

# International Meme Chemistry Olympiad, July 2021 Solutions

Solutions by Daniil Kargin, 53rd IChO silver medalist  
Problems by Daniil Kargin, Evan Grishkjan and Vladislav Tishchenko

June 30th, 2021

## Contents

|          |  |           |
|----------|--|-----------|
| <b>1</b> | <b>Introduction</b>  | <b>2</b>  |
| <b>2</b> | <b>Amateur League</b>  | <b>3</b>  |
| 2.1      | Problem <i>A</i> . Little Ian, analysis! . . . . .                       | 3         |
| 2.2      | Problem <i>B</i> . Compounds that break relationships . . . . .          | 6         |
| 2.3      | Problem <i>C</i> . Blood Magic and Jonathan . . . . .                    | 10        |
| 2.4      | Problem <i>D</i> . Amquid Limonia, Liqueic Ionid and other MLG . . . . . | 15        |
| 2.5      | Problem <i>E</i> . Expand, Evolve, Thermodynamics . . . . .              | 19        |
| 2.6      | Problem <i>F</i> . Traces of DNA in pickle juice . . . . .               | 24        |
| 2.7      | Problem <i>G</i> . How to understand Julia . . . . .                     | 30        |
| 2.8      | Problem <i>H</i> . LIL BO' CHEM . . . . .                                | 34        |
| <b>3</b> | <b>Pro League</b>  | <b>40</b> |
| 3.1      | Problem <i>A</i> . Little Ian's trips . . . . .                          | 40        |
| 3.2      | Problem <i>B</i> . Colour becomes Power . . . . .                        | 52        |
| 3.3      | Problem <i>C</i> . Elements go bang . . . . .                            | 57        |
| 3.4      | Problem <i>D</i> . Amquid Limonia, Liqueic Ionid and other MLG . . . . . | 61        |
| 3.5      | Problem <i>E</i> . Traces of DNA in pickle juice . . . . .               | 68        |
| 3.6      | Problem <i>F</i> . Vapour of muriomorphosis . . . . .                    | 79        |
| 3.7      | Problem <i>G</i> . RD Corp. and Mechanisms . . . . .                     | 85        |
| 3.8      | Problem <i>H</i> . LIL BO' CHEM . . . . .                                | 90        |
| <b>4</b> | <b>Conclusion</b>  | <b>95</b> |

# 1 Introduction

The document you are currently reading are the official Meme Chemistry Olympiad July 2021 problem solutions. The Grading Manual was devised according to this document, thus use this text as a reference when reviewing your marked assignment. The Authors suggest considering the solutions of the Problems as worked examples as well as an official document. If some of the solutions still remain unclear, feel free to email us at [memechemistryolympiad@gmail.com](mailto:memechemistryolympiad@gmail.com)! The Olympiad Problems were written mostly by Daniil Kargin, Evan Griskjan and Vladislavs Tischenko, although we must also acknowledge Jonathan for his contributions to Amateur-Problem E and Pro-Problem G and other Olympiad development advice. A huge shoutout to Julia for providing the beautiful illustrations to the paper! If you are a Meme Chemistry Olympiad participant reading this, please take a moment to thank yourself for the work supplied in participation-this is the only driving force of the project!

A bit more onto the chemistry part: this problems were mostly composed by high school students, although not the most random ones: most of the Meme-ChO authors are current or former IChO participants. In order to reduce cluttering, we mostly assume that these rules apply to the Problems when solving **unless stated otherwise in the Problem text**:

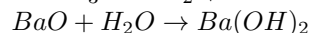
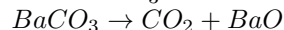
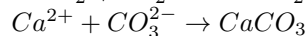
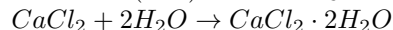
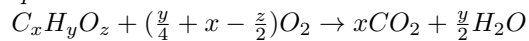
1. Take the molar masses needed in the calculations rounded to the nearest integer except chlorine. ( $M_{Cl}=35.5$  g/mol)
2. All gases described in the Problems are assumed to be ideal gases unless not stated otherwise.
3. Use as many significant digits as you wish in your answer.
4. We consider an answer to be numerically correct if it falls within a 5% range of our calculated answer.
5. All conditions described in the Problems are assumed to be standard conditions unless not stated otherwise.
6. In all problems, assume enthalpy and entropy changes to be independent of temperature. Also assume that, when liquids are mixed, the new volume is the sum of their individual volumes.

## 2 Amateur League

### 2.1 Problem A. Little Ian, analysis!

Little Ian the Chemist was working part-time in an analytical chemistry lab. He was assigned to work at the Janitis Gas Analyzer machine. The Janitis Gas Analyzer machine works in the following manner: First, the gases being analysed get pumped into a tube filled with anhydrous calcium chloride. The gases which pass through the calcium chloride get bubbled into three sequential Drechsel gas bottles filled with concentrated aqueous barium hydroxide. The remaining gas is ejected outside and the volume of the gas being ejected is measured as well as its density. Little Ian asked his girlfriend Johanna to inhale the gases ejected because their fume hood is malfunctioning. Recently, a sample confiscated from an illegal laboratory was delivered to the lab for Ian to analyse. It contained a single compound consisting of carbon, hydrogen and oxygen. We'll refer to this molecule as compound X. Little Ian conducted the following test to determine the molecular formula of compound X: After orally ingesting a few grams of the substance, bewildered by his curiosity, he took 8.540g of compound X and burned it in a sealed flask. Then, the hot gases produced by the reaction were pumped into the Janitis Gas Analyzer machine. Little Ian has noted down that the Janitis Gas Analyzer machine ejected no gas at all. Then, Little Ian took apart the Janitis Gas Analyzer and weighed the calcium chloride inside. The weight of calcium chloride after passing the gases through it was 59.28g. Because he forgot to weigh the anhydrous calcium chloride before putting it inside the Janitis Gas Analyzer, Little Ian dissolved the calcium chloride in water and added sodium carbonate until a precipitate stopped forming. He filtered off and dried the precipitate, its mass being 50.00g. Then, Little Ian took apart the Drechsel bottles with aqueous barium hydroxide while noting that the solution in the first and second jars was opaque. He filtered all the solutions from the Drechsel jars and heated the precipitate collected at 1800C during the night. Afterwards, the treated precipitate was dissolved in 2L of water, forming a solution with pH 13.69. Neglect the change of density of the solution as well as the mass of water spent in the reaction.

*A-1 Write down all the 6 balanced reaction equations that describe the chemical processes described in the text.*



*A-2 Calculate the molar mass of compound X. It is less than 200 g/mol.*

*A-3 Calculate the molecular formula of compound X.*

First, let us determine the mass and amount of hydrogen that was present in

the compound. We know that the calcium chloride absorbed the water that was produced on combustion of compound X. To determine the initial mass of the compound, we first determine the amount of moles of calcium chloride present in the Janitis Gas Analyzer.

$$n_{CaCO_3} = \frac{m_{CaCO_3}}{M_{CaCO_3}}$$

Thus,  $n_{CaCO_3} = \frac{50.00}{100} = 0.5 \text{ mol}$ , and due to stoichiometry  $n_{CaCO_3} = n_{CaCl_2} = 0.5 \text{ mol}$ . And the mass of anhydrous calcium chloride Little Ian inserted in the machine is equal to  $0.5 \cdot 111 = 55.5 \text{ g}$ . From this, we determine the amount of water vapour absorbed by calcium chloride, it is equal to the difference between the factual mass of calcium chloride Little Ian collected and the mass of pure calcium chloride.  $m_{H_2O} = 59.28 - 55.50 = 3.78 \text{ g}$ . Converting into moles,  $n_{H_2O} = \frac{3.78}{18} = 0.21 \text{ mol}$ . This correlates to  $0.42 \text{ mol}$  of hydrogen atoms in the compound X sample. Then, we determine the amount of carbon atoms in the system. To do this, we need to determine the amount of carbon dioxide absorbed by the barium hydroxide solution.

$$pH = -\log[H^+] \quad K_W = [H^+] \cdot [OH^-] \quad [OH^-] = \frac{n_{OH^-}}{V_{solution}}$$

By using these equations, we determine  $n_{CO_2}$  produced:  $[OH^-] = 10^{-14} - 13.69 = 0.49M$ , and thus  $n_{BaO} = 0.49 \text{ mol}$  and  $n_{CO_2} = n_{BaO} = 0.49 \text{ mol}$ . Using simple logic, we conclude that the amount of carbon atoms in the sample equals  $0.49 \text{ mol}$ . To determine the amount of oxygen in the sample, we subtract the mass of hydrogen and carbon atoms from the total mass of the sample the rest must be oxygen atoms!  $m_{O_2} = 8.540 - 12 \cdot 0.49 - 1 \cdot 0.42 = 8.540 - 5.880 - 0.420 = 2.24 \text{ g}$ . This, in turn, corresponds to  $\frac{2.24}{16} = 0.14 \text{ mol}$ . By simplifying the mole ratio, we obtain  $n_C : n_H : n_O = 7 : 6 : 2$ . The molecular formula with the minimal integer coefficients is  $C_7H_6O_2$ , whose molar mass is  $122 \text{ g/mol}$ . The next smallest molar mass molecular formula with integer coefficients is  $C_{14}H_{12}O_4$ , but its molar mass exceeds  $200 \text{ g/mol}$ .

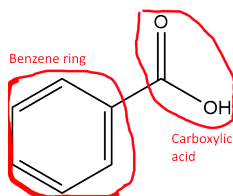
Little Ian also dissolved some compound X in some water and produced an acidic solution. He also added some ferric chloride to the solution and witnessed formation of a light yellow precipitate. Little Ian also mixed some X with a base and some ethyl chloride and produced a pleasantly-smelling compound.

*A-4 Determine the structural formula of compound X.*

*A-5 Determine the functional groups present in compound X. Circle them on your drawing and write down their names next to the functional group circled.*

The compound produces an acidic solution in water, so it must have some sort of an acidic proton. One might suspect compound X bears a carboxylic acid functional group. This hypothesis is confirmed by the esterification reaction that proceeds with ethyl chloride. Thus, the compound has a carboxylic acid  $-CO_2H$  group in its structure, the remaining part having the molecular

formula  $C_6H_5$  which beautifully correlates with a phenyl substituent. Thus, the compound is benzoic acid, and its structural formula is



Little Ian wanted to determine the  $pK_a$  of compound X. To do that he decided to do the following experiment: he dissolved 0.244g of compound X in 100 mL of water, waited until compound X fully dissolved and measured the pH of the solution formed. The pH of the solution containing compound X was equal to 2.96. We can assume that water autoprotolysis can be negated in this experiment.

*A-6 Estimate the  $pK_a$  of compound X. Hint:  $pK_a$  is equal to the negative decimal logarithm of the acid dissociation constant of compound X. If you failed to calculate the molecular mass of compound X assume it is equal to 183 g/mol (It is not the true molecular mass of the compound)*

$$K_a = \frac{[H^+] \cdot [PhCO_2^-]}{[PhCO_2H]} \quad pK_a = -\log K_a \quad pH = -\log[H^+]$$

The solution in discussion is uncharged, thus this equality is usable:

$$[H^+] = [PhCO_2^-]$$

We can also write the following equation relating the total amount of benzoic acid species:

$$[PhCO_2H] + [PhCO_2^-] = [PhCO_2H]_{initial}$$

$$[PhCO_2H]_{initial} = \frac{n_{PhCO_2H}}{V_{solution}}$$

By expressing the undissociated acid from the expression above, and substituting into the benzoic acid balance, we obtain the following expression for  $K_a$ :

$$K_a = \frac{[H^+]^2}{[PhCO_2H]_{initial} - [H^+]}$$

And, finally, by taking the negative decimal logarithm of the two sides, we obtain this expression for  $pK_a$ :

$$pK_a = 2 \cdot pH + \log\left(\frac{n_{PhCO_2H}}{V_{solution}} - 10^{-pH}\right)$$

By substituting the numbers in the formula, we obtain:  $pKa = 2 * 2.96 + \log(\frac{0.002}{0.1} - 10^{-2.96}) = 4.20$

Little Ian also wanted to analyse a compound containing an unknown element we'll call element Z. Little Ian burned some binary compound (we'll call it compound Y) containing 82.35 % Z by mass and let the gases through the Janitis Gas Analyzer machine. He noted that the mass of the anhydrous calcium chloride inside the apparatus increased, as well as 3.59L of a gas with a density of 1.25kg\*m<sup>-3</sup> at a pressure of 755 Torr at a temperature of 17C was ejected from the machine. (Assume this gas is an ideal gas)

*A-7 Calculate the molar mass of the gas ejected from the Janitis Gas Analyzer.*

*A-8 Determine the molecular formula of the gas mentioned above.*

*A-9 Determine the formula of compound Y.*

To calculate the molar mass we must recall that  $\rho = \frac{m}{V} = \frac{M \cdot n}{V}$ . Thus, the easiest way to tackle this problem is to calculate its molar mass from the ideal gas equation.

$$pV = nRT \quad M = \frac{\rho \cdot RT}{p}$$

By inserting the numbers we obtain:  $M = \frac{1.25 \cdot 8.314 \cdot 290}{755 \cdot 133} = 0.030 \text{ kg/mol}$  This corresponds either to ethane  $C_2H_6$  or nitrogen monoxide,  $NO$ . It is quite obvious that ethane can not form as a combustion product, thus the gas is nitrogen monoxide. To determine the molecular formula of compound Y, we assume it contains nitrogen (element Z). Because the calcium chloride mass also increased after burning the compound and passing the gases into the Janitis Gas Analyzer, it must contain hydrogen. Thus, it is some of nitrogen hydrides, either ammonia or hydrazine. Let us test the mass fraction on hydrogen in ammonia, first:  $w_H = \frac{14}{14+3} = 82.35\%$  which corresponds to the mass fraction of hydrogen in compound Y. Thus, compound Y is ammonia  $NH_3$ .

## 2.2 Problem B. Compounds that break relationships

Chemist Peter wanted to get a Nobel prize. So, he spent lots of time in his lab and finally invented a chemical method that, in his opinion, would be worth a Nobel prize. The first person whom Peter showed his discovery was his incredibly beloved... friend Anne. Basically, Peter claimed that he'd discovered that hydrochloric acid dissolved copper. Anne, who also was a chemist, highly doubted Peter's claims. But, because she considered that Peter is a good friend of hers, she decided to have a look at his lab and witness how Peter dissolved some copper in hydrochloric acid. Peter and Anne ventured inside the chemistry lab where Peter conducted his experiments. Peter took his hydrochloric acid and poured it into a beaker. He also added in a piece of copper and stepped away, showing the reaction to Anne, and hoping to impress her. Anne was quite

shocked when the copper did indeed dissolve, forming a nice green solution. Anne asked Peter to carry out the same reaction again, but now in her lab and using her reagents. In Anne's lab Peter repeated the same experiment successfully, but now using Anne's reagents, and impressing Anne so much that she began considering him a potential relationship partner. When Anne recreated the experiment again after Peter left, nothing happened to copper. After that Anne started suspecting Peter in some hidden machinations with hydrochloric acid that he'd carried out. She asked the security officer working in her lab to show her the security camera footage so that she could unveil the truth behind Peter's magical hydrochloric acid. Anne was very disappointed with her discovery. It appeared that while Anne left the lab in order to visit the bathroom Peter had mixed the hydrochloric acid in the beaker with some liquid from a large plastic bottle he'd brought with him in his bag. Anne was furious and decided to debunk Peter's hydrochloric acid mystery. The next day she met Peter in the canteen and quietly stole the plastic bottle from his bag while Peter was aimlessly staring at her for the whole time they were sitting at the lunch table. Now, when she had the big plastic bottle with Peter's "magic additive" Anne could analyse it and determine the compounds Peter'd mixed in it.

*B-1 Explain why copper doesn't dissolve in hydrochloric acid.*

The standard reduction potential of the redox pair  $Cu^{2+}/Cu$  is greater than the standard reduction potential of the redox pair  $H^+/H_2$ , thus  $Cu^{2+}$  ions are more preferably reduced to  $Cu^0$  than  $H^+$  ions to  $H_2$  in the solution.

*B-2 Suggest how the compound in the plastic bottle might take part in the reaction of copper dissolution.*

It might either form soluble complexes with the copper (2+) ions formed during the dissolution process, or serve as an oxidising agent to oxidise Cu to  $Cu^{2+}$  ions.

Anne decided to measure the pH of the mysterious reagent. She used some pH test strips and determined that the solution inside the white bottle was slightly acidic. During the experiment Anne behaved carelessly and didn't wear lab gloves. Unfortunately she spilled some of Peter's reagent on her hand, and after a few minutes she suddenly felt pain as a white chemical burn formed on her skin. Because she was a strong-hearted chemist, Anne endured the pain from the burns and continued her analysis.

Anne mixed some of Peter's reagent with acidified potassium dichromate and observed formation of a strange dark-blue compound. She liked its colour, although it vanished after a few minutes. Anne also mixed the reagent with acidified potassium iodide, forming a brown-coloured solution. The same reagent also reacted weirdly with acidified potassium permanganate, producing a gas. Peter's reagent also reacted incredibly violently with neutral potassium permanganate, producing a gas and a basic brown solution.

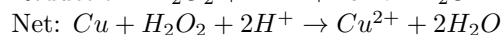
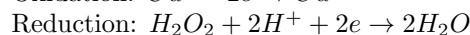
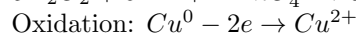
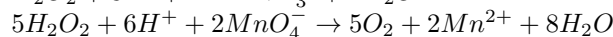
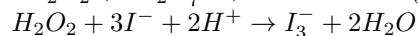
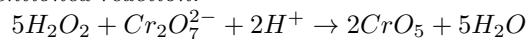
*B-3 Determine the molecular formula of Peter's reagent. Hint: it's inor-*

ganic.

The fact that Peter's reagent reacts both with oxidising and reducing agents, as well as produces a gas when oxidised by permanganate, suggests it being hydrogen peroxide. This is proved by formation of the chromium peroxide upon addition to acidified dichromate.

*B-4 Write reaction equations describing the reactions of Peter's reagent and potassium dichromate, potassium iodide in excess and potassium permanganate in acid.*

*B-5 Write the reaction equation of copper dissolving in the mix of Peter's reagent and hydrochloric acid as well as the redox half reactions of the aforementioned reaction.*



Anne took 70 mL of the Peter's reagent solution and weighed it. The weight of the solution was equal to 77.7 g.

*B-6 Determine the density of the Peter's reagent Anne stole from Peter.*

$$\rho = \frac{m}{V}$$

By substituting into the formula, we obtain  $\rho = \frac{77.7}{70} = 1.11 \text{ g} \cdot \text{cm}^{-3}$

Anne mixed 10.00mL of Peter's reagent with excessive potassium iodide in acidic medium. The mixture produced was transferred into a 1L volumetric flask and diluted up to the mark with deionised water. Anne measured a 40.00mL aliquot of that solution using a pipette (of course, following all safety precautions and pipetting that solution by mouth) and titrated it with 0.200M sodium thiosulfate. She required 20.00mL of titrant to reach the stoichiometric point.

*B-7 Anne is such a pro in Analytical Chemistry that she can run titrations without using an indicator. Still, which indicator should she have used in the procedure?*

*B-8 How is this titration procedure called? (Not titration without an indicator, but the procedure described above. . . .)*

*B-9 Determine the molarity of the solution of Peter's reagent Anne had obtained earlier.*

*B-10 Determine the molality of Peter's reagent.*

The titration procedure Anne is carrying out is iodometric titration. This procedure is mainly used to determine concentrations of reducing or oxidising agents. In the reaction, iodide is usually oxidised to iodine, which afterwards is



titrated (either directly or back-titrated) using sodium thiosulfate. To determine the presence of iodine, starch is usually used as an indicator.

Let us now determine the molarity of Peter's reagent! To do it, let's first write down the reaction equation between iodine and sodium thiosulfate:  $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ . Now, we can determine the amount of sodium thiosulfate Anne needed to titrate her aliquot:  $n_{Na_2S_2O_3} = V_{Na_2S_2O_3} \cdot c_{Na_2S_2O_3}$ , by substituting the numbers we get:  $n_{Na_2S_2O_3} = 20.00 \cdot 10^{-3} \cdot 0.200 = 4 \cdot 10^{-3} \text{ mol}$ . Because of stoichiometry, the amount of iodine in the sample is twice as low, and the total amount of iodine in the 1L volumetric flask is  $n_{I_2} = \frac{4 \cdot 10^{-3} \cdot 0.5}{0.04} = 0.05 \text{ mol}$ . We know that this amount of iodine corresponds to an equimolar amount of hydrogen peroxide, thus:  $c_{H_2O_2} = \frac{0.05}{0.01} = 5M$ . To determine the molality (not to be confused with molarity!) a following formula is used:

$$c_m = \frac{n_{\text{compound}}}{m_{\text{solvent}}}$$

Let us assume that we have a liter of solution. Then, its mass will be equal to  $\rho \cdot V = 1.11 \cdot 1000 = 1110g$ . We know that this solution contains 5 moles of hydrogen peroxide, and the rest must be water. Numerically,  $m_{H_2O} = 1110 - 5 \cdot 34 = 940g$ . And, finally,  $c_m = \frac{5}{0.94} = 5.32 \text{ mol} \cdot \text{kg}^{-1}$ .

Anne wanted to prepare 100 mL of the copper-eating hydrochloric acid solution to show it to Peter. She had a 36% hydrochloric acid ( $\rho = 1.20 \text{ g/mL}$ ) solution by hand.

*B-11 Determine the molarity of the hydrochloric acid in Anne's lab.*

Using a similar logic than earlier, let's imagine that we have a liter of such acid. Then, its mass must equal  $1200g$ , from which  $1200 \cdot 0.36 = 432g$  are HCl. To determine the molarity, we only need to convert this mass of hydrogen chloride into moles, and it comes up to be  $\frac{432}{36.5} = 11.84 \text{ mol}$ . This in turn results in that the molar concentration of the acid is  $c = \frac{11.84}{1} = 11.84M$ .

Anne wanted to make the solution as efficient as possible, so she decided to mix the reagents stoichiometrically. We can assume that the volume of the solution equals the volumes of components combined.

*B-12 Determine the volume of Peter's reagent and hydrochloric acid needed to prepare the copper-eating solution.*

*B-13 Calculate the density of the solution formed.*

*B-14 Calculate how much copper can be dissolved in this solution. Take into account only the reaction between hydrochloric acid, Peter's reagent and copper metal, although Anne is definitely skilled enough as an Analytical chemist to force any reaction, but this skill of Anne shall be ignored here.*

A stoichiometrical mix implies that the compounds are mixed in a molar ratio equal to the ratio of the stoichiometric coefficients in the reaction. Thud, the amount of hydrogen chloride must be twice the amount of hydrogen peroxide. Let us imagine that  $x$  liters of the HCl solution and  $y$  liters of the peroxide

solution are mixed together to form 100 mL of a stoichiometric solution. This results in this system of two simultaneous equations:

$$\begin{cases} x + y = 0.1 \\ 11.84 \cdot x = y \cdot 5 \cdot 2 \end{cases}$$

By solving the simultaneous equations, we obtain:

$$\begin{cases} x = 0.046 \\ y = 0.054 \end{cases}$$

The density of the solution is calculated as follows:

$$\rho_{solution} = \frac{m_{solution}}{V_{solution}} = \frac{m_{HCl} + m_{H_2O_2}}{V_{HCl} + V_{H_2O_2}}$$

And, by knowing the volumes of compounds and having determined the densities earlier, we obtain:  $\rho = \frac{46 \cdot 1.20 + 54 \cdot 1.11}{46 + 54} = 1.15 \text{ g} \cdot \text{cm}^{-3}$

This solution can maximally dissolve  $n_{H_2O_2} = 5 \cdot 0.054 = 0.27 \text{ mol}$ , which in turn correlates to  $0.27 \cdot 64 = 17.28 \text{ g}$ .

### 2.3 Problem C. Blood Magic and Jonathan

Jonathan decided to make some blood. He found out that he can make three compounds that kinda resemble blood. He called them compounds **A**, **B** and **C**. Jonathan didn't spend a lot of time thinking and immediately began synthesising these compounds.

Compound **A** contains element **X**. To prepare **A** Jonathan needed to prepare an intermediate **D**. To prepare the intermediate **D** Jonathan reacted some gas **E** containing 82.36% by mass of element **X** with some compound **F** whose molecular structure is similar to that of silicon dioxide. Compound **F** doesn't contain element **X**, its molar mass is 38 times more than the molar mass of hydrogen gas. The intermediate **D** is mixed with compound **G**, which is a transition metal chloride containing 65.54% chlorine by mass. The product of the reaction is compound **A** and compound **H**.

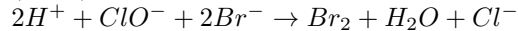
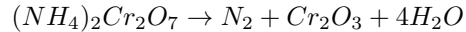
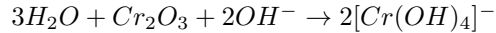
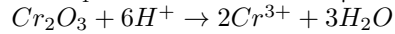
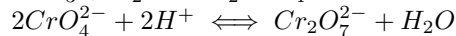
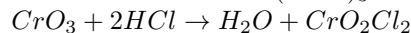
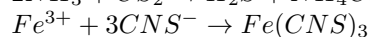
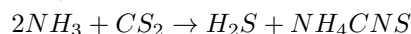
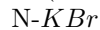
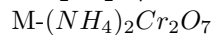
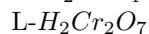
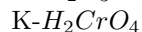
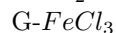
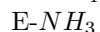
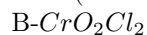
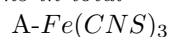
Another compound that looks like blood is compound **B**. It is prepared by reacting oxide **I**— with gaseous hydrogen chloride at 0C with sulfuric acid present. Oxide **I** contains metal **Y**. Oxide **I** can be reduced to a green oxide **J**, which reacts both with alkali and acids. Oxide **I** reacts with water, forming an interesting acid **K**, which equilibrates with acid **L**. The equilibrium shifts towards formation of **L** on addition of acid. Acid **L** produces interesting salts, for example compound **M**, which is produced by mixing **L** with aqueous **E**. Compound **M** decomposes on heating, one of the decomposition products being **J**. 7.56g of **M** produces 4.56g of **J** on decomposition.

Compound **C** is the scariest compound of the trio. It also has the simplest molecular formula. It contains element **Z**. Compound **C** can be produced, for

example, by mixing some compound **N**, containing 66.23% element **Z**, with some industrial bleach in an acidic medium. Element **Z** forms anions similar to those of bleach and potassium chlorate. One of those anions can be encountered in compound **O**. Compounds **O** and **N** react in acidic medium, also forming compound **C**. Compound **O** decomposes on heating, producing **N** and oxygen gas. Compound **O** contains 28.74% oxygen.

*C-1 Determine the molecular formulas of compounds **A-O** and elements **X**, **Y** and **Z**.*

*C-2 Write equations describing each reaction described in the text. 11 equations in total*



Jonathan decided to prepare some of compound **A** because it was the least toxic of them all. He had prepared some of the reagents needed for the synthesis. Jonathan “borrowed” a cylinder containing **E** from a chemical reagents shop. The 2L cylinder filled with **E** was at a pressure of 8.05 bar at room temperature. Assume **E** in the cylinder behaves as an ideal gas.

C-3 Determine the mass of **E** in the cylinder. If you failed to determine the molecular formula of **E**, assume its molar mass is equal to 10 g/mol.

From the ideal gas law:

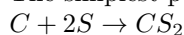
$$n = \frac{pV}{RT}$$

And by substituting the numbers, we obtain  $n = \frac{805 \cdot 2}{8.314 \cdot 298} = 0.65 \text{ mol}$   
 $m_{NH_3} = 0.65 \cdot 17 = 11.05 \text{ g}$ .

Jonathan also prepared some compound **F**. He managed to produce 2.85g of **F**.

C-4 Write down a reaction equation that may be used to produce **F**.

The simplest possible equation is something like:



Then, Jonathan carried out the reaction between **E** and **F**. The reaction Jonathan carried out has the yield of 73%. The product **D** reacts with **G** quantitatively, this means, the yield of the reaction is equal to 100%. But, Jonathan didn't manage to source chemically pure **G**, he only managed to buy some technical-grade **G** in an electronics hardware store. He calculated that technical-grade **G** contained 87% by mass of compound **G**. Jonathan used almost all of **G** he had in an electronics project to etch a few PCBs, so he had only 11.21g of technical-grade **G** at his disposal.

C-5 Calculate the total yield of **A** little Ian will produce.

At first we need to calculate the amount of carbon disulfide Jonathan managed to produce. It is not hard to determine that  $n_{CS_2} = \frac{2.85}{76} = 0.0375 \text{ mol}$  We have earlier determined that Jonathan had 0.65 mol of ammonia in his cylinder, which is definitely an excess.

Thus, in the first reaction,  $n_{NH_4CNS} = 0.0375 \cdot 0.73 = 0.027375 \text{ mol}$ .

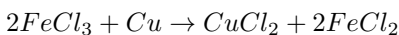
Now, let us determine the amount of pure ferric chloride Jonathan owns. It is equal to  $11.21 \cdot 0.87 = 9.7527 \text{ g}$ . This, in turn, is used to determine the moles of ferric chloride:  $n_{FeCl_3} = \frac{9.7527}{162.5} = 0.06 \text{ mol}$ .

We can again see from the stoichiometry that ammonium thiocyanate is the limiting reagent, thus  $n_{Fe(CNS)_3} = 9.133 \cdot 10^{-3} \text{ mol}$ .

And, finally,  $m_{Fe(CNS)_3} = 2.10 \text{ g}$ .

C-6 Explain why Jonathan uses **G** to etch PCBs. Write down the reaction equation. Hint: Etching a PCB (printed circuit board) is a process of removing copper plated on a sheet of plastic. To avoid removing copper from traces and electrical connections, a protective film is applied on the copper where it should not dissolve.

Ferric chloride can oxidise copper in large concentrations:



*C-7 How is the property of  $\mathbf{J}$  of reacting with both acids and alkali called? Name at least three more such oxides.*

This property is called amphotericity. More such oxides are for example  $Al_2O_3$ ,  $PbO$  and  $ZnO$ .

Jonathan was inspired by crazy experiments of his mentor Little Ian the Chemist and decided to burn some sodium. Little Ian generously provided Jonathan a small amount of sodium for his experiments. So, Jonathan burnt a bit of sodium in the presence of air and weighed the reaction product. His reaction produced a miniscule clump of burning products of a mass 16030g. Jonathan was worried that sodium didn't react completely, so he threw in the clump in a bathtub filled with ice-cold water. He noticed that 112L (at STP) of a gas were produced while the clump was dissolving. Afterwards he poured in hydrochloric acid inside the bathtub until the pH was neutral. He poured in about two jars of 36% HCl ( $\rho = 1.2 \text{ g/mL}$ ), which accounted for 35.8L of the acid.

*C-8 Which two products are formed when sodium is burned on air?*

*C-9 Which pH level is considered neutral? Prove that in pure water the pH is equal to that level.*

*C-10 Write down all reaction equations describing the chemical reactions Jonathan carried out. total 6 equations*

*C-11 Calculate the mass of the sodium chunk Jonathan burned. Assume all reactions happened with 100% yield.*

When sodium is burned on air, two products form: sodium oxide  $Na_2O$  and sodium peroxide  $Na_2O_2$ .

Neutral water has a pH of 7. To prove it, let us use the pH definition:

$$pH = -\log[H^+]$$

In neutral water no other ions except for  $H^+$  and  $OH^-$  are present, and because the net charge of water is zero,

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

And, knowing the expression for the water ion product,  $K_w$ :

$$K_w = [OH^-] \cdot [H^+]$$

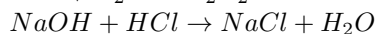
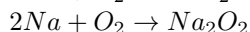
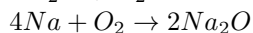
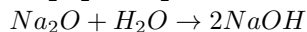
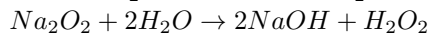
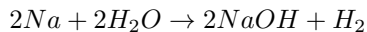
we can easily prove that in neutral water this equation holds true:

$$K_w = [H^+]^2$$

$$10^{-14} = 10^{-2pH}$$

$$pH = 7$$

Jonathan carried out such reactions:



To determine the mass of the sodium chunk, we will debunk the mystery from the bottom:

The gas evolved when Jonathan threw the combustion products into his bathtub should be hydrogen from the reaction between unburnt sodium and water. Then,  $n_{H_2} = \frac{112}{22.4} = 5 \text{ mol}$ . And  $n_{Na,unburnt} = 10 \text{ mol}$ .

The rest of the combustion products is a mixture of sodium peroxide and sodium oxide with a mass  $m = 16030 - 230 = 15800 \text{ g}$ .

We now need to determine the amount of HCl Jonathan needed to neutralise the sodium hydroxide produced in the solution. This is quite easy to be done:

1. The mass of the hydrochloric acid Jonathan spent is equal to  $35.8 \cdot 1.2 = 42.96 \text{ kg}$
2. The mass of HCl in that acid equals  $42.96 \cdot 0.36 = 15465.6 \text{ g}$
3. The amount of HCl in moles thus equals  $\frac{15465.6}{36.5} = 424 \text{ mol}$ .

Now, we can write out two simultaneous equations relating the amounts of sodium oxide and sodium peroxide in the combustion products. Let us imagine that the combustion products consist of  $x$  moles  $Na_2O$  and  $y$  moles of  $Na_2O_2$ . Then, we obtain two equations to describe the situation:

$$\begin{cases} 2x + 2y = 424 \\ 62x + 78y = 15800 \end{cases}$$

By solving the equation system, we obtain:

$$\begin{cases} x = 46 \\ y = 166 \end{cases}$$

Now, we determine the total amount of sodium:

$$n_{Na-initial} = n_{Na-unburnt} + 2 \cdot n_{Na_2O_2} + 2 \cdot n_{Na_2O}$$

And, by substituting in the numbers, we obtain:

$$n_{Na-initial} = 10 + 2 \cdot 46 + 2 \cdot 166 = 434 \text{ mol}$$

This amount of sodium, in turn, correlates to  $434 \cdot 23 = 9982 \text{ g}$

Little Ian, Jonathan's mentor, was very keen on collecting spheres of elements. Being honest, the chunk of sodium Jonathan burned also was spherical.

*C-12 Calculate the radius of the sodium sphere Jonathan had burned.  $\rho_{Na} = 0.97 \text{ g/mL}$ . If you failed to calculate the mass of sodium Little Ian the Chemist gave to Jonathan assume it is 23000g (It is not the correct answer).*

First, let us determine the volume of the sodium sphere:

$$V = \frac{m}{\rho} = \frac{9982}{0.97} = 10291 \text{ cm}^3$$

Then, using the sphere volume formula:

$$V_{\text{sphere}} = \frac{4}{3} \cdot \pi \cdot r^3$$

we can determine the radius of the sphere, it being equal to  $r = \sqrt[3]{\frac{3V}{4\pi}} =^3 \sqrt{\frac{3 \cdot 10291}{3.14 \cdot 4}} = 13.5 \text{ cm}$

## 2.4 Problem D. Amquid Limonia, Liquic Ionid and other MLG

Ross the Amateur Chemist decided to assert his dominance over Little Olavs. To do this, he decided to make Olavs do some experiments in a very strange solvent where chemistry seemed to work wrong. . . . Ross dissolved 2.08g of zinc metal in his "super solvent" as he now calls it. Zinc dissolved in it, producing a gas that occupied 0.79L at 298K and 1 bar (Assume it's ideal). This gas also had a density of 1.21 g/L. After Ross evaporated the "super solvent" from the flask, he weighed the solid product formed, its mass being 6.048g.

Ross hoped that Olavs would be too confused about the identity of the "super solvent", but unfortunately Little Olavs was a very skilled Inorganic chemist and he almost immediately figured out the formula of the "super solvent".

*D-1 Determine the chemical formula of the "super solvent". It is a binary compound.*

*D-2 Determine the chemical formula of the gas that was produced in the reaction between the "super solvent" and zinc metal. Write down the reaction equation describing that process.*

First, let us determine what was the gas evolved in the reaction. Knowing that  $\rho = \frac{m}{V}$  we can express the density from the ideal gas equation:

$$pV = \frac{m}{M} \cdot RT$$

$$M = \frac{\rho RT}{p}$$

By substituting the numbers in the formula, we obtain  $M = \frac{1.21 \text{ g/L} \cdot 8.314 \cdot 298}{100 \text{ kPa}} = 30 \text{ g/mol}$ . This corresponds either to ethane  $C_2H_6$  or nitrogen monoxide  $NO$ . Nitrogen monoxide seems to be a more viable option.

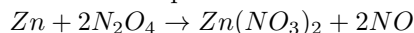
Then, it must be so that the zinc metal is left behind in the solid precipitate. Most probably, the precipitate is some sort of a  $Zn^{2+}$  compound. We can determine the molar mass of the anion because we know it has to correspond to the zinc mole count. Thus, for a compound  $ZnX_a$  we can write down such an equation:

$$\frac{m_{Zn}}{M_{Zn}} = \frac{m_{Compound}}{M_{Zn} + a \cdot M_X}$$

We only need to solve the equation two times, for compounds  $ZnX_2$  and  $ZnX$ .

| Formula | $M_X$ | Possible formula(-s) |
|---------|-------|----------------------|
| $ZnX_2$ | 62    | $Zn(NO_3)_2$         |
| $ZnX$   | 124   | nothing adequate     |

Thus, the compound formed is zinc nitrate  $Zn(NO_3)_2$ . The "super solvent" must thus be a nitrogen oxide. The only nitrogen oxide that could react like this is dinitrogen tetroxide  $N_2O_4$ . It is a dimer of nitrogen dioxide  $NO_2$ , because at a 1 bar pressure  $NO_2$  can not exist in liquid as a monomer. The reaction equation for this process is as follows:



Afterwards, it was Little Olavs' turn to strike. Little Olavs developed a whole research paper on exotic MLG solvents, so he easily could destroy Ross the Amateur Chemist's hopes to solve any problem in their chemical duel. As a warming exercise (which Ross already failed, disappointing Olavs by a lot) Little Olavs decided to show Ross some chemistry of quite a famous solvent. Olavs referred to it as Amquid Limonia. Because Amquid Limonia was not stable at room temperature, Little Olavs used dry ice to keep it chill which is of course not MLG. As the first experiment, Little Olavs carried out an amazing reaction: he dissolved barium nitrate and ammonium chloride in two separate test tubes containing Amquid Limonia and mixed them together. He observed a white precipitate - barium chloride! Also, Little Olavs had added a small portion of Amquid Limonia into water with phenolphthalein added into it, producing a pink solution. Ross the Amateur Chemist could not explain that chemistry that he'd observed. . . . It is known that Little Olavs prepared Amquid Limonia by condensing a gas with a molar mass 17 g/mol.

*D-3 What solvent bears the name of Amquid Limonia?*

Well, it is obvious that the solvent is Liquid Ammonia, hence the word play in its name.

*D-4 Explain how the metathesis reaction Little Olavs carried out could happen in Amquid Limonia if it's impossible in water.*

Ammonium salts are well soluble in liquid ammonia due to them being acids in the medium. Nitrate salts are also soluble because of the strong hydrogen



bonding. On the other hand, barium chloride can not bond so well with liquid ammonia molecules, thus it precipitates out of the solution.

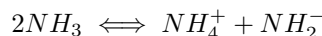
Little Olavs also knew that Amquid Limonia is very similar to water in its chemical properties. For example, it also can undergo autoprotolysis (self-proton exchange) and produce something similar to hydronium and hydroxide ions in aqueous media.

*D-5 Write the reaction equation describing autoprotolysis of Amquid Limonia.*

In water the autoprotolysis reaction is such:



Thinking analogically with liquid ammonia, one of the two molecules loses a proton and becomes negatively charged, and another molecule picks that proton up, forming a cation. We obtain such an equation:



Now, Little Olavs decided to prank Ross even more by forcing him to calculate some acid-base equilibria in Amquid Limonia, threatening to otherwise send a video of Ross struggling to calculate the concentration of water in water to Ross' friend Anastasia, who Ross was secretly admiring. In neutral Amquid Limonia Ross managed to measure that the concentration of the protonated species was equal to  $10^{-15}$  M.

*D-6 Help Ross calculate the Kw analogue of Amquid Limonia in order to avoid being humiliated by Little Olavs. Hint: Kw is equal to the product of the concentration of the protonated species and the deprotonated species in the solvent, for Amquid Limonia it is also true.*

Kw is calculated by using the following formula:

$$Kw = [NH_4^+] \cdot [NH_2^-]$$

In neutral liquid ammonia no other ions are present. Still, the solution must have a zero net charge, thus  $[NH_4^+] = [NH_2^-]$ . From this, we conclude that

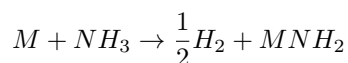
$$Kw = [NH_4^+]^2 = 10^{-30}$$

Phew, Ross finally completed the first task designed by Olavs to destroy Ross in a chemical duel. The next task Olavs gave to Ross was to dissolve his favourite metal in Amquid Limonia, just for fun. Little Olavs gave Ross 1.3g of his favourite metal and forced him to throw it into Amquid Limonia. After

some time, they collected a precipitate after evaporating Amquid Limonia directly into the air of the lab (as everybody knows, fume hoods are not MLG enough for Little Olavs), its mass being 1.83g.

*D-7 Determine the chemical formula of Olavs' favorite metal. Do not forget that Olavs still threatens to send videos of Ross failing to solve these problems to Anastasia, the love of Ross' life, and he needs help.*

The reaction of metals with liquid ammonia are well known. Alkali metals produce an alkali metal amide and hydrogen, and less active metals produce metal ammine complexes (*mostly hexacoordinated*). Let us first check the amide formation reaction:



From the stoichiometry of the reaction, we obtain a following equation:

$$\frac{m_{metal}}{M_{metal}} = \frac{m_{amide}}{M_{metal} + 16}$$

And by solving it, we obtain the value  $M_{metal} = 39 \text{ g/mol}$ , which corresponds to potassium. Thus, Olavs' favourite metal is potassium  $K$ .

The next task Ross was given was comparably easy to accomplish. He just needed to prepare the strongest base that could exist in Amquid Limonia.

*D-8 What compound can be the strongest base in the medium of Amquid Limonia?*

In water, the theoretically strongest base is hydroxide ion  $OH^-$ . Thus, in liquid ammonia the strongest base is the amide ion  $NH_2^-$ .

*D-9 Tick the boxes next to the name of the reagents Ross could use to prepare such a solution.*

|                                 |                                  |                                       |                                    |
|---------------------------------|----------------------------------|---------------------------------------|------------------------------------|
| <input type="checkbox"/> $NaOH$ | <input type="checkbox"/> $NEt_3$ | <input type="checkbox"/> $N(iPr)_2Li$ | <input type="checkbox"/> $MeLi$    |
| <input type="checkbox"/> $BuLi$ | <input type="checkbox"/> $NaOEt$ | <input type="checkbox"/> $K_2CO_3$    | <input type="checkbox"/> $H_2SO_4$ |

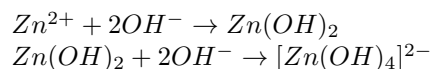
All bases that are stronger than the amide will work. Those are:

- LDA  $LiN(iPr)_2$
- $BuLi$
- $MeLi$

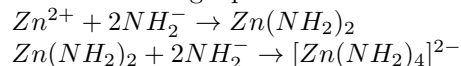
Little Olavs got his hands on two solutions in Amquid Limonia: a solution of zinc nitrate and a basic solution Ross'd prepared earlier. Upon addition of the basic solution to a solution of zinc nitrate a precipitate occurred, which then dissolved again when Olavs added even more base.

*D-10 Write the reaction equations describing this process as well as the equations describing a similar process, but in aqueous medium.*

In water this reaction would work like this:



Thus, knowing that in liquid ammonia the reaction would work similarly, we obtain the following equations:

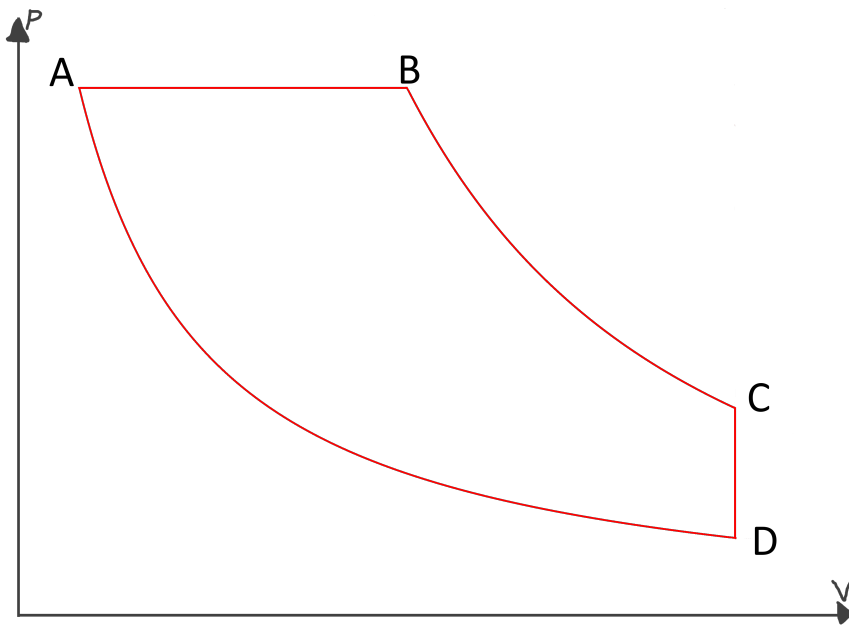


## 2.5 Problem E. Expand, Evolve, Thermodynamics

Vladislavs the Biochemist needed a freezer to store dead bodies. He could not manufacture one himself, so he decided to ask his friend Big Rolands to build one for him.

Big Rolands was a physicist himself, so he decided to make a somewhat efficient freezer not to disappoint Vladislavs, but not the most effective one—Vladislavs didn't pay him for doing his job... Big Rolands designed a completely gas-phase freezer because he thought it'd be easier to construct and to maintain. In this problem you can assume that all gases described are ideal gases and that the ideal gas law applies to them in full extent.

The freezer works using a closed thermodynamic cycle containing one adiabat, one isobar, one isotherm and one isochore. It uses some amount of an ideal monatomic gas circulating in it.



This thermodynamic cycle is plotted in the coordinates of p-V on the picture above.

At point A the temperature is equal to 258K, the volume of the gas in the machine is equal to 50L, the pressure is equal to 600 kPa. In point B the volume occupied by the gas equals 175L, in point C—300L. A-D is an isotherm, B-C is

an adiabat.

E-1 Determine the amount of the gas (in moles) in the freezer.

E-2 Complete this table about the state functions of the gas in the freezer at points A,B,C and D.

| Point | p,kPa | V,L | T,K |
|-------|-------|-----|-----|
| A     | 600   | 50  | 258 |
| B     |       | 175 |     |
| C     |       | 300 |     |
| D     |       |     |     |

From the ideal gas equation:

$$n = \frac{pV}{RT} = \frac{50 \cdot 600}{8.314 \cdot 258} = 14 \text{ mol}$$

The A → B transition is an isobar (*it is visible from the graph that pressure is constant*), thus from the ideal gas law:

$$\frac{T_1}{T_2} = \frac{V_1}{V_2}$$

And:  $p_B = p_A = 600 \text{ kPa}$ ,  $T_B = \frac{175 \cdot 258}{50} = 903 \text{ K}$

The B → C transition is an adiabat (*it is given in the introduction*), thus from the adiabat equation:

$$p_1 \cdot V_1^{\frac{5}{3}} = p_2 \cdot V_2^{\frac{5}{3}}$$

And, from this equation we obtain that  $p_C = \frac{600 \cdot 175^{\frac{5}{3}}}{300^{\frac{5}{3}}} = 244 \text{ kPa}$  And, from the ideal gas equation, we can determine  $T_C = \frac{244 \cdot 300}{14 \cdot 8.314} = 629 \text{ K}$

The C → D transition is an isochore (*it is visible from the graph that the volume is constant*), thus from the ideal gas law:

$$\frac{p_1}{p_2} = \frac{T_1}{T_2}$$

And,  $V_D = 300 \text{ L}$

The A → D transition is an isotherm (*it is given in the introduction*), thus from the ideal gas law:

$$p_1 V_1 = p_2 V_2$$

$T_D = 258 \text{ K}$   $p_D = \frac{600 \cdot 50}{300} = 100 \text{ kPa}$

The complete table looks like this:

| Point | p,kPa | V,L | T,K |
|-------|-------|-----|-----|
| A     | 600   | 50  | 258 |
| B     | 600   | 175 | 903 |
| C     | 244   | 300 | 629 |
| D     | 100   | 300 | 258 |

E-3 Which direction from point B must you go to make a freezer? What will happen if you go the other way around?

The needed direction is towards A. Otherwise, the work done by the gas will be positive, and the freezer will turn into a heat engine.

E-4 Calculate the work done on the gas during one cycle.

E-5 Calculate the heat removed from the colder side of the system by the gas during one cycle.

The work can be determined from the First Law of thermodynamics:

$$\Delta U = q + w$$

Thus, on the part A  $\rightarrow$  D the temperature does not change, so internal energy does not change, and:

$$q = -w = -nRT \cdot \ln\left(\frac{V_D}{V_A}\right)$$

And we obtain that  $q_{A \rightarrow D} = +53807 \text{ J}$ , and  $w_{A \rightarrow D} = -53807 \text{ J}$

On the part D  $\rightarrow$  C the volume does not change, so no work happens. Thus,

$$\Delta U = q$$

And, knowing that  $U = \frac{3}{2} \cdot nRT$ , we can transform the First Law into

$$q = \frac{3}{2} \cdot (T_D - T_C)$$

And we obtain that  $q_{D \rightarrow C} = +64774 \text{ J}$ ,  $w_{D \rightarrow C} = 0 \text{ J}$ .

On the part C  $\rightarrow$  B the process is adiabatic, thus  $q = 0$  and the First Law is expressed as:

$$\Delta U = w$$

Knowing that  $U = \frac{3}{2} \cdot nRT$ , we obtain:  $q_{C \rightarrow B} = 0$ ,  $w_{C \rightarrow B} = +47839 \text{ J}$

On the part B  $\rightarrow$  A the pressure is constant, thus the First Law can be expressed as such:

$$q = \Delta U - w = \frac{3}{2}nR(T_A - T_B) - p_{B \rightarrow A} \cdot (V_A - V_B)$$

And, by substituting the numbers we obtain  $w_{B \rightarrow A} = +75000 \text{ J}$  and  $q_{B \rightarrow A} = -187613 \text{ J}$

The total work in the cycle equals  $-53807 + 47839 + 75000 = +69032 \text{ J} = 69 \text{ kJ}$ .

The heat removed by the freezer is all the heats with a "+" sign (heats with a + sign mean that the gas in the freezer accepts heat from some source, heats with a - sign mean that the gas gives that heat away). The total heat equals  $q = 53807 + 64774 = 118581 \text{ J} = 118.6 \text{ kJ}$ .

Vladislavs' freezer for dead bodies is a small thermally insulated room with the following measures: height=2m, length=2m, width=4m. Vladislavs wanted to know how much energy will he need to completely cool down the air in his room and to sustain the temperature. The density of air is  $\rho = 1.225 \text{ kg/m}^3$  and the specific heat capacity of air is  $c = 0.718 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ . Vladislavs still didn't learn any thermodynamics, so let us help him in his calculations!

If you failed to calculate the amount of heat removed by the machine during one cycle, assume it is equal to 170 kJ in the rest of the problem. Or, use the heat value you have calculated. If you failed to calculate the work required to do the cycle, assume it is equal to 50 kJ, which, of course, is not the right answer.

*E-6 Calculate the amount of heat that needs to be removed from the air in Vladislavs' freezer so that it cools down from 25C to -15C.*

*E-7 How many cooling machine cycles must be carried out to remove this much heat? Hint: the machine can not perform a non-integer amount of cycles.*

*E-8 How much work will be needed to do this cooling operation?*

First, let us determine the volume of the room.  $V = abc = 2 \cdot 2 \cdot 4 = 16 \text{ m}^3$

Then, we need to find the mass of air in the room, we can do it knowing its density:  $m = \rho \cdot V = 16 \cdot 1.225 = 19.6 \text{ kg}$ . And, by using the formula:

$$q = cm\Delta T$$

we find the heat required to cool the freezer!  $q = 19.6 \cdot 40 \cdot 0.718 = 563 \text{ kJ}$ .

One cooling cycle removes 118.6 kJ of heat, thus to remove 563 kJ Vladislavs needs to carry out  $\frac{563}{118.6} = 4.74$  cycles. But, because the machine can do only integer amounts of cycles, he actually needs to carry out 5 cycles to complete the cooling.

Each cycle requires 69 kJ of work to complete, thus 5 cycles require  $5 \cdot 69 = 345 \text{ kJ}$ .

Vladislavs also noted that if the room is cooled down, the cooler is shut down and the room is left to itself it heats up back to the initial temperature in the course of two hours. He decided to periodically switch on the cooling machine to sustain the temperature in the freezer.

*E-9 How often will Vladislavs need to switch on the machine? Note that we can assume it does one cooling cycle immediately compared to the time the room requires to heat up.*

To cool down the room from room temperature to -15C Vladislavs needs 5 cooling cycles. Assuming that the heat loss is constant, it is quite clear that Vladislavs needs to run his machine every  $\frac{120}{5} = 24 \text{ min}$  to sustain the temperature in his room at an optimal level.

Vladislavs finally prepared the whole machine, gave Big Rolands some of the money he promised and began experimenting with freezing dead bodies. Vladislavs decided to visit the local farm and found a dead body of a mutant

pickle. He gently placed it in a bag and carried it back to his lab. There, he weighed it and prepared it for freezing. The mass of the pickle in Vladislavs' disposal was equal to 80 kg. As it is known, pickles consist mainly of water, so we can assume the mutant pickle also consisted mainly of water. Because of the huge heat capacity of water compared to other compounds found in pickles, we can assume that thermodynamically the pickle is equivalent to 72 kg worth of pure water in terms of heat capacity. You might need some heat capacity information in this task, everything you might need is located in this table:

| $C_m(ice)$                           | $\Delta_{fusion}H(ice)$  | $C_m(water)$                         |
|--------------------------------------|--------------------------|--------------------------------------|
| $37.7 J \cdot mol^{-1} \cdot K^{-1}$ | $333.6 kJ \cdot kg^{-1}$ | $75.4 J \cdot mol^{-1} \cdot K^{-1}$ |

*E-10 Calculate the amount of work that Vladislavs needs to supply to the cooling machine in order to freeze the dead mutant pickle from  $T=25C$  to  $T=-15C$ . Show your calculations. Do not forget that the cooling machine can not do non-integer amounts of work cycles!*

Using the formulas

$$q = n \cdot C_m \cdot \Delta T \quad q = m \cdot \Delta_{fusion}H$$

we can determine the heat required. First, let us find out the amount of moles of water in the dead mutant pickle. By simple calculations, we obtain  $n_{H_2O} = \frac{72 \cdot 10^3}{18} = 4 \cdot 10^3 mol$ .

Now, let's actually determine the heat needed. First, the water needs to be cooled down to 0C, then it must be frozen completely and then the produced ice must be cooled down to -15C. By substituting the numbers into the formula, we obtain that  $q = 72 \cdot 333.6 + 4 \cdot 15 \cdot 37.7 + 4 \cdot 25 \cdot 75.4 = 33821 kJ$

To remove this heat,  $\frac{33821}{118.6} = 285.2$  cycles are required. Because of the machine limitations, this comes up to 286 cycles.

The work then comes to be  $286 \cdot 69 = 19.734 MJ$

If you failed to calculate the work in E-10, use the value of 29 MJ in the rest of the problem.

Vladislavs realised that it'd be lots of energy needed to cool down the dead mutant pickle. So, he asked his friend Big Rolands to help him again. Big Rolands suggested Vladislavs use the power of electricity to power his machine. To complete this feat, Vladislavs extracted the electric motor from his washing machine and connected it to the cooling machine. The electric motor has a power rating of 380W.

*E-11 Calculate how long must the motor power the cooler in order to freeze only the dead mutant pickle inside the freezer.*

Knowing that  $1W = 1J \cdot s^{-1}$ , we can express the work in the following manner:

$$w = P \cdot t$$

And by substituting the numbers, we obtain that  $t = \frac{19734}{0.380} = 51932 s = 14.4 h$ .

Still, Vladislavs' freezer was leaking heat (see above), and he needed to consider this factor, too. Help him conduct his experiments!

*E-12 Determine the fraction of the motor power (in %) that will be spent to counter heat leaks in the freezer.*

*E-13 Determine the time Vladislavs will actually need to freeze the dead mutant pickle, taking into account the heat losses in the freezer.*

The easiest way to solve the problem is to think like this:

One heating cycle is needed every 24 minutes. To perform it, 69 kJ of energy are needed. During those 24 minutes, the motor produces  $24 \cdot 60 \cdot 0.380 = 547.2 \text{ kJ}$  of power. Thus, to counter the leaks  $\frac{69}{547.2} = 12.6\%$  of the motor power are spent.

Taking this fact into account, the real efficiency of the motor is in fact  $100 - 12.6 = 87.4\%$ . So, the time needed to perform the cooling of the dead mutant pickle will increase and be equal  $\frac{14.4}{0.874} = 16.5 \text{ h}$ .

Vladislavs also wanted to increase the size of his freezer. But, for this machine there are limitations to the size of the room being cooled because of the heat losses. We can assume that the time period in which a cycle must be run to sustain the room temperature is inversely proportional to the volume of the room. For example, if a room of volume  $4 \text{ m}^3$  needs to be cooled every 8 minutes to be sustained at  $-15\text{C}$ , a room of volume  $2 \text{ m}^3$  needs to be cooled every 16 minutes to sustain its temperature.

*E-14 Assuming that Vladislavs still uses his 380W motor to power the cooling machine, calculate the minimum time between two cycles of the machine so that the motor is able to sustain the temperature.*

*E-15 Determine the maximum volume of the freezer Vladislavs can keep at  $-15\text{C}$  using his 380W motor and the same cooling machine.*

During the minimum cooling time the motor must be able to supply the 69 kJ of heat required to actually perform a cooling cycle. Thus, we can easily find the time, it being  $t = \frac{69}{0.38} = 181 \text{ s} = 3 \text{ min}$ .

Knowing the fact that the time between cooling operations is inversely proportional to the room volume, we obtain such an equation:

$$24 \cdot 16 = 3 \cdot V_{max}$$

From which we can obtain  $V_{max} = 128 \text{ m}^3$ .

## 2.6 Problem F. Traces of DNA in pickle juice

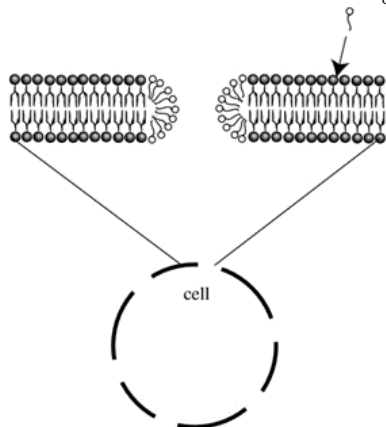
Someone from a little known country drank a potion he synthesized at his chemistry lab and turned into a pickle near a domestic monument. The police didn't like it (turning into a pickle is seen as disrespectful in his country), but weren't surveilling the area, so they're now suspecting three people - Big Nauris, Medium Ritums, and Little Olavs. Let's help the police find the true culprit.

When a person turns into a pickle, lots of pickle juice is emitted and splattered all around. That pickle juice contains muriocytes (Latin - muria, brine +



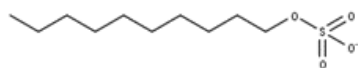
Greek kytos, cell) - the biological precursor cells which the human pickle body is made up of. The police found pickle juice splattered all over the monument, collected samples and took it to the lab of Vladislavs the Biochemist.

To determine the culprit, we will need to use gel electrophoresis to compare the DNA of muriocytes of the three suspects and that in the sample. Vladislavs promptly extracted the nucleus DNA from these cells, but, as expected, found it in low concentration. He now needs to conduct the polymerase chain reaction - an enzymatic reaction used to magnify the concentration of DNA. Help Vladislavs conduct this reaction. First, the culprit's DNA is extracted from the muriocytic nucleus. For that, the muriocytes have to be lysed - their lipid bilayer membranes disintegrated with a surfactant. The surfactant integrates into the cellular membrane and generates pores in it, as follows:



Source: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2504493/>

The anion in sodium dodecyl sulfate (SDS), a surfactant often used for cellular lysis, is shown below:



*F-1 Indicate which part of the anion is the tail and which is the head, if the porated cell in the figure is placed in water.*

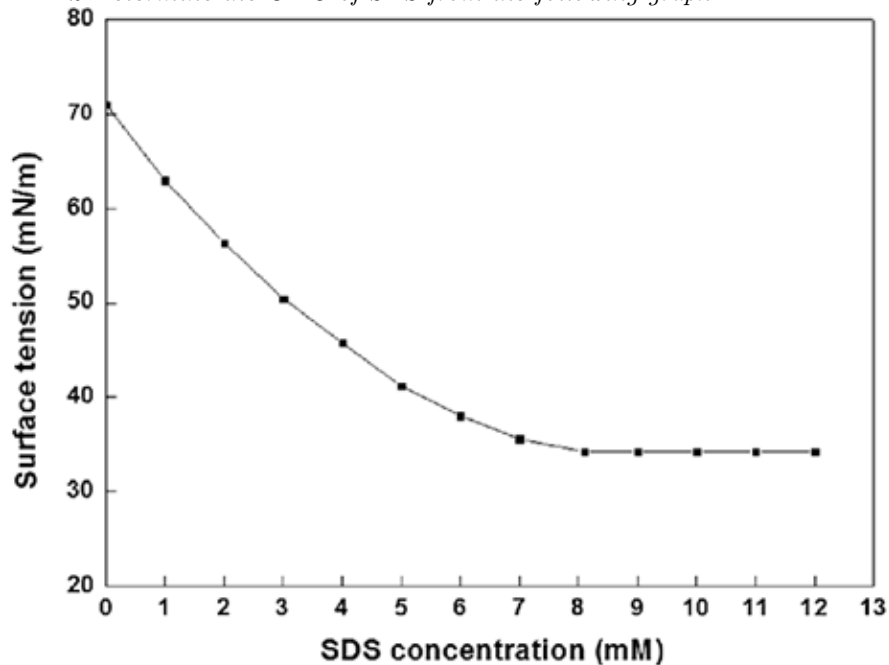
The tail of the SDS molecule must be hydrophobic, thus it has to be the carbon chain. The head is hydrophilic, and it has to be the sulfonate group.



The critical micelle concentration (CMC) is the concentration of surfactant

at which all further added surfactant forms micelles. Up until CMC, the surface tension of the surfactant solution keeps changing, but after - stays constant.

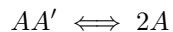
*F-2 Determine the CMC of SDS from the following graph:*



It is quite obvious from the graph that the CMC of the SDS surfactant equals 8 mM.

Phew, that lysis procedure sure was quite a bit of work. Now, the extracted DNA has to be amplified using the polymerase chain reaction. The polymerase chain reaction is an in vitro procedure where the DNA is duplicated once per cycle. The cycles are repeated many times to ensure an appropriate final concentration of DNA. We will consider only one part of the PCR - melting.

Melting is the stage where the DNA has to be dissociated. The chemical equation for dissociation of DNA is as follows:



*F-3 Assuming no dissociated DNA was present at the start of the reaction, express the reaction equilibrium constant  $K$  from the initial concentration of the DNA dimer and final concentration of DNA monomers.*

Let us imagine that  $[AA']_0$  is the initial concentration of the DNA dimer,  $[AA]$  is the final concentration of the DNA dimer and  $[A]$  the final concentration

of the DNA monomer. Then, we can write down the equilibrium constant expression for this reaction:

$$K = \frac{[A]^2}{[AA']}$$

Because there was no initial DNA monomer present, we can conclude that the DNA monomer concentration was produced only from the DNA dimer. Because one molecule of DNA dimer dissociated into two DNA dimer molecules, we can write the following relation between the initial DNA concentration and the final DNA concentration:

$$[AA']_0 - \frac{1}{2} \cdot [A] = [AA']$$

And by substituting this expression in the equilibrium constant definition, we obtain:

$$K = \frac{[A]^2}{[AA']_0 - \frac{1}{2} \cdot [A]}$$

Vladislavs determined that at 298K the equilibrium constant  $K$  for the melting stage of PCR is equal to  $4.20 \cdot 10^{-6}$ . He also measured that after reaching equilibrium the concentration of monomer DNA was equal to 16  $\mu$ M.

*F-4 Determine the initial concentration of dimer DNA that Vladislavs had in the murioocyte cell.*

By substituting in the earlier obtained equilibrium constant expression, we obtain the following equation:

$$4.20 \cdot 10^{-6} = \frac{(16 \cdot 10^{-6})^2}{[AA']_0 - \frac{1}{2} \cdot (16 \cdot 10^{-6})}$$

And by solving the equation, we obtain  $[AA']_0 = 69 \mu$ M

Vladislavs decided to increase the concentration of DNA to carry out his tests using PCR.

*F-5 If the desired concentration of DNA is 0.035M and the amount of DNA doubles every PCR cycle, calculate the necessary amount of cycles Vladislavs need to carry out on the murioocyte DNA.*

The initial DNA concentration  $[AA']_0$  equals  $69 \cdot 10^{-6}$  M. After the first PCR cycle, the DNA concentration will be equal to  $2 \cdot [AA']_0$ , after the second cycle  $2 \cdot 2 \cdot [AA']_0 = 2^2 \cdot [AA']_0$ ..., and after the n-th PCR cycle the DNA concentration will be equal to  $2^n \cdot [AA']_0$ . Thus, we obtain such an equation:

$$2^n \cdot 69 \cdot 10^{-6} = 0.035$$

To solve it, we transform it to a form:

$$2^n = \frac{0.035 \cdot 10^6}{69}$$

Which, after logarithmating, gives:

$$n = \frac{\ln\left(\frac{0.035 \cdot 10^6}{69}\right)}{\ln(2)} = 9 \text{ times}$$

Thus, Vladislavs needs to carry out the PCR 9 times to obtain such a DNA concentration in his sample.

OK... Now, thanks to your help, the muriocytic DNA was amplified. For forensic analysis, it now must be cleaved by a restriction endonuclease. The DNA is cleaved at particular spots which match the enzymes. This will yield a certain amount of DNA fragments which is unique to a particular person. The number of these fragments can then be determined by gel electrophoresis. By comparing the number of such fragments amongst suspects and with the muriocytic fragments, we can determine the true culprit.

After cleaving the DNA, Vladislavs then decided to try to conduct a gel electrophoresis on the DNA fragments he'd produced earlier. Unfortunately, the gel electrophoresis did not separate the fragments well and he couldn't count the amount of the fragments in the muriocytes.

So, Vladislavs decided to carry out another test. He used some enzyme that could bind to the DNA fragment in an irreversible reaction. The interesting thing about this reaction is that in every person it occurs as a different-order reaction kinetically. So, Vladislavs decided to measure out the rate of the reaction at different enzyme and fragment concentrations for each test subject's muriocytes and the muriocytes found on the monument.

He plotted his data in four tables:

| Name of Subject | Big Nauris   |            |                     |
|-----------------|--------------|------------|---------------------|
| Trial No.       | [Fragment],M | [Enzyme],M | rate, $10^{-3}$ M/s |
| 1               | 0.01         | 0.05       | 0.851               |
| 2               | 0.02         | 0.05       | 1.825               |
| 3               | 0.05         | 0.10       | 9.330               |

| Name of Subject | Medium Ritums |            |                     |
|-----------------|---------------|------------|---------------------|
| Trial No.       | [Fragment],M  | [Enzyme],M | rate, $10^{-3}$ M/s |
| 1               | 0.01          | 0.05       | 0.725               |
| 2               | 0.02          | 0.05       | 1.665               |
| 3               | 0.05          | 0.10       | 8.706               |

| Name of Subject | Little Olavs |            |                     |
|-----------------|--------------|------------|---------------------|
| Trial No.       | [Fragment],M | [Enzyme],M | rate, $10^{-3}$ M/s |
| 1               | 0.01         | 0.05       | 1.621               |
| 2               | 0.02         | 0.05       | 2.623               |
| 3               | 0.05         | 0.10       | 12.311              |

| Name of Subject | Monument Sample |            |                     |
|-----------------|-----------------|------------|---------------------|
| Trial No.       | [Fragment],M    | [Enzyme],M | rate, $10^{-3}$ M/s |
| 1               | 0.06            | 0.05       | 5.681               |
| 2               | 0.12            | 0.05       | 9.228               |
| 3               | 0.04            | 0.08       | 7.879               |

The reaction rate can be expressed using this equation:

$$r = k \cdot [Frag]^a \cdot [Enz]^b$$

where [Frag] and [Enz] are molar concentrations of the DNA fragment and the enzyme respectively; a and b are reaction orders in respect to fragment and enzyme of the reactions, k is a constant, it is unchanged for every person. The reaction orders with respect to both reagents of the culprit and the monument muriocyte should be almost the same.

*F-6 Determine the reaction orders with respect to both enzyme and DNA fragment of every sample. Do not forget to show your calculations, too! Fill this table:*

| Name            | Order with respect to [Frag] | Order with respect to [Enz] |
|-----------------|------------------------------|-----------------------------|
| Big Nauris      |                              |                             |
| Medium Ritums   |                              |                             |
| Little Olavs    |                              |                             |
| Monument Sample |                              |                             |

*F-7 Calculate the rate constant k of this reaction.*

Here, only the detailed calculations for the monument sample are shown. The orders can be calculated in a similar fashion for Big Nauris', Medium Ritums' and Little Olavs' samples, too! We strongly encourage the reader to try and do it themselves as an exercise.

We can write three rate law expressions for three trials described in the problem:

$$\begin{cases} 5.681 \cdot 10^{-3} = k \cdot (0.06)^\alpha \cdot (0.05)^\beta \\ 9.228 \cdot 10^{-3} = k \cdot (0.12)^\alpha \cdot (0.05)^\beta \\ 7.879 \cdot 10^{-3} = k \cdot (0.04)^\alpha \cdot (0.08)^\beta \end{cases}$$

The fact that the variables are in the exponent are not really nice, we should try to linearize the equation. A nice way to linearize such equations is to logarithmate both sides of every equation, from which we obtain:

$$\begin{cases} \ln(5.681 \cdot 10^{-3}) = \ln(k \cdot (0.06)^\alpha \cdot (0.05)^\beta) \\ \ln(9.228 \cdot 10^{-3}) = \ln(k \cdot (0.12)^\alpha \cdot (0.05)^\beta) \\ \ln(7.879 \cdot 10^{-3}) = \ln(k \cdot (0.04)^\alpha \cdot (0.08)^\beta) \end{cases}$$

By using the logarithm properties:

$$\ln(ab) = \ln(a) + \ln(b) \quad \ln(a^b) = b \cdot \ln(a)$$

we can transform the system into a linear system:

$$\begin{cases} \ln(5.681 \cdot 10^{-3}) = \ln(k) + \alpha \cdot \ln(0.06) + \beta \cdot \ln(0.05) \\ \ln(9.228 \cdot 10^{-3}) = \ln(k) + \alpha \cdot \ln(0.12) + \beta \cdot \ln(0.05) \\ \ln(7.879 \cdot 10^{-3}) = \ln(k) + \alpha \cdot \ln(0.04) + \beta \cdot \ln(0.08) \end{cases}$$

This equation system is linear and is quite easy to solve. By solving the system, we obtain:

$$\begin{cases} k = e^{0.6918} = 2 \\ \alpha = 0.7 \\ \beta = 1.3 \end{cases}$$

Thus, for the monument sample the reaction order with respect to [Frag] is 0.7 and the reaction order with respect to [Enz] is 1.3.

The reaction rate constant is the same for every person,  $k = 2 \text{ M}^{-1} \cdot \text{s}^{-1}$ .

In an analogical manner, rate constants for every suspect can be determined. They are filled in into the table below:

| Name            | Order with respect to [Frag] | Order with respect to [Enz] |
|-----------------|------------------------------|-----------------------------|
| Big Nauris      | 1.1                          | 0.9                         |
| Medium Ritums   | 1.2                          | 0.8                         |
| Little Olavs    | 0.7                          | 1.3                         |
| Monument Sample | 0.7                          | 1.3                         |

With this data, Vladislavs the Biochemist managed to determine the identity of the culprit. And his name was... *[CLASSIFIED]*

*F-8 Who was the culprit?*

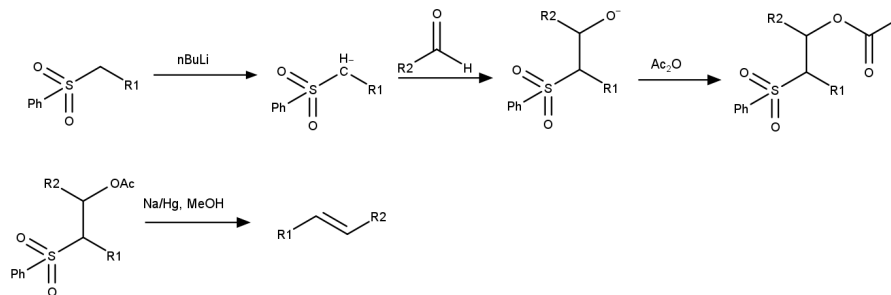
The reaction rate data of Little Olavs matches the reaction rate data from the monument sample, thus Little Olavs is guilty of turning into a pickle in front of a monument.

## 2.7 Problem G. How to understand Julia

High school student Julia decided to study Organic Chemistry. She has already learnt all Organic Chemistry in her high school textbook, and she decided to have a look at such a thing as named reactions. Some chemist friend told Julia about one very interesting reaction called Julia Olefination. She thought that it'd be great to recreate the reaction bearing the same name as her but she didn't really know how the reaction worked. Let's explore Julia olefination together with Julia!

The Julia olefination reaction happens in two main stages: substitution and reduction.

The Julia olefination reaction proceeds according to this scheme:



First of all, the initial phenyl sulfone is mixed with n-butyllithium and then an aldehyde. The product is then mixed with acetic anhydride to form an ester. The sulfone ester is reduced by sodium amalgam in methanol, forming the trans-double bond.

*G-1 What is sodium amalgam and how is it made?*

Sodium amalgam is an alloy of sodium and mercury. It is usually prepared by dissolving chunks of solid sodium in mercury at room temperature. *At room temperature mercury is liquid.*

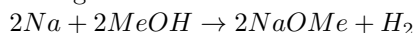
*G-2 Which role does butyllithium have in the substitution phase? Hint: have a closer look at the changes in the structure of the molecule that occur after adding BuLi.*

Butyllithium takes off a proton adjacent to the  $-\text{SO}_2\text{Ph}$  group in the molecule. Thus, it works as a base. It is worth to be mentioned that  $\text{BuLi}$  is a very strong base - sodium hydroxide would not be able to deprotonate this sulfone.

Julia discovered that during the reduction stage of Julia olefination the first reaction that happens is an E1cb elimination of acetic acid, forming the unsaturated sulfone which is then reduced by sodium amalgam. E1cb elimination needs quite a strong base present to kickstart the process.

*G-3 What base is formed in the reductive mixture of Na/Hg and methanol? Write the name of the base as well as the reaction equation describing its formation.*

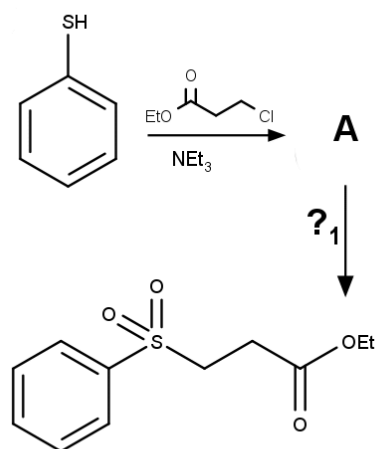
The base formed is sodium methoxide,  $\text{NaOMe}$ . The reaction equation describing its formation is as follows:



*G-4 Why is sodium amalgam rather than metallic sodium being used in the Julia olefination?*

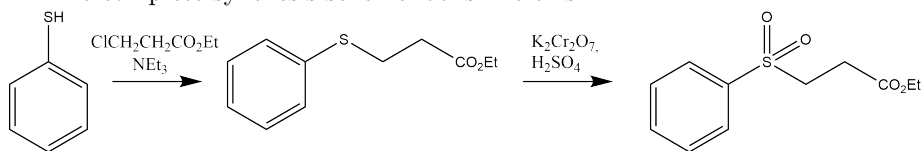
Sodium amalgam is less reactive than metallic sodium. If we used metallic sodium in methanol it would immediately react with methanol, leaving no sodium available to react with the sulfone and to reduce it. Also, sodium amalgam is much more convenient to use, is not as explosive and does not float on top of the reaction mixture.

Julia first needed to make a sulfone to do the Julia olefination. Thus, Julia made the following synthesis scheme for the sulfone (see abbreviation deciphering in Organic Chemistry Info Sheet):



*G-5 Determine the intermediate **A** and the reagent **?<sub>1</sub>** in Julia's synthesis.*

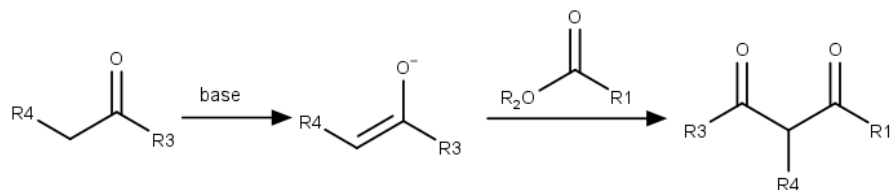
The complete synthesis scheme looks like this:



It is worth mentioning that any oxidiser will work as **?<sub>1</sub>**, not only the dichromate/sulfuric acid mixture.

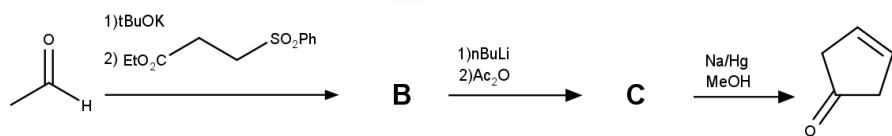
Julia got her hands on some sodium amalgam generously provided by Little Ian aka Mr. White Powder A and began planning the Julia olefination she'd planned to complete. She also wanted to test out her knowledge of the Claisen ester condensation reaction, which is used to fuse a carbonyl compound with an ester. The scheme of the Claisen ester condensation is as follows:





The Claisen condensation is a special type of the Aldol reaction. This reaction involves an enolizable carbonyl compound which is converted into an enolate using a strong base such as LDA. The enolate then substitutes the ester and forms a 1,3-dicarbonyl compound.

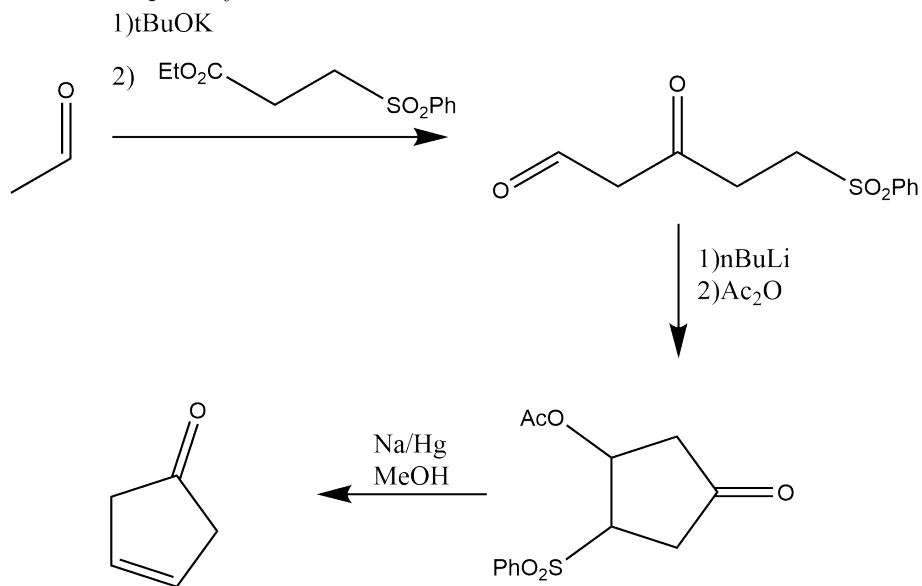
Julia decided to make an interesting Julia olefination. Julia made the synthesis following the scheme below. This Julia olefination reaction is very interesting because it doesn't produce a trans-double bond as it is supposed to, but rather a cis-one.



G-6 Determine the intermediates **B** and **C** in Julia's synthesis.

G-7 Why wasn't the double bond formed trans-oriented?

The complete synthesis scheme looks like this:



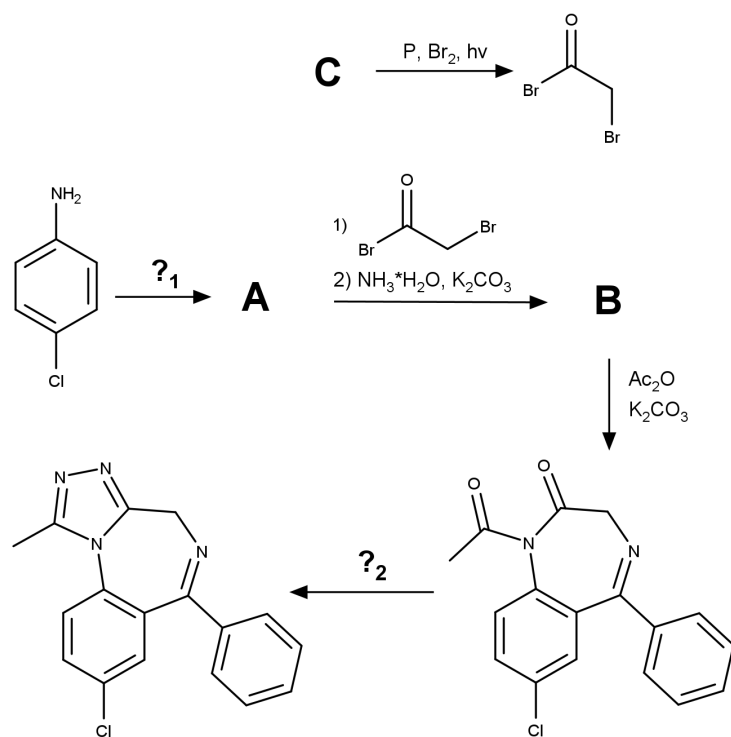
The produced bond is not trans-oriented because of the ring strain it'd induce

in a trans-configuration. Thus, the bond **must** be cis in order for the cyclic structure to be possible.

## 2.8 Problem H. LIL BO' CHEM

Gustav the High school student decided to become a Pharma Boss. He discovered that pharmacists need to sell any sort of drugs, so Nick decided to make some at home to sell. He made a few synthesis schemes, but unfortunately Gustav's father came into Gustav's room and seized part of his synthesis schemes, saying that drawing is a waste of time and that Gustav should become a lawyer. Although, it didn't stop Gustav from completing his plans, and he still had enough of the schemes intact to restore the syntheses.

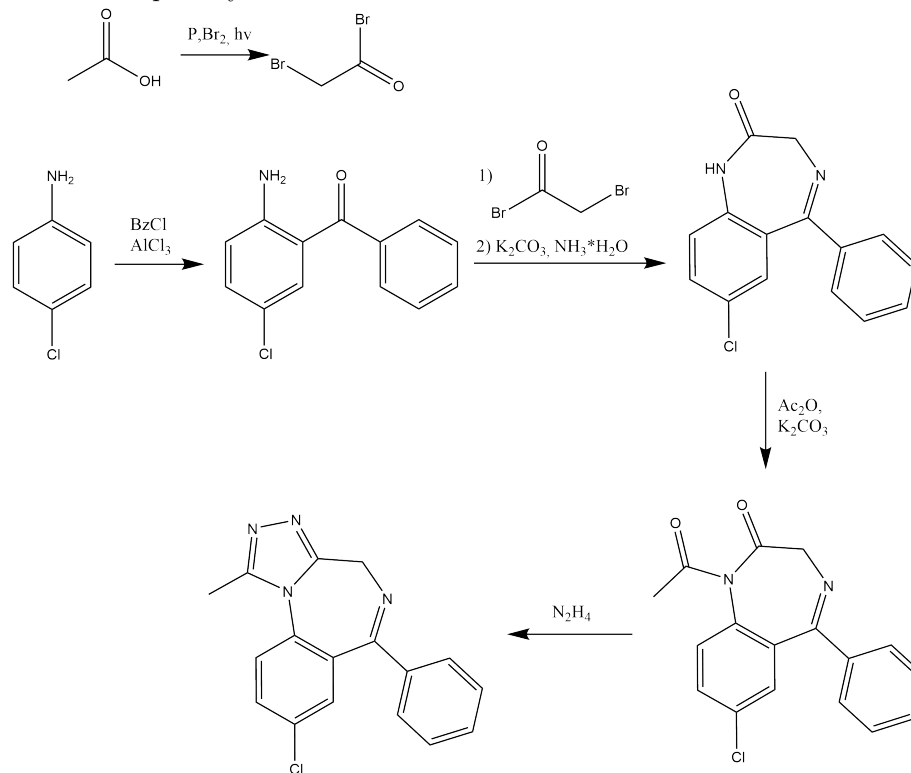
Gustav decided that his potential buyers will need to calm their anxiety down after seeing the mess in his room/lab/shop, and thought that adding a sedative such as alprazolam to his stock will be useful. He made an easy to follow synthesis scheme, but unfortunately it didn't quite survive the attack of Gustav's dad.



H-1 Determine the intermediates **A-C** and the reagents  $?_1$  and  $?_2$  in the synthesis scheme.

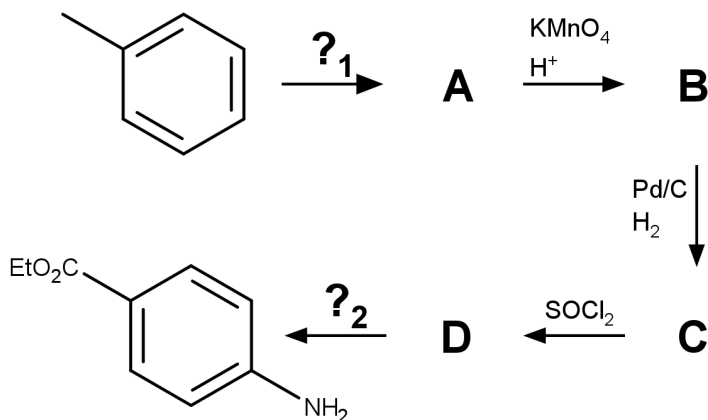
H-2 Why is NBS (*N*-bromosuccinimide) not a good reagent for producing the  $\alpha$ -bromoacetophenone?

The complete synthesis scheme looks like this:



NBS is a bad reagent for such bromination because it can not produce an acyl bromide (*NBS is a source of electrophilic bromine*). Also, if we assume that the reaction with NBS would work, the produced acyl bromide would immediately be attacked by the succinimide ion formed, thus making the reaction useless.

Gustav also thought that it'd be a great idea to add some medication to numb the pain of buyers who injure their legs when they maneuver themselves between the heaps of junk in his room, so he decided to sell benzocaine.

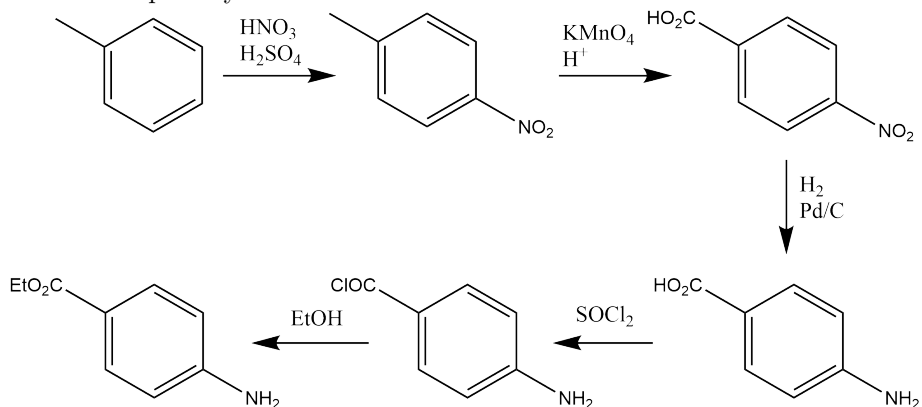


H-3 Determine the intermediates **A-D** and reagents  $?_1$  and  $?_2$  in this synthesis scheme.

H-4 Explain which process the reaction of **C** and  $\text{SOCl}_2$  is pushed forward by.

H-5 Which side products form during the toluene  $\rightarrow$  **A** conversion?

The complete synthesis scheme looks like this:



The reaction of **B** and  $\text{SOCl}_2$  is pushed forward by the production of  $\text{SO}_2$  gas as one of the products.  $\text{SO}_2$  leaves the reaction vessel, thus shifting the equilibrium to the right.

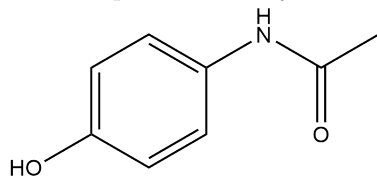
The toluene  $\rightarrow$  **A** conversion proceeds with formation of a ortho-nitrated product as well as a mixture of di- and trinitrotoluenes.

Gustav wanted to prepare a drug so common as aspirin. Though, he wanted to prepare something similar to aspirin, but not an exact replica. He found a name of a compound with similar properties to aspirin - N-(4-hydroxyphenyl)acetamide.

H-6 Draw the molecular formula of that compound.

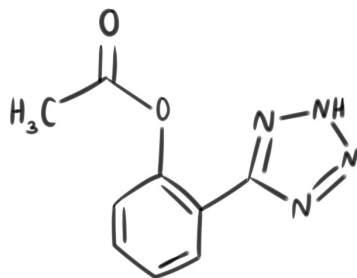
H-7 What is a more common name for this compound?

The compound with this IUPAC name is trivially called paracetamol/acetaminophen. This compound is a very common medication.

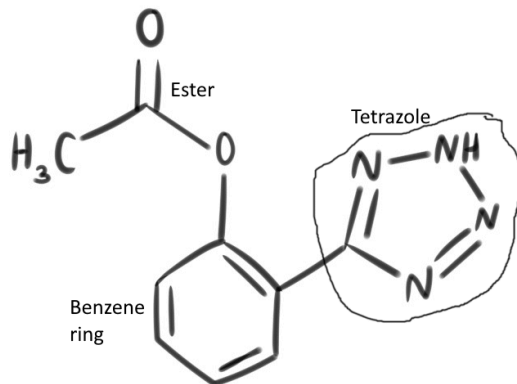


paracetamol

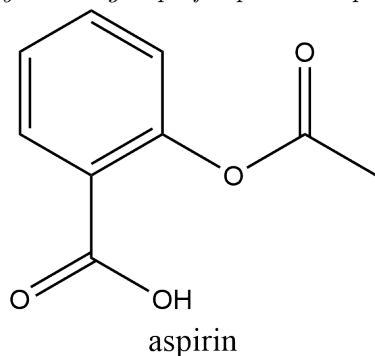
A very common substitute for a carboxylic acid functional group in drug chemistry is a tetrazole group. It has almost the same pKa and is mostly deprotonated inside the human organism. Gustav decided that his analog of aspirin will have the carboxylic acid group replaced by a tetrazole group. He decided to name the compound Gustavopirin. Gustav drew the molecular formula of Gustavopirin on a sheet of paper so that it'd be easier for him to make the compound synthesis scheme.



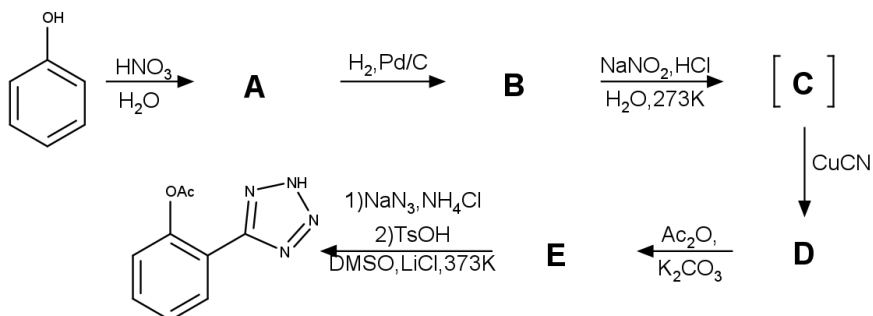
H-8 Determine all the functional groups in Gustavopirin and circle the tetrazole group on the drawing. Write names of each functional group on the drawing.



H-9 Draw the molecular formula of aspirin. Hint: in Gustavopirin the carboxylic acid group of aspirin is replaced by a tetrazole group.



Gustav also devised a synthesis scheme for Gustavopirin. It is not very complicated but still is an interesting one to have a look at. Unfortunately, this synthesis scheme also did not survive the attack of Gustav's mother, so a decent part of it is missing.



Intermediate **C** is an unstable particle that Gustav immediately reacted with copper (i) cyanide to avoid any product losses.

H-10 Determine the structural formulas of intermediates **A-E**.

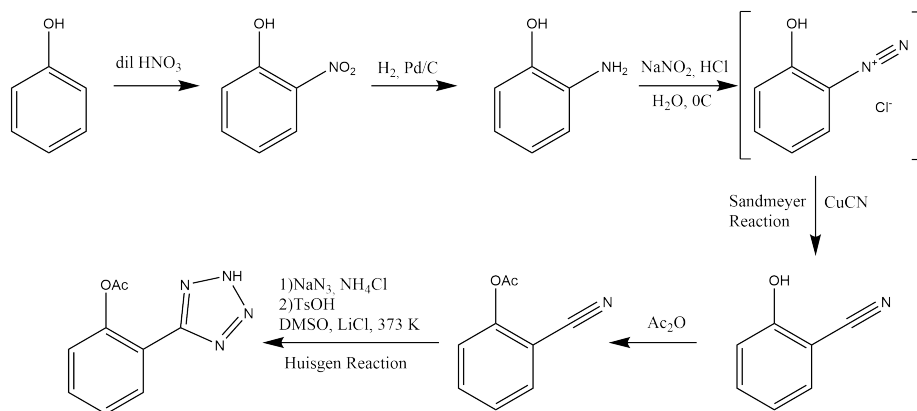
H-11 What makes **C** so unstable in aqueous medium? Explain it.

H-12 How is the reaction between **C** and copper (i) cyanide called?

H-13 Why is dilute nitric acid used as a reagent for phenol nitration? Why concentrated nitric acid in a mixture with concentrated sulfuric acid must be used to nitrate benzaldehyde?

H-14 Is **A** the only product of the reaction between phenol and dilute nitric acid? Draw the structural formula of the other reaction product or write "no by-product" as an answer.

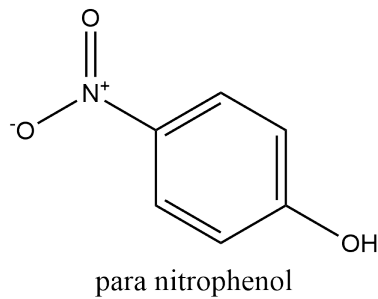
The complete synthesis scheme looks like this:



**C** is very unstable to hydrolysis, because it can easily throw away a nitrogen gas molecule, shifting the hydrolysis reaction to the right.

The reaction between aryldiazonium salts such as **C** with  $Cu^I$  salts is called the *Sandmeyer Reaction*. The diazonium group is switched to the anion of the  $Cu^I$  salt.

Dilute nitric acid is used in phenol nitration to avoid over-nitration. The by-product is para-nitrophenol as well as a mixture of di- and trinitrophenols.



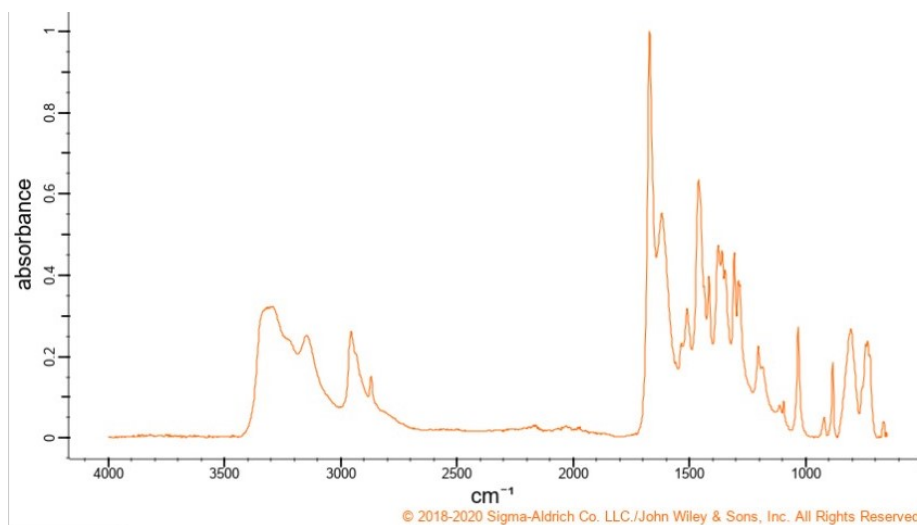
## 3 Pro League

### 3.1 Problem A. Little Ian's trips

Little Ian the Chemist was working part-time in an analytical chemistry lab. He was assigned to work at the Janitis Gas Analyzer machine. The Janitis Gas Analyzer machine works in the following manner: First, the gases being analysed get pumped into a tube filled with anhydrous calcium chloride. The gases which pass through the calcium chloride get bubbled into three sequential Drechsel gas bottles filled with concentrated aqueous barium hydroxide. The remaining gas is ejected outside and the volume of the gas being ejected is measured as well as its density. Little Ian asked his girlfriend Johanna to inhale the gases ejected because their fume hood is malfunctioning. Recently, a sample confiscated from an illegal laboratory was delivered to the lab for Ian to analyse. It contained a single compound consisting of carbon, hydrogen, oxygen and one more element we'll call element Z. We'll refer to this molecule as compound X. Little Ian conducted the following test to determine the molecular formula of compound X: After orally ingesting a few grams of the substance, bewildered by his curiosity, he took 6.825g of compound X and burned it in a sealed flask. Then, the hot gases produced by the reaction were pumped into the Janitis Gas Analyzer machine. Little Ian has noted down that the Janitis Gas Analyzer machine ejected 3.59L of a gas with a density of  $1.2525\text{kg}\cdot\text{m}^{-3}$  at a pressure of 755 Torr at a temperature of 17C directly into Johanna's lungs. (Assume this gas is an ideal gas) Then, Little Ian took apart the Janitis Gas Analyzer and weighed the calcium chloride inside. The weight of calcium chloride after passing the gases through it was 60.225g. Because he forgot to weigh the anhydrous calcium chloride before putting it inside the Janitis Gas Analyzer, Little Ian dissolved the calcium chloride in water and added sodium carbonate until a precipitate stopped forming. He filtered off and dried the precipitate, its mass being 50.000g. Then, Little Ian took apart the Drechsel bottles with aqueous barium hydroxide while noting that the solution in the first and second jars was opaque. He filtered all the solutions from the Drechsel jars and heated the precipitate collected at 1800C during the night. Afterwards, the treated precipitate was dissolved in 2L of water, forming a solution with pH 13.48. Neglect the change of density of the solution as well as the mass of water spent in the reaction.

The IR spectrum of compound X:





Assume that all reactions have 100% yield and every gas that can be absorbed by a compound inside the Janitis Gas Analyzer is fully absorbed.

*A-1 Determine the element called element Z.*

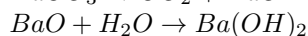
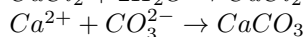
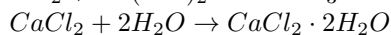
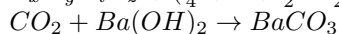
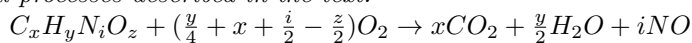
First, we determine the molar mass and the chemical formula of the gas being ejected.

To calculate the molar mass we must recall that  $\rho = \frac{m}{V} = \frac{M \cdot n}{V}$ . Thus, the easiest way to tackle this problem is to calculate its molar mass from the ideal gas equation.

$$pV = nRT \quad M = \frac{\rho \cdot RT}{p}$$

By inserting the numbers we obtain:  $M = \frac{1.25 \cdot 8.314 \cdot 290}{755 \cdot 133} = 0.030 \text{ kg/mol}$  This corresponds either to ethane  $C_2H_6$  or nitrogen monoxide,  $NO$ . It is quite obvious that ethane can not form as a combustion product, thus the gas is nitrogen monoxide  $NO$  and element Z is nitrogen  $N$ .

*A-2 Write down all the 6 balanced reaction equations that describe the chemical processes described in the text.*



*A-3 Calculate the molecular formula of compound X.*

From the ideal gas equation, we determine the amount of  $NO$  produced on combustion. It comes equal to 0.150 mol.

Next, let us determine the mass and amount of hydrogen that was present in the compound. We know that the calcium chloride absorbed the water that was produced on combustion of compound X. To determine the initial mass of the compound, we first determine the amount of moles of calcium chloride present in the Janitis Gas Analyzer.

$$n_{CaCO_3} = \frac{m_{CaCO_3}}{M_{CaCO_3}}$$

Thus,  $n_{CaCO_3} = \frac{50.00}{100} = 0.5 \text{ mol}$ , and due to stoichiometry  $n_{CaCO_3} = n_{CaCl_2} = 0.5 \text{ mol}$ . And the mass of anhydrous calcium chloride Little Ian inserted in the machine is equal to  $0.5 \cdot 111 = 55.5 \text{ g}$ . From this, we determine the amount of water vapour absorbed by calcium chloride, it is equal to the difference between the factual mass of calcium chloride Little Ian collected and the mass of pure calcium chloride.  $m_{H_2O} = 60.225 - 55.50 = 4.725 \text{ g}$ . Converting into moles,  $n_{H_2O} = \frac{4.725}{18} = 0.2625 \text{ mol}$ . This correlates to  $0.525 \text{ mol}$  of hydrogen atoms in the compound X sample. Then, we determine the amount of carbon atoms in the system. To do this, we need to determine the amount of carbon dioxide absorbed by the barium hydroxide solution.

$$pH = -\log[H^+] \quad K_W = [H^+] \cdot [OH^-] \quad [OH^-] = \frac{n_{OH^-}}{V_{solution}}$$

By using these equations, we determine  $n_{CO_2}$  produced:  $[OH^-] = 10^{-14} - 13.48 = 0.300M$ , and thus  $n_{BaO} = 0.300 \text{ mol}$  and  $n_{CO_2} = n_{BaO} = 0.300 \text{ mol}$ . Using simple logic, we conclude that the amount of carbon atoms in the sample equals  $0.300 \text{ mol}$ . To determine the amount of oxygen in the sample, we subtract the mass of hydrogen, nitrogen and carbon atoms from the total mass of the sample—the rest must be oxygen atoms!  $m_{O_2} = 6.825 - 12 \cdot 0.300 - 1 \cdot 0.525 - 0.150 \cdot 14 = 0.600 \text{ g}$ . This, in turn, corresponds to  $\frac{0.600}{16} = 0.0375 \text{ mol}$ .

We obtain the following mole ratio for the compound:  $C : H : N : O = 0.300 : 0.525 : 0.150 : 0.0375$ . By dividing the ration by the smallest factor,  $0.0375$ , we obtain:  $C : H : N : O = 8 : 14 : 4 : 1$ . And, the simplest molecular formula of compound X comes up to be  $C_8H_{14}N_4O$ .

*A-4 Calculate the degree of unsaturation of compound X.*

Degree of unsaturation is calculated using the following formula:

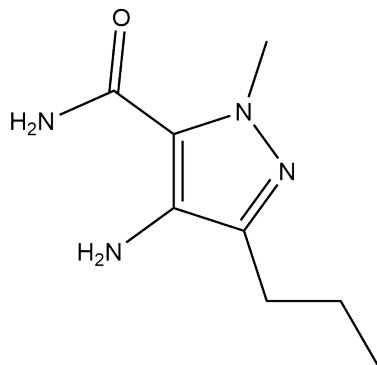
$$DOS = \frac{2C + 2 + N - H}{2} = \frac{16 + 2 + 4 - 14}{2} = 4$$

*A-5 Determine the functional groups present in compound X.*

From the IR spectra of compound X it must contain a carbonyl group due to the stretch at  $1650 \text{ cm}^{-1}$ . Thus, the broad band at  $3000 \text{ cm}^{-1}$  must belong to a hydrogen-bonded OH or NH group, but because there is only one oxygen

atom in the molecule (and it is already located in the carbonyl group), it comes up to be an amine group.

*Author's note: compound X is actually a precursor to the drug Viagra, and for information's sake its structural formula looks like this:*



As you see, there are amine groups and an amide carbonyl present in the molecule.

Little Ian also was given a sample with the molecular formula  $C_6H_8N_2O_2S$ . The compound will be referred to as compound Y. Little Ian carried out another Janitis Gas Analyzer test but he was very hungry and ate the piece of paper where all the experimental data collected was recorded. The only information Little Ian could recall was the mass of compound Y being combusted: 5.160g. But, he still somehow needs to file the lab report, so he decided to estimate the data he should have collected using calculations.

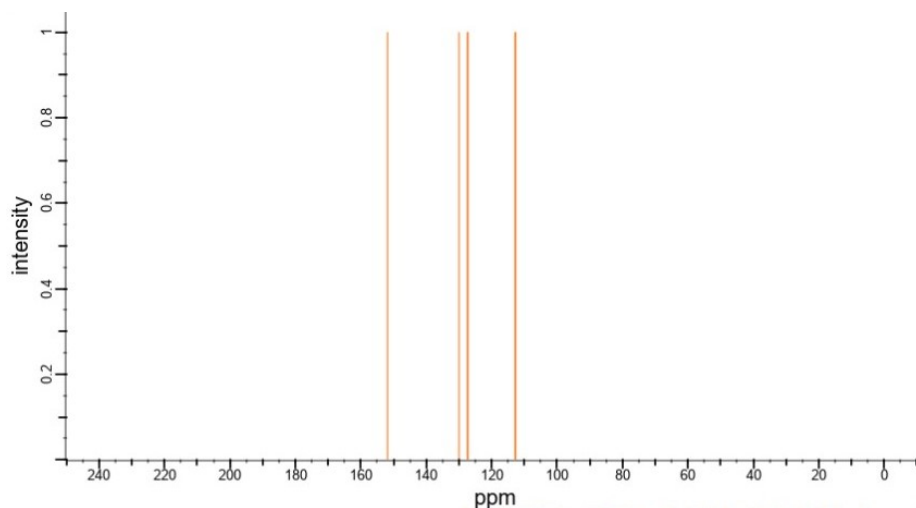
*A-6 Calculate the volume and density of the gas that will be ejected from the Janitis Gas Analyzer after the experiment at the same temperature and pressure as in the first experiment.*

*A-7 Calculate the pH of the solution that will be formed from the precipitate in the Drechsel bottles after Little Ian conducted the Janitis Gas Analyzer experiment.*

The ejected gas will still be nitrogen monoxide, its density unchanged-1.2525 kg/m<sup>3</sup>.

The amount of nitrogen monoxide will be double the amount of compound Y. The amount of compound Y is equal to  $\frac{5.160}{6 \cdot 12 + 8 + 2 \cdot 14 + 32 + 2 \cdot 16} = 0.030 \text{ mol}$ . Thus, the volume of nitrogen monoxide equals  $\frac{0.030 \cdot 2 \cdot 30}{1.2525} = 1.34 \text{ L}$ . The barium hydroxide will absorb sulfur dioxide and carbon dioxide, thus  $nBaCO_3 = 0.030 \cdot 7 = 0.21 \text{ mol}$  and pH in the barium hydroxide solution will be equal to  $14 + \log(0.21) = 13.32$ .

The <sup>13</sup>C NMR spectrum of compound Y is below.



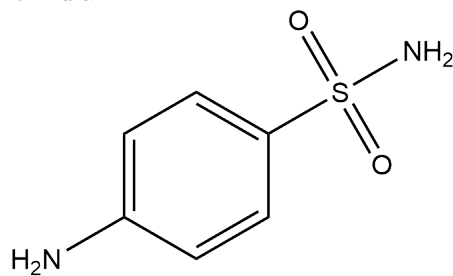
The  $^{13}\text{C}$  NMR spectrum of compound Y.

*A-8 Determine the structural formula of compound Y.*

*A-9 Write a balanced reaction equation describing combustion of compound Y.*

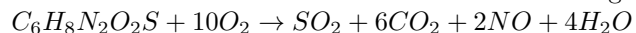
*A-10 How is compound Y being used nowadays?*

From the  $^{13}\text{C}$  NMR shifts we can see that the aromatics are para-substituted and also contain an electron-withdrawing and electron-donating group. Thus, compound Y is a common antiseptic sulfanilamide with the following structural formula:



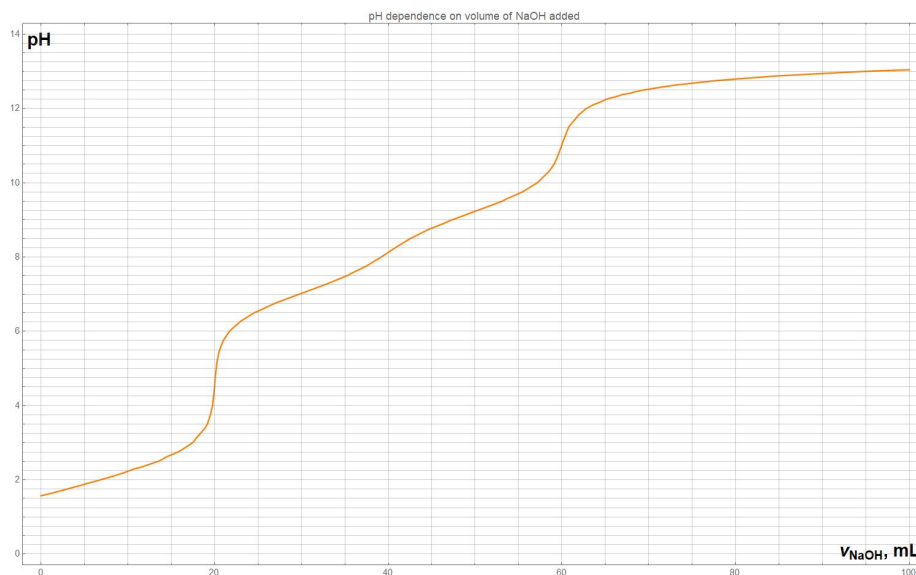
sulfanilamide

The combustion of sulfanilamide can be described using this equation:



On the next day in the lab, a coworker came to Little Ian and asked him to store some of his acid for a period of time. Little Ian agreed, so the coworker gave Little Ian about a kilogram of a compound Little Ian's coworker referred to as "acid". Little Ian wanted to know whether this acid had any interesting properties, so he decided to borrow some of the acid from the jar and to run some experiments. He took 1.42g of the "acid" and dissolved it in 80.00 mL

of deionized water. Then he inserted a pH meter in the solution and started titrating it with 0.500 M aqueous sodium hydroxide. He plotted the pH of the solution against the volume of added base and got the following graph:



He also made a mass spectral analysis of the compound, its mass being 142 g/mol and elemental analysis being O 45.07% H 2.11 % .

*A-11 Determine the molecular formula of the "acid" .*

Let us imagine that we have one mole of the "acid" and calculate the amounts of different elements present in it. In 1 mol of "acid" there are  $\frac{142 \cdot 0.4507}{16} = 4 \text{ mol}$  of O atoms and  $\frac{142 \cdot 0.0211}{1} = 3 \text{ mol}$  of H atoms. This structure reminds of phosphoric acid,  $H_3PO_4$ . Let us calculate the mass of the non-hydrogen or oxygen atom(-s) in the molecule.  $m = 142 \cdot (1 - 0.4507 - 0.0211) = 75 \text{ g}$ . If we check whether there are elements with an atomic mass of 75, we discover that arsenic is a viable option. Even more, arsenic acid  $H_3AsO_4$  is a stable compound. Thus, the "acid" is arsenic acid  $H_3AsO_4$

*A-12 Indicate all the stoichiometric points on the titration curve.*

Stoichiometric points are reached when the acid and base are mixed equimolarly for each proton in the acid. First, calculate the amount of arsenic acid in the solution:  $n = \frac{1.42}{142} = 0.01 \text{ mol}$ . Thus, at the equivalence points the amount of added base is equal to 0.01, 0.02 and 0.03 mol respectively. This, in turn, correlates to  $V_{NaOH} = \frac{0.01}{0.5} = 20 \text{ mL}$ ,  $\frac{0.02}{0.5} = 40 \text{ mL}$  and  $\frac{0.03}{0.5} = 60 \text{ mL}$

*A-13 Derive the expression for the titration curve in terms of the added titrant volume (in mL), pH and other constant values.  $K_w = 1.0 \cdot 10^{-14}$*

First, in order to simplify the formulas, we'll refer to the  $H_3AsO_4$  species as  $H_3A$ , the  $H_2AsO_4^-$  species as  $H_2A$ , the  $HAsO_4^{2-}$  species as  $HA$  and the  $AsO_4^{3-}$  species as  $A$ . Because arsenic acid is weak (you can see it from the graph due to buffering), it has acid dissociation constants. We'll call them  $K_{a1}$ ,  $K_{a2}$  and  $K_{a3}$ . Their expressions are as follows:

$$K_{a1} = \frac{[H_2A] \cdot [H^+]}{[H_3A]} \quad K_{a2} = \frac{[HA] \cdot [H^+]}{[H_2A]} \quad K_{a3} = \frac{[A] \cdot [H^+]}{[HA]}$$

We definitely know that the amount of acid Little Ian added initially is constant, thus we obtain the following equation:

$$n_{H_3AsO_4(\text{initial})} = n_A + n_{HA} + n_{H_2A} + n_{H_3A}$$

We can see that we can not just neglect the change of the volume of the solution (we can, but we still would need to account for it while solving A-16...), so that we can easily switch to concentrations. It is quite obvious that by dividing everything in the equation above by the total volume of the solution we can express the same equation in more convenient terms:

$$[A] + [HA] + [H_2A] + [H_3A] = \frac{n_{\text{initial}}}{V_{\text{initial}} + V_{\text{titrant}}}$$

When we add sodium hydroxide into the solution, we introduce  $Na^+$  ions to the system. The net charge still must remain zero, however. So, we can write this expression to describe it (the coefficients before  $[A]$  and  $[HA]$  are needed because one such ion needs more than one positively charged ion to result in zero net charge):

$$3[A] + 2[HA] + [H_2A] + [OH^-] = [H^+] + [Na^+]$$

Now, we need to express  $[A]$ ,  $[HA]$ ,  $[H_2A]$  and  $[OH^-]$  as functions of  $[H^+]$ . Here, a full calculation for  $[H_2A]$  will be shown,  $[A]$  and  $[HA]$  can be expressed similarly, we will only show the final derived expression. The derivation of these expression is strongly advised as an exercise to the reader.

The derivation proceeds in a following manner:

1. First, express  $[H_3A]$  from the  $K_{a1}$  expression:

$$[H_3A] = \frac{[H_2A] \cdot [H^+]}{K_{a1}}$$

2. Analogically, express  $[HA]$  from the  $Ka_2$  expression:

$$[HA] = \frac{Ka_2 \cdot [H_2A]}{[H^+]}$$

3. A more difficult one, express  $[A]$  by combining the constant expressions:

$$Ka_2 \cdot Ka_3 = \frac{[A] \cdot [H^+]^2}{[H_2A]}$$

And, express  $[A]$  from the expression obtained:

$$[A] = \frac{Ka_2 \cdot Ka_3 \cdot [H_2A]}{[H^+]^2}$$

4. Substitute the obtained species concentration expressions into the total concentration equation:

$$\frac{Ka_2 \cdot Ka_3 \cdot [H_2A]}{[H^+]^2} + \frac{Ka_2 \cdot [H_2A]}{[H^+]} + [H_2A] + \frac{[H_2A] \cdot [H^+]}{Ka_1} = \frac{n_{initial}}{V_{initial} + V_{titrant}}$$

5. We see that  $[H_2A]$  can be taken out of the left part as a common factor, and, by dividing both sides of the equation with the other factor, we obtain:

$$[H_2A] = \frac{\frac{n_{initial}}{V_{initial} + V_{titrant}}}{1 + \frac{Ka_2}{[H^+]} + \frac{[H^+]}{Ka_1} + \frac{Ka_2 \cdot Ka_3}{[H^+]^2}}$$

Analogically, following expressions can also be obtained:

$$[A] = \frac{\frac{n_{initial}}{V_{initial} + V_{titrant}}}{1 + \frac{[H^+]}{Ka_3} + \frac{[H^+]^2}{Ka_3 \cdot Ka_2} + \frac{[H^+]^3}{Ka_3 \cdot Ka_2 \cdot Ka_1}}$$

$$[HA] = \frac{\frac{n_{initial}}{V_{initial} + V_{titrant}}}{1 + \frac{Ka_3}{[H^+]} + \frac{[H^+]}{Ka_2} + \frac{[H^+]^2}{Ka_2 \cdot Ka_1}}$$

The concentration of hydroxide ions can be calculated very easily, knowing the concentration of proton species.

$$[OH^-] = \frac{Kw}{[H^+]}$$

And, the concentration of sodium ions is simply equal to  $\frac{n_{Na^+}}{V_{solution}}$ , or:

$$[Na^+] = \frac{c_{NaOH} * V_{titrant}}{V_{titrant} + V_{initial}}$$

Finally, by substituting everything into the zero net charge equation, we obtain the titration curve equation:

$$\frac{c_{NaOH} * V_{titrant}}{V_{titrant} + V_{initial}} + [H^+] = 3 \cdot \frac{\frac{n_{initial}}{V_{initial} + V_{titrant}}}{1 + \frac{[H^+]}{K_{a3}} + \frac{[H^+]^2}{K_{a3} \cdot K_{a2}} + \frac{[H^+]^3}{K_{a3} \cdot K_{a2} \cdot K_{a1}}} + 2 \cdot \frac{\frac{n_{initial}}{V_{initial} + V_{titrant}}}{1 + \frac{K_{a3}}{[H^+]} + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a2} \cdot K_{a1}}} + \frac{\frac{n_{initial}}{V_{initial} + V_{titrant}}}{1 + \frac{K_{a2}}{[H^+]} + \frac{[H^+]}{K_{a1}} + \frac{K_{a2} \cdot K_{a3}}{[H^+]^2}} + \frac{K_w}{[H^+]}$$

A-14 Indicate the region of the curve where Little Ian's acid is predominantly in its free form (fully protonated).

A-15 Determine the  $pK_a$ (-s) and the acid constant(-s) for the "acid" using the graph. Indicate the points on the graph you used to determine the  $pK_a$ (-s) and explain why you chose them.

In the areas between the equivalence points (e.g.  $25 < V_{titrant} < 35$ ) we can approximate the behaviour of the acid species using the buffer equation. Thus,

$$pH = pK_{a1} + \log \left( \frac{[H_2A]}{[H_3A]} \right)$$

for  $V_{titrant} < 20 \text{ mL}$  If  $[H_3A] > [H_2A]$  the logarithm sign is negative, than we conclude that  $H_3A$  is the major species when  $pH < pK_{a1}$ , and the  $pK_{a1}$  value can be determined like this:

The easiest way to simplify the buffer equation is to make the log term equal zero. This is achieved when  $[H_3A] = [H_2A]$ . Then, we obtain:

$$pH = pK_a \quad \text{if } [H_3A] = [H_2A]$$

By simple calculations, we obtain that this equation is true when  $V_{titrant} = 10 \text{ mL}$ . Thus, the free acid is predominant in the region  $V_{titrant} \in [0, 10) \text{ mL}$ .

By the method earlier described we can obtain all three  $pK_a$  values with a decent level of precision:

- $pK_{a1} = 2.25$  - the point taken was  $V_{titrant} = 10 \text{ mL}$ .
- $pK_{a2} = 7.00$  - the point taken was  $V_{titrant} = 30 \text{ mL}$ .
- $pK_{a3} = 9.25$  - the point taken was  $V_{titrant} = 50 \text{ mL}$ .

We can also calculate the acid constants for the acid:

$$K_a = 10^{-pK_a}$$

Thus,

- $K_{a1} = 5.62 \cdot 10^{-3}$
- $K_{a2} = 1.00 \cdot 10^{-7}$



- $Ka_3 = 5.62 \cdot 10^{-10}$

A-16 Which changes could be observed in the titration curve if Little Ian used ammonium hydroxide of the same concentration rather than sodium hydroxide?  $Ka_{NH_4^+/NH_3} = 5.6 \cdot 10^{-10} = Kb$

Ammonium hydroxide is a weak base, thus the titration curve peaks would be less visible. Also, ammonium hydroxide is not strong enough to take the last proton off the hydroarsenate ion, thus only two peaks will be visible in the titration curve.

A-17 Derive the formula for the titration curve of the same sample of Little Ian's acid with 0.500M aqueous ammonium hydroxide in terms of  $V_{NH_3 \cdot H_2O}$ ,  $V_{initial}$ ,  $Ka_n$ ,  $Kb$  and pH. Do not ignore the change of the volume of the solution.  $Kw=1.0 \cdot 10^{-14}$

We have already expressed the titration curve of sodium hydroxide. If we write down the equation of the zero net total charge, the only species that is changed is the ammonium ion species. Thus, we only need to derive a few equations to describe the dependence of ammonium ion concentration as a function of pH.

First of all, we have the fact that the total sum of ammonium species concentration is equal to the amount of ammonia added:

$$[NH_4^+] + [NH_3] = \frac{n_{NH_3 \cdot H_2O}(initial)}{V_{initial} + V_{titrant}}$$

We also have the expression for  $Kb$ :

$$Kb = \frac{[NH_3] \cdot [H^+]}{[NH_4^+]}$$

By expressing  $[NH_3]$  from the constant and substituting into the ammonia net amount expression, we obtain

$$[NH_4^+] + \frac{Kb \cdot [NH_4^+]}{[H^+]} = \frac{n_{NH_3 \cdot H_2O}(initial)}{V_{initial} + V_{titrant}}$$

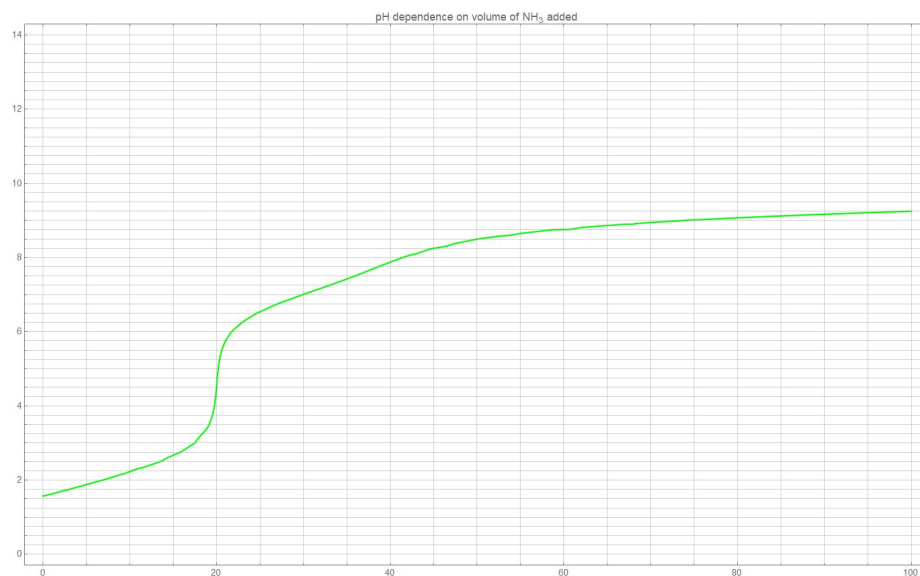
From this equation we can express  $[NH_4^+]$  in a similar fashion to the expression of  $[H_2A]$  :

$$[NH_4^+] = \frac{\frac{c_{NH_3 \cdot H_2O} \cdot V_{titrant}}{V_{initial} + V_{titrant}}}{1 + \frac{Kb}{[H^+]}}$$

And, finally, we can substitute  $[NH_4^+]$  instead of  $[Na^+]$  in the titration curve expression obtained in A-13:

$$\begin{aligned} \frac{\frac{c_{NH_3 \cdot H_2O} \cdot V_{titrant}}{V_{initial} + V_{titrant}}}{1 + \frac{Kb}{[H^+]}} + [H^+] &= 3 \cdot \frac{\frac{n_{initial}}{V_{initial} + V_{titrant}}}{1 + \frac{[H^+]}{Ka_3} + \frac{[H^+]^2}{Ka_3 \cdot Ka_2} + \frac{[H^+]^3}{Ka_3 \cdot Ka_2 \cdot Ka_1}} + \\ + 2 \cdot \frac{\frac{n_{initial}}{V_{initial} + V_{titrant}}}{1 + \frac{Ka_3}{[H^+]} + \frac{[H^+]}{Ka_2} + \frac{[H^+]^2}{Ka_2 \cdot Ka_1}} &+ \frac{\frac{n_{initial}}{V_{initial} + V_{titrant}}}{1 + \frac{Ka_2}{[H^+]} + \frac{[H^+]}{Ka_1} + \frac{Ka_2 \cdot Ka_3}{[H^+]^2}} + \frac{Kw}{[H^+]} \end{aligned}$$

*Just to show the difference, I plotted the graph of this curve. You can see that the slope is less steep and one equivalence point is missing. The y axis is the pH value of the solution, the x axis represents the volume of titrant added (in mL).*



Little Ian and another coworker Robert were incredibly bored during the working day in the lab. So they decided to play a chemistry guessing game while waiting for a synthesis to finish. The game has the following rules: Little Ian took some of the “acid” he obtained earlier and dissolved it in water. Afterwards he poured in a random amount of base and measured the pH of the formed solution. Then Little Ian and Robert took guesses to determine which species of the acid is dominant at these conditions. The loser paid the canteen bill for the both, so the stakes were high. Little Ian wanted to prepare himself so he calculated a formula that’d allow him to win.

*A-18 Derive the formulas that express molar fractions of each component in*

the mixture in terms of pH and acid constant(-s) for the “acid”. Ignore water autoprotolysis in this question.

A-19 Determine which species will be predominant in Little Ian’s solution at:

- pH 4.75
- pH 7.5
- pH 9.8
- pH 1

Solving this problem is very easy if you have managed to solve the previous ones. We suggest the readers to try and solve it on their own using the titration curve equation derived earlier before looking at the solution.

The molar fraction of a species is represented using this formula:

$$X_A = \frac{n_A}{n_{mixture}}$$

In our case, we have already calculated the concentrations of three acid species out of four as a function of pH. We also need to express the concentration of the  $H_3A$  species in a similar manner. Again, we strongly advise that the readers try and derive expression themselves as an exercise by using the  $[H_2A] = f(pH)$  derivation shown above. The final expression obtained for  $[H_3A]$  is equal to:

$$[H_3A] = \frac{\frac{n_{initial}}{V_{initial} + V_{titrant}}}{1 + \frac{Ka_1}{[H^+]} + \frac{Ka_1 \cdot Ka_2}{[H^+]^2} + \frac{Ka_1 \cdot Ka_2 \cdot Ka_3}{[H^+]^3}}$$

Let us try to calculate  $X_{H_3A}$ . From the definition,

$$n_{H_3A} = \frac{n_{initial}}{1 + \frac{Ka_1}{[H^+]} + \frac{Ka_1 \cdot Ka_2}{[H^+]^2} + \frac{Ka_1 \cdot Ka_2 \cdot Ka_3}{[H^+]^3}}$$

and by substituting into the molar fraction definition,

$$X_{H_3A} = \frac{1}{1 + \frac{Ka_1}{[H^+]} + \frac{Ka_1 \cdot Ka_2}{[H^+]^2} + \frac{Ka_1 \cdot Ka_2 \cdot Ka_3}{[H^+]^3}}$$

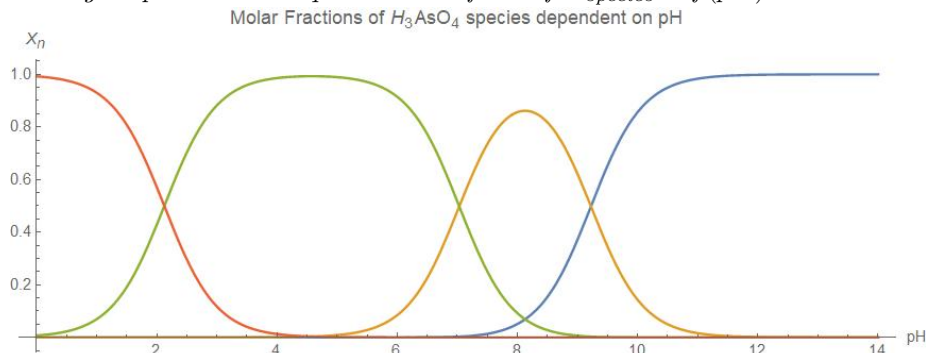
Analogically, we can express:

$$X_A = \frac{1}{1 + \frac{[H^+]}{Ka_3} + \frac{[H^+]^2}{Ka_3 \cdot Ka_2} + \frac{[H^+]^3}{Ka_3 \cdot Ka_2 \cdot Ka_1}}$$

$$X_{HA} = \frac{1}{1 + \frac{Ka_3}{[H^+]} + \frac{[H^+]}{Ka_2} + \frac{[H^+]^2}{Ka_2 \cdot Ka_1}}$$

$$X_{H_2A} = \frac{1}{1 + \frac{Ka_2}{[H^+]} + \frac{[H^+]}{Ka_1} + \frac{Ka_2 \cdot Ka_3}{[H^+]^2}}$$

I again plotted those equations in a form of  $X_{species} = f(pH)$



We can determine the dominant species either by solving the full molar fraction equations (which, of course, is stupid) or by using the buffer equation which is a good approximation here:

$$pH = pKa + \log \left( \frac{[A]}{[HA]} \right)$$

From the buffer equation, species predominance can be divided like this:

1.  $H_3AsO_4$  if  $pH \in [0; 2.25)$
2.  $H_2AsO_4^-$  if  $pH \in (2.25; 7)$
3.  $HAsO_4^{2-}$  if  $pH \in (7; 9.25)$
4.  $AsO_4^{3-}$  if  $pH \in (9.25; 14]$

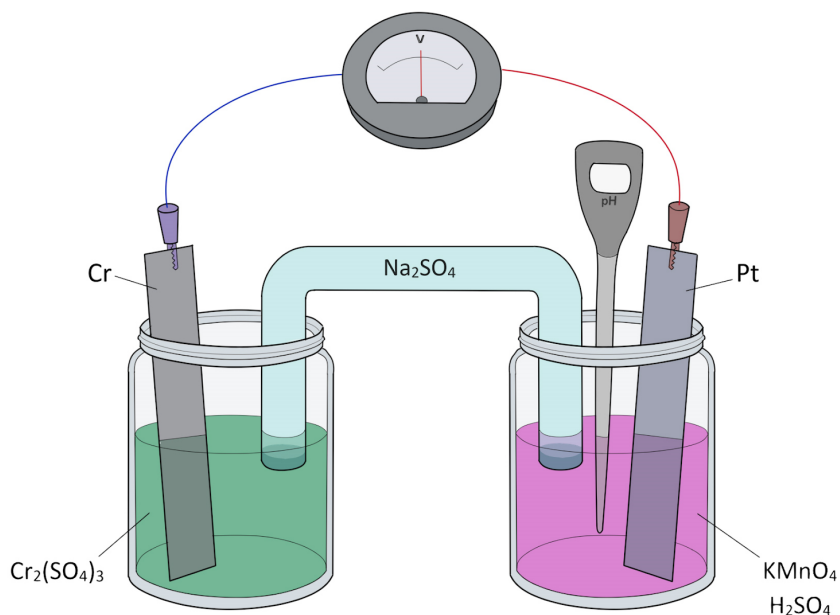
And, by correlating pH to the dominant species, we obtain the following answers:

- pH 4.75- $H_2AsO_4^-$
- pH 7.5- $HAsO_4^{2-}$
- pH 9.8- $AsO_4^{3-}$
- pH 1- $H_3AsO_4$

### 3.2 Problem B. Colour becomes Power

Nauris the Chemist was very busy with grading National Olympiad papers for the whole night. Exhausted, in the morning he decided that he was fed up with working for the Government and began scheming a coup. To overthrow the Government, he needed to gain political power, but with great power comes great responsibility, so he first wanted to try his hands on the power in a galvanic cell. Help him prepare for surveilling the Government's inner affairs as an

outsider by analyzing a device he stole from his student Anastasia the Pickle.



The device consists of two previously emptied pickle jars with solutions of potassium permanganate in sulfuric acid and chromium (iii) sulfate. In the respective pickle jars, a platinum electrode and a chromium electrode are inserted. The jars are connected by a sodium sulfate salt bridge. A voltmeter is connected with its “-” pin to the chromium electrode and to the platinum electrode with its “+” pin. Also, a pH meter is submerged into the pickle jar containing acidified potassium permanganate. Nauris was so angry at the Government that his hands were shaking and he managed to spill some manganese (ii) sulfate solution into the permanganate pickle jar so that the concentration of  $Mn^{2+}$  in the pickle jar became 0.05M.

Some electrochemical redox potentials that might be useful in the task.

| Redox pair        | $E_{red}^0$ , V |
|-------------------|-----------------|
| $Cr^{3+}/Cr^0$    | -0.74           |
| $H^+/H_2$         | 0.00            |
| $MnO_4^-/Mn^{2+}$ | +1.51           |
| $H_2O/H_2, OH^-$  | -0.83           |
| $O_2, H^+/H_2O$   | +1.23           |

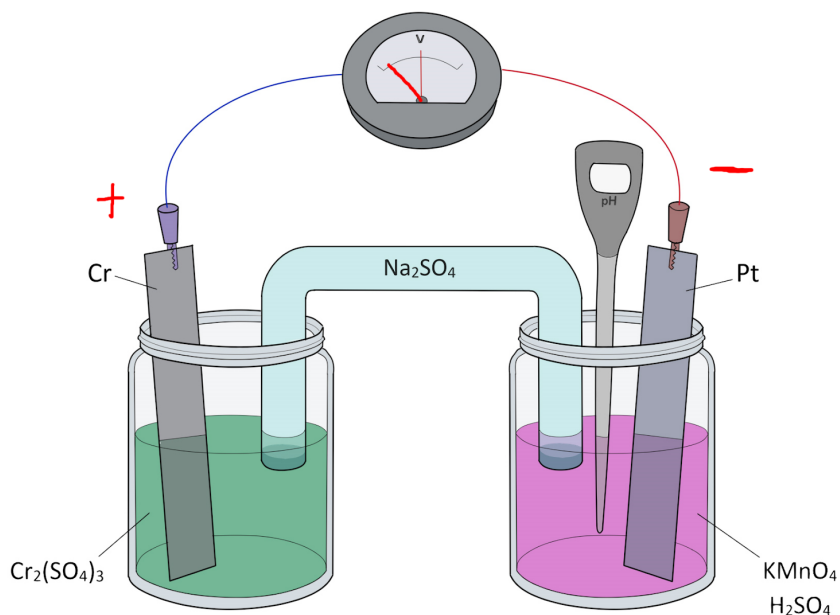
B-1 Determine the direction the voltmeter arrow will turn when the voltmeter

is connected to the pickle jars. Assume that it'd turn opposite to the direction of the electron flow in the circuit.

B-2 Determine the cathode and the anode of the galvanic cell. Indicate the galvanic cell's polarity by drawing a "+" and a "-" sign at the corresponding electrodes.

The electrons flow from the anode to the cathode. The cathode is the electrode where reduction occurs, thus it must be the platinum/permanganate electrode.

The anode is the electrode where oxidation occurs, and it is the chromium electrode, thus the voltmeter arrow will turn counterclockwise.

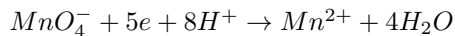


B-3 Write the anode and the cathode half-reactions occurring in the galvanic cell and calculate its standard potential.

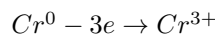
B-4 Write the cell's total net reaction equation.

B-5 Write Nauris's cell's structural formula using common cell notation (e.g.  $Ag(s)|AgNO_3(aq)||CuSO_4(aq)|Cu(s)$ )

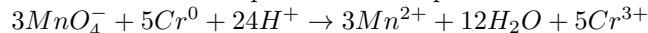
On the cathode, reduction of permanganate ions occurs. The half reaction is as follows:



On the anode, the oxidation of chromium metal happens. The half reaction is as follows:



The total reaction equation comes up to be:



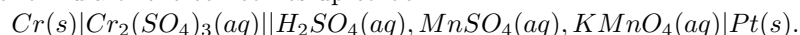
The standard potential of the cell is calculated using this formula:

$$E_{cell}^0 = E_{red}^0 + E_{ox}^0$$

In our case,

$$E_{cell}^0 = 0.74 + 1.51 = +2.25 V$$

The galvanic cell notation uses the | symbol to represent phase boundaries and the || symbol to represent a salt bridge between two separated cells. Thus, the formula of the cell comes up to be



Nauris wanted to determine the concentration of chromium in the jar filled with the green solution. He took a 10mL sample of the green solution in one of the pickle jars, diluted it to 100mL and decided to carry out a photometric titration using EDTA. First, in a 2cm cuvette a sample containing 0.055M  $Cr^{3+}$  an excessive amount of EDTA and acid to pH 4.0 was added by Nauris, the absorption at  $18350\text{ cm}^{-1}$  was equal to 22. Assume that the samples follow the Lambert-Beer absorption law. Then Nauris added an excess of EDTA to his sample, waited until the colour completely changed and also measured the absorbance. The absorbance reading of the sample Nauris collected from the green solution in the galvanic cell and diluted was equal to 8.

*B-6 Calculate the molar absorption coefficient of the  $Cr^{3+}/EDTA$  complex.*

*B-7 Calculate the concentration of  $Cr^{3+}$  in the green solution.*

From the Lambert-Beer law,

$$A = \epsilon lc$$

we can determine the molar absorption coefficient of the  $Cr^{3+}/EDTA$  complex simply by substituting in the numbers.

$$\epsilon = \frac{22}{0.055 \cdot 2} = 200\text{ M}^{-1} \cdot \text{cm}^{-1}$$

And the concentration of the green solution then comes up to be:

$$c = \frac{8}{2 \cdot 200} \cdot 10 = 0.2\text{ M}$$

The  $Cr^{3+}/EDTA$  complex absorbs at two wavelengths: it has a very strong and broad absorption band at  $18350\text{ cm}^{-1}$  and slight absorption at  $25000\text{ cm}^{-1}$ .

*B-8 Estimate the color of the  $Cr^{3+}/EDTA$  complex.*

To determine the wavelength of the absorption band the following formula is used:

$$\lambda = \tilde{\nu}^{-1}$$

And the absorption wavelengths come up to be 545 nm and 400 nm.

The strongest absorption is at 545 nm which corresponds to green, thus the color of the  $Cr^{3+}/EDTA$  complex is violet.

Then, Nauris recorded the readings of the pH meter. The pH in the permanganate solution was reported to be 2.00. After that he connected the electrodes with a nichrome wire, thus closing the electrical circuit and resonating with the anticipation of his political power. The galvanic cell produced an electromotive force of 2.085 V.

*B-9 Calculate the concentration of permanganate ions in the galvanic cell. Assume that the reaction happens at  $T=298K$ .*

The Nernst equation for Nauris' cell is as follows:

$$E = E^0 - \frac{RT}{zF} \ln \left( \frac{[Cr^{3+}]^5 \cdot [Mn^{2+}]^3}{[MnO_4^-]^3 \cdot [H^+]^{24}} \right)$$

From which the permanganate ion concentration is expressed as:

$$[MnO_4^-] = \sqrt[3]{e^{-\frac{zF}{RT} \cdot (E^0 - E)} \cdot \frac{[Cr^{3+}]^5 \cdot [Mn^{2+}]^3}{[H^+]^{24}}}$$

And, by substituting the numbers we obtain  $[MnO_4^-] = 0.38 M$

Nauris left the circuit working until the reaction fully stopped. The reaction stopped after 2h 24min because the chromium electrode fully dissolved, its mass being 1.56g. We can assume that the whole reaction occurred with a constant voltage  $V=2V$ . Now Nauris wants to determine the amount of power in his hands.

*B-10 Calculate the current in the galvanic cell electrical circuit during the process.*

The amount of chromium dissolved equals  $\frac{1.56}{52} = 0.03 mol$ , thus the current through the wire equals  $\frac{z \cdot n \cdot F}{t} = \frac{0.03 \cdot 3 \cdot 96485}{8640} = 1 A$ .

*B-11 Calculate the power of the galvanic cell (in W) and the total work made by the galvanic cell (in J).*

Assuming that the potential of the cell was constant, we can determine the power of the cell:

$$P = V \cdot I = 2 W$$

And the work can be determined as follows:

$$w = \int_0^t P(t) dt = P \cdot t = 17.28 kJ$$



The remaining permanganate solution Nauris transferred into an Erlenmeyer flask and started titrating it with an acidified 1M  $H_2O_2$  solution. He required 31.00 mL of the titrant until he reached the end point of titration.

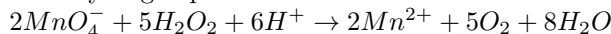
*B-12 Why didn't Nauris add an indicator while titrating? How did he determine the titration endpoint?*

*B-13 Write the reaction equation for the titration process.*

*B-14 Calculate the initial volume of the permanganate solution in the galvanic cell.*

Permanganometric titration does not need an indicator because the endpoint is determined by the discoloration of the permanganate solution.

The reaction equation describing titration of potassium permanganate with acidified hydrogen peroxide is as follows:



The initial volume of the solution is determined using its concentration.

First, the galvanic cell consumed  $0.03 \cdot \frac{3}{5} = 0.018 \text{ mol}$  of permanganate ions in the initial solution.

Then, the rest of the permanganate was titrated, the amount of permanganate being  $0.031 \cdot 1 \cdot \frac{2}{5} = 0.0124 \text{ mol}$ , and the total amount of permanganate thus comes up to be  $0.018 + 0.0124 = 0.0304 \text{ mol}$ . This, in turn, correlates to  $\frac{0.0304}{0.38} \cdot 1000 \text{ mL} = 80.00 \text{ mL}$  of the permanganate solution.

Nauris also wanted to try and recharge his galvanic cell by connecting it to a DC power supply in reverse polarity. This would allow him to control even more electric (and hopefully, political) power.

*B-15 Will Nauris be able to recharge his galvanic cell? Prove it by writing the cathode and anode half-reaction equations as well as the total reaction equation.*

No, he will not be able to do so. On the cathode the most electrochemically viable reduction will occur, that is a mixture of the hydrogen reduction reaction and the chromium reduction reaction  $Cr^{3+} + 3e \rightarrow Cr^0$ . On the anode, the most viable oxidation is the oxidation of water (its potential is larger), thus the anode reaction will be  $2H_2O - 4e \rightarrow O_2 + 4H^+$ .

The total reaction equation comes up to be  $4Cr^{3+} + 6H_2O \rightarrow 12H^+ + 3O_2$ .

*B-16 How is the electrochemical process that Nauris decided to carry out called?*

This electrochemical process is called electrolysis.

### 3.3 Problem C. Elements go bang

Little Ian recently was occupied in an Inorganic Chemistry lab. There, his girlfriend Johanna the Inorganic Chemist told him about some very cool element we'll refer to as element **X**. Little Ian became very interested in element **X**

because of its high psychedelic and destructive abilities. Little Ian took 0.92g of a blue solid **H** and began heating it in a sealed 1L flask filled with argon at 298K. Among the products, Ian collected 0.25g of a black solid. After cooling to 390K, the pressure in the flask went up from 1 bar at the beginning of the experiment to 2.16 bar. **A** was produced during this reaction. **B** is obtained when oxidising compound **E**, which in turn contains 82,35% element **X**. **B** is notable for being a stable free radical. **A** can also be produced on decomposition of oxide **F** which contains 74.07% oxygen. Little Ian let **A** and **B** into a tube filled with dry ice and collected **C**, a bluish liquid. **C** was mixed with sodium hydroxide, producing **D**. Little Ian also prepared another blue compound by dissolving his favourite metal **Y** in **E** in a dry ice bath. Unfortunately, the nice colour disappeared by heating back to room temperature, but at least Little Ian now had compound **G** which contained 58,97% **Y**. Little Ian mixed aqueous **H** with some sodium hydroxide and produced a blue precipitate and a solution of compound **I**. Then Little Ian mixed compounds **I** and **G** and produced the most important intermediate - **J**. **J** was then mixed with aqueous lead(ii) nitrate and produced Little Ian's most favourite compound- **K**. Compounds **J** and **K** are incredibly dangerous because of their toxicity and thermal instability. All of the compounds **A-K** contain element **X**.

*C-1 Determine the molecular formulas of compounds **A-K**, and elements **X** and **Y**.*

A- $NO_2$

B- $NO$

C- $N_2O_3$

D- $NaNO_2$

E- $NH_3$

F- $N_2O_5$

G- $NaNH_2$

H- $Cu(NO_3)_2 \cdot 6H_2O$

I- $NaNO_3$

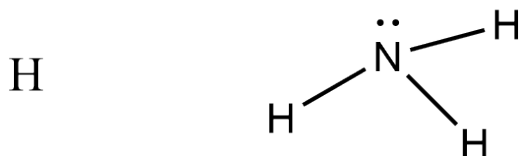
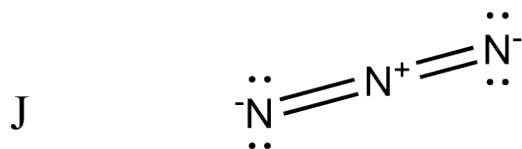
J- $NaN_3$

K- $PbN_6$

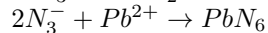
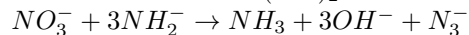
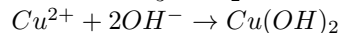
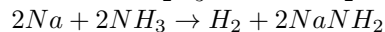
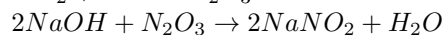
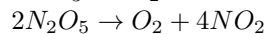
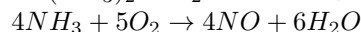
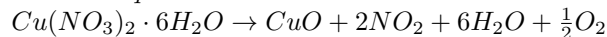
X- $N$

Y- $Na$

*C-2 Draw Lewis dot structures of compound **B** and the anions of **J** and **H**.*



C-3 Write reaction equations describing all the chemical processes in the text. total 9 equations



C-4 Explain why did the blue colour disappear after heating the mixture of **E** and **Y**.

The dissolution of sodium in liquid ammonia produces free electrons. On heating the electrons reduce ammonia, releasing hydrogen. The colour of the solution is due to solvated electrons, thus on heating the solution becomes discoloured because there are no solvated electrons to colour it.

Little Ian also loved element **Z**. It is quite similar in its properties to element **X**, but they still do differ. Element **Z** exists in different allotropes. Little Ian got some unstable and reactive **Z1** which on heating produced **Z2**. Little Ian mixed a bit of **Z** with **Y** and heated them together. The compound **L** produced in the reaction reacts vigorously with some water, producing a gas **M**. **M** burns very well on air, forming **O**. **O** is also formed when **Z1** or **Z2** is burned on air. **O** reacts with water and forms a compound **S** with 3,06% hydrogen. Little Ian mixed some **Z** with chlorine and received two different products **P** and **R**, with

22,55% **Z** and 14,87% **Z** respectively. **P** is not really stable on air, it produces **Q**. **Q** and **R** react with water and form the same product **S**. **M** can react with hydrogen iodide to form **T**, which is a very unstable compound. **T** can react with iodine and form **N** which contains 10,88% **Z**. **N** can be mixed with **Z1** and be partially hydrolysed, forming **T** and **S**.

*C-5 Determine the molecular formulas of compounds L-T and element Z as well as the allotropes Z1 and Z2.*

L- $Na_3P$

M- $PH_3$

N- $P_2I_4$

O- $P_4O_{10}$

P- $PCl_3$

Q- $POCl_3$

R- $PCl_5$

S- $H_3PO_4$

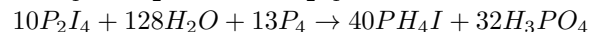
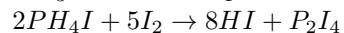
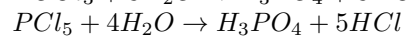
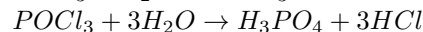
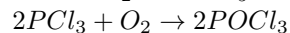
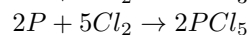
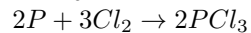
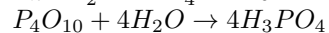
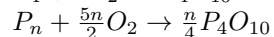
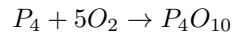
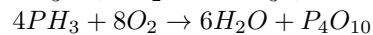
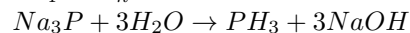
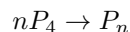
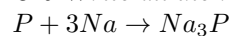
T- $PH_4I$

Z-P

Z1- $P_4$  white phosphorus

Z2- $P_n$  red phosphorus

*C-6 Write all the reaction equations described in the text. total 15 equations*



A multitude of compounds containing **Z** are used very widely in organic synthesis. One of them, the compound with the formula  $ZPh_3$  is used in a multitude of reactions because of **Z**'s very interesting chemical properties.  $ZPh_3$  is used as one of the reagents in the following named reactions:

- A highly stereoselective reaction used to couple acids and alcohols
- A coupling reaction to form olefins

- A substitution reaction to selectively replace hydroxyl groups with halogens

*C-7 Name the reactions mentioned above and briefly describe the reaction conditions, products formed and the reagents needed. (no need for mechanisms)*

The first reaction mentioned is the Mitsunobu Reaction:

- Reagents for coupling: acid, alcohol,  $PPh_3$  and DEAD
- Products:  $PPh_3O$ , ester,  $EtO_2C - NH - NH - CO_2Et$
- also works with other substrates, e.g. thiols
- Inverse stereoselectivity

The second reaction mentioned is the Wittig Reaction:

- Reagents for coupling: carbonyl compound, phosphonium ylide  $R - (C^- - P^+ Ph_3) - R'$
- Products: olefin,  $PPh_3O$
- Modifications exist such as the Horner-Wadsworth-Emmons Olefination
- Stereochemistry depends on the nature of the substrate -stabilised ylides are E-selective, others are Z-selective

The third reaction is the Appel Reaction:

- Reagents: alcohol,  $PPh_3$ ,  $CHal_4$
- Products: halogen-substituted molecule,  $CHHal_3$ ,  $PPh_3O$

*C-8 Explain which property of **Z** is the reason for usage of **Z** in such reactions.*

The strength of the P=O bond formed in the reaction is so big that the formation of this bond is the driving force of this reaction.

*C-9 Determine the molecular geometry of compounds **E**, **P** and **R**.*

E-trigonal pyramidal

P-trigonal pyramidal

R-trigonal bipyramidal

### 3.4 Problem D. Amquid Limonia, Liquec Ionid and other MLG

Ross the Amateur Chemist decided to assert his dominance over Little Olavs. To do this, he decided to make Olavs do some experiments in a very strange solvent where chemistry seemed to work wrong. . . . Ross dissolved 2.08g of zinc metal in his "super solvent" as he now calls it. Zinc dissolved in it, producing a gas that occupied 0.79L at 298K and 1 bar (Assume it's ideal). This gas also

had a density of 1.21 g/L. After Ross evaporated the “super solvent” from the flask, he weighed the solid product formed, its mass being 6.048g.

Ross hoped that Olavs would be too confused about the identity of the “super solvent”, but unfortunately Little Olavs was a very skilled Inorganic chemist and he almost immediately figured out the formula of the “super solvent”.

*D-1 Determine the chemical formula of the “super solvent”. It is a binary compound.*

*D-2 Determine the chemical formula of the gas that was produced in the reaction between the “super solvent” and zinc metal. Write down the reaction equation describing that process.*

First, let us determine what was the gas evolved in the reaction. Knowing that  $\rho = \frac{m}{V}$  we can express the density from the ideal gas equation:

$$pV = \frac{m}{M} \cdot RT$$

$$M = \frac{\rho RT}{p}$$

By substituting the numbers in the formula, we obtain  $M = \frac{1.21 \text{ g/L} \cdot 8.314 \cdot 298}{100 \text{ kPa}} = 30 \text{ g/mol}$ . This corresponds either to ethane  $C_2H_6$  or nitrogen monoxide  $NO$ . Nitrogen monoxide seems to be a more viable option.

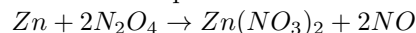
Then, it must be so that the zinc metal is left behind in the solid precipitate. Most probably, the precipitate is some sort of a  $Zn^{2+}$  compound. We can determine the molar mass of the anion because we know it has to correspond to the zinc mole count. Thus, for a compound  $ZnX_a$  we can write down such an equation:

$$\frac{m_{Zn}}{M_{Zn}} = \frac{m_{Compound}}{M_{Zn} + a \cdot M_X}$$

We only need to solve the equation two times, for compounds  $ZnX_2$  and  $ZnX$ .

| Formula | $M_X$ | Possible formula(-s) |
|---------|-------|----------------------|
| $ZnX_2$ | 62    | $Zn(NO_3)_2$         |
| $ZnX$   | 124   | nothing adequate     |

Thus, the compound formed is zinc nitrate  $Zn(NO_3)_2$ . The “super solvent” must thus be a nitrogen oxide. The only nitrogen oxide that could react like this is dinitrogen tetroxide  $N_2O_4$ . It is a dimer of nitrogen dioxide  $NO_2$ , because at a 1 bar pressure  $NO_2$  can not exist in liquid as a monomer. The reaction equation for this process is as follows:



Afterwards, it was Little Olavs’ turn to strike. Little Olavs developed a whole research paper on exotic MLG solvents, so he easily could destroy Ross the Amateur Chemist’s hopes to solve any problem in their chemical duel. As a warming exercise (which Ross already failed, disappointing Olavs by a lot) Little Olavs decided to show Ross some chemistry of quite a famous solvent. Olavs

referred to it as Amquid Limonia. Because Amquid Limonia was not stable at room temperature, Little Olavs used dry ice to keep it chill which is of course not MLG. As the first experiment, Little Olavs carried out an amazing reaction: he dissolved barium nitrate and ammonium chloride in two separate test tubes containing Amquid Limonia and mixed them together. He observed a white precipitate - barium chloride! Also, Little Olavs had added a small portion of Amquid Limonia into water with phenolphthalein added into it, producing a pink solution. Ross the Amateur Chemist could not explain that chemistry that he'd observed. . . . It is known that Little Olavs prepared Amquid Limonia by condensing a gas with a molar mass 17 g/mol.

*D-3 What solvent bears the name of Amquid Limonia?*

Well, it is obvious that the solvent is Liquid Ammonia, hence the word play in its name.

*D-4 Explain how the metathesis reaction Little Olavs carried out could happen in Amquid Limonia if it's impossible in water.*

Ammonium salts are well soluble in liquid ammonia due to them being acids in the medium. Nitrate salts are also soluble because of the strong hydrogen bonding. On the other hand, barium chloride can not bond so well with liquid ammonia molecules, thus it precipitates out of the solution.

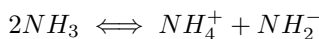
Little Olavs also knew that Amquid Limonia is very similar to water in its chemical properties. For example, it also can undergo autoprotolysis (self-proton exchange) and produce something similar to hydronium and hydroxide ions in aqueous media.

*D-5 Write the reaction equation describing autoprotolysis of Amquid Limonia.*

In water the autoprotolysis reaction is such:



Thinking analogically with liquid ammonia, one of the two molecules loses a proton and becomes negatively charged, and another molecule picks that proton up, forming a cation. We obtain such an equation:



Now, Little Olavs decided to prank Ross even more by forcing him to calculate some acid-base equilibria in Amquid Limonia, threatening to otherwise send a video of Ross struggling to calculate the concentration of water in water to Ross' friend Anastasia, who Ross was secretly admiring. In neutral Amquid Limonia Ross managed to measure that the concentration of the protonated

species was equal to  $10^{-15}$  M.

*D-6 Help Ross calculate the  $K_w$  analogue of Amquid Limonia in order to avoid being humiliated by Little Olavs. Hint:  $K_w$  is equal to the product of the concentration of the protonated species and the deprotonated species in the solvent, for Amquid Limonia it is also true.*

$K_w$  is calculated by using the following formula:

$$K_w = [NH_4^+] \cdot [NH_2^-]$$

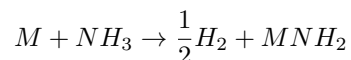
In neutral liquid ammonia no other ions are present. Still, the solution must have a zero net charge, thus  $[NH_4^+] = [NH_2^-]$ . From this, we conclude that

$$K_w = [NH_4^+]^2 = 10^{-30}$$

Phew, Ross finally completed the first task designed by Olavs to destroy Ross in a chemical duel. The next task Olavs gave to Ross was to dissolve his favourite metal in Amquid Limonia, just for fun. Little Olavs gave Ross 1.08g of his favourite metal and forced him to throw it into Amquid Limonia. After some time, they collected a precipitate after evaporating Amquid Limonia directly into the air of the lab (as everybody knows, fume hoods are not MLG enough for Little Olavs), its mass being 5.67g.

*D-7 Determine the chemical formula of Olavs' favorite metal. Do not forget that Olavs still threatens to send videos of Ross failing to solve these problems to Anastasia, the love of Ross' life, and he needs help.*

The reaction of metals with liquid ammonia are well known. Alkali metals produce an alkali metal amide and hydrogen, and less active metals produce metal ammine complexes (*mostly hexacoordinated*). Let us first check the amide formation reaction:

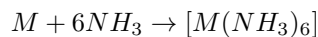


From the stoichiometry of the reaction, we obtain a following equation:

$$\frac{m_{metal}}{M_{metal}} = \frac{m_{amide}}{M_{metal} + 16}$$

By solving the equation, we obtain  $M_{metal} = 3.8$ , thus it is not the amide.

Alkaline earth metals react with liquid ammonia in a different fashion-a hexacoordinated metal ammine complex forms. The reaction is as follows:



From the stoichiometry of the reaction, we obtain the following equation:

$$\frac{m_{metal}}{M_{metal}} = \frac{m_{complex}}{M_{metal} + 102}$$



By solving the equation, we obtain  $M_{metal} = 24$  which corresponds to the alkaline earth metal magnesium. Thus, Olavs' favourite metal is magnesium  $Mg$ .

The next task Ross was given was comparably easy to accomplish. He just needed to prepare the strongest base that could exist in Amquid Limonia.

*D-8 What compound can be the strongest base in the medium of Amquid Limonia?*

In water, the theoretically strongest base is hydroxide ion  $OH^-$ . Thus, in liquid ammonia the strongest base is the amide ion  $NH_2^-$ .

*D-9 Tick the boxes next to the name of the reagents Ross could use to prepare such a solution.*

$NaOH$       $NEt_3$       $N(iPr)_2Li$       $MeLi$   
  $BuLi$       $NaOEt$       $K_2CO_3$       $H_2SO_4$

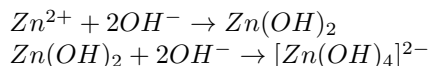
All bases that are stronger than the amide will work. Those are:

- LDA  $LiN(iPr)_2$
- $BuLi$
- $MeLi$

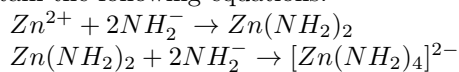
Little Olavs got his hands on two solutions in Amquid Limonia: a solution of zinc nitrate and a basic solution Ross'd prepared earlier. Upon addition of the basic solution to a solution of zinc nitrate a precipitate occurred, which then dissolved again when Olavs added even more base.

*D-10 Write the reaction equations describing this process as well as the equations describing a similar process, but in aqueous medium.*

In water this reaction would work like this:



Thus, knowing that in liquid ammonia the reaction would work similarly, we obtain the following equations:



Sadly, Ross still managed to solve these problems, so Little Olavs decided to present to him a challenge Ross never would be able to solve...

So, Olavs gave Ross a jug of a superacid. This superacid is prepared via the reaction between concentrated hydrogen fluoride and antimony pentafluoride. Olavs considered fluoroantimonic acid to be very MLG because it could dissolve almost anything.

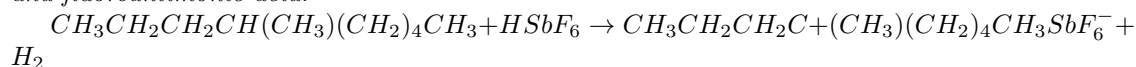
*D-11 Explain why fluoroantimonic acid is so strong.*

The extremely high fluorine affinity of antimony shifts the equilibrium of the reaction  $HF + SbF_5 \rightleftharpoons H^+ + SbF_6^-$  completely to the right. Also, the

counter ion is not nucleophilic.

Olavs then dissolved some 4-methylnonane in the superacid.

*D-12 Write the reaction equation describing the reaction between 4-methylnonane and fluoroantimonic acid.*

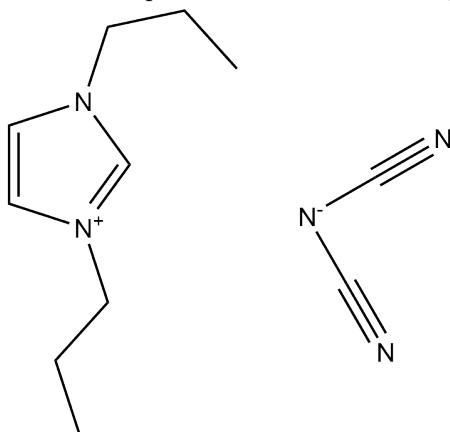


The next compound Ross was forced to work with by Little Olavs was 1,3-dipropylimidazolium dicyanamide. This compound is liquid at room temperature, which makes it very MLG, so it's the reason Olavs liked it so much.

*D-13 Which type of lattice does 1,3-dipropylimidazolium dicyanamide have? Draw the molecular formula of this compound.*

molecular ionic atomic metallic

The compound has an ionic lattice, its structure being:



Little Olavs decided to increase the MLG level in his mixture even more. First, he tried crystallising the compound. He determined that the density of the compound was equal to 1.2 g/mL. The compound formed a cesium chloride-type lattice. We can use the close-packed spheres assumption on this compound.

*D-14 Calculate the parameter of the lattice cell of 1,3-dipropylimidazolium dicyanamide. If you failed to determine its molar mass, assume it is 260 g/mol.*

The cesium chloride lattice contains 1 molecule of a compound. The molecular formula of 1,3-dipropylimidazolium dicyanamide is  $\text{C}_{11}\text{H}_{17}\text{N}_5$ , and its molecular mass is 219 g/mol. Thus, the mass of one molecule is equal to  $\frac{219}{6.02 \cdot 10^{23}} = 3.64 \cdot 10^{-22}$  g. From the density expression  $\rho = \frac{m}{V}$  we obtain that the volume of one lattice cell is  $3.03 \cdot 10^{-22}$  cm<sup>3</sup>. Because the cesium chloride lattice is cubic, its parameter is connected to the cell volume using this formula:  $V = a^3$ , thus  $a = \sqrt[3]{V} = \sqrt[3]{3.03 \cdot 10^{-22}} = 6.7 \cdot 10^{-10}$  m. The parameter of the lattice cell of the

MLG Liquic Ionid is equal to 6.7 Å

Afterwards Olavs decided that the achieved degree of MLG was not sufficient, and he decided to mix his compound with water. In water, a following series of reactions occurs, describing water autoprotolysis:



The reaction (1) is reversible, its equilibrium constant  $K$  at 298K being equal to  $1.8 \cdot 10^{-16}$  and its expression:  $K = \frac{[H^+][OH^-]}{[H_2O]}$

*D-15 Prove that in pure water the ion product  $K_w$  is equal to  $1.0 \cdot 10^{-14}$ .*

The concentration of water in water is  $\frac{1000}{18} = 55.56M$  thus by substituting  $[H_2O]$  in the equilibrium constant expression we obtain  $[OH^-] \cdot [H^+] = 1.00 \cdot 10^{-14}$  which corresponds to the water ion product  $K_w$  value.

*D-16 Explain, using the nucleophile-electrophile theory, why the reaction between  $H^+$  and water proceeds fully.*

A good nucleophile has a high-energy HOMO, for the water molecule it is the  $2sp^3$  orbital on the oxygen atom. A good electrophile has a low energy LUMO, the LUMO of the proton is the empty  $1s$  orbital, making the proton the best electrophile out there. The resulting bond between the two atoms is quite strong, thus the reaction is thermodynamically favourable and proceeds fully.

In Olavs' MLG solution, this was not quite true... Nevertheless, knowing that he is a very cool Inorganic Chemist who knows what he does, Olavs dissolved some water in his solution he'd patented as Liquic Ionid. Afterwards he measured the standard potential of the reaction  $2H^+ + 2e \rightarrow H_2$  against the SHE, receiving the value of -0.504V. Olavs neither added any acid to the mixture, nor chose such a solvent that could interact with water autoprotolysis. The only thing he also knew was the density of the solution - it was equal to 1.10g/mL.

*D-17 Calculate the concentration and the molar fraction of water in Olavs' Liquic Ionid. Use only equation (1) and its equilibrium constant expression to describe the protolytic processes in the Liquic Ionid.*

Let us write down the Nernst equation for the potential of the hydrogen evolution reaction:

$$E = E^0 - \frac{RT}{zF} \ln \left( \frac{p_{H_2}}{[H^+]^2} \right)$$

Because standard potentials are given, the Nernst equation can be converted to the form:

$$E = E^0 - \frac{0.0592}{z} \log \left( \frac{1}{[H^+]^2} \right)$$

Because the system is uncharged, we obtain such an equation for the charge balance:

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

And, by expressing  $[H^+]$  from the equilibrium constant of reaction (1) we obtain:

$$K \cdot [H_2O] = [H^+]^2$$

By substituting into the Nernst equation we end up with such expression for  $[H_2O]$ :

$$[H_2O] = \frac{1}{K} \cdot 10^{-\frac{2(E^0 - E)}{0.0592}} = 0.05 \text{ M}$$

1L of this solution has the mass of 1100 g. Out of those 1100g 0.9g are water, thus the mass of 1,3-dipropylimidazolium dicyanamide equals 1099.1 g, which corresponds to 5.02 mol. Thus, the molar fraction of water is  $\frac{0.05}{0.05+5.02} = 0.99\%$ .

At this moment, Little Olavs was happy enough about the MLG level of the Liquic Ionid to stop his experiments and to leave his lab and Ross behind. Ross, unfortunately, failed Little Olavs' challenge and as a punishment Olavs sent the video of him struggling to determine the water concentration in water to his love Anastasia, breaking Ross' heart. . . .

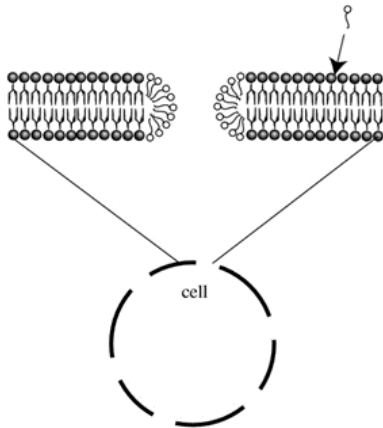
### 3.5 Problem E. Traces of DNA in pickle juice

Someone from a little known country drank a potion he synthesized at his chemistry lab and turned into a pickle near a domestic monument. The police didn't like it (turning into a pickle is seen as disrespectful in his country), but weren't surveilling the area, so they're now suspecting three people - Big Nauris, Medium Ritums, and Little Olavs. Let's help the police find the true culprit.

When a person turns into a pickle, lots of pickle juice is emitted and splattered all around. That pickle juice contains muriocytes (Latin - muria, brine + Greek kytos, cell) - the biological precursor cells which the human pickle body is made up of. The police found pickle juice splattered all over the monument, collected samples and took it to the lab of Vladislavs the Biochemist.

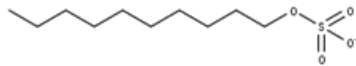
To determine the culprit, we will need to use gel electrophoresis to compare the DNA of muriocytes of the three suspects and that in the sample. Vladislavs promptly extracted the nucleus DNA from these cells, but, as expected, found it in low concentration. He now needs to conduct the polymerase chain reaction - an enzymatic reaction used to magnify the concentration of DNA. Help Vladislavs conduct this reaction.

First, the culprit's DNA is extracted from the muriocytic nucleus. For that, the muriocytes have to be lysed - their lipid bilayer membranes disintegrated with a surfactant. The surfactant integrates into the cellular membrane and generates pores in it, as follows:



Source: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2504493/>

The anion in sodium dodecyl sulfate (SDS), a surfactant often used for cellular lysis, is shown below:



E-1 Indicate which part of the anion is the tail and which is the head, if the porated cell in the figure is placed in water.

The tail of the SDS molecule must be hydrophobic, thus it has to be the carbon chain. The head is hydrophilic, and it has to be the sulfonate group.

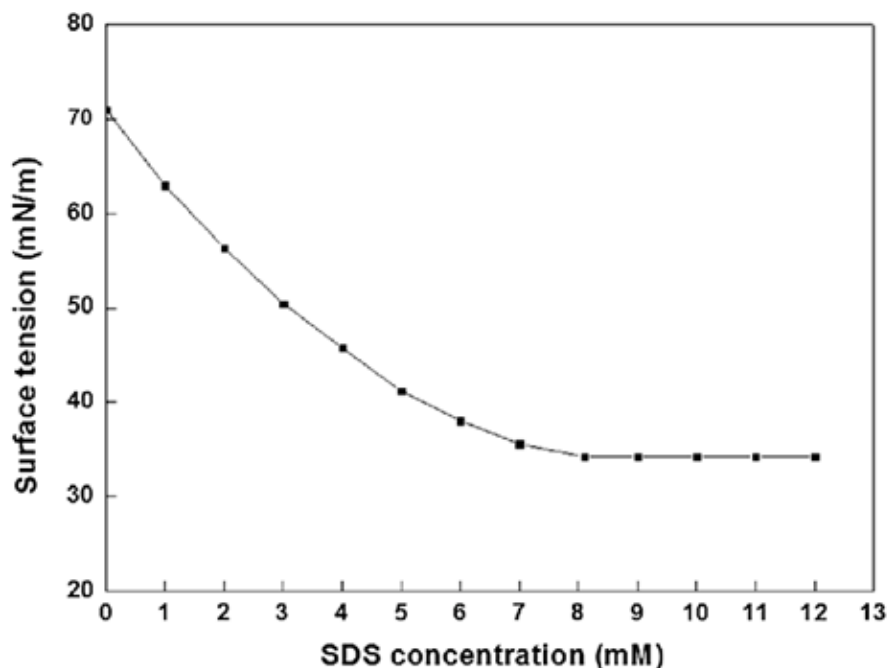


E-2 Such strongly ionic surfactants are not always used since they tend to denature (change the structure of) proteins. Is this a problem for Vladislavs the Biochemist in this experiment? Why?

In this situation, it is absolutely not a problem for Vladislavs because he does not really care about the structure of proteins in the cells-he needs DNA which is not a protein.

The critical micelle concentration (CMC) is the concentration of surfactant at which all further added surfactant forms micelles. Up until CMC, the surface tension of the surfactant solution keeps changing, but after - stays constant.

E-3 Determine the CMC of SDS from the following graph:



It is quite obvious from the graph that the CMC of the SDS surfactant equals 8 mM.

Vladislavs the Biochemist is kind of surprised by the strength of the interaction of the dodecyl sulfate's anionic moiety with water. The potential of the ion-dipole interaction is as follows:

$$V = -k \cdot \frac{|q|\mu}{r^2}$$

The separation distance  $r$  can be estimated as half of the oxygen atom van der Waals radius ( $r = 152 \text{ pm}$ ) and half of the water molecule's length along its principal axis ( $l = 28.7 \text{ pm}$ );  $k = 9.0 \cdot 10^9 \text{ N} \cdot \text{m}^2 \cdot \text{C}^{-2}$ ,  $\mu = 6.17 \cdot 10^{-30} \text{ C} \cdot \text{m}$ .

*E-4 Determine the charge on each oxygen atom (remember that sulfate anion exhibits resonance) and the interaction potential of the dodecyl sulfate with water's dipole. Will it interact with the hydrogenic or oxygenic face of water?*

Because of the resonance, the charge on each oxygen atom comes up to be  $-1/3$ . The dodecyl sulfate will interact with the hydrogenic face of water. By substituting the numbers in the potential formula, we obtain the interaction potential equals

$$9.0 \cdot 10^9 \cdot \frac{\frac{1}{3} \cdot 1.6 \cdot 10^{-19} \cdot 6.17 \cdot 10^{-30}}{((14.35 + 76) \cdot 10^{-12})^2} = 3.63 \cdot 10^{-19} \text{ J}$$

*E-5 Assume that every sulfate anionic oxygen interacts with two water molecules. Per pore made in the murioctytic membrane, 69 dodecyl sulfate anions integrate into the membrane. Assuming negligible hydrophobic interactions, calculate the enthalpy change from the formation of one pore in the membrane if water's dipole is  $6.17 \cdot 10^{-30} \text{ C} \cdot \text{m}$ .*

The formation of a pore results in  $2 \cdot 69 = 138$  interactions. Thus,  $\Delta H = 138 \cdot 3.63 \cdot 10^{19} = 5.01 \cdot 10^{-17} \text{ J}$ .

Vladislavs conducted a cell counting experiment and determined that the absorption of the 10 mL sample of the mixture he took, diluted to 100 mL, is 1.80. The molar absorption of the dye that Vladislavs used (one dye molecule binds to one cell) is  $3330 \text{ M}^{-1} \cdot \text{cm}^{-1}$ . Vladislavs intends to add 0.5 M SDS to 100 mL of collected murioctytes to lyse them. *Edit: the length of the cuvette is equal to 1 cm*

*E-6 Determine the total number of cells in the 100 mL cell suspension.*  
From the Lambert-Beer Law,

$$N = \frac{A}{\epsilon l} \cdot N_A = 3.25 \cdot 10^{20} \text{ cells}$$

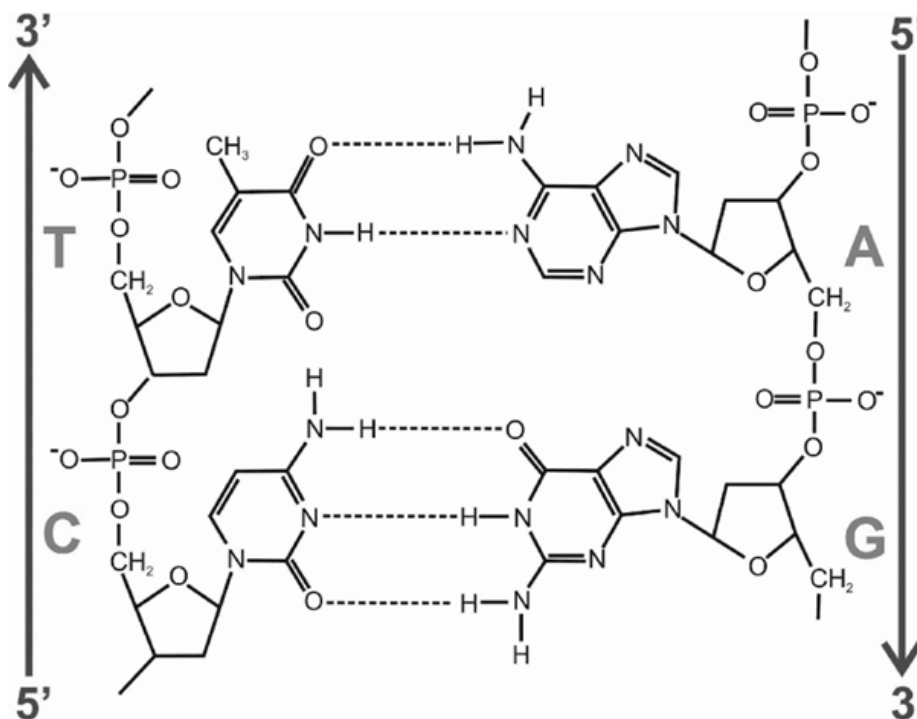
Help Vladislavs determine the amount of SDS that he should add. Assume that a negligible amount of micelles are formed before CMC, that SDS forms micelles only when integrated into the membrane. On average, 420 pores are formed in a cell.

*E-7 Determine the volume of SDS that should be added and the heat thus evolved.*

The amount of SDS required to porate one cell is  $69 \cdot 420 = 28980 \text{ molecules}$ . Thus, the amount of SDS to lyse all the cells is equal to  $\frac{28980 \cdot 3.25 \cdot 10^{20}}{6.02 \cdot 10^{23}} = 15.6 \text{ mol}$ . The enthalpy of this reaction equals  $420 \cdot 3.25 \cdot 10^{20} \cdot 5.01 \cdot 10^{-17} = 6838 \text{ kJ}$ . The volume of SDS comes up to be 31.2L *Yes, the number is a bit inadequate for 100 mL, but it is a meme olympiad.....*

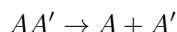
Phew, that lysis procedure sure was quite a bit of work. Now, the extracted DNA has to be amplified using the polymerase chain reaction. A 10 mL sample is taken for the reaction. The polymerase chain reaction is an in vitro procedure where the DNA is duplicated once per cycle. The cycles are repeated many times to ensure an appropriate final concentration of DNA. We will consider only one part of the PCR - melting.

Melting is the stage where the DNA has to be dissociated. The dimerization of DNA is mediated by hydrogen bonds, as demonstrated below:



Source: <https://www.researchgate.net/publication/327500345/figure/fig6/AS:668188459139077@1536319951907/Section-of-the-Watson-Crick-DNA-structure-showing-hydrogen-bonds-connecting-the.png>

The chemical equation for dissociation of DNA is as follows:



E-8 Assuming no initially present dissociated DNA, express the equilibrium constant  $K$  from the initial concentration of DNA dimers and final concentration of each DNA monomer.

Because one molecule of DNA dissociates into two monomer molecules, the constant expression is as follows ( $[AA']^0$  is the initial concentration of the DNA dimer, and  $[A]$  and  $[A']$  are the corresponding concentrations of the DNA monomers.) Thus, the expression of  $K$  is:

$$K = \frac{[A] \cdot [A']}{[AA']^0 - [A]} = \frac{[A]^2}{[AA']^0 - \frac{1}{2}[A]}$$

E-9 Determine  $K$  if the concentration of each monomer of DNA is 99% of that of initial dimerized DNA, assuming there are 46 DNA molecules per cell.

The concentration of DNA in the solution equals  $\frac{3.25 \cdot 10^{20} \cdot 46}{6.02 \cdot 10^{23}} = 2.48 \cdot 10^{-1} M$ . Thus, the final concentration of DNA is  $2.48 \cdot 10^{-3} M$ . And the equilibrium



concentrations of the monomers are thus  $2.46 \cdot 10^{-1} M$ . The equilibrium constant then is

$$K = \frac{(2.46 \cdot 10^{-1})^2}{2.48 \cdot 10^{-3}} = 24.4$$

*E-10 The strength of the average hydrogen bond in DNA is found to be approximately 4 J/mol. If the enthalpy of dissociation is 204 kJ/mol, and the total number of base pairs is 20069, determine the number of A-T and G-C pairs, respectively, in each DNA molecule.*

Let us imagine that 1 mol of DNA has  $x$  A-T pairs and  $y$  G-C pairs. One A-T pair has two hydrogen bonds, thus its enthalpy of dissociation is 8 J/mol. One G-C pair has 3 hydrogen bonds, thus its enthalpy of dissociation is 12 J/mol

Then, we obtain the following two simultaneous equations that can describe the situation:

$$\begin{cases} x + y = 20069 \\ 8x + 12y = 204000 \end{cases}$$

By solving the simultaneous equations, we obtain:

$$\begin{cases} x = 9207 \\ y = 10862 \end{cases}$$

The DNA molecule has 9207 A-T pairs and 10862 C-G pairs.

*E-11 If  $K$  of dissociation at 298 K is 0.01, determine the temperature at which it will reach the  $K$  you calculated in E-9.*

We can relate the Gibbs energy of the reaction to its equilibrium constant by the following formula:

$$\Delta G = -RT \ln K = \Delta H - T \Delta S$$

From which,

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

And, by substituting numbers we can find the entropy change of the reaction:

$$\Delta S = R \ln K + \frac{\Delta H}{T} = 646 J \cdot mol^{-1} \cdot K^{-1}$$

And, we can express the equilibrium constant as a function of temperature:

$$K = e^{\frac{\Delta S}{R} - \frac{\Delta H}{RT}}$$

By solving the equation, we obtain  $T = 329 K$ .

*E-12 If the desired concentration of DNA is 1 M and the amount of DNA doubles every cycle, calculate the minimum number of cycles.*

The initial DNA concentration  $[AA']_0$  equals  $2.48 \cdot 10^{-1} M$ . After the first PCR cycle, the DNA concentration will be equal to  $2 \cdot [AA']_0$ , after the second cycle  $2 \cdot 2 \cdot [AA']_0 = 2^2 \cdot [AA']_0$ ...., and after the n-th PCR cycle the DNA concentration will be equal to  $2^n \cdot [AA']_0$ . Thus, we obtain such an equation:

$$2^n \cdot 2.48 \cdot 10^{-1} = 1$$

To solve it, we transform it to a form:

$$2^n = \frac{1}{2.48 \cdot 10^{-1}}$$

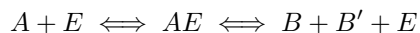
Which, after logarithmating, gives:

$$n = \frac{\ln\left(\frac{1}{2.48 \cdot 10^{-1}}\right)}{\ln(2)} = 4 \text{ times}$$

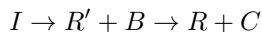
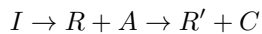
Thus, Vladislavs needs to carry out the PCR 4 times to obtain such a DNA concentration in his sample.

OK... Now, thanks to your help, the murioctytic DNA has been amplified. For forensic analysis, it now must be cleaved by a restriction endonuclease. The DNA is cleaved at particular spots which match the enzymes. This will yield a certain amount of DNA fragments which is unique to a particular person. The number of these fragments can then be determined by gel electrophoresis. By comparing the number of such fragments amongst suspects and with the murioctytic fragments, we can determine the true culprit.

Restriction endonucleases follow Michaelis-Menten kinetics. A represents the concentration of cleavage sites:



Let us take a particular fragment C. The fragment needs to be cleaved by two different endonucleases in order to be yielded. There are then two paths to such a fragment:



All elementary reactions proceed through Michaelis-Menten kinetics. The rate of such reactions is expressed as follows:

$$v = V_{max} \cdot \frac{[S]}{K_M + [S]}$$

$$\frac{1}{v} = \frac{1}{V_{max}} \cdot \left( \frac{K_M}{[S]} + 1 \right)$$

*E-13 Write the total rate for disappearance of the initial DNA, [I].*

The rate of disappearance of DNA is a sum of two reactions by two enzymes. Their rates are respectively:

$$\frac{dI}{dt}(A) = -V_{max-A} \cdot \frac{[I]}{1 + K_M A/[I]}$$

$$\frac{dI}{dt}(B) = -V_{max-B} \cdot \frac{[I]}{1 + K_M B/[I]}$$

$$\frac{dI}{dt} = - \left( V_{max-A} \cdot \frac{[I]}{1 + K_M A/[I]} + V_{max-B} \cdot \frac{[I]}{1 + K_M B/[I]} \right)$$

$$v = \frac{V_{max}}{1 + \frac{K_M}{[S]}} = V_{max} \cdot \left( 1 - \frac{K_M}{[S]} + \frac{K_M}{[S]^2} - \dots \right)$$

Vladislavs wants to play engineer and approximate the Michaelis-Menten rate expression. However, can he really do that?

*E-14 Write out the rate of reaction of an endonuclease with DNA as an infinite series using the formula for the Taylor series of  $\frac{1}{1+x} = 1 - x + x^2 - x^3 + \dots$*

$$\frac{dI}{dt} = - \left( (V_{max-A} + V_{max-B}) \cdot \left( 1 - \frac{K_M A + K_M B}{[I]} + \frac{K_M A + K_M B}{[I]^2} - \dots \right) \right)$$

*E-15 Can you approximate the rate law using the above series in the form  $k(1-x)$  if the reaction rate is 50% of the maximum rate? Also determine the maximum ratio of  $\frac{K_M}{[S]}$  when the ratio of the precise value and approximation is up to 103% or over 97%, whichever requirement is stricter. Will Vladislavs using the approximation lead to overestimation or underestimation of the rate?*

*Problem can not be solved due to lack of constant values*

*E-16 The association of the enzymes with DNA is slow. Can you, in this case, use the steady state approximation on the rate of generation of A and B? Write the expression of a steady state approximation applied to A and B. What kind of information about A and B is deduced from this expression?*

The steady state expression can be applied to Michaelis-Menten kinetics:

$$k_1 \cdot [I] = k_2 \cdot [R][A]$$

$$k_3 \cdot [I] = k_4 \cdot [R'][B]$$

The A and B intermediates do not assemble in the system.

Finally, Vladislavs wants to use gel electrophoresis to find the true culprit. For that, he needs to use a dye. The dye will associate with the DNA

molecules, and thus the DNA molecules, moved according to their weight in the electrophoresis procedure, will be visible under UV light. If the pattern of a particular suspect's set of DNA matches that of the muricocytic DNA, the true culprit is found.

The equilibrium constant for association of the dye to a DNA fragment is 16 at 293K. The equation is as follows:



The air conditioning machine in the lab broke, so Vladislavs wants to find the maximum temperature at which the dyed DNA molecules will be visible.

*E-17 If the dye's association enthalpy is -31.7 kJ/mol, the concentration of dye is 0.5 M, and the concentration of DNA is 1 M, express the concentrations B-DNA and B as a function of temperature.*

The equilibrium constant can be related to the Gibbs free energy change of the reaction:

$$\Delta G = -RT \ln K = \Delta H - T \Delta S$$

We can determine the entropy change of the reaction:

$$\Delta S = \frac{\Delta H}{T} + R \ln K = -85.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Let us make an ice table *For the readers unfamiliar, an ice table correlates initial and equilibrium concentrations of the components in a reaction mixture.*

| Reagent | B     | DNA   | B-DNA |
|---------|-------|-------|-------|
| i       | 0.5   | 1.0   | 0     |
| c       | -x    | -x    | +x    |
| e       | 0.5-x | 1.0-x | x     |

We can express the equilibrium constant from the Gibbs free energy:

$$K = e^{\frac{\Delta S}{R} - \frac{\Delta H}{RT}}$$

And also we obtain the expression for the equilibrium constant as:

$$K = \frac{[B - DNA]}{[B] \cdot [DNA]} = \frac{x}{(0.5 - x)(1 - x)}$$

And, we obtain the following expression:

$$e^{\frac{-85.1}{8.314} - \frac{-31700}{8.314T}} = \frac{x}{(0.5 - x)(1 - x)}$$

By solving which, we get:

$$x = \frac{1 + 1.5E - \sqrt{1 + 3E + 0.25E^2}}{2E} \quad \text{where } E = e^{-10.2 + \frac{3182}{T}}$$

The minus sign before the square root comes from the implication that  $0 < x < 0.5$ , the sign is checked by calculating  $x$  for temperatures such as 300K.

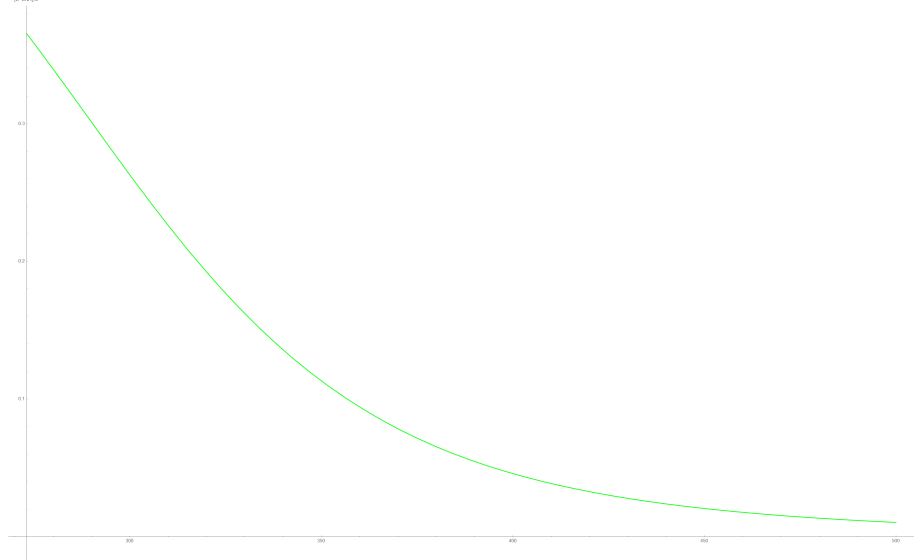
Thus, the concentration of B-DNA is equal to

$$[B - DNA] = \frac{1 + 1.5E - \sqrt{1 + 3E + 0.25E^2}}{2E} \quad \text{where } E = e^{-10.2 + \frac{3182}{T}}$$

And the concentration of the free dye:

$$[B] = 0.5 - \frac{1 + 1.5E - \sqrt{1 + 3E + 0.25E^2}}{2E} \quad \text{where } E = e^{-10.2 + \frac{3182}{T}}$$

I plotted the concentration of [B-DNA] as a function of temperature, the graph is below:



A 1 mL sample of this mixture is now placed in the gel for electrophoresis.

The mixture is now irradiated by UV light. Assume that the remaining B is dispersed throughout the gel (bad assumption, I know), and the electrophoresis pattern (with only the solvent and B-DNA) takes up  $\frac{1}{5}$  of the gel's volume. The quantum yield for fluorescence of the dye molecule is 0.7. The minimum light intensity for detection against the background light intensity is A. Assume that the background light is coming only from the remaining B (the room is dark). The molar absorption for all B-containing species is  $5000 M^{-1} \cdot cm^{-1}$ .

*E-18 Express the temperature at which B-DNA is no longer detectable as a function of A.*

*THIS PROBLEM WILL NOT BE GRADED DUE TO THE LACK OF THE  $I_{in}$  AND  $l$  VALUES! Still, here is a general solution:*

The quantum yield for fluorescence is expressed like this:

$$\Phi = \frac{I_{fluorescence}}{I_{incident}}$$

From the definition of A, we obtain:

$$A = I_{B-DNA} - IB$$

From the definition of absorbance we obtain:

$$10^{-Abs} = \frac{I_{out}}{I_{in}}$$

$$1 = 10^{-Abs} = \frac{I_{absorbed}}{I_{in}}$$

where  $I_{in}$  is the incoming light intensity Thus, we can obtain:

$$I_{absorbed} = I_{in} \cdot (1 - 10^{-Abs})$$

And

$$I_{absorbed} = I_{in} \cdot \Phi \cdot (1 - 10^{-Abs})$$

Because the [B-DNA] complex occupies  $\frac{1}{5}$ , its concentration becomes:

$$[B - DNA] = 5 \cdot \frac{1 + 1.5E - \sqrt{1 + 3E + 0.25E^2}}{2E} \quad \text{where } E = e^{-10.2 + \frac{3182}{T}}$$

And,

$$[B] = 0.5 - \frac{1 + 1.5E - \sqrt{1 + 3E + 0.25E^2}}{2E} \quad \text{where } E = e^{-10.2 + \frac{3182}{T}}$$

From the Lambert-Beer law:

$$Abs = \epsilon lc$$

we obtain:

$$A = 0.7I_{In} \cdot \left( 10^{5000 \cdot l \cdot \left( 0.5 - \frac{1 + 1.5 \cdot E - \sqrt{1 + 3 \cdot E + 0.25 \cdot (E)^2}}{2 \cdot E} \right)} - 10^{25000 \cdot l \cdot \frac{1 + 1.5 \cdot E - \sqrt{1 + 3 \cdot E + 0.25 \cdot (E)^2}}{2 \cdot E}} \right)$$

where  $E = e^{-10.2 + \frac{3182}{T}}$

And so, through all this effort, Vladislavs determined the culprit to be [CLASSIFIED].

### 3.6 Problem F. Vapour of muriomorphosis

Little John lives in a time when people have been genetically engineered to gain the ability to transform into pickles. This transformation - scientifically termed muriomorphosis - is initiated by interaction of one of many types of ligands with a muriomorphotic receptor on the surface of the oral and nasal cavities. The interaction sets off a cascade of biochemical reactions. Little John has been assigned to work with molecule X - one out of many ligands that can interact with the muriomorphotic receptor that Little John (and everyone) has.

However, Little John is afraid to get anywhere near the substance. Since the molecule interacts with receptors inside the nose, breathing it in might be able to cause the transformation, which Little John is extremely cautious of (he's never done it before). Therefore, Little John wants to make sure that the vapour pressures of the substance at room temperature are not excessive and will not turn him into a pickle.

First, let us estimate the strength of the intermolecular interaction that holds the substance together. The electric dipole of molecule X is low, so we can assume that the interactions are dispersion-like. Dispersion interaction strength can be approximated as follows, by the London formula:

$$V = -\frac{3}{4} \cdot \alpha'^2 \cdot I \cdot \frac{1}{r^6}$$

where  $\alpha'$  is the polarizability volume,  $I$  is the ionization energy, and  $r$  is the radius of the molecule.

*F-1 The molecule has a globular shape. What assumptions should be made in this calculation? Mark Yes or No for each assumption.*

|            |   |
|------------|---|
| <i>yes</i> | The ionization energy should be approximately uniform across the surface of the molecule. |
| <i>no</i>  | The molecule is small.  |
| <i>no</i>  | The molecule is inorganic.  |
| <i>yes</i> | The molecule is organic.  |

To estimate the polarizability volume, we can use the Clausius-Mossotti equation:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho * N_A}{3M\varepsilon_0} \cdot \left( \alpha + \frac{\mu^2}{3kT} \right)$$

where  $\varepsilon_r$  is the electric relative permittivity of the substance, and  $\mu$  is the permanent dipole.

Some clever scientists (who are NOT afraid of turning into pickles) collected data on the dependence of density and relative permittivity of molecule X on temperature:

| $T, ^\circ C$ | $\rho, g \cdot cm^{-3}$ | $\varepsilon_r$ |
|---------------|-------------------------|-----------------|
| 0             | 0.99                    | 12.5            |
| 20            | 0.99                    | 11.4            |
| 40            | 0.99                    | 10.8            |

Also given is the molar mass of molecule X = 4206.9 g/mol, as determined using a mass spectrometer.  $\epsilon_0 = 8.8 \cdot 10^{-12} F \cdot m$ .

F-2 To use linear regression to determine the polarizability volume, the equation has to be linearized. As in  $y = ax + b$ , write out the  $y$ ,  $a$ , and  $b$  terms that describe the Clausius-Mossotti equation.

|   |   |
|---|---|
| y | $\frac{\epsilon_r - 1}{\epsilon_r + 2}$             |
| a | $\frac{\rho \cdot N_A \cdot \mu^2}{9M\epsilon_0 k}$ |
| b | $\frac{\alpha \rho N_A}{3M\epsilon_0}$              |
| x | $\frac{1}{T}$                                       |

F-3 Using linear regression, determine the polarizability volume of molecule X.

F-4 The spherical molecule X has 37 surface atoms, with 4.00 Å<sup>2</sup> molecular surface area per each atom. Determine the surface area of the molecule, and thus its radius.

F-5 Using the ionization energy 2001 kJ · mol<sup>-1</sup>, determine the dispersion interaction energy and (assume to be equal in magnitude) vaporization enthalpy.

Let us make a table of values we'll use to calculate the linear regression:

| T   | $\frac{1}{T}$   | $\epsilon_r$ | $\frac{\epsilon_r - 1}{\epsilon_r + 2}$ |
|-----|-----------------|--------------|---|
| 273 | $\frac{1}{273}$ | 12.5         | $\frac{11.5}{14.5}$                     |
| 293 | $\frac{1}{293}$ | 11.4         | $\frac{10.4}{13.4}$                     |
| 313 | $\frac{1}{313}$ | 10.8         | $\frac{9.8}{12.8}$                      |

And, now we use linear regression to determine the  $a$  and  $b$  coefficients of the line equation:

$$a = 58.924$$

$$b = 0.5765$$

$$r^2 = 0.9908$$

We know that

$$b = \frac{\alpha \rho N_A}{3M\epsilon_0}$$

Thus, we can express  $\alpha$ :

$$\alpha = \frac{3bM\epsilon_0}{\rho N_A}$$

Polarizability volume is expressed as follows:

$$\alpha' = \frac{\alpha}{4\pi\epsilon_0}$$

Thus, the polarizability volume of this molecule is:

$$\alpha' = \frac{3bM}{4\pi\rho N_A}$$



And numerically, it is:

$$\alpha' = 9.71 \cdot 10^{-28} \text{ m}^3$$

To determine the interaction energy, we should determine the radius of the molecule. To do it, we first determine the surface area of the molecule. It comes up to be  $37 \cdot 4.00 = 148 \text{ \AA}^2$ . The surface area of the sphere is connected to its radius:

$$A_{\text{sphere}} = 4\pi r^2$$

From which, we obtain:

$$r = \sqrt{\frac{37}{\pi}} = 3.43 \cdot 10^{-10} \text{ m}$$

Then, by substituting into the London formula:

$$V = -\frac{3}{4} \cdot \alpha'^2 \cdot I \cdot \frac{1}{r^6}$$

we obtain the numerical answer:

$$V = -869 \text{ MJ/mol}$$

*Again, the answer is a bit crazy.....*

The vaporization enthalpy is said to be equal to the interaction energy, being

$$\Delta_{\text{vap}}H = +869 \text{ MJ/mol}$$

*F-6 Some more clever scientists who are not afraid of becoming pickles found the vapour pressure of molecule X at 200 K to be 2 Pa. Estimate the vapour pressure at 298 K.*

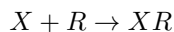
*PROBLEM NOT COUNTED TOWARD FINAL GRADE DUE TO INADEQUATE NUMBERS*

*F-7 Thus, assuming the enthalpies and entropies of vapourization to be independent of temperature, determine the entropy of vapourization.*

*PROBLEM NOT COUNTED TOWARD FINAL GRADE DUE TO INADEQUATE NUMBERS*

OK, so we've calculated a bunch of nonsensical data. But Little John wants real answers, now. Will it (how quickly will it) turn him into a pickle?

Assume the vapour of molecule X behaves like an ideal gas. It interacts with the receptor according to the following elementary reaction:



F-8 Deduce the [concentration-based] rate law for the reaction, assuming  $p_X$  and  $[R]$  are known.

From the ideal gas equation we can express the concentration of X:

$$[X] = \frac{n_X}{V}$$

$$p_X V = n_X RT$$

Thus,

$$[X] = \frac{p_X}{RT}$$

The concentration-based rate law is then as follows:

$$r = k \cdot [R] \cdot \frac{p_X}{RT}$$

Receptors can be imagined as little protrusions from the walls of the oral and nasal cavities. The collision flux (number of collisions of molecule X with the wall per unit area per time interval) can be calculated as follows:

$$Z = \frac{p}{\sqrt{2\pi mkT}}$$

F-9 Calculate the collision flux of molecule X at 298 K.

**PROBLEM NOT COUNTED TOWARD FINAL GRADE DUE TO IMPOSSIBILITY OF PRESSURE CALCULATION**

The probability of a molecule X that is heading for the wall of hitting a murimorphotic receptor is 0.0021. The projection of the receptoral molecular surface onto the cavity's "wall" (assuming it is flat) has an area of 400 Å<sup>2</sup>.

F-10 Estimate the number of receptors in the cavity per unit area.

Let us imagine that we have 1m<sup>2</sup> of the wall. Then, the area of the receptors will be 0.0021 m<sup>2</sup>. The amount of receptors comes up to be  $\frac{0.0021}{400 \cdot 10^{-20}} = 5.25 \cdot 10^{14}$  receptors/m<sup>2</sup>.

F-11 The activation energy of the ligand-receptor interaction is 74 kJ/mol. Calculate the probability that the ligand will have enough energy to associate with the receptor.

Let us first determine the minimum speed the molecule needs to have to interact with the receptor:

$$E = \frac{1}{2}mv^2$$

$$v = \sqrt{\frac{2E_a}{M}}$$

$$v = \sqrt{\frac{2 \cdot 74000}{4.2069}} = 187.56 \text{ m/s}$$

From the Maxwell-Boltzmann distribution:

$$f(v) = 4\pi \cdot \left( \frac{M}{2\pi RT} \right)^{3/2} \cdot v^2 \cdot e^{-\frac{Mv^2}{RT}}$$

we can determine the fraction of molecules whose kinetic energy is equal or less than the minimum requirement:

$$\int_0^{\infty} f(v)dv = 1$$

Thus, we can determine the fraction of molecules with a speed greater than 187.58 m/s:

$$P_{v>187.58} = 1 - \int_0^{187.58} f(v)dv$$

Substituting in the numbers:

$$P_{v>187.58} = 1 - \int_0^{187.58} 4\pi \cdot \left( \frac{4.2069}{2\pi \cdot 8.314 \cdot 298} \right)^{3/2} \cdot v^2 \cdot e^{-\frac{4.2069v^2}{8.314 \cdot 298}} dv = 0.646$$

The Arrhenius factor can be approximated using the following formula:

$$A = \frac{p_{correctorientation} \cdot (S_{ligand} + S_{receptor}) \cdot N_A}{2} \cdot \sqrt{\frac{8kT}{\pi\mu}}$$

where S is the surface area of the molecule, and  $\mu$  is the reduced mass  $\frac{m_a \cdot m_b}{m_a + m_b}$  of the two molecules. The molar mass of the receptor molecule is 3000 g/mol.

*F-12 Finally, assuming that only a third of the orientations of molecule X hitting the receptor are appropriate for the reaction, and assuming that a collision with appropriate orientation and energy will lead to a reaction, calculate the rate constant of the reaction at 298 K.*

First, we need to determine the Arrhenius factor:

$$A = \frac{p_{correctorientation} \cdot (S_{ligand} + S_{receptor}) \cdot N_A}{2} \cdot \sqrt{\frac{8kT}{\pi\mu}}$$

Numerically, we obtain:

$$A = \frac{1/3 \cdot (148 \cdot 10^{-20} + 400 \cdot 10^{-20}) \cdot 6.02 \cdot 10^{23}}{2} \cdot \sqrt{\frac{8 \cdot 298 \cdot 8.314}{\pi \cdot \frac{3 \cdot 4.2069}{3+4.2069}}} = 3.3 \cdot 10^7 M^{-1} \cdot s^{-1}$$

From the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

we calculate the rate constant:

$$k = 3.525 \cdot 10^{-6} \text{ M}^{-1} \cdot \text{s}^{-1}$$

*F-13 Calculate the initial reaction rate using the collision flux. To calculate it, think about the probability of each collision leading to the association reaction.*

*PROBLEM NOT COUNTED TOWARD FINAL GRADE DUE TO IMPOSSIBILITY OF PRESSURE CALCULATION*

*F-14 Thus calculate the concentration of muriomorphotic receptors. Using this information (hint: you must equate the two rate expressions), and assuming that the concatenation of the two cavities is spherical, estimate the total number of muriomorphotic receptors in the cavity. Another hint: you have receptors per area unit and receptors per volume unit. Think about how spherical surface area can be converted to spherical volume.*

*PROBLEM NOT COUNTED TOWARD FINAL GRADE DUE TO IMPOSSIBILITY OF PRESSURE CALCULATION*

*F-15 The equilibrium constant of ligand association to the muriomorphotic receptor is 11. Estimate the dissociation reaction rate constant.*

The equilibrium constant is expressed like this:

$$K = \frac{k_{\text{forward}}}{k_{\text{backward}}}$$

Thus,  $k_{\text{backward}} = 3.205 \cdot 10^{-7} \text{ M}^{-1} \cdot \text{s}^{-1}$

Little John only needs a total of 1000 receptor associations to transform into a pickle. The total volume of the oral and nasal cavities is  $5 \text{ dm}^3$ .

*F-16 Using the following formula:*

$$kt = \frac{1}{[B]_0 - [A]_0} \cdot \ln \left( \frac{[B] \cdot [A]_0}{[B]_0 \cdot [A]} \right)$$

*and ignoring the dissociation, calculate the time within which that number will be reached (time that Little John has to run out of the room out of fear).*

*PROBLEM NOT COUNTED TOWARD FINAL GRADE DUE TO IMPOSSIBILITY OF PRESSURE CALCULATION*

*F-17 Clever Chemist Zane is studying molecule Y, which has a transition state during association with the receptors that has more in-phase pi interactions. The activation energy has been shifted by 10 kJ/mol. Has the activation energy increased or decreased? Calculate the new activation energy.*

The in-phase pi interactions reduce the activation energy, making the transition state more energetically favourable. Thus, the new activation energy will

equal 64 kJ/mol.

*F-18 Calculate the new rate constant and the time within which Little Zane will transform into a pickle.*

The Arrhenius factor is given to be unchanged. Thus, from the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

we calculate the rate constant:

$$k = 1.995 \cdot 10^{-4} M^{-1} \cdot s^{-1}$$

*The time can not be calculated because the pressure data is unavailable. This part of the question will not be counted towards the final grade.*

Why does Little John even have to study this molecule X? Something far worse than a complete transformation is a partial transformation into a pickle. It can happen if receptor association is thermodynamically too weak, and not all the cells coordinate well enough during the transformation. Consequences are usually permanent and may include brain damage, green and juicy skin, internal aches, and degradation of muscular tissue. Little John, as the voluntary protector of mankind, has been tasked with determining if molecule X can cause this occurrence.

The partial transformation occurs if less than 25% of receptors are activated at equilibrium.

*F-19 Calculate the equilibrium number of ligand-receptor complexes, assuming none are initially present. Will molecule X cause a partial transformation?*

*PROBLEM NOT COUNTED TOWARD FINAL GRADE DUE TO IMPOSSIBILITY OF PRESSURE CALCULATION*

*F-20 Assuming the dissociation constant and initial vapour pressure remain the same, what is the equilibrium number of ligand-receptor complexes of molecule Y? Is molecule Y safer to use?*

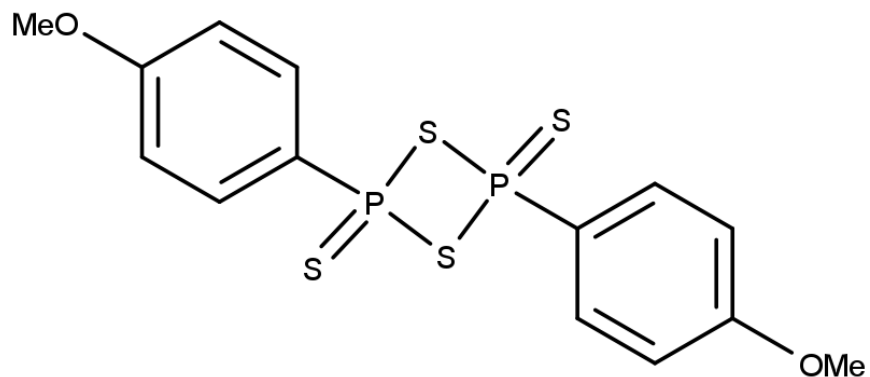
*PROBLEM NOT COUNTED TOWARD FINAL GRADE DUE TO IMPOSSIBILITY OF PRESSURE CALCULATION*

Thank you for helping Little John make the right choice for his phobias.

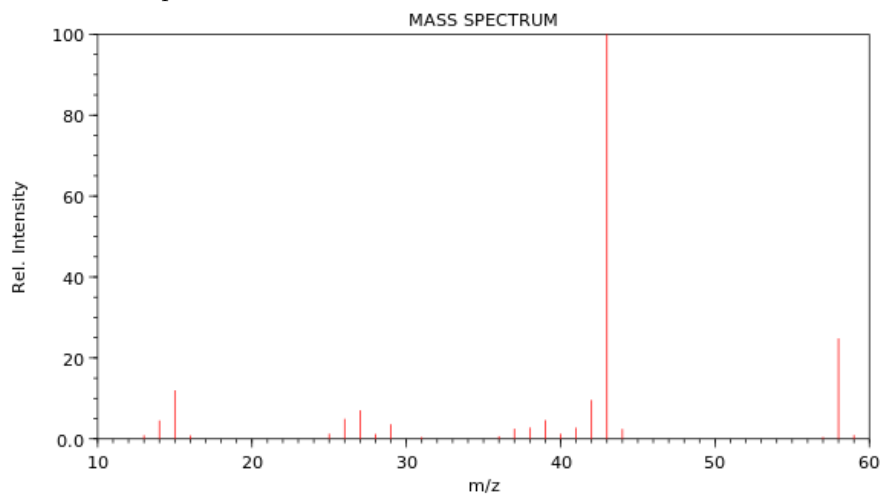
### 3.7 Problem G. RD Corp. and Mechanisms

Daniel decided to apply for an Organic Chemist job in RD Corp. Because of the enormous number of applicants to the position, Ross the Chemist, the lead chemist in the company, decided to carry out an Organic Chemistry exam for all applicants. Daniel studied hard before applying (he even got an IChO gold medal before university), but still he was very worried that he might fail the test. The day of the exam finally came, and Daniel nervously went into the

examination lab accompanied by Ross the Chemist and a stack of papers. The first task Daniel had to complete was very simple: he had to mix reagent **L** and some compound **O**. Reagent **L** has such a structural formula:



Compound **O**, on the other hand, has two peaks in its  $^{13}\text{C}$  NMR spectrum, and such a mass spectrum:



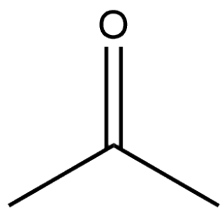
NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

*G-1 What is the true name for reagent **L**?*

Reagent **L** is Lawesson's reagent.

*G-2 Deduce the name and structural formula of compound **O**.*

Compound **O** is acetone. Its structural formula is such:



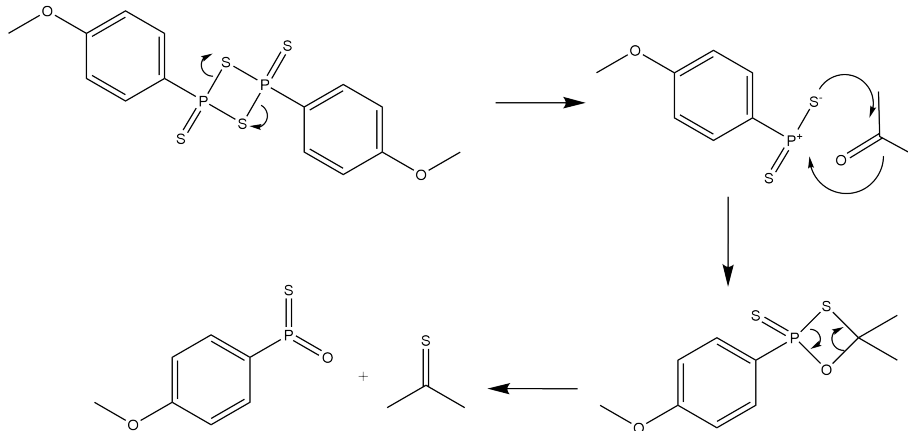
acetone

G-3 Draw the structural formula of the reaction product between **O** and reagent **L**.

G-4 Draw a curly-arrow mechanism for the reaction in G-3.

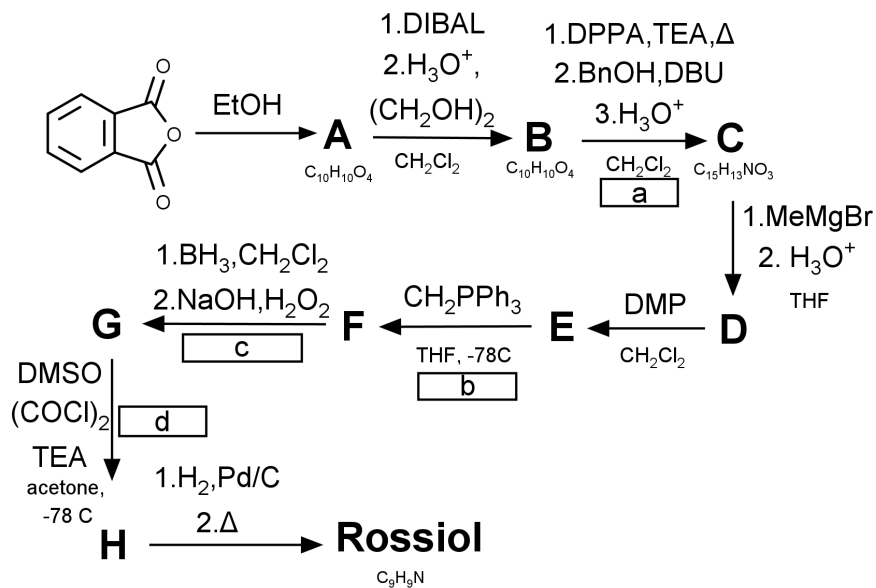
G-5 Which named reaction is very similar to this reaction?

The mechanism for the reaction is as follows:

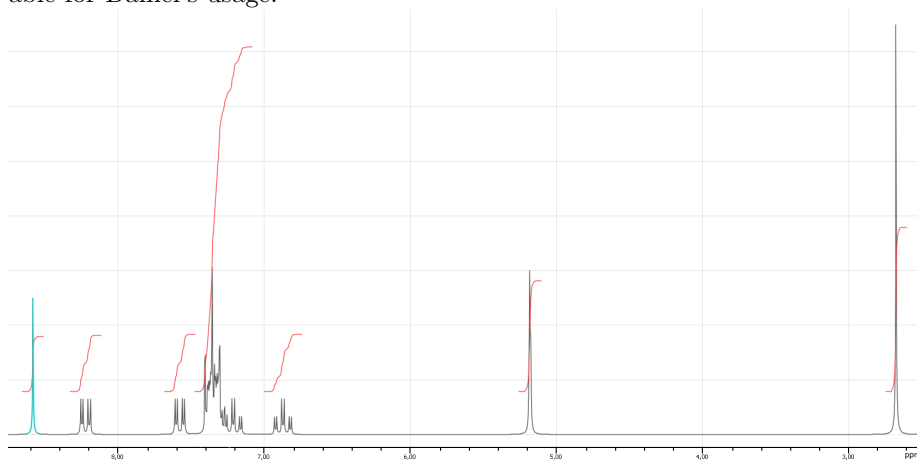


It is interesting that the reaction resembles the Wittig reaction in most of the parts.

The next task Ross the Chemist gave to Daniel is to prepare compound **Rossiol**. Of course, the synthesis is not complete (it is a very tough exam), so Daniel needed to first deduce the intermediates in the synthesis. The empirical formulas for some intermediates are known: A:  $C_{10}H_{10}O_4$ ; B:  $C_{10}H_{10}O_4$ ; C:  $C_{15}H_{13}NO_3$ ; Rossiol:  $C_9H_9N$



There is also an  $^1\text{H}$  NMR spectrum (150 MHz, simulated) of compound **E** available for Daniel's usage.

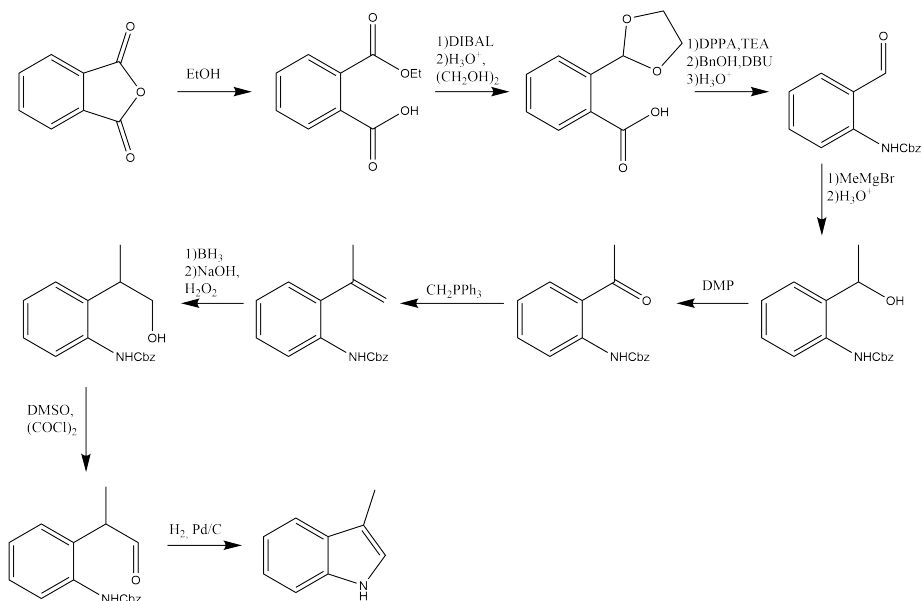


A simulated  $^1\text{H}$  NMR spectrum of compound **E**. The ratio of integrals is as follows (from left to right): 1:1:1:6:1:2:3

*G-6 Determine the structural formulas of compounds **A-H** and **Rossiol**. Draw them without indicating stereochemistry.*

The complete synthesis scheme looks like this:





*G-7 What are the names of the reactions a-d?*

Reaction **a** is the Curtius Rearrangement.

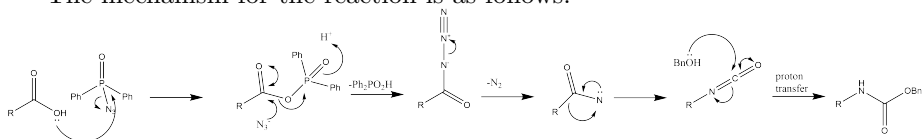
Reaction **b** is the Wittig Reaction.

Reaction **c** is the hydroboration-oxidation reaction.

Reaction **d** is the Swern Oxidation.

*G-8 Draw a curly-arrow mechanism for reaction a.*

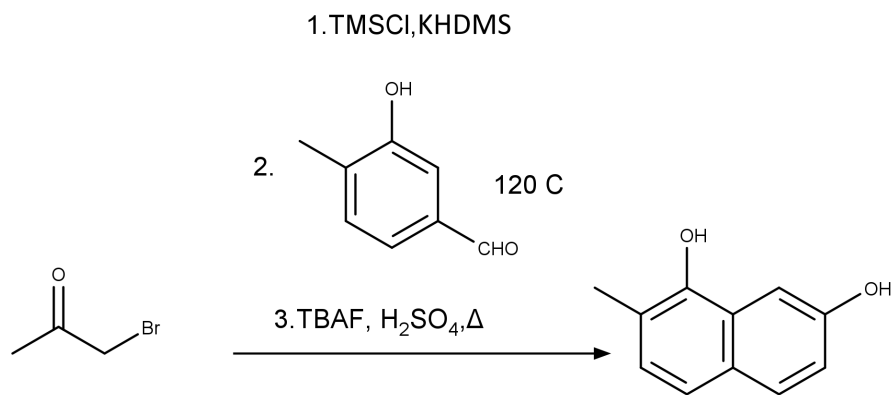
The mechanism for the reaction is as follows:



*G-9 Suggest a way to prepare the reagent  $\text{CH}_2\text{PPh}_3$  for the reaction b.*

The easiest way to prepare such a compound is by first mixing  $\text{PPh}_3$  with methyl iodide, afterwards adding a strong base such as  $\text{BuLi}$ .

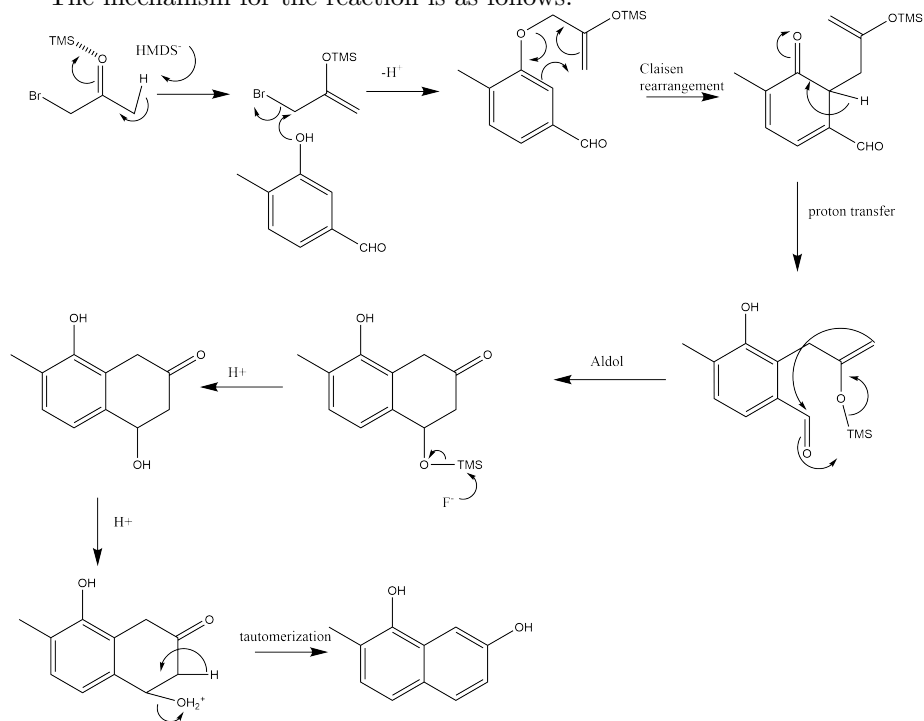
The last challenge Ross the Chemist presented to Daniel was to complete this reaction successfully:



G-10 Draw a curly-arrow mechanism for this reaction.

G-11 If there are any name reactions as steps in the mechanisms, write down their names in your mechanism.

The mechanism for the reaction is as follows:

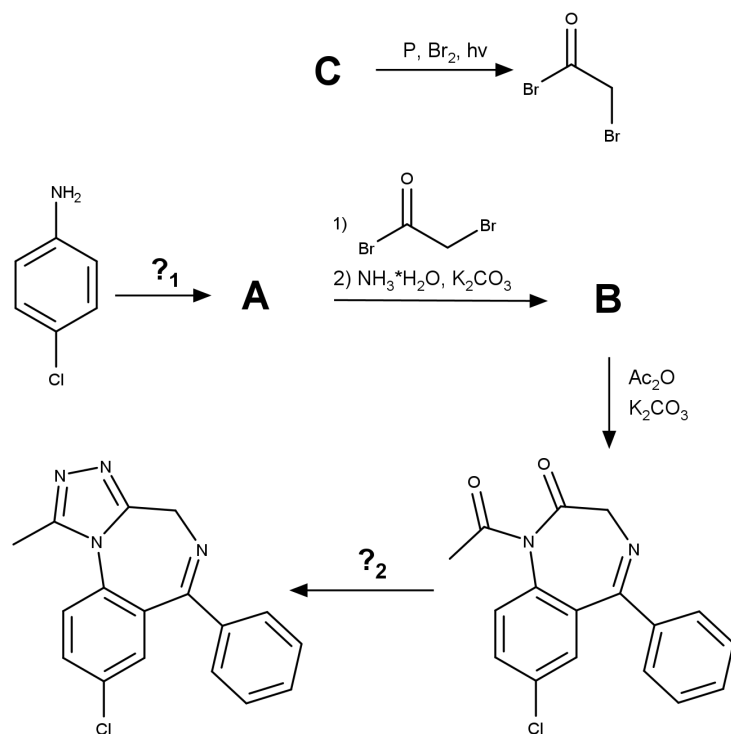


### 3.8 Problem H. LIL BO' CHEM

Gustav the High school student decided to synthesise some medicines at home to sell. He made a few synthesis schemes, but unfortunately Gustav's father

came into Gustav's room and seized part of his synthesis schemes, saying that drawing is a waste of time and that Gustav should become a lawyer. Although, it didn't stop Gustav from completing his plans, and he still had enough of the schemes intact to restore the syntheses.

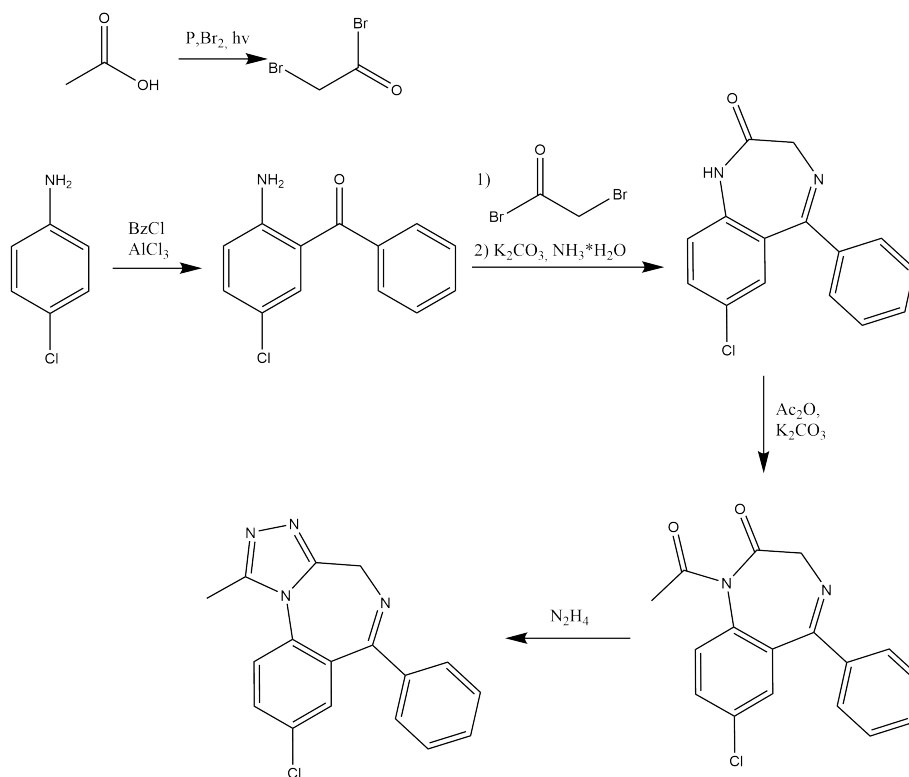
Gustav decided that his potential buyers will need to calm their anxiety down after seeing the mess in his room/lab/shop, and thought that adding a sedative such as alprazolam to his stock will be useful. He made an easy to follow synthesis scheme, but unfortunately it didn't quite survive the attack of Gustav's dad.



H-1 Determine the intermediates **A-C** and the reagents  $?_1$  and  $?_2$  in the synthesis scheme.

H-2 Why is NBS (*N*-bromosuccinimide) not a good reagent for producing the  $\alpha$ -bromoacetophenone?

The complete synthesis scheme looks like this:



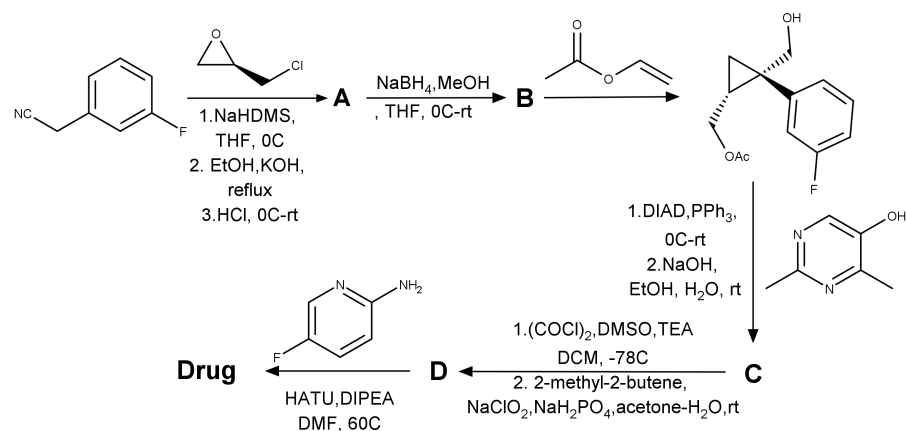
NBS is a bad reagent for such bromination because it can not produce an acyl bromide (*NBS is a source of electrophilic bromine*). Also, if we assume that the reaction with NBS would work, the produced acyl bromide would immediately be attacked by the succinimide ion formed, thus making the reaction useless.

*H-3 What is the name of the reaction 4-chloroaniline  $\rightarrow$  A?*

It is a Friedel-Crafts acylation reaction.

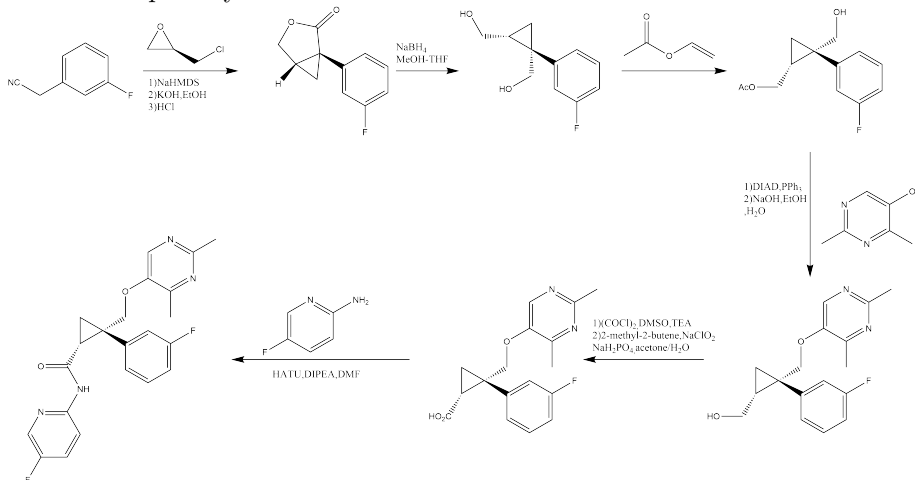
Then, Gustav planned to prepare some pharmacological compounds that'd help him sleep better. He found a molecular formula of a drug that counters insomnia online and designed a synthesis. Sadly, this molecule also didn't survive Gustav's dad and his raid. Gustav recalled the following information:

- **A** contains two oxygen atoms and no nitrogen atoms
- The molar mass of **Drug** is 410.4 g/mol



H-4 Determine the structural formulas of compounds **A-D** and **Drug** in the synthesis.

The complete synthesis scheme looks like this:



H-5 What are the names of two reactions used in step **C** → **D**? Why is 2-methyl-2-butene used in the second reaction of the step?

The first reaction used is Swern Oxidation.

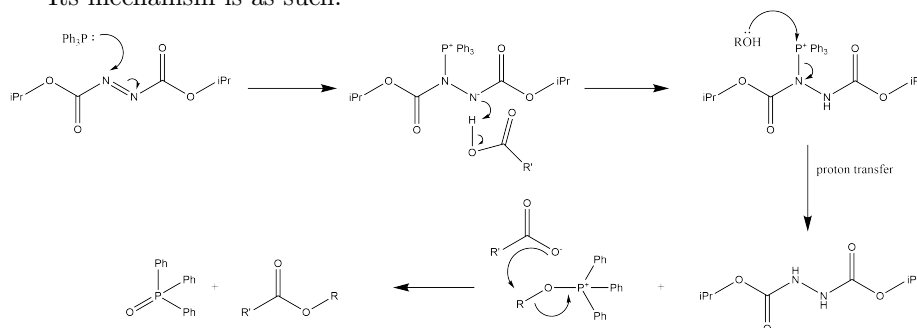
The second reaction used is Pinnick Oxidation.

During the Pinnick Oxidation sodium hypochlorite forms as a reaction product, and because of its unpredictable side reactions, 2-methyl-2-butene is added as a hypochlorite scavenger to the reaction mixture.

H-6 Draw the mechanism of the reaction step resulting in **C** ( $PPh_3$ , DIAD, .....). What is the name of this reaction?

This reaction is called Mitsunobu Reaction.

Its mechanism is as such:



## 4 Conclusion

The authors would like to apologise for the inconsistencies in the Pro League physical Chemistry problems. We will try to improve them the next time around...

The next Meme Chemistry Olympiad will be held in autumn 2021, not to miss out the fun keep an eye at our social media and our website!

We hoped that the solutions were clear to the reader not only as a book of solutions but also as a guide on how to solve similar problems. The goal of the contest was to promote self-study, after all! If something still is unclear to the reader, do not feel shy to email the authors at *memechemistry-olympiad@gmail.com* and ask your questions there!

Good luck!