}{298.15} + (-\ 2R)ln\tfrac{5000}{1000}$$

$$= +248.71\ \mathrm{J\ mol^{-1}\ K^{-1}}\ (3\ \mathrm{s.f.})$$

Using the equation

$$\Delta G_r = \Delta H_r - T\Delta S_r$$

$\Rightarrow \Delta G_r = 170.50 - (5000)(\tfrac{+248.71}{1000}) = -1073.05\ \mathrm{kJ\ mol^{-1}}$ (5 s.f.) $= -1070\ \mathrm{kJ\ mol^{-1}}$ (3 s.f.)

The value of ΔG decreases when temperature increases, which is expected for a reaction that is spontaneous at only high temperatures.

Extra: Derivation of temperature-dependent ΔH and ΔS equations

For ΔH, from Hess's Law,

$$\Delta H_r^{\emptyset} = \sum H^{\emptyset}(products) - \sum H^{\emptyset}(reactants)$$

Differentiating both sides with respect to temperature T (this allows us to find how small changes in temperature will affect $\Delta H_r^{\emptyset}$),

$$\frac{d\Delta H_r^{\emptyset}}{dT} = \sum \frac{dH^{\emptyset}}{dT}(products) - \sum \frac{dH^{\emptyset}}{dT}(reactants)$$

From the definition of C_p (see derivation of $C_{p,m} = C_{v,m} + R$),

$$C_p = \frac{dH}{dT} \text{ at constant pressure}$$

$$\therefore \frac{d\Delta H_r^{\emptyset}}{dT} = \sum C_p^{\emptyset}(products) - \sum C_p^{\emptyset}(reactants)$$

$$= \Delta_r C_p^{\emptyset}$$

$$\Rightarrow d\Delta H_r^{\emptyset} = \Delta_r C_p^{\emptyset}\, dT$$

Integrating both sides w.r.t. T,

$$\int_{T_1}^{T_2} d\Delta H_r^{\emptyset} = \int_{T_1}^{T_2} \Delta_r C_p^{\emptyset}\, dT$$

$$\Delta H_r^{\emptyset}(T_2) - \Delta H_r^{\emptyset}(T_1) = \int_{T_1}^{T_2} \Delta_r C_p^{\emptyset}\, dT$$

$$\Rightarrow \Delta H_r^{\emptyset}(T_2) = \Delta H_r^{\emptyset}(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\emptyset}\, dT \text{ (shown)}$$

For ΔS, at constant pressure, from the definition of entropy,

$$dS = \frac{dq_{p,rev}}{T} = \frac{dH}{T}$$

since ΔH = q.

Again from Hess's Law,

$$\Delta S_r^{\emptyset} = \sum S^{\emptyset}(products) - \sum S^{\emptyset}(reactants)$$

Differentiating both sides with respect to temperature T,

$$\frac{d\Delta S_r^{\emptyset}}{dT} = \sum \frac{dS^{\emptyset}}{dT}(products) - \sum \frac{dS^{\emptyset}}{dT}(reactants)$$

$$= \sum \frac{dH^{\emptyset}}{TdT}(products) - \sum \frac{dH^{\emptyset}}{TdT}(reactants)$$

$$= \frac{1}{T}\left[\sum \frac{dH^{\emptyset}}{dT}(products) - \sum \frac{dH^{\emptyset}}{dT}(reactants)\right]$$

$$= \frac{1}{T}\left[\sum C_p^{\emptyset}(products) - \sum C_p^{\emptyset}(reactants)\right]$$

$$= \frac{1}{T}\Delta_r C_p^{\varnothing}$$

$$\Rightarrow d\Delta S_r^{\varnothing} = \frac{1}{T}\Delta_r C_p^{\varnothing}\, dT$$

Integrating both sides w.r.t. T,

$$\int_{T_1}^{T_2} d\Delta S_r^{\varnothing} = \int_{T_1}^{T_2} \frac{1}{T}\Delta_r C_p^{\varnothing}\, dT$$

$$\Delta S_r^{\varnothing}(T_2) - \Delta S_r^{\varnothing}(T_1) = \int_{T_1}^{T_2} \frac{1}{T}\Delta_r C_p^{\varnothing}\, dT$$

$$\Rightarrow \Delta S_r^{\varnothing}(T_2) = \Delta S_r^{\varnothing}(T_1) + \int_{T_1}^{T_2} \frac{1}{T}\Delta_r C_p^{\varnothing}\, dT \text{ (shown)}$$

Problem prepared by: George Zhou

Problem 39: ✌ 💣⍓⬧⧫♏❒♓□◆⬧ 💣♏⬧⬧♋♑♏

[5 points]

You and your band of time travellers have received a mysterious message which appears to be a bit garbled. The message is given as follows:

```
MgGe / SrTlCrCrTlAgBaK / SrPbTlFe / GeNaBa / HCoBaRbMgLiCr /
GeNaBaTlPbPt / TlSr / PbBaCrLiGeMgCuMgGePt / GeNaLiGe / FeLiHH /
LiInK / BaInBaPbCaPt / LiPbBa / CsTlGeNa / CsBiGe /
KMgSrSrBaPbBaInGe / FeLiInMgSrBaHGeLiGeMgTlInH / TlSr / GeNaBa /
HLiFeBa / GeNaMgInCa / — / Li / HTlFeBaAgNaLiGe /
BiInSrLiFeMgCrMgLiPb / RbTlInRbBaCoGeMgTlIn / SrTlPb / GeNaBa /
LiCuBaPbLiCaBa / FeMgInK. / SrBiPbGeNaBaPbFeTlPbBa, / GeNaBa /
BaNiBiLiGeMgTlIn / Ba / MgH / BaNiBiLiCr/ / Fe / Rb /
HNiBiLiPbBaK, / MgIn / AgNaMgRbNa / BaInBaPbCaPt / MgH / CoBiGe
/ BaNiBiLiCr / GeTl / FeLiHH, / FeBiCrGeMgCoCrMgBaK / CsPt /
GeNaBa / HNiBiLiPbBa / TlSr / GeNaBa / CuBaCrTlRbMgGePt / TlSr /
CrMgCaNaGe, / HNaTlAgBaK / GeNaLiGe / CuBaPbPt / HFeLiCrCr /
LiFeTlBiInGeH / TlSr / FeLiHH / FeLiPt / CsBa /
RbTlInCuBaPbGeBaK / MgInGeTl / Li / CuBaPbPt / CrLiPbCaBa /
LiFeTlBiInGe / TlSr / BaInBaPbCaPt / LiInK / CuMgRbBa /
CuBaPbHLi. / GeNaBa / FeLiHH / LiInK / BaInBaPbCaPt / AgBaPbBa /
MgIn / SrLiRbGe / BaNiBiMgCuLiCrBaInGe, / LiRbRbTlPbKMgInCa /
GeTl / GeNaBa / SrTlPbFeBiCrLi / FeBaInGeMgTlInBaK /
CsBaSrTlPbBa. / GeNaMgH / AgLiH / KBaFeTlInHGePbLiGeBaK / CsPt /
RbTlRbZnRbPbTlSrGe / LiInK / AgLiCrGeTlIn / MgIn /
InMgInBaGeBaBaIn / GeNaMgPbGePt / GeAgTl /
BaHgCoBaPbMgFeBaInGeLiCrCrPt.
```

You know the following information about the message:

- The message uses a substitution cipher.
- Each letter in the original text has been replaced by an element in the message.
- Each letter corresponds to only one element, and each element corresponds to only one letter.
- Characters like dashes, commas and full stops have not been represented.
- Whether the original letter in the original message was uppercase or lowercase does not matter.
- Each slash represents a spacing between words.
- The message is taken from a scientific text.

- Letters have not been assigned elements randomly: there is an **underlying rule** governing the chemical symbols used. In the derivation of this rule, each letter has a certain value or number which is useful in deriving this rule.

Consider the element used to encode the letter “S”. Deduce its corresponding number according to the aforementioned underlying rule.

Leave your answer to the nearest integer. Neglect any units.

Solution:

0

You can start by running a bit of frequency analysis on the text (online cryptographic tools may help). Out of the elements, Ba appears most often (64x) followed by Ge (49x), Li (42x), Tl (35x) and In (34x). We can start by supposing that Ba = **E**.

MgGe / SrTlCrCrTlAg**E**K / SrPbTlFe / GeNa**E** / HCo**E**RbMgLiCr / GeNa**E**TlPbPt / TlSr / Pb**E**CrLiGeMgCuMgGePt / GeNaLiGe / FeLiHH / LiInK / **E**In**E**PbCaPt / LiPb**E** / CsTlGeNa / CsBiGe / KMgSrSr**E**Pb**E**InGe / FeLiInMgSr**E**HGeLiGeMgTlInH / TlSr / GeNa**E** / HLiFe**E** / GeNaMgInCa / — / Li / HTlFe**E**AgNaLiGe / BiInSrLiFeMgCrMgLiPb / RbTlInRb**E**CoGeMgTlIn / SrTlPb / GeNa**E** / LiCu**E**PbLiCa**E** / FeMgInK. / SrBiPbGeNa**E**PbFeTlPb**E**, / GeNa**E** / **E**NiBiLiGeMgTlIn / **E** / MgH / **E**NiBiLiCr / Fe / Rb / HNiBiLiPb**E**K, / MgIn / AgNaMgRbNa / **E**In**E**PbCaPt / MgH / CoBiGe / **E**NiBiLiCr / GeTl / FeLiHH, / FeBiCrGeMgCoCrMg**E**K / CsPt / GeNa**E** / HNiBiLiPb**E** / TlSr / GeNa**E** / Cu**E**CrTlRbMgGePt / TlSr / CrMgCaNaGe, / HNaTlAg**E**K / GeNaLiGe / Cu**E**PbPt / HFeLiCrCr / LiFeTlBiInGeH / TlSr / FeLiHH / FeLiPt / Cs**E** / RbTlInCu**E**PbGe**E**K / MgInGeTl / Li / Cu**E**PbPt / CrLiPbCa**E** / LiFeTlBiInGe / TlSr / **E**In**E**PbCaPt / LiInK / CuMgRb**E** / Cu**E**PbHLi. / GeNa**E** / FeLiHH / LiInK / **E**In**E**PbCaPt / Ag**E**Pb**E** / MgIn / SrLiRbGe / **E**NiBiMgCuLiCr**E**InGe, / LiRbRbTlPbKMgInCa / GeTl / GeNa**E** / SrTlPbFeBiCrLi / Fe**E**InGeMgTlIn**E**K / Cs**E**SrTlPb**E**. / GeNaMgH / AgLiH / K**E**FeTlInHGePbLiGe**E**K / CsPt / RbTlRbZnRbPbTlSrGe / LiInK / AgLiCrGeTlIn / MgIn / InMgIn**E**Ge**EE**In / GeNaMgPbGePt / GeAgTl / **E**HgCo**E**PbMgFe**E**InGeLiCrCrPt.

Now, we need to consider a few common letter groups: these can include the 6 letter word **E**in**E**PbCaPt which appears 4 times, the two three letter words ending in E: GeNa**E** (10 appearances, 2 as part of words) and LiPb**E** (3 appearances), or the 8 letter InMgIn**E**Ge**EE**In. Although this last group has one appearance, it is very helpful as it also has another triply repeated letter (In). The only common word that has this pattern is **NINETEEN**, which gives us In = **N**, Mg = **I**, Ge = **T**.

IT / SrTlCrCrTlAg**E**K / SrPbTlFe / **T**Na**E** / HCo**E**Rb**I**LiCr / **T**Na**E**TlPbPt / TlSr / Pb**E**CrLi**TI**Cu**IT**Pt / **T**NaLi**T** / FeLiHH / Li**N**K / **ENE**PbCaPt / LiPb**E** / CsTl**T**Na / CsBi**T** / K**I**SrSr**E**Pb**ENT** / FeLi**NI**Sr**E**H**T**Li**TI**Tl**N**H / TlSr / **T**Na**E** / HLiFe**E** / **T**Na**IN**Ca / — / Li / HTlFe**E**AgNaLi**T** /

Bi**N**SrLiFe**I**Cr**I**LiPb / RbTl**N**Rb**E**Co**TI**Tl**N** / SrTlPb / **T**Na**E** / LiCu**E**PbLiCa**E** / Fe**IN**K. / SrBiPb**T**Na**E**PbFeTlPb**E**, / **T**Na**E** / **E**NiBiLi**TI**Tl**N** / **E** / **I**H / **E**NiBiLiCr / Fe / Rb / HNiBiLiPb**E**K, / **IN** / AgNa**I**RbNa / **ENE**PbCaPt / **I**H / CoBi**T** / **E**NiBiLiCr / **T**Tl / FeLiHH, / FeBiCr**TI**CoCr**IE**K / CsPt / **T**Na**E** / HNiBiLiPb**E** / TlSr / **T**Na**E** / Cu**E**CrTlRb**IT**Pt / TlSr / Cr**I**CaNa**T**, / HNaTlAg**E**K / **T**NaLi**T** / Cu**E**PbPt / HFeLiCrCr / LiFeTlBi**NT**H / TlSr / FeLiHH / FeLiPt / Cs**E** / RbTl**N**Cu**E**Pb**TE**K / **INT**Tl / Li / Cu**E**PbPt / CrLiPbCa**E** / LiFeTlBi**NT** / TlSr / **ENE**PbCaPt / Li**N**K / Cu**I**Rb**E** / Cu**E**PbHLi. / **T**Na**E** / FeLiHH / Li**N**K / **ENE**PbCaPt / Ag**E**Pb**E** / **IN** / SrLiRb**T** / **E**NiBi**I**CuLiCr**ENT**, / LiRbRbTlPbK**IN**Ca / **T**Tl / **T**Na**E** / SrTlPbFeBiCrLi / Fe**ENTI**Tl**NE**K / Cs**E**SrTlPb**E**. / **T**Na**I**H / AgLiH / K**E**FeTl**N**H**T**PbLi**TE**K / CsPt / RbTlRbZnRbPbTlSr**T** / Li**N**K / AgLiCr**T**Tl**N** / **IN** / **NINETEEN** / **T**Na**I**Pb**T**Pt / **T**AgTl / **E**HgCo**E**Pb**I**Fe**ENT**LiCrCrPt.

Lots of helpful points appear now: **ENE**PbCaPt is probably **ENERGY**, **T**Na**E** is probably **THE**, and with **T**NaLi**T** becoming **TH**Li**T**, we can guess that the word is **THAT**. Also, considering the preceding "**IN** / **NINETEEN**", **T**Na**I**Pb**T**Pt / **T**AgTl is likely to be the rest of a year: **THIRTY** / **TWO**. Fe**ENTI**Tl**NE**K is one of **MENTIONED** or **MENTIONER**, the former being more likely since R is already another element. We thus deduce Pb = **R**, Ca = **G**, Pt = **Y**, Na = **H**, Li = **A**, Ag = **W**, Tl = **O**, Fe = **M**, K = **D**.

IT / Sr**O**CrCr**OWED** / Sr**ROM** / **THE** / HCo**E**Rb**IA**Cr / **THEORY** / **O**Sr / **RE**Cr**ATI**Cu**ITY** / **THAT** / **MA**HH / **AND** / **ENERGY** / **ARE** / Cs**OTH** / CsBi**T** / **DI**SrSr**ERENT** / **MANI**Sr**E**H**TATION**H / **O**Sr / **THE** / H**AME** / **THING** / — / **A** / H**OMEWHAT** / Bi**N**Sr**AMI**Cr**IAR** / Rb**ON**Rb**E**Co**TION** / Sr**OR** / **THE** / **A**Cu**ERAGE** / **MIND**. / SrBi**RTHERMORE**, / **THE** / **E**NiBi**ATION** / **E** / **I**H / **E**NiBi**A**Cr / **M** / Rb / HNiBi**ARED**, / **IN** / **WHI**Rb**H** / **ENERGY** / **I**H / CoBi**T** / **E**NiBi**A**Cr / **TO** / **MA**HH, / **M**BiCr**TI**CoCr**IED** / Cs**Y** / **THE** / HNiBi**ARE** / **O**Sr / **THE** / Cu**E**Cr**O**Rb**ITY** / **O**Sr / Cr**IGHT**, / H**HOWED** / **THAT** / Cu**ERY** / H**MA**CrCr / **AMO**Bi**NT**H / **O**Sr / **MA**HH / **MAY** / Cs**E** / Rb**ON**Cu**ERTED** / **INTO** / **A** / Cu**ERY** / Cr**ARGE** / **AMO**Bi**NT** / **O**Sr / **ENERGY** / **AND** / Cu**I**Rb**E** / Cu**ER**H**A**. / **THE** / **MA**HH / **AND** / **ENERGY** / **WERE** / **IN** / Sr**A**Rb**T** / **E**NiBi**I**Cu**A**Cr**ENT**, / **A**RbRb**ORDING** / **TO** / **THE** / Sr**ORM**BiCr**A** / **MENTIONED** / Cs**E**Sr**ORE**. / **THI**H / **WA**H / **DEMON**H**TRATED** / Cs**Y** / Rb**O**RbZnRb**RO**Sr**T** / **AND** / **WA**Cr**TON** / **IN** / **NINETEEN** / **THIRTY** / **TWO** / **E**HgCo**ERIMENTA**CrCr**Y**.

At this point, we can continue guessing words (in fact, there are many words which are quite easy to guess at this point), but we can also deduce the main topic of the paragraph.

This can be easily seen in the sentence "**MA**HH / **AND** / **ENERGY** / **ARE** / Cs**OTH** / CsBi**T** / **DI**SrSr**ERENT** / **MANI**Sr**E**H**TATION**H / **O**Sr / **THE** / H**AME** / **THING**" – which we can easily interpret as "**MASS** / **AND** / **ENERGY** / **ARE** / **BOTH** / **BUT** / **DIFFERENT** / **MANIFESTATIONS** / **OF** / **THE** / **SAME** / **THING**". The topic of the passage is mass-energy equivalence. Similarly, the mysterious "**M**" being its own word in the sentence "**THE** / **E**NiBi**ATION** / **E** / **I**H / **E**NiBi**A**Cr / **M** / Rb / HNiBi**ARED**" should bring to mind "**THE** / **EQUATION** / **E** / **IS** / **EQUAL** / **M** / **C** / **SQUARED**". Lastly, what "**THEORY** / **O**Sr / **RE**Cr**ATI**Cu**ITY**" could mass-energy equivalence be related to but the "**THEORY** / **OF** / **RELATIVITY**"? We thus find that H = **S**, Cs = **B**, Bi = **U**, Sr = **F**, Ni = **Q**, Cr = **L**, Rb = **C**, Cu = **V**.

IT / **FOLLOWED** / **FROM** / **THE** / **S**Co**ECIAL** / **THEORY** / **OF** / **RELATIVITY** / **THAT** / **MASS** / **AND** / **ENERGY** / **ARE** / **BOTH** / **BUT** / **DIFFERENT** / **MANIFESTATIONS** / **OF** / **THE** / **SAME** / **THING** / – / **A** / **SOMEWHAT** / **UNFAMILIAR** / **CONCE**Co**TION** / **FOR** / **THE** / **AVERAGE** / **MIND**. / **FURTHERMORE**, / **THE** / **EQUATION** / **E** / **IS** / **EQUAL** / **M** / **C** / **SQUARED**, / **IN** / **WHICH** / **ENERGY** / **IS** / Co**UT** / **EQUAL** / **TO** / **MASS**, / **MULTI**Co**LIED** / **BY** / **THE** / **SQUARE** / **OF** / **THE** / **VELOCITY** / **OF** / **LIGHT**, / **SHOWED** / **THAT** / **VERY** / **SMALL** / **AMOUNTS** / **OF** / **MASS** / **MAY** / **BE** / **CONVERTED** / **INTO** / **A** / **VERY** / **LARGE** / **AMOUNT** / **OF** / **ENERGY** / **AND** / **VICE** / **VERSA**. / **THE** / **MASS** / **AND** / **ENERGY** / **WERE** / **IN** / **FACT** / **EQUIVALENT**, / **ACCORDING** / **TO** / **THE** / **FORMULA** / **MENTIONED** / **BEFORE**. / **THIS** / **WAS** / **DEMONSTRATED** / **BY** / **COC**Zn**CROFT** / **AND** / **WALTON** / **IN** / **NINETEEN** / **THIRTY** / **TWO** / **E**HgCo**ERIMENTALLY**.

We are nearly done and it remains for us to find the last few missing letters. "**S**Co**ECIAL**" and "**MULTI**Co**LIED**" correspond to "**SPECIAL**" and "**MULTIPLIED**" respectively, telling us that Co = **P**. Meanwhile, "**E**HgCo**ERIMENTALLY**" shows that Hg = **X**. Lastly, mass-energy equivalence was first demonstrated experimentally by "**COCKCROFT** / **AND** / **WALTON** / **IN** / **NINETEEN** / **THIRTY**/ **TWO**", so Zn = **K**. The final message is:

IT / **FOLLOWED** / **FROM** / **THE** / **SPECIAL** / **THEORY** / **OF** / **RELATIVITY** / **THAT** / **MASS** / **AND** / **ENERGY** / **ARE** / **BOTH** / **BUT** / **DIFFERENT** / **MANIFESTATIONS** / **OF** / **THE** / **SAME** / **THING** / – / **A** / **SOMEWHAT** / **UNFAMILIAR** / **CONCEPTION** / **FOR** / **THE** / **AVERAGE** / **MIND**. / **FURTHERMORE**, / **THE** / **EQUATION** / **E** / **IS** / **EQUAL** / **M** / **C** / **SQUARED**, / **IN** / **WHICH** / **ENERGY** / **IS** / **PUT** / **EQUAL** / **TO** / **MASS**, / **MULTIPLIED** / **BY** / **THE** / **SQUARE** / **OF** / **THE** / **VELOCITY** / **OF** /

LIGHT, / SHOWED / THAT / VERY / SMALL / AMOUNTS / OF / MASS / MAY / BE / CONVERTED / INTO / A / VERY / LARGE / AMOUNT / OF / ENERGY / AND / VICE / VERSA. / THE / MASS / AND / ENERGY / WERE / IN / FACT / EQUIVALENT, / ACCORDING / TO / THE / FORMULA / MENTIONED / BEFORE. / THIS / WAS / DEMONSTRATED / BY / COCKCROFT / AND / WALTON / IN / NINETEEN / THIRTY / TWO / EXPERIMENTALLY.

This is an excerpt from a recording made by Albert Einstein for the documentary *Atomic Physics*. The encoding system is given as follows (the two greyed out letters are not present in the cryptogram, and their identity is not needed for the question)

A	B	C	D	E	F	G	H	I	J	K	L	M
Li	Cs	Rb	K	Ba	Sr	Ca	Na	Mg	Al	Zn	Cr	Fe
N	O	P	Q	R	S	T	U	V	W	X	Y	Z
In	Tl	Co	Ni	Pb	H	Ge	Bi	Cu	Ag	Hg	Pt	Au

Reading from left to right, the sequence Li-Cs-Rb-K-Ba... should evoke the electrochemical series of metals (a relative of the reactivity series which sorts the orders purely based on standard reduction potentials). Indeed, all these elements are sorted in order of their standard electrode potentials. By definition, the standard reduction potential of the H^+/H_2 system is 0.00V, so the final answer is 0.

Problem prepared by: Brennan Ting

Problem 40: Just A Couple Of Atoms

[12 points]

Proton nuclear magnetic resonance spectroscopy (^1H NMR) is used to determine the number and types of hydrogen atoms in a molecule. One unique strength of ^1H NMR is **spin-spin coupling**, which arises from the nuclear spin of ^1H ($I = ½$).

In the ^1H NMR spectrum of 1,1,2-trichloroethane, the protons labelled H_a and H_b are spin-coupled to each other. The H_b protons generate their own magnetic field that have a 50% chance of aligning with the external field and 50% chance of aligning against it. The effective magnetic field experienced by H_a is hence more shielded in half of the molecules and less shielded in the other half, causing a splitting of the H_a signal.

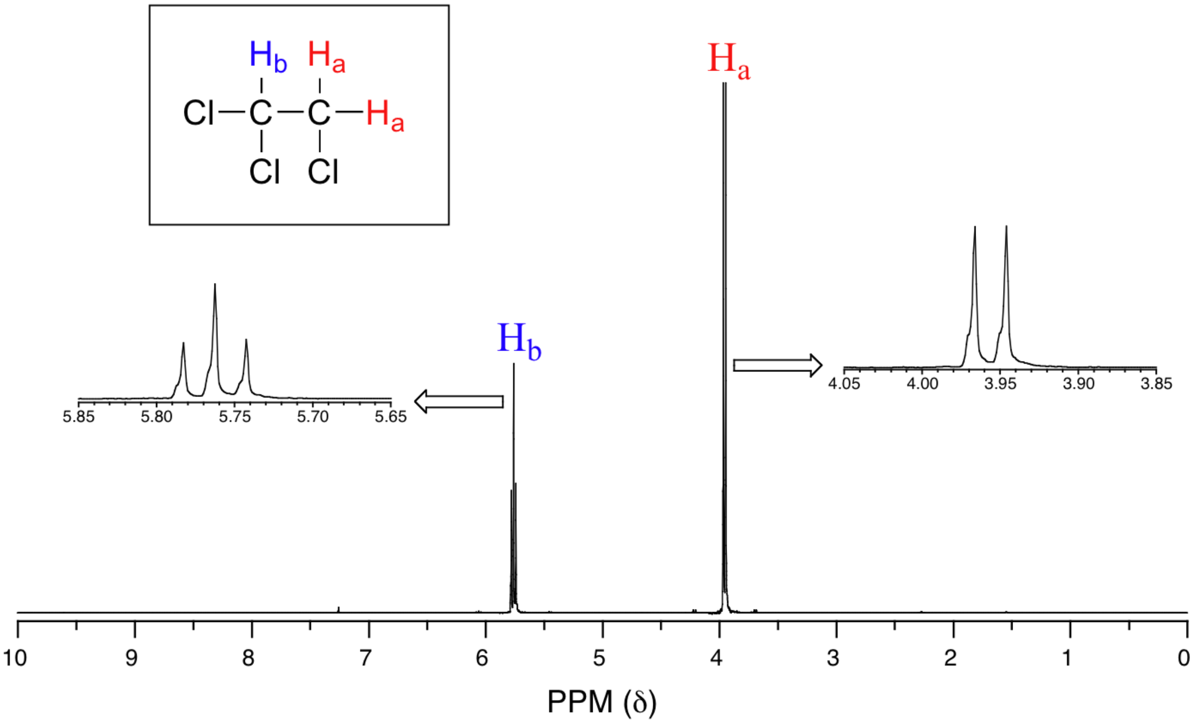


Figure 1: ^1H NMR Spectrum of 1,1,2-trichloroethane.

This can be represented by a splitting diagram, where $^3J_{HH}$ = 7 Hz is a typical coupling constant between vicinal hydrogens on saturated carbons. The subscript HH refers to the atoms involved, and the superscript 3 refers to the number of bonds in between the protons.

In most cases, protons only couple with neighbouring protons 3 bonds away (on adjacent carbon atoms). However, long-range coupling is observed in aromatic and allylic protons.

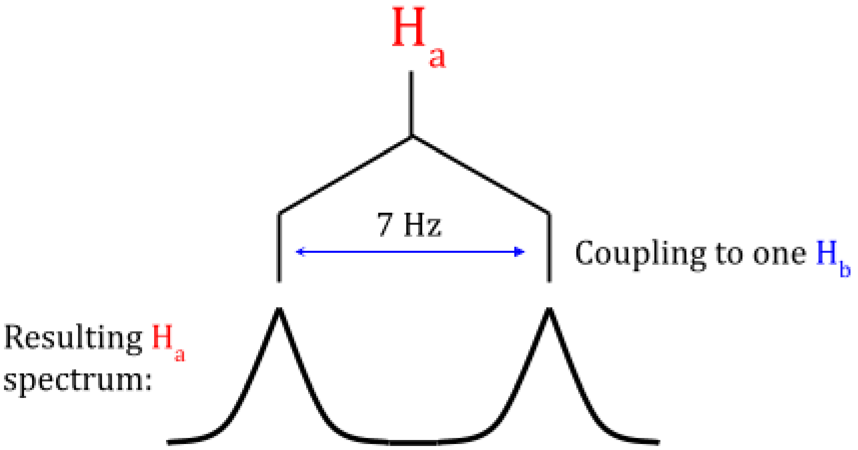


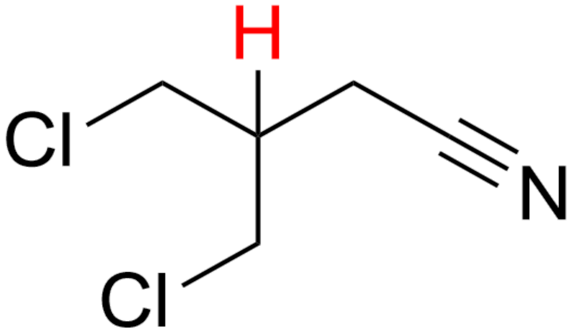
Figure 2: Splitting diagram for the H_a protons.

The final number of peaks in the signal depends on the number of *different* neighbouring hydrogens and the coupling constants involved.

How a signal is split due to coupling is called its **multiplicity**. This could be a singlet (s) when coupling is absent, a doublet (d), a triplet (t), or even combinations like a doublet of doublets (dd) or doublet of triplets (dt) if there are different coupling constants involved. In 1,1,2-trichloroethane, the *single* H_b proton causes the H_a signal to be split *once* into a *doublet*. Conversely, the *two* H_a protons cause the H_b signal to be split *twice* into a *triplet*.

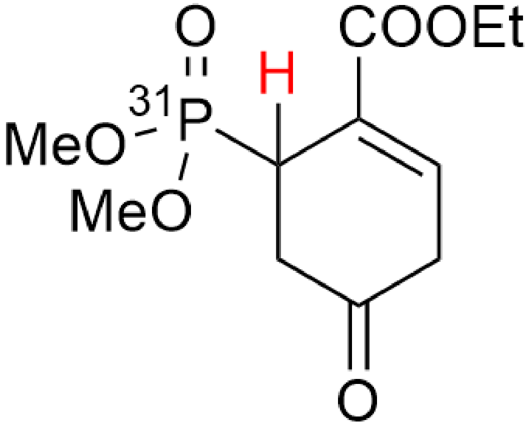
Another thing to note is how the H_a signal looks twice as strong as the H_b. Technically, the **area** under the signal is twice as large. This is called **integration**. A signal corresponding to 1 proton has an integration of 1H, a 2 proton signal has an integration of 2H, and so on.

(a) In the following molecule, how many peaks will the signal for the red proton theoretically have? Assume the only coupling interactions are between protons. **[2 points]**



Protons need not interact with neighbouring protons only. NMR-active nuclei also include phosphorus-31, which also has a nuclear spin of ½.

(b) A very precise ^{1}H NMR spectrum for the following molecule is obtained.



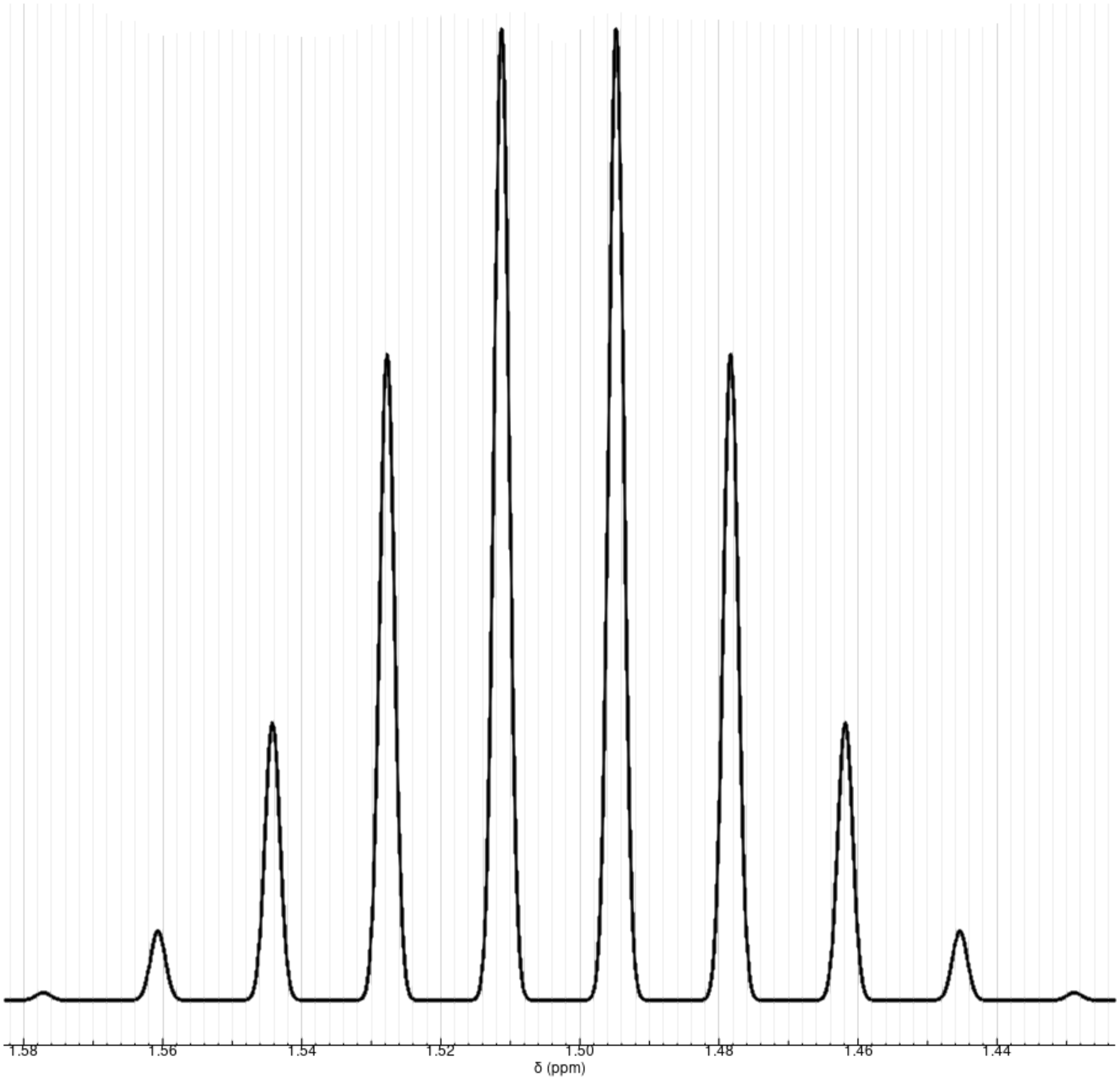
The coupling constants in this molecule are:

- $^3J_{HH}$ (Alkane) = 8 Hz
- $^4J_{HH}$ (Allylic) = 2.4 Hz
- $^2J_{PH}$ = 22 Hz

List the separations, in Hz, of all the peaks obtained in the signal for the red proton, from left to right. Assume that there are no coupling interactions other than those listed. **[3 points]**

Input your answer as [number],[number],[number] … , without any spaces.
Leave all numbers to 1 decimal place.

(c) In the ^{1}H NMR spectrum of isobutane, $HC(CH_3)_3$, the signal for the tertiary proton is a 1H “dectet” with 10 peaks.



How many times taller is the largest peak than the smallest peak? **[2 points]**
Leave your answer as an integer.

For the following parts, you should use the ^{1}H NMR chemical shifts and list of coupling constants found in the ***data sheet****.*

A fluorobenzene **A** has the molecular formula $C_{12}H_{15}OF$. Its ^{1}H NMR spectrum is recorded as follows (assume that fluorine does **not** couple with hydrogen):

δ / ppm	Integration	Multiplicity	J / Hz
1.43	6H	s	-
2.34	3H	s	-
5.04	1H	dd	16.79, 1.36
5.10	1H	dd	10.88, 1.36
6.13	1H	dd	16.79, 10.88
6.80	1H	dd	2.43, 0.54
6.97	1H	dd	2.43, 7.91
7.33	1H	dd	7.91, 0.54

A may be produced from the S_N1 reaction of a phenol with an alkyl bromide.

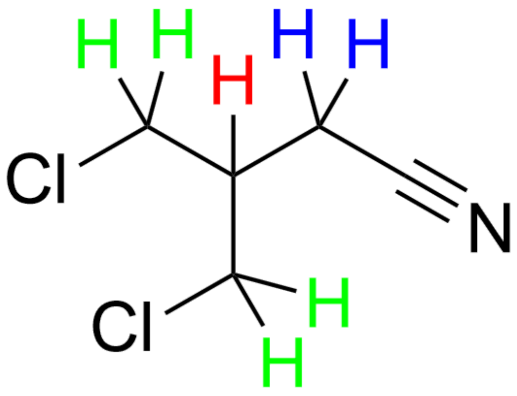
When **A** was heated to 200 °C, a compound **C** with the same molecular formula as **A** was obtained. The ^{1}H NMR spectrum of **C** shows 2 aromatic hydrogens with $J = 2.08$ Hz. A 2H doublet and three separate 3H signals are also present. **C** also exhibits intramolecular hydrogen bonding.

(d) Deduce the structure of **A**. **[3 points]**

(e) Deduce the structure of **C**. **[2 points]**

Solution:

(a) 15



The green protons are all chemically equivalent, but they are different from the blue protons.

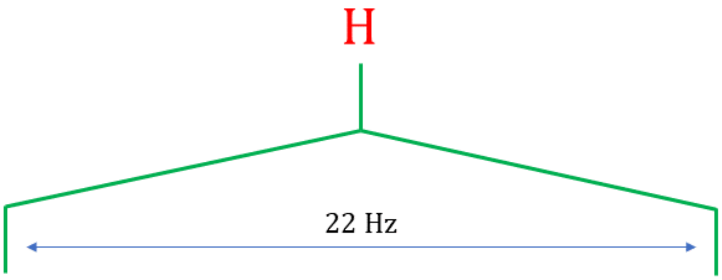
The 2 blue protons split the signal of the red proton 2 times to form a **triplet**. Then, the 4 green protons split **each** of the resulting peaks 4 times to form a **triplet of quintuplets**. Hence the theoretical number of peaks for the red proton is $3 \times 5 = 15$.

In practice, however, it would be impossible to see all 15 peaks without a very precise ^{1}H NMR machine. The signal for the red proton would appear as a “multiplet” with an indiscernible number of peaks.

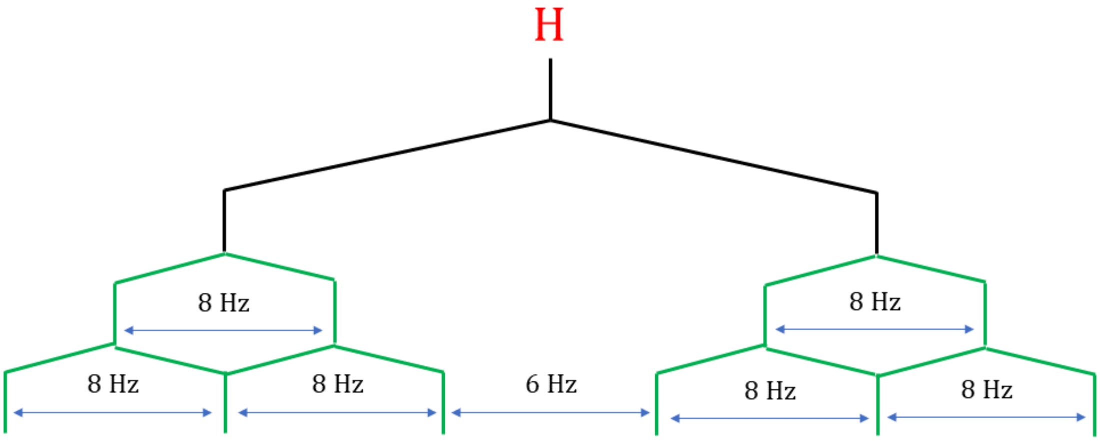
(b) 2.4,5.6,2.4,5.6,2.4,3.6,2.4,5.6,2.4,5.6,2.4

The resulting signal for the red H will be a **doublet of triplet of doublets** (dtd), since it couples to phosphorus-31, then to the 2 neighbouring hydrogens, then to the distant allylic hydrogen, forming 2 x 3 x 2 = 12 peaks.

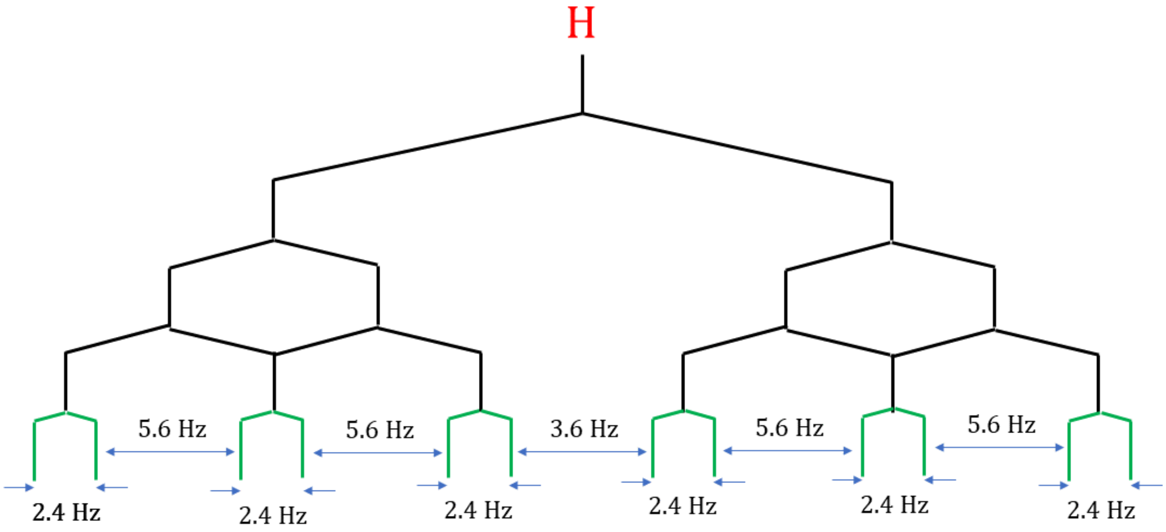
Start by drawing the splitting diagram just for ^{31}P, since it has the largest coupling constant. The single ^{31}P splits the 1H signal into a doublet:



The two alkyl hydrogens split the doublet further. **Each** of the 2 peaks is now split into 3, producing 6 peaks in total.



Finally, the single allylic hydrogen splits **each** of the 6 peaks into 2 again, producing the final 12 peaks.



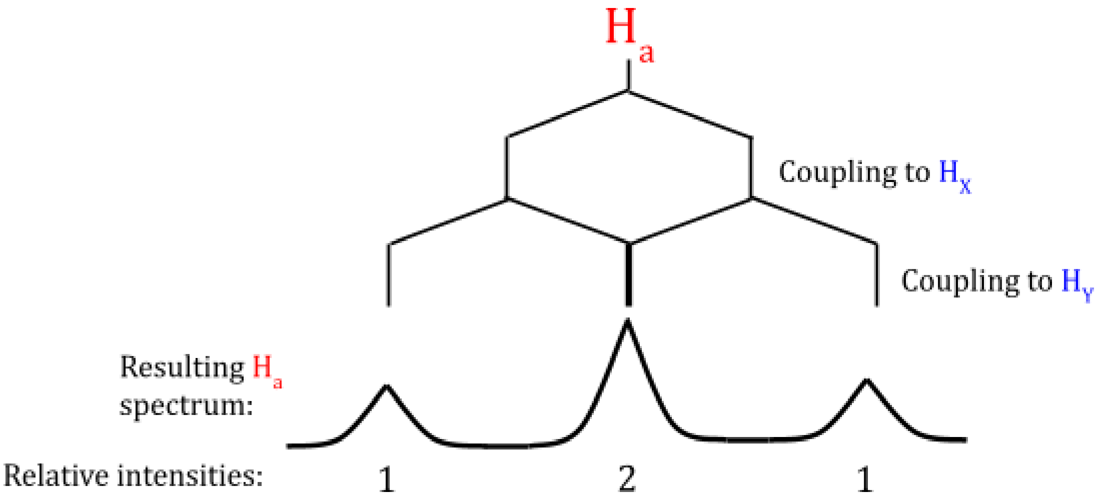
(Diagrams not drawn to scale)

The order of couplings is immaterial, but you should use the largest first because it avoids having the lines crossing messily.

(c) 126

Consider the splitting pattern when the tertiary hydrogen (H_a) couples to just 2 equivalent neighbours (H_X and H_Y). There are 3 cases:

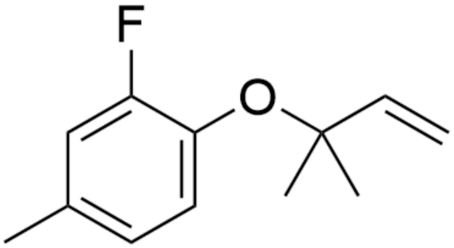
- **Both** H_X and H_Y are aligned **with** the applied field → H_a experiences *less* shielding.
- H_X is aligned **with** the applied field but H_Y is aligned **against** (and **vice versa**) → effect cancels out so the shielding experienced by H_a is the *same* as if there was *no* interaction. However, there are 2 cases, so this peak is twice as high.
- **Both** H_X and H_Y are aligned **against** the applied field → H_a experiences *more* shielding.



For 2 equivalent neighbours, the resulting pattern is a 1:2:1 triplet. For 3 equivalent neighbours, the pattern is a 1:3:3:1 quadruplet.

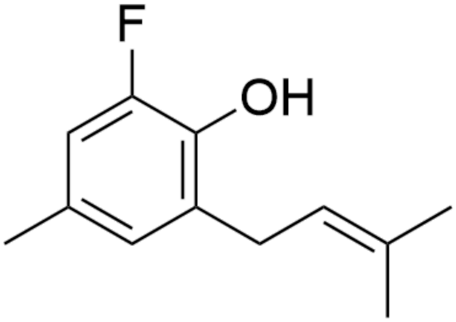
For *n* equivalent neighbours, the ratio of the peaks' intensities is given by the *n*th row of Pascal's triangle (because this is essentially a binomial distribution). Hence, for 9 equivalent neighbours in the case of isobutane, the largest peak is $\mathbf{{}^9C_4 = 126}$ times taller than the smallest.

(d)



A

(e)

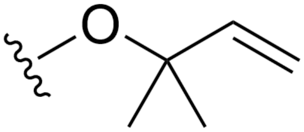


C

For **A**, We can group the signals in the table into three sections (luckily, they are already arranged in order of chemical shifts).

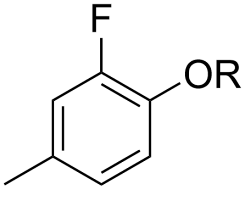
The first two, with chemical shifts of 1-2 Hz, originate from alkyl protons. The integration tells us there are two identical methyl groups, as well as a third methyl group more downfield, possibly benzylic. The next three signals have chemical shifts of 5-6 Hz, lying in the range for alkene protons. Since there are *three* distinct signals, the molecule must contain an alkene (confirmed using the molecule's degree of unsaturation) that is *mono*-substituted. Finally, the last three signals have chemical shifts of 6.5-7 Hz, which are aromatic protons.

Since **A** can be prepared from a phenol and an alkyl bromide, it is a phenol ether, and since the substitution is an S_N1 reaction, the other (alkyl) carbon bonded to the oxygen (referred to as C*) is most likely tertiary. How can we fit three groups around it? Because the 6H signal for the 2 methyl groups is a singlet, the carbon attached to them is quaternary. Attaching these two methyl groups to C*, the last bond must be to the mono-substituted alkene. Hence the alkyl half of the ether is:

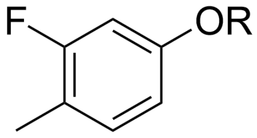


We will abbreviate this as OR. The final methyl group bonds directly to the benzene ring.

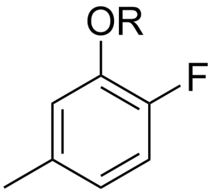
How should the three groups (F, CH_3, OR) be arranged around the benzene ring? Between the three aromatic protons, we have $J = 0.54$, 2.43 and 7.91 Hz, which correspond to *ortho*, *meta* and *para* coupling respectively. With all three types of coupling present, the six possible structures for **A** are as follows:



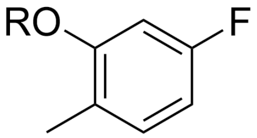
A1



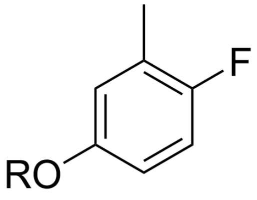
A2



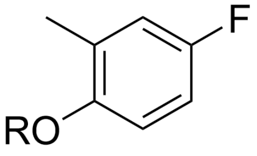
A3



A4



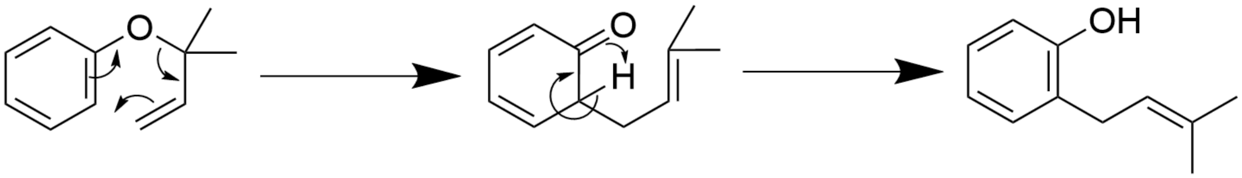
A5



A6

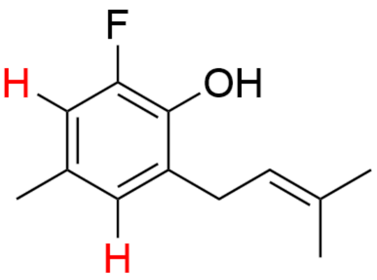
With no other information, we move on to part (c) first. The reaction **A** → **C** hints at a rearrangement since the molecular formula is unchanged. **C** only has 2 aromatic protons (*meta* to each other), as well as a -CH2- group and three distinct methyl groups.

You may recognise this as an aromatic Claisen rearrangement:

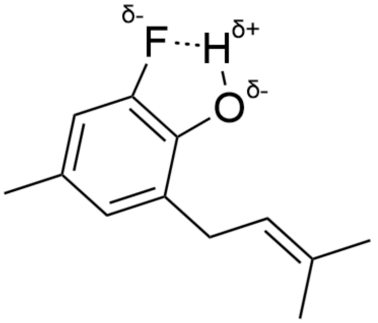


Observe that the Claisen rearrangement adds a new alkyl group *ortho* to the existing alcohol. Hence, the correct structure for part (b) is **A1** since:

1. Only its rearrangement product has the remaining two aromatic protons *meta* to each other (this rules out **A2, A3, A4** and **A5**)



2. Intramolecular hydrogen bonding is possible between the adjacent F and OH groups in its rearrangement product (this rules out **A6**)



Finally, **C** is simply the Claisen rearrangement product of **A1**, and we are done.

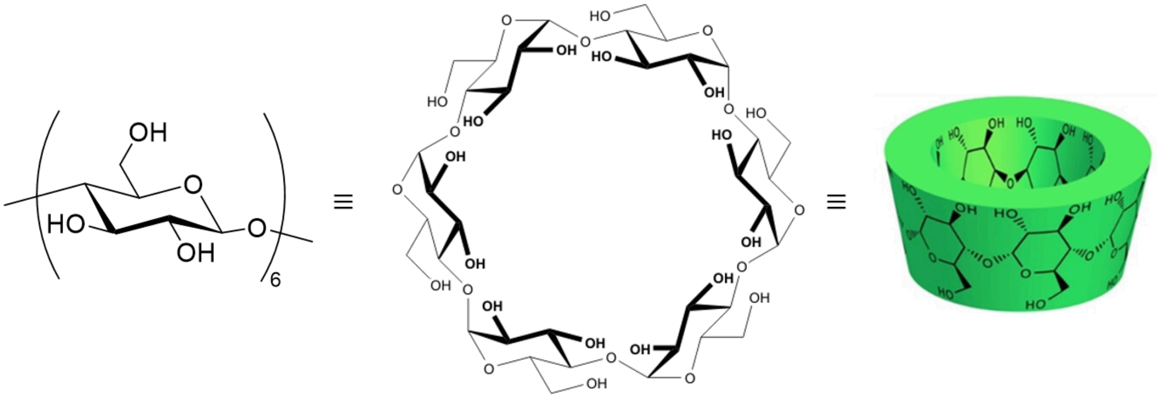
Problem prepared by: Wang Jiahua

Problem 41: Cyclodextrins

[8 points]

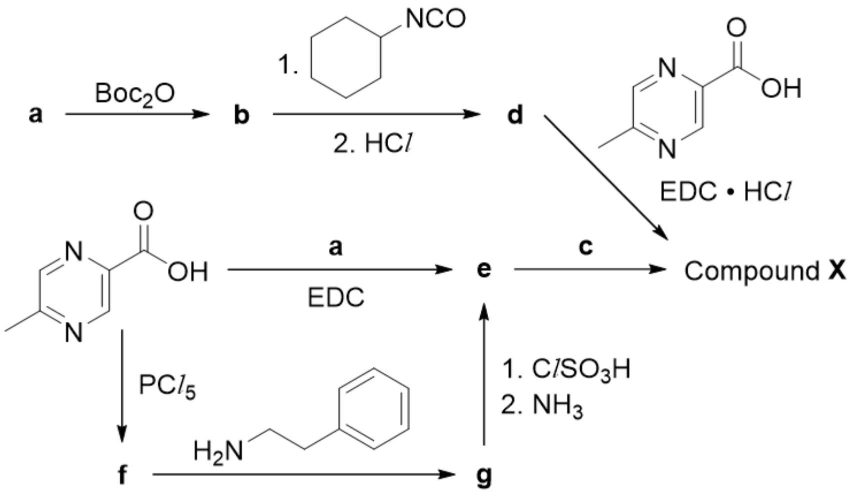
Cyclodextrins are a family of cyclic oligosaccharides consisting of glucose subunits joined by α-1,4 glycosidic bonds. Cyclodextrins are commonly used in food, pharmaceutical and drug delivery. Typically, cyclodextrins contain a number of glucose monomers ranging from 6 to 8 units in a ring.

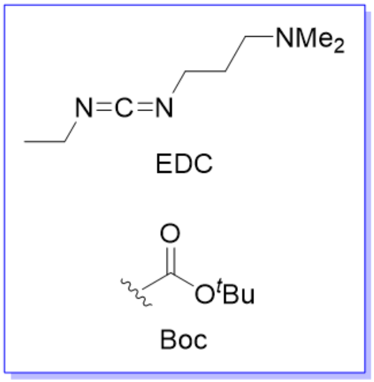
In α-cyclodextrin (α-CD), the 6 glucose subunits are linked end to end via α-1,4 linkages. The resulting three-dimensional structure of α-CD has the shape of a tapered cylinder. The structure of α-CD is shown below.



A group of researchers recently found that compound **X** can form inclusion complexes with α-CD, in which compound **X** is contained in the cavity of α-CD. Compound **X** is a drug that treats a certain endocrinological disorder.

Three different synthetic routes for compound **X** are shown in the diagram below.

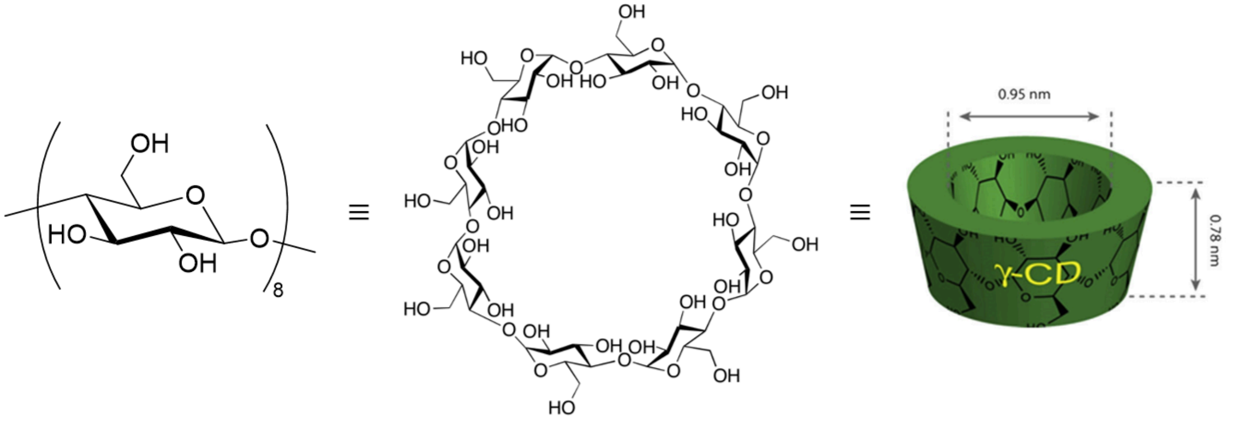




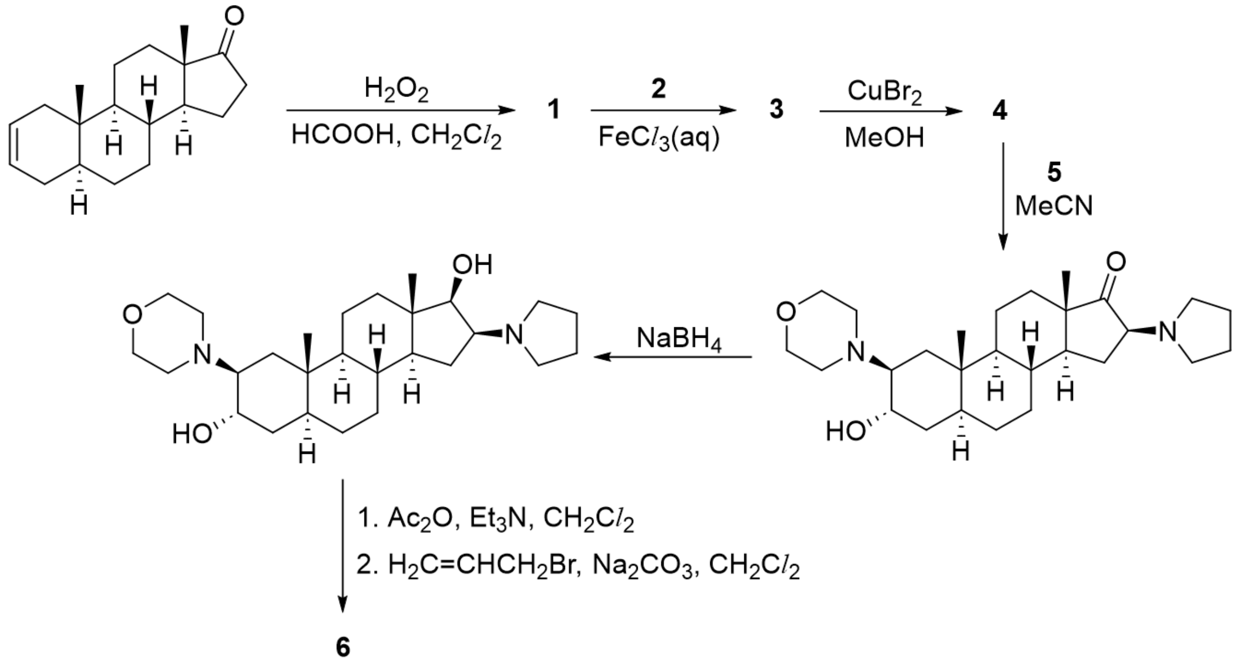
(a) Draw the structure of compound **e**. **[2 points]**

(b) Draw the structure of compound **X**. **[2 points]**

Similar to α-CD, γ-cyclodextrin (γ-CD) consists of 8 glucose molecules linked together to form a structure that resembles a truncated cone.

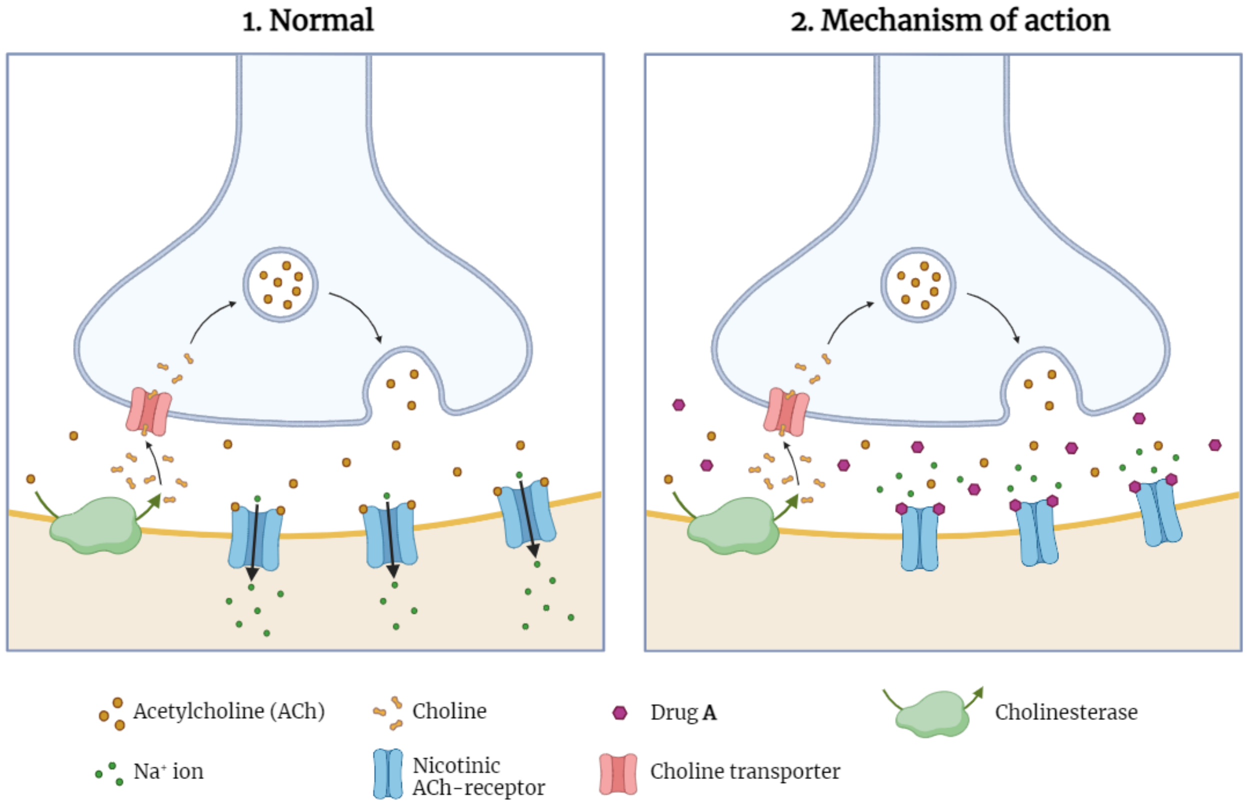


Another group of researchers found that modified γ-CDs could serve as host molecules for a certain drug **A**. A total synthesis scheme of drug **A** (compound **6**) is shown below.



(c) Draw the structure of compound **4** with stereochemistry. **[2 points]**

The mechanism of action of drug **A** in the human body is shown in the diagram below.



Credits: Diagram was drawn using BioRender.

You are given the following further information:

- Acetylcholine (Ach) is a neurotransmitter. Ach causes the conduction of muscle action potential to occur which subsequently induces skeletal muscle contraction.
- Choline is an essential nutrient required to make acetylcholine.
- Nicotinic acetylcholine receptors (nAchR) are receptor polypeptides that respond to acetylcholine.
- Cholinesterase is an enzyme that catalyses the hydrolysis of choline-based esters.

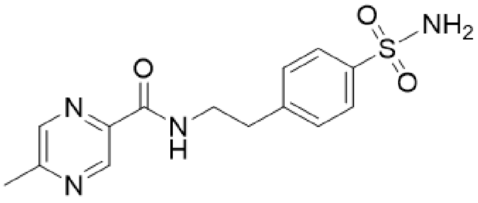
(d) State whether each of the **4** statements given above are true (T) or false (F).

[2 points]

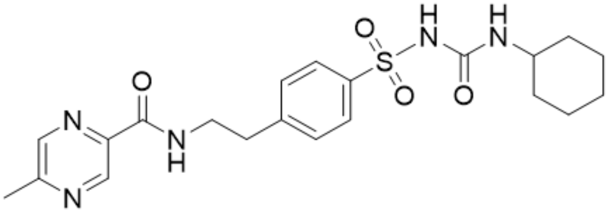
1. Drug **A** is a competitive antagonist.
2. Drug **A** prevents muscle contraction from occurring, inducing paralysis.
3. By forming host-guest complexes with drug **A**, the modified γ-CDs enhance the intended effects of drug **A**.
4. Should drug **A** be used in surgical procedures, the use of modified γ-CDs would reduce the risk of fatality of administering drug **A**.

If the statement is true, indicate T. If the statement is false, indicate F. Leave your answer as a concatenated string of ***four capital letters****. For example, if your answers are true, true, true, false, leave your answer as TTTF.*

Solution:

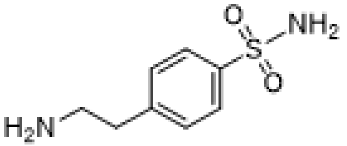


(a)

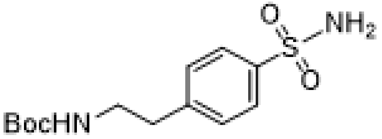


(b)

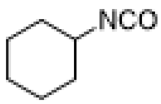
The structures of compounds **a** to **g** and **X** are shown below:



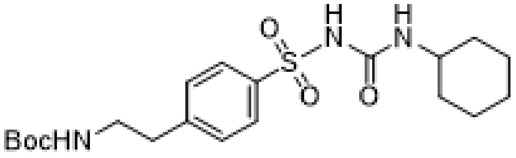
a



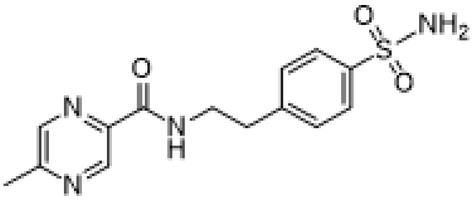
b



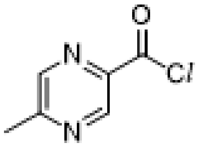
c



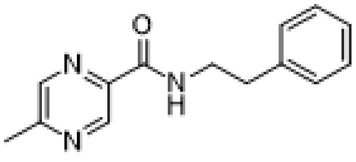
d



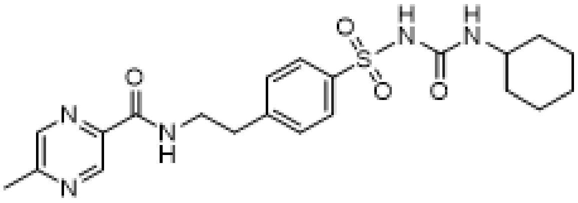
e



f

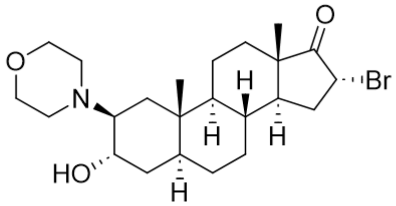


g

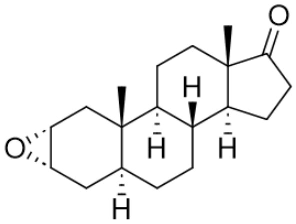


X

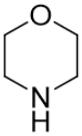
(c)



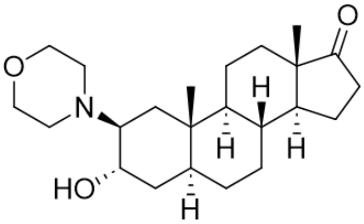
The structures of compounds **1** to **6** are shown below:



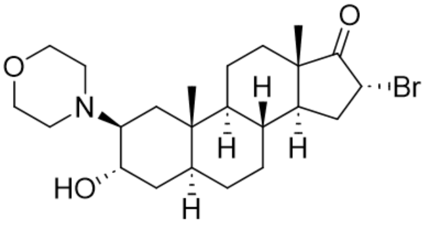
1



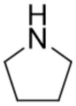
2



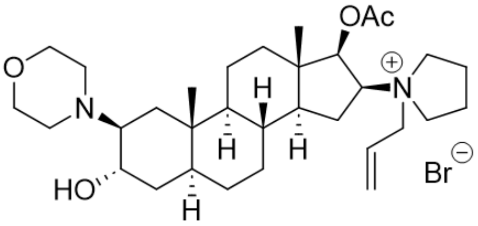
3



4



5



6

(d) TTFT

1. Drug **A** is a competitive antagonist.

Drug **A** (rocuronium bromide) acts by competitively binding to nAchR at the motor endplate (**competitive antagonist**) which prevents Ach from binding onto nAchR. Hence, statement 1 is **true**.

2. Drug **A** prevents muscle contraction from occurring, inducing paralysis.

Since drug **A** prevents Ach from binding onto nAchR, the conduction of muscle action potential is prevented, and muscle contraction does not occur, thereby inducing paralysis. Hence, statement 2 is **true**.

3. By forming host-guest complexes with drug **A**, the modified γ-CDs enhance the

intended effects of drug **A**.

By forming host-guest complexes with drug **A**, the modified γ-CDs reverse the paralysis induced by drug **A** as the complex prevents drug **A** from competitively binding to the nAchR site. Hence, statement 3 is **false**.

4. Should drug **A** be used in surgical procedures, the use of modified γ-CDs would reduce the risk of fatality of administering drug **A**.

Since drug **A** induces paralysis as muscle contraction cannot occur, this may lead to respiratory arrest or even death. Hence, the reversal of neuromuscular block at the end of surgery is often necessary to speed up the recovery of a patient's muscle function. Since the modified γ-CDs can reverse the paralysis induced by drug **A**, Ach can bind to nAchR once again and skeletal muscle contraction can occur, greatly reducing the risk of fatality when administering drug **A** during surgery. Hence, statement 4 is **true**.

Problem prepared by: Ranen Yong