7th Chemistry Race: Questions and Solutions



7th February 2026

Question A.1 (Václav Verner): Electronic

How many electrons does a single (neutral) molecule of benzene contain?

Solution:

Benzene has the formula of C_6H_6 and the number of electrons is equivalent to all the proton numbers in the molecule added together, giving $6 \times 6 + 6 \times 1 = 42$ electrons in a single molecule of benzene.

Question A.2 (Supatpong Juntarawatt): Chromium extraction

Chromium can be found in nature as various types of ores, such as chromite ($FeCr_2O_4$). To extract chromium from chromite, alkaline roasting under basic conditions is used, followed by leaching and acidic dimerisation. The reaction scheme is shown below. All chemical equations are balanced.

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \longrightarrow 8\,\text{  } + 2\,Fe_2O_3 + 8\,CO_2$$

$$2\,\text{} + 2\,H^+ \longrightarrow \text{  } + H_2O + 2\,Na^+$$

Suggest the chemical formulae of and .

Solution:

From the first equation, 8 formula units of must consist of 8 chromium, 16 sodium, and 32 oxygen atoms. Therefore, is Na_2CrO_4.

From the second reaction, a formula unit of must have 2 sodium, 2 chromium, and 7 oxygen atoms, so is $Na_2Cr_2O_7$.

Question A.3 (Daniel Čičovský): Bengal fire

A popular school demonstration experiment is the so-called Bengal fire. Its mechanism involves adding an oxidizer to the fuel, and optionally a compound that colors the flame.

The reaction can be initiated by a flame or by adding another chemical. Match the individual chemicals to their role in the process.

1. Fuel	A Starch
2. Oxidiser	B Potassium chlorate
3. Flame colouring	C Copper(II) chloride
4. Initiator	D Concentrated sulfuric acid

Solution:

Fuel: A. starch

Oxidizer: B. potassium chlorate

Flame colouring: C. copper(II) chloride

Initiation: D. concentrated sulfuric acid.

Question A.4 (Tatiana Nemirovich): Pretty heavy

How much heavier is a molecule of D_2O compared to H_2O, in kg?

Solution:

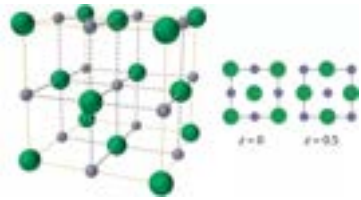
It is heavier by two neutrons, therefore the difference is 3.35×10^{-27} kg.

Question A.5 (V. Verner, T. Nemirovich): Crystallographic

The picture shows the crystal lattice of table salt (NaCl). You can see that the crystal adopts the geometry of an anion face-centred lattice with vacant tetrahedral holes, while the cations occupy octahedral holes. The coordination number of both anions and cations in this compound is 6. This salt crystallises as colourless cubic crystals with $a = b = c$ and $\alpha = \beta = \gamma = 90°$.

Your task is to determine what molar percentage of this compound is sodium. To help you, we provide the following data. The density is $2170\,\mathrm{kg\,m^{-3}}$. Its solubility in ammonia is $21.5\,\mathrm{g\,L^{-1}}$. $E(Na^+/Na) = -2.71\,V$ and $E(Cl_2/Cl^-) = 1.36\,V$. The ground term of Na^+ is $^1S_0$. The ionic radius of Cl^- is 181 pm, the characteristic sodium spectral doublet is at 588.99 nm and 589.56 nm.

The decomposition temperature of cesium carbonate is 610 °C (1130 °F), its molar magnetic susceptibility is -3.18×10^5 μm^3 g^{-1} and it is specifically toxic to testes.

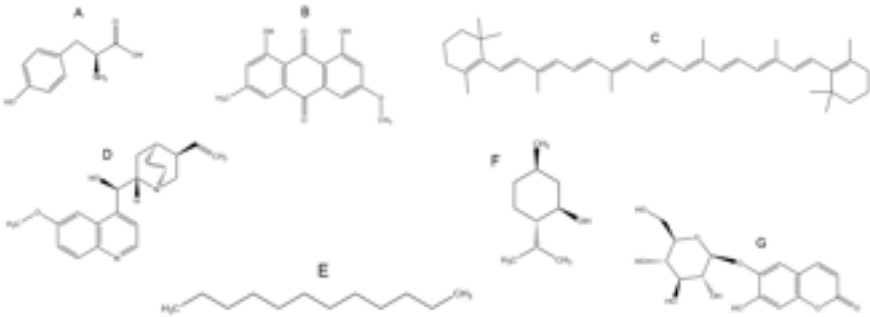


Solution:

Table salt, NaCl, has a Na:Cl ratio of 1:1, so sodium makes up 50 %.

Question A.6 (Daniel Čičovský): Fluorescence

Fluorescence is a phenomenon exhibited by many molecules. In this process, electrons in molecules are excited by light of a specific wavelength, and when the electron returns to its original energy level, light with a longer wavelength is emitted. Many organic substances in living systems are capable of visible light fluorescence under specific illumination. Typically, these are compounds that contain conjugated double bonds or an aromatic ring. Using these rules, select from the options the substances that are likely to fluoresce intensely.



Solution:

All compounds except E and F contain conjugated double bonds or a benzene ring.

Question B.1 (Adam Tywoniak): Implausible is not impossible

It has almost become a rule that the introductory presentation to a Chemistry Race reminds you that unreal transmutations such as

$$\mathrm{Al + Cu \longrightarrow Au + Cl}$$

are not accepted as correct answers. Today, let's have a look at one transformation that might not be common, but it satisfies the balance of electrons and nucleons. Give the identity of particle X (mass number, element symbol, charge) that undergoes the following nuclear decay, liberating an electron:

$$\mathrm{X \longrightarrow {}^{10}_{5}B^{5+} + e^-}$$

Solution:

Since the element boron is defined by having 5 protons, then an atom of $^{10}_{5}\mathrm{B}$ also has 5 neutrons. Given its charge of 5+, it has no electrons whatsoever. A free electron contains no neutrons or protons, which gives it a mass number of 0, and has a negative charge. To satisfy both the conservation of charge and of mass number, particle X must have a charge of 4+ and mass number of 10. This corresponds to a beryllium cation of $^{10}_{4}\mathrm{Be}^{4+}$ with 4 protons, a mass of 10 and no electrons. The implausible transformation in its entirety is then

$$\mathrm{{}^{10}_{4}Be^{4+} \longrightarrow {}^{10}_{5}B^{5+} + e^-}$$

Question B.2 (Tatiana Nemirovich): Motively active

Hydrogen sulfide is primarily known as a gas with an unpleasant odor reminiscent of rotten eggs. Scientists have, however, discovered that this gas plays a key role in biological processes, including reproduction. In the human body, $\mathrm{H_2S}$ acts as an important signalling molecule that influences a variety of functions, from regulating blood pressure to supporting sperm. In sperm, $\mathrm{H_2S}$ improves motility and increases the chances of successful fertilisation of the egg.

$\mathrm{H_2S}$ production in sperm is mediated by enzymes such as cystathionine-β-synthase (CBS) and cystathionine-γ-lyase (CSE), which catalyse the conversion of amino acids to $\mathrm{H_2S}$. This gas subsequently activates signalling pathways that increase cyclic guanosine monophosphate (cGMP) levels, leading to smooth muscle relaxation

and improved blood flow in the reproductive organs. H_2S also acts as an antioxidant, protecting sperm from oxidative stress and supporting their energy metabolism, thereby ensuring optimal motility and viability.

Write down which proteinogenic amino acid is key for H_2S production.

Solution:

In order to create H_2S, an amino acid containing sulphur must be used. Cysteine is correct; methionine is not, because the methyl group (CH_3) blocks the conversion.

Source of inspiration: Kadlec, M., Ros-Santaella, J. L., & Pintus, E. (2020). "The Roles of NO and H_2S in Sperm Biology: Recent Advances and New Perspectives", *International journal of molecular sciences*, 21(6), 2174. DOI: 10.3390/ijms21062174

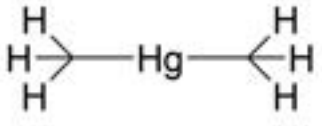
Question B.3 (Kotchapun Saritsiri): The 'Super Toxic' Compound

On 14th August 1996, Karen Wetterhahn, an American professor of chemistry at Dartmouth College, was studying an interaction between a toxic metal ion and a DNA repair protein. However, she spilled several drops of a compound she used onto her latex-gloved hand. Wetterhahn took all recommended precautions but she was not quick enough. Three months after the accident, Wetterhahn began experiencing a significant weight loss, loss of balance and slurred speech. Three weeks after the first neurological symptoms appeared, Wetterhahn's condition began to deteriorate and on June 8 1997, she was removed from life support and pronounced dead, less than a year after her initial exposure. The compound was considered "super toxic" at the time but the later test revealed that it can permeate several kinds of latex gloves and enter the skin within about 15 seconds. Give the structural formula of the compound. The compound consists of 9 atoms. The central atom is a toxic metal that is known for its popularity among the alchemists because of its distinctive state at room temperature. The groups bonded to the central atom are identical and each consists of 2 types of atoms. One is the most abundant element in the universe while the other one is found in the hardest mineral.

Solution:

There are 9 atoms in the compound; 1 is the central atom so each group bonded to the central atom has 4 atoms. The group is methyl ($-CH_3$) as hydrogen is the most abundant element in the universe while carbon is found in diamonds, the hardest mineral. The central atom is mercury (Hg), which is liquid at room temperature.

Alchemists believed mercury had magical properties that could not only transform lead into gold, but also help humans achieve immortality. The symptoms Wetterhahn experienced were from mercury poisoning due to exposure to dimethylmercury ($Hg(CH_3)_2$), which is the mysterious compound. The shape of the compound is shown below.



Question B.4 (Tadeáš Grabic, Jiří Vestfál): Czechoslovak

As part of an agreement between the Czech Republic and Slovakia, several Slovak chemists participate in the Czech national round of the Chemistry Olympiad. In return, Czech chemists then participate in the Slovak round. Last year's Slovak Olympiad took place in Košice, a picturesque city in the far east of Slovakia. The starting point for Czech chemists was Prague.

Traveling from Prague to Košice can be done by train, which takes about 8 hours. An alternative, less environmentally friendly option, is a regular flight on the Prague-Košice route, with a flight time of 1 hour and 10 minutes. The jet engines of a Boeing 737-800, the plane used by the Czech chemists, consume $3217.6\,\ell$ of aviation fuel per hour. Aviation fuel is kerosene, approximated here as dodecane, with a density of $0.79\,\mathrm{g\,ml^{-1}}$.

After a one-way flight (the Chemistry Olympiad budget is not unlimited), calculate

$$\frac{\text{Mass of } CO_2 \text{ in atmosphere}}{\text{Mass of } CO_2 \text{ in atmosphere before flight}}$$

The mass of the atmosphere is $5.157 \times 10^{18}\,\mathrm{kg}$, and the initial O_2 content is 21 % and the CO_2 content is 0.043 %. Do not neglect the oxygen consumed during the combustion of aviation fuel. Round the result to two decimal places.

Solution:

The mass of carbon dioxide in the entire atmosphere is so large that even a single flight, despite releasing a considerable amount of CO_2, does not change the total mass enough to affect the first two decimal places, so the answer will be 1.00.

Question B.5 (Václav Verner): Chemistry Race cooks

A talented chemist named Štěpán decided to become the chef for the Chemistry Race organizers' gathering. As both a professional chemist and a practically Michelin-level cook, he wanted to impress everyone by preparing steak with potatoes, steamed vegetables, and a tarragon sauce.

But what a disaster! By mistake, Štěpán brought 20 g of powdered estrogen from the lab instead of 20 g of dried estragon (a.k.a. tarragon)! He managed to dissolve it in the hot sauce, and luckily, he didn't taste it while cooking – that could have had some unpleasant consequences…

The typical estrogen dose for males undergoing hormone therapy is 4 mg per day. If 10 male and two female organizers attended the Chemistry Race gathering, and each person ate the same amount of the estrogen sauce, by how many times did each male organizer exceed the daily hormone therapy dose? (Ignore the differences in biochemistry between males and females.)

Solution:

The total amount of estrogen was 20 000 mg. This was divided among 12 organizers, so each received

$$\frac{20\,000}{12} = 1666.67\,\text{mg}.$$

Since the daily dose is 4 mg, each organizer exceeded it by

$$\frac{1666.67}{4} = 417$$

times.

Question B.6 (Václav Verner): Anhydrous metal halides

Some metal halides cannot be dehydrated by simple heating of the hydrate, because it will lead to decomposition. The prime example of this is iron(III) chloride hexahydrate, where the products of decomposition are Fe_2O_3, HCl and H_2O.

One of the methods in which you can actually dehydrate this salt is by addition of non-metal chlorides, which gives only gaseous products besides the anhydrous salt. Your task is to write the balanced equation of the dehydration of $FeCl_3 \cdot 6\,H_2O$ by $SOCl_2$. Use the smallest integer coefficients.

Solution:

$$\mathrm{FeCl_3 \cdot 6\,H_2O + 6\,SOCl_2 \longrightarrow FeCl_3 + 6\,SO_2 + 12\,HCl}$$

Question C.1 (Adam Přáda): Gold diggers

SEX was discovered in Denmark by William Christopher Zeise in 1823, which has delighted many. Given this huge achievement, he was awarded a silver medal by the Royal Danish Academy of Sciences and Letters and was knighted by the Danish king. However, by now SEX is mostly used by the gold diggers. Since SEX can be dangerous to health, in most countries regulations are in place to avoid children being exposed to SEX. Appropriate latex protection can reduce the risks associated with SEX and, when utilised responsibly, SEX can be beneficial to humanity.[1]

Sodium Ethyl Xanthate (SEX) is used as a so-called flotation agent in the mining industry for the recovery of gold, silver, copper or nickel. The gold containing rock is ground and mixed with water to make a slurry. The golden ore (typically pyrite) is separated from the slurry by addition of SEX resulting in a creation of froth that can be collected. Usually, about 100 g of SEX per metric ton of rock is needed for flotation. The rock contains about 5 ppm of gold by weight and the fractional recovery of gold is about 80 %. How much SEX do you need to obtain 1 g of gold? Give your answer in grams.

Solution:

We know how much SEX is needed for an amount of rock, so we need to calculate how much rock we need for 1 g of gold. Since the fractional recovery is 80 %, the actual amount of gold in the rock must be $1/0.8 = 1.25\,\mathrm{g}$. Gold is 5 ppm by weight, so the mass fraction of gold in the rock is 5×10^{-6}.

$$m_{\mathrm{gold}} = m_{\mathrm{rock}} \times 5 \times 10^{-6}$$

$$m_{\mathrm{rock}} = 250\,\mathrm{kg}$$

We know that the amount of SEX is 100 g per 1000 kg, so the final answer is that we need 25 g of SEX to get 1 g of gold.

[1] Citation needed.

Question C.2 (Ondřej Daněk): A metre-long alkane

How many carbon atoms must a linear alkane consist of, to have a total length of 1 metre when in the ideal conformation with maximal length? Assume that the C-C bonding angles are exactly 109.5° (the same as a regular tetrahedral molecule, when rounded). The length of C-C bond is assumed to be exactly 154 pm and the length of C-H bond is exactly 110 pm.

Solution:

Each C–C bond in the fully extended zig-zag chain contributes only part of its length along the axis, equal to:

$$154\,\text{pm} \times \cos\left(\frac{180°–109.5°}{2}\right) = 125.8\,\text{pm}$$

Each terminal C–H bond adds:

$$110\,\text{pm} \times \cos\left(\frac{180°–109.5°}{2}\right) = 89.9\,\text{pm}$$

The total length of an n-carbon chain is therefore:

$$L = (n-1) \times 125.8\,\text{pm} + 2 \times 89.9\,\text{pm} = (n-1) \times 125.8\,\text{pm} + 179.8\,\text{pm}$$

Using the conversion $1\,\text{m} = 10^{12}\,\text{pm}$ gives

$$10^{12}\,\text{pm} = (n-1) \times 125.8\,\text{pm} + 179.8\,\text{pm}$$

Hence:

$$n - 1 = \frac{10^{12}\,\text{pm} - 179.8\,\text{pm}}{125.8\,\text{pm}} = 7\,951\,476\,938$$

The alkane must therefore contain 7 951 476 939 carbon atoms to reach a total length of 1 metre. During the competition, anything between 7 950 000 000 and 7 960 000 000 was accepted.

Question C.3 (Adam Přáda): Spunk

Spunk is a brand of Danish salty liquorice candy. It's named after a nonsensical word (like skibidi) invented by the fictional character Pippi Longstocking from the pen of a Swedish author Astrid Lindgren. The main ingredients of this candy are (percentage by mass):

Sugar: 40 %; Starch: 38 %; Salmiak (ammonium chloride): 5 %; Salt (sodium chloride): 0.82 %.

A common person might be worried when looking at the ingredients, since ammonium chloride looks more like a lab chemical rather than something you want to eat. Let's see whether there is actually something to worry about. Below, you will find the oral LD_{50} (the dose that kills 50 % of individuals) for each of the main ingredients (as measured for mice, but let us assume it is the same for humans): Sucrose: $29.7\,g\,kg^{-1}$ of body mass; Starch: $33.9\,g\,kg^{-1}$ of body mass; Ammonium chloride: $1.65\,g\,kg^{-1}$ of body mass; Sodium chloride: $3\,g\,kg^{-1}$ of body mass.

Answer the following questions: (1) How much Spunk will kill you if ingested? (with 50 % chance) (2) Which ingredient kills you first? Assume you weigh 60 kg.

Solution:

It is, indeed, the suspicious ammonium chloride that kills you first, but you would still have to eat 1980 g or approximately 1000 pastilles, which seems an unlikely danger given the strong astringent salty taste.

$$m(\text{Spunk}) = \text{LD}_{50} \times \frac{m(\text{body})}{w(\text{substance})}$$

	Sugar	Starch	NH_4Cl	NaCl
Fraction	0.4	0.38	0.05	0.0082
LD_{50} $g\,kg^{-1}$	29.7	33.9	1.65	3
g per body	1782	2034	99	180
Spunk g	4455	5353	1980	21951

Question C.4 (Adam Horák): (Non)reactive

The noble gases form Group 18 of the periodic table and are characterized by their very low chemical reactivity due to their fully filled valence electron shells. This group includes helium, neon, argon, krypton, xenon, and radon. These elements are inherently very stable and form very few compounds, which often require extreme conditions for their preparation.

The most well-known exceptions are xenon fluorides, such as XeF_2, XeF_4, and XeF_6, which are used as very strong oxidizing agents.

In 2000, according to Gemini, the first compound of argon was discovered. The newly described compound contains three elements, including 1.67 % hydrogen and 31.69 % fluorine by mass.

Determine the empirical formula of this compound.

Solution:

The first compound of argon was discovered in 2000 and consists of three elements with mass fractions of
1.65 % of hydrogen, 31.69 % of fluorine and 66.64 % of argon. If we assume sample of mass 100 g, masses of given elements are 1.67 g of H, 31.69 g of F, and 66.64 g of Ar. Calculation of the amount of substance leads to

$$n = \frac{m}{M}$$
$$n(\mathrm{H}) = \frac{1.67}{1.01} = 1.65\,\mathrm{mol}$$
$$n(\mathrm{F}) = \frac{31.69}{19.00} = 1.668\,\mathrm{mol}$$
$$n(\mathrm{Ar}) = \frac{66.64}{39.95} = 1.668\,\mathrm{mol}$$

Dividing by the smallest value (1.65) we get H : F : Ar $\approx$ 1 : 1 : 1. Empirical formula is then HArF.

Question C.5 (Adam Tywoniak): Habemus fumum

The Papal conclave of May 2025 attracted considerable worldwide attention. Crowds gathered to observe the smoke rising from Sistine Chapel, the colour of which indicated whether a new head of the Roman Catholic church was elected after each round of voting. Let's focus on one perhaps overlooked aspect of this process: the chemistry of combustion producing said smoke. While the visible part of black smoke consists of soot particles, white smoke has a component of water vapour-based aerosols.

It has been published that the mixture used to form black smoke in 2013 consisted of potassium perchlorate, anthracene and sulfur. The white smoke was formed by burning a mix of potassium chlorate, lactose and Greek pitch, a type of pine resin.

Balance the formula below that corresponds to the three-component reaction producing black smoke. (Anthracene is a hydrocarbon derived from naphthalene in the same way that naphthalene is derived from benzene.)

For simplicity, let us assume that no additional (atmospheric) oxygen is consumed, that the starting mixture contains approximately equal masses of anthracene and

sulfur which result in their respective molar ratio of 1:11, and that half of the total amount of carbon is turned into elemental C.

$$KClO_4 + C_{14}H_{10} + S \longrightarrow C + CO_2 + SO_2 + H_2O + KCl$$

Solution:

The ratios given are satisfied by the balanced equation:

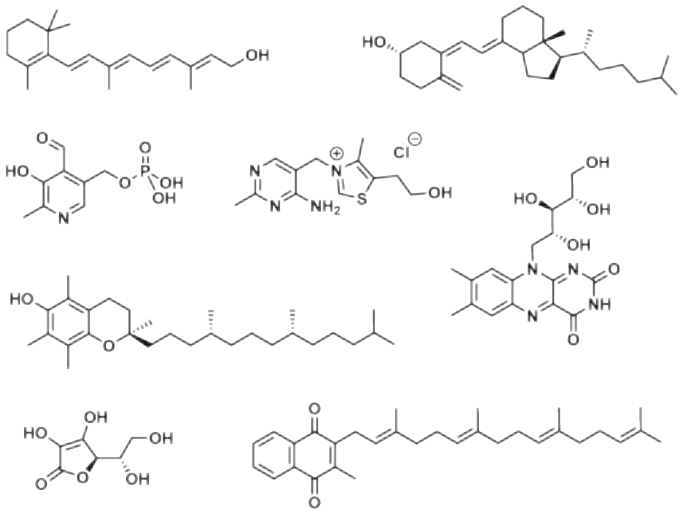
$$41\,KClO_4 + 4\,C_{14}H_{10} + 44\,S \longrightarrow 28\,C + 28\,CO_2 + 44\,SO_2 + 20\,H_2O + 41\,KCl$$

Question C.6 (Jiří Ledvinka): Olestra

Olestra is a group of substances approved in 1996 by the FDA (not to confuse with AfD) for use as a non-caloric fat substitute in foods.

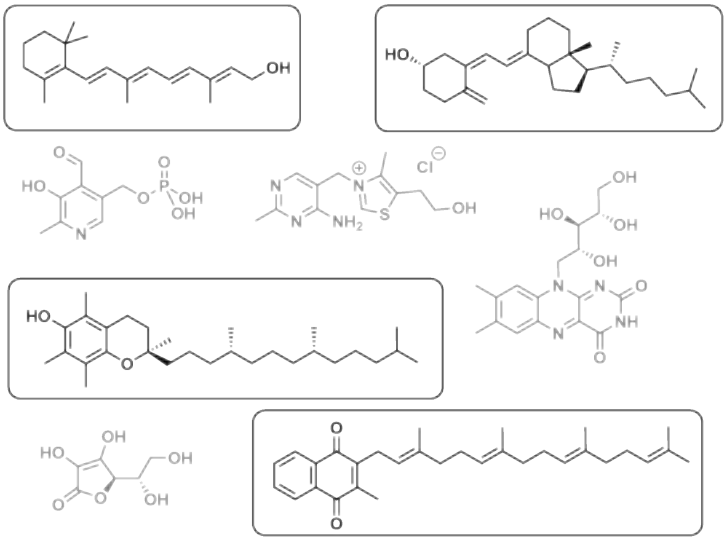
Olestra consists of sucrose esters with 6 to 8 fatty acid chains. Compared to natural fats (glycerol triesters), Olestra molecules are so bulky and sterically protected against enzymatic degradation that they are not absorbed in the intestine and pass through the digestive tract unchanged. This sometimes causes diarrhea.

The second adverse effect is that the extremely hydrophobic Olestra binds some vitamins and thus prevents their intake from food. From the vitamins shown below, select those 4 molecules that Olestra binds the most and prevents their intake from food.



Solution:

Since Olestra is strongly hydrophobic, it also binds hydrophobic vitamins. Of the listed vitamin structures, the lipophilic ones are evident - they practically only have an aliphatic skeleton with a minimum of polar functional groups.



Question D.1 (Supatpong Juntarawatt): Yellowish coins

Agent FE0000 has stumbled upon several yellowish "coins" floating everywhere during one of his travels. His colleagues confirmed that the coin was made of gold, silver, and copper. However, he was still curious about the quantitative composition of the coin sample. Excess nitric acid was added to 10 g of the coin sample. There were 2.96 g of a dark yellow solid remaining when the reaction had been completed.

Afterwards, he added an excess NaCl solution to the blue solution obtained from the previous stage, where he got 4.30 g of white powder. If he adds an excess amount of Fe powder to reduce Cu ions in the solution after filtering AgCl away, calculate the mass of copper he should obtain at the end in grams to 1 decimal point.

Solution:

Mass of Au (the dark yellow solid, as Au does not react with nitric acid) in the sample is 2.96 g.
Mass of Ag in the sample is

$$\frac{4.3}{143.32} \times 107.87 = 3.24\,\text{g}$$

noting that the white powder is AgCl, according to the question.

Mass of Cu in the sample is

$$10 - 2.96 - 3.24 = 3.80\,\text{g}.$$

Question D.2 (Supatpong Juntarawatt): Hard Water

When water from natural sources passes through porous minerals like limestone or gypsum, the concentration of divalent ions like Ca^{2+} increases. This is called hard water, whose properties include the formation of limescale (deposits of $CaCO_3$) in pipes and appliances, and lime soap with a sodium stearate, the main component in soap (making bubbles impossible to form when showering with hard water).

พิชญุตม์ [Pichayut] wants to analyse the hardness of groundwater in his hometown. He added a few drops of Eriochrome Black T indicator and ammonia-based pH 10 buffer (5 mL) to 50 mL of the water sample in his flask. After that, the sample is titrated against 0.38 % w/v EDTA ($C_{10}H_{12}N_2Na_4O_8$), which forms 1:1 complex with Ca^{2+}, until the solution changes from wine red into blue.

At the end, he used 45.00 mL of EDTA solution. Assuming that the hardness of his groundwater only stems from the presence of Ca^{2+}, calculate the water hardness of the sample in dGH (degree of general hardness). Take note that 1 dGH is defined as 10 mg of CaO per litre. Assume the density of all solutions equals the density of water.

Solution:

Concentration of EDTA solution

$$c = \frac{0.38\,\text{g}}{0.1\,\ell} \times \frac{1\,\text{mol}}{380\,\text{g}} = 0.01\,\text{mol}\,\ell^{-1}$$

Moles of EDTA used for the titration

$$n = 0.01\,\text{mol}\,\ell^{-1} \times 45.00 \times 10^{-3}\,\ell = 4.5 \times 10^{-4}\,\text{mol}$$

Thus, the concentration of Ca^{2+} in groundwater is:

$$Ca^{2+} = \frac{4.5 \times 10^{-4}\,\text{mol}}{50 \times 10^{-3}\,\ell} = 9 \times 10^{-3}\,\text{mol}\,\ell^{-1}$$

Converting the units into dGH, the water hardness is:

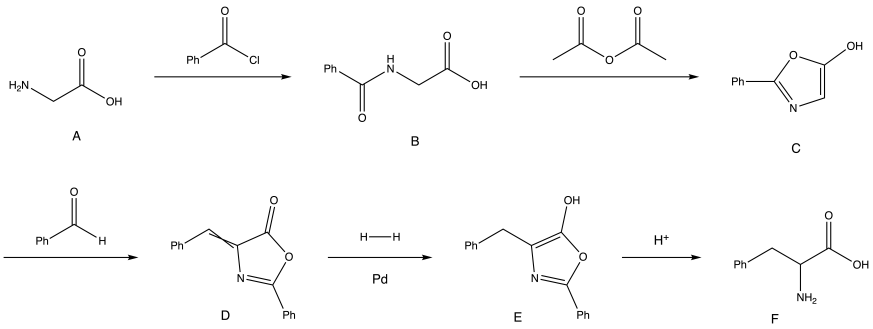
$$9 \times 10^{-3}\,\text{mol}\,\ell^{-1} \times \frac{1000 \times 56\,\text{mg}}{1\,\text{mol} \times 10} = 50.4\,\text{dGH}$$

Question D.3 (Václav Verner): Erlenmeyer's

Richard August Carl Emil Erlenmeyer (28 June 1825 – 22 January 1909), known simply as Emil Erlenmeyer, was a German chemist known for contributing to the early development of the theory of chemical structure and formulating the Erlenmeyer rule regarding tautomer equilibria. He also designed the Erlenmeyer flask, a specialized apparatus ubiquitous in chemistry laboratories, which is named after him.

In 1863 he became associate professor at the University of Heidelberg. In 1868 he was hired as a full professor in Munich to take charge of the laboratories of the new Munich Polytechnic School, a post which he held until he retired from teaching in 1883. His work mostly focused on theoretical chemistry, where he suggested the structural formula for naphthalene. Erlenmeyer's practical investigations were concerned mostly with aliphatic compounds. In 1859 he synthesised aminohexanoic acid and proceeded to study the general behavior of albuminoids on hydrolysis. He worked out methods to determine the relative amounts of leucine and tyrosine, which are produced during the degradation of several substances of this class. His investigations in the aromatic series include isomerism of the cinnamic acids and the synthesis of tyrosine from phenylalanine (1882). In 1875, by nitrating benzoic acid, Erlenmeyer disproved the prevalent opinion that more than three nitrobenzoic acids exist.

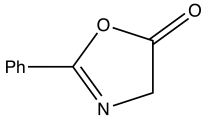
He is also known for his synthesis of racemic alfa-amino acids called the Erlenmayer azlactone amino acid synthesis. You may see the scheme of this series of reactions below, this particular synthesis is for the canonical amino acid Phenylalanine. Your task is to determine the tautomer (isomer differing by hydrogen and pi-bonds) of compound C which should be more stable than the one drawn given the Erlenmayer rule. Note: crossed double bond means that Z/E isomer is undefined.



Solution:

As we know from the task, the Erlenmayer rule is concerning tautomerism and the only tautomerism compound C can go through is keto/enol. Enamine/imine cannot occur, since the enamine form would require a triply bonded oxygen or a carbon with five bonds (a double bond from a benzene core). The keto/enol yields us with a lactone, which obeys the Erlenmayer rule since keto compounds are generally more stable than enols.

Author's note: With compound C, the enol form might be more stable than regular enol compounds because of the conjugated oxazol system forming in this form. However, various publications regarding this actual compound and vendors selling it all agree, that even in this case, the keto form (2-phenylazlactone) is the prevalent one.



2-phenyloxazol-5(4*H*)-one

Question D.4 (Neil Waterson): FOOF

Dioxygen difluoride, FOOF, contains an O-O bond. Despite being a single bond the barrier to rotation of the bond is almost identical to the bond dissociation energy of the O-F bond. In addition, the bond length is almost as short as a O=O bond. Dioxygen difluoride reacts to form dioxygenyl salts (and a gas as the only byproduct). These contain the O_2^+ ion.

Write down the balanced equation for the reaction of dioxygen difluoride with phos-

phorus pentafluoride (which react in a 1:1 molar ratio). During the reaction the phosphorus does not change its oxidation state.

Solution:

A salt containing O_2^+ must be formed, so the negative ion must be PF_6^- if phosphorus remains in the same oxidation state. Analysis of the stoichiometric coefficients reveals that additional fluorine must be produced.

$$2\,O_2F_2 + 2\,PF_5 \longrightarrow 2\,O_2PF_6 + F_2$$

Question D.5 (Adam Horák): Investment task

At the end of December 2021, the Chinese government ordered the closure of a bromine production plant in the city of 寿光 [Shouguang] (Eastern China) as part of air pollution control measures commonly applied during the winter. This step significantly reduced the local supply of this raw material, leading to a substantial increase in the commodity price (according to the Bromine Price Index on the Business Analytiq website, by 440 %). At that time, 2 斤 of bromine would cost approximately 70.07 元.

As savvy businessmen, you decided to extract bromine from seawater and sell it to maximize profit. You have all the necessary chemical equipment, 1 cubic 丈 of seawater ($\rho = 0.75926$ 两 per cubic 寸), 10 斤 of MnO_2, and 10 升 of 37 % HCl. The bromide content in seawater is about $69\,\mathrm{mg}\,\ell^{-1}$.

Calculate how many mg of elemental bromine you can obtain from 1 kg of seawater if your process efficiency is 82 %. Round the result to the nearest mg. Neglect any side reactions and approximate seawater as a solution of salts and bromide anions.

1 USD	≈ 6.37 元 (2021 rate)	1 寸	≈ 3.33 cm
1 USD	≈ 7.23 元 (average Q2 2025 rate)	1 尺	≈ 33.3 cm
1 两	= 50 g	1 丈	≈ 3.33 m
1 斤	= 0.5 kg	1 升	≈ 1 ℓ

Solution:

0.75926 两 per cubic 寸 corresponds to a density of $1.025\,\mathrm{g\,m}\ell^{-1} = 1.025\,\mathrm{kg}\,\ell^{-1}$ of water. 1 kg of water corresponds to approximately $0.9756\,\ell$.

The bromide content is $0.9756\,\ell \times 69\,\mathrm{mg}\,\ell^{-1} \approx 67.317\,\mathrm{mg}$ of bromide = 67.317 mg of bromine (mass is conserved, only molar quantity changes).

Considering an 82 % process efficiency: 67.317 mg $\times 0.82 \approx 55.2$ mg of bromine per 1 kg of seawater. Rounded to the nearest integer, that is55 mg.

Question D.6 (Vadim Kablukov): Junger Fritz

Little Fritz has been tasked with some homework: to fill a vessel of $1 \times 2 \times 200$ m with a gaseous diatomic to reach atmospheric pressure. Little Fritz miscalculated something, though. In his calculations, he was working with a temperature of 25 °C and 15 % loss of original material, and bought his materials according to that. But when he arrived at his destination, he found out that the temperature is 15 °C and the losses are going to be around 35 %. To his surprise, though, the atmospheric pressure was exactly the same as he was working with. What percent of the original amount of substance will Fritz need to fill the vessel?

Solution:

According to the ideal gas law $pV = n\mathrm{R}T$, at constant pressure and volume the amount of gas is inversely proportional to the temperature in kelvins. Fritz originally calculated with a temperature of 25 °C (298.15 K) and losses of 15 %.

The actual temperature is 15 °C (288.15 K) and losses are 35 %. The ratio of the new required amount of gas to the original one is

$$\frac{n_2}{n_1} = \frac{T_1}{T_2} = \frac{298.15}{288.15} = 1.0347$$

Originally, Fritz expected 15 % loss, so he bought:

$$\frac{n_1}{1 - 0.15} = \frac{n_1}{0.85} = 1.1765 \times n_1$$

Considering the 35 % losses, Fritz must buy:

$$\frac{n_2}{1 - 0.35} = \frac{n_2}{0.65} = 1.5926 \times n_1$$

The ratio of the new required amount to the original one is

$$\frac{1.5926 \times n_1}{1.1765 \times n_1} = 1.354$$

or about 135 %. Therefore, Fritz will need approximately 35 % more gas than he originally calculated.

Question E.1 (Quyll Pavlakovic): More (or less?) polonium

In 2006, Alexander Litvinenko was poisoned using an estimated 10.0 µg of $^{210}_{84}$Po, with a half life of 138 days. As a very small proportion of you discovered last year, in the alternate lore of Chemistry Race, Andrey Lugovoy and Dmitri Kovtun instead possess a sample of $^{206}_{84}$Po, with a much shorter half life of 8.81 days. What mass of $^{206}_{84}$Po would the agents require to have the same initial radioactive activity as with the $^{210}_{84}$Po?

Solution:

Dividing 138 days by 8.81 days finds that $^{210}_{84}$Po has a half life 15.7 times greater than $^{206}_{84}$Po. This means that $^{206}_{84}$Po has an activity 15.7 times greater for the same number of moles.

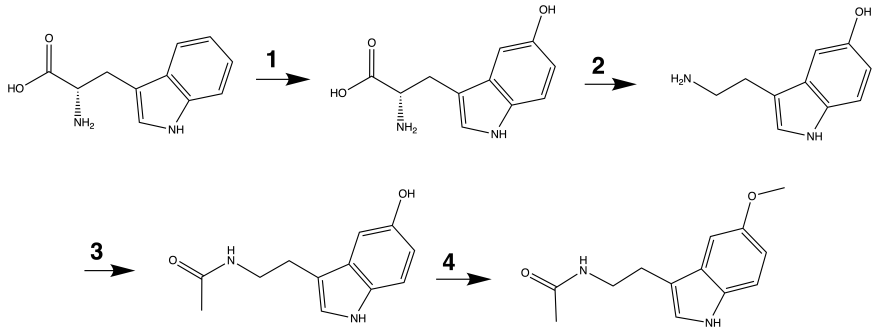
Factoring in that $^{206}_{84}$Po has a lower atomic mass than $^{210}_{84}$Po, the mass of $^{206}_{84}$Po required is:

$$10\,\mu g \times \frac{206}{210} \times \frac{1}{15.7} = 0.626\,\mu g = 626\,ng$$

Question E.2 (Václav Verner): Biosynthesis of melatonin

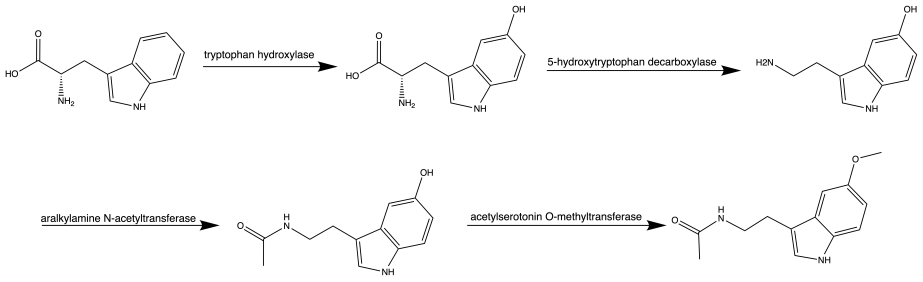
Biosynthesis is a phenomenon in biochemistry, when we talk about synthesising complex molecules from readily available precursors in the human body by enzymes.You are given a blank biosynthetic pathway for melatonin (the sleepy sleepy hormone), where you may see the first reactant – tryptophan – and the product – melatonin. Based on the structures of the products, assign the correct enzyme names for each step from the list below.

A – 5-hydroxytryptophan decarboxylase
B – acetylserotonin *O*-methyltransferase
C – 5-hydroxytryptophan *O*-methyltransferase
D – aralkylamine *N*-acetyltransferase
E – melatonin *N*-acetyltransferase
F – tryptophan decarboxylase
G – tryptophan hydroxylase
H – aralkylamine *O*-methyltransferase



Solution:

Each of the enzyme names correspond to the reaction change, therefore the correct solution is:
1 – G, 2 – A, 3 – D, 4 – B.



Question E.3 (Ošamarben Ládaň): Hotter than a burning bush

9 out of 11 people surveyed at a networking event of chemistry "professionals" agree that burning jet fuel is capable of melting structural steel, such as that found in modern high-rise buildings. The melting point of steel is approximately in the range of 1370 °C - 1540 °C, depending on the exact alloy used. Dodecane (which we use to approximate jet fuel) has an enthalpy of combustion of $-7513\,\mathrm{kJ\,mol^{-1}}$ (taking gaseous H_2O as a product). The dodecane is assumed to react stoichiometrically with air, which is 23.2 % oxygen by mass. The reactants are initially at 20 °C, however become significantly hotter as a result of the combustion. We will assume that

the products of the reaction (as well as the unreacted air) have the same specific heat as normal air, at $1.005\,\mathrm{kJ\,kg^{-1}\,K^{-1}}$ and we will neglect any heat associated with phase changes of any reactant or product.[2] Calculate the maximum achievable temperature by the combustion in °C.

Solution:

The balanced equation for the complete combustion of dodecane is

$$\mathrm{C_{12}H_{26}} + \frac{37}{2}\,\mathrm{O_2} \longrightarrow 12\,\mathrm{CO_2} + 13\,\mathrm{H_2O}\ \cdot$$

One mole of dodecane has a mass of 170 g. The amount of oxygen required is

$$18.5\,\mathrm{mol} \times 32\,\mathrm{g\,mol^{-1}} = 592\,\mathrm{g\ O_2}.$$

Since air is 23.2 % oxygen by mass, the total mass of air needed is

$$592/0.232 = 2552\,\mathrm{g}.$$

The total mass of the reacting mixture is therefore

$$170\,\mathrm{g} + 2552\,\mathrm{g} = 2722\,\mathrm{g} = 2.722\,\mathrm{kg}.$$

The enthalpy of combustion of one mole of dodecane is 7513 kJ. This energy is assumed to heat the entire 2.722 kg of gas. Using the relation $Q = m \cdot c \cdot \Delta T$, the temperature rise is

$$\Delta T = \frac{Q}{m \times c} = \frac{7513}{2.722 \times 1.005} = 2746\,\mathrm{K}.$$

Adding this temperature increase to the initial 20 °C gives a final temperature of $20 + 2746 = 2766$ °C.

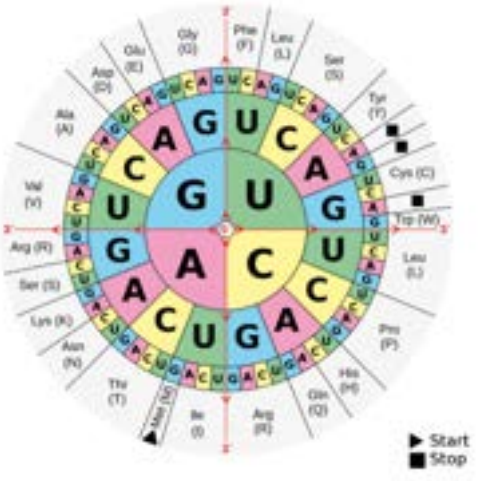
As ChatGPT would tell you: "Under these simplified assumptions, the adiabatic flame temperature is about 2766 °C. This value is much higher than the melting point of steel, but the approximation is unrealistic because real combustion products do not have the same heat capacity as air. In reality, dissociation of CO_2 and H_2O at high temperatures limits the flame temperature, and actual jet fuel flames reach around 2100 °C under optimal conditions. The theoretical result simply represents an upper limit based on the assumptions made." As you can see, that has not made it better, since 2100 is still much higher than 1540.

[2] This is a wildly incorrect approximation

Question E.4 (Václav Verner): Central dogma

DNA is the key component to life. It encodes proteins, which get created through subsequent transcription and translation of DNA. But have you ever thought about how effective this process actually is? And we are not talking about errors in translation or transcription, but about mass. The organizing team came up with an apparently random DNA strand whose complementary strand is 5'-GCCTCTTCG-3' ($M = 2852\,\mathrm{Da}$ rounded to an integer and omitting phosphate counterions).

Calculate, how many times on average (it does not have to be an integer) would this strand of DNA need to be converted to a protein to get the same mass of peptide as the DNA strand weighs itself.



Solution:

The molecular weight of the final peptide, which is Ala-Ser-Ser, is

$$89 + 2 \times 105 - 2 \times 18 = 263\,\mathrm{Da}$$

(The protonation of the amine and deprotonation of the carboxylate do not change the molecular mass.) The number of times this process will have to be repeated is given by

$$\frac{M(\mathrm{DNA})}{M(\mathrm{pep})} = \frac{2852}{263} = 10.84\ .$$

Question E.5 (Tatiana Nemirovich): Christmassy

At one of the Christmas parties of a research group at the Academy of Sciences, held in the apartment of an eccentric scientist who, besides his passion for science, also had the unusual hobby of making YouTube videos, a bizarre situation occurred. Amid laughter, debates, and Christmas melodies, one of the scientists, likely a bit more cheerful from alcohol, lost his balance and almost vomited into a strange box placed under the table.

When he recovered and the colleagues around him examined the box, they discovered it was not just some old crate. It was a mass spectrometer, set to measure negatively charged ions. What would have happened if the accident had actually occurred and he had vomited into it?

The peaks of which element would the spectrometer measure with the greatest intensity, and how many of those peaks would appear in the spectrum? The stomach contents can be approximated as primarily consisting of the main component of gastric juice.

Solution:

The main component of gastric juice is HCl, so the mass spectrometer would measure chloride anions (Cl^-). Since chlorine has two stable isotopes, the spectrum would show two peaks.

Question E.6 (Filip Hůlek): Fireflies

Fireflies create light through the following chemical reaction:

$$\text{Luciferin} + \text{ATP} + \text{O}_2 \longrightarrow \text{Oxyluciferin} + \text{AMP} + \text{PP} + \text{Light}$$

The period of their flickering is dependent on temperature. In the firefly species *Nipponoluciola cruciata*, the period was measured to be 3.3 s at 13 °C, but decreased to 1.9 s at 25 °C. Use these data to estimate the activation energy required for the oxidation of luciferin in $\text{kJ}\,\text{mol}^{-1}$. The dependence of the flicker period on temperature is governed by the Arrhenius equation.

Solution:

The Arrhenius equation is

$$k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{\mathrm{R}T}}$$

For the ratio of two rate constants, we have

$$\frac{k_2}{k_1} = \mathrm{e}^{\left(\frac{E_\mathrm{a}}{\mathrm{R}T_1} - \frac{E_\mathrm{a}}{\mathrm{R}T_2}\right)}$$

Since the period and the rate constant are inversely proportional, we obtain

$$\frac{t_1}{t_2} = \mathrm{e}^{\left(\frac{E_\mathrm{a}}{\mathrm{R}T_1} - \frac{E_\mathrm{a}}{\mathrm{R}T_2}\right)}$$

After substituting the temperatures in kelvins, we find $E_\mathrm{a} = 32.6\,\mathrm{kJ\,mol^{-1}}$

Question F.1 (Supatpong Juntarawatt): Coloured Salts

Alkali halides, such as NaCl and KBr, are usually colourless in their pure form. However, when exposed to X-ray radiation or alkali metal vapour, they can develop colour centres, causing them to appear coloured.

A common type of colour centre is the F-centre (*Farbe*, colour in German), which forms when an electron gets trapped in a missing halide ion within the crystal lattice. The trapped electrons can be modelled as three-dimensional particle in a box, where the energy of absorbed light is defined by the 'size' of the crystal lattice, a, which acts as an electron cage:

$$\Delta E = \frac{1}{a^{1.8}}$$

The value of 1.8 is derived from empirical data, whereas an actual particle in a box model would predict 2. Cherprang has been given 4 white crystals which are different alkali chlorides: LiCl, NaCl, KCl, and RbCl. However, after evacuating from her lab due to an earthquake, she forgot which crystal belongs to each chloride salt. She irradiated all salt samples with X-ray, yielding yellow, orange, blue, and violet crystals.

Match the colour of irradiated alkali chloride crystals with their chemical formula. Note that the observed colour of a compound is a complementary colour of the absorbed wavelength (i.e., the colours are located across from each other on a colour wheel). All solids in question share the same crystal structure.

Solution:

The ionic radius of alkali cation is larger down the group, from Li^+ to Rb^+. Thus, the 'size' of crystal lattice (a) increases. This would mean that the absorbed energy for exciting the trapped electron would decrease from LiCl to RbCl.

The complementary colours of yellow, orange, blue, and violet are violet, blue, orange, and yellow respectively. The energy decreases from violet, blue, yellow to orange. Therefore, the colour mainly absorbed by irradiated LiCl, NaCl, KCl, and RbCl are violet, blue, yellow to orange. The observed colours are respectively yellow, orange, violet, and blue.

Question F.2 (Supatpong Juntarawatt): Cativa Process

Sissel decided to get rid of methanol she obtained from a botched attempt during homemade moonshine production. Luckily, she had learned that there is a catalytic process that can convert toxic methanol along with a toxic gas into acetic acid, a main component in vinegar: the Cativa process. Unfortunately, she didn't completely remember the process—leading to some chemicals left blank in the catalytic cycle: acid **A** and toxic gas **Z**.

Indicate whether these statements are true or false:

(i) Addition of chlorine water to acid **A** would see no colour change.

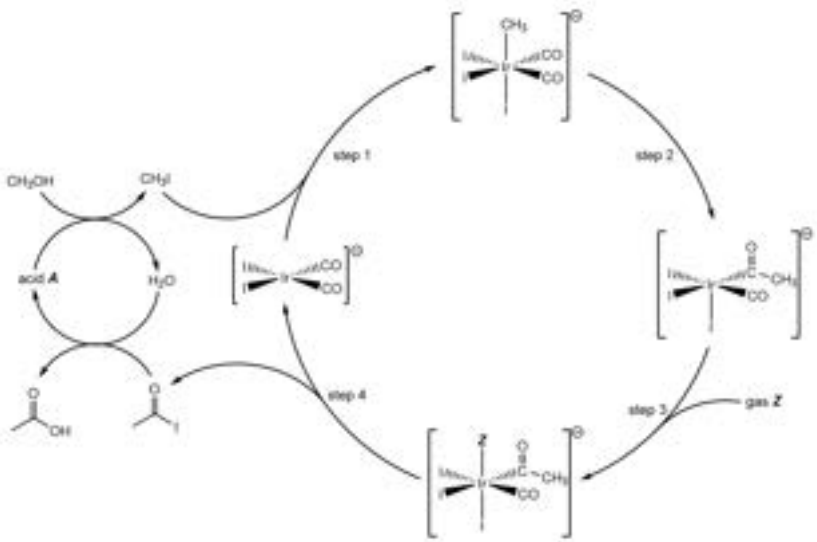
(ii) The oxidation state of Ir in $[Ir(CO)_2I_2]^-$ is +1.

(iii) The step involving conversion of CH_3COI into CH_3COOH is nucleophilic addition reaction, with water as a nucleophile.

(iv) The identity of gas **Z** is carbon monoxide.

(v) If Sissel has 320.42 g of methanol, she would need 245 mℓ of gas **Z** (assuming ideal gas behaviour) at 298 K, 101.325 kPa to completely convert all methanol into acetic acid via this process.

Hint: Treat each ligand as either an ion or a Lewis base that has no formal charge.



Solution:

(i) It can be deduced from the catalytic cycle that A is hydroiodic acid (HI). Since the halogens are less oxidising down the group, Cl_2 is more oxidising than I_2. Thus, the halogen displacement reaction would occur:

$$Cl_2 + 2\,I^- \longrightarrow I_2 + 2\,Cl^-$$

The colour of the solution would darken as a result of dissolved iodine, so the statement is false.

(ii) Each CO has a charge of 0, whilst each iodide ions has a –1 charge. Thus, the oxidation number of Ir in $[Ir(CO)_2I_2]^-$ is

$$-1 - (2 \times (-1)) = +1,$$

making the statement true.

(iii) Although it is through that water acts as a nucleophile attacking electrophilic C=O, the iodide acts as a leaving group after the reaction. Hence, the reaction is not nucleophilic addition akin to those in carbonyls. Instead, the reaction is nucleophilic substitution, making the statement false.

(iv) Comparing between the starting material and the products (both the Ir species and CH_3COI) in step 4, one atom each of C and O is missing in the starting

intermediate. Therefore, gas Z is CO, making the statement true.

(v) Number of moles of methanol is

$$n = \frac{320.42}{32.042} = 10\,\text{mol}$$

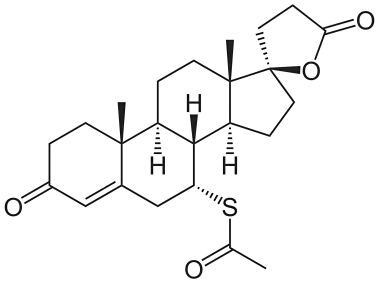
It can be observed that the stoichiometry ratio of methanol to gas Z is 1:1. Thus, the number of moles of gas Z required is also 10 mol, which is

$$V = \frac{n\text{R}T}{p} = \frac{10 \times 8.314 \times 298}{101325} = 244.5\,\ell$$

of gas Z needed, making the statement false.

Question F.3 (Tatiana Nemirovich): Ms. Donald Trump

The internet never fails when it comes to wild rumors about the health of famous people. And once the topic turns to Donald Trump's medical condition, things escalate quickly. Lately, online discussions have spread the theory that the current U.S. president is taking a drug called Aldactone – supposedly for heart problems. People point to his frequent leg swelling, visibly enlarged veins, and occasional shortness of breath, which, according to online experts, "look exactly like what happens after taking diuretics." The structure of spironolacton is in the following figure.



Under the commercial name Aldactone hides the compound spironolactone, a commonly used diuretic – a medication that helps the body get rid of excess water and salt, relieves the heart, lowers blood pressure, and is also used in the treatment of edema, liver cirrhosis, or certain forms of acne. There would be nothing unusual about that… if spironolactone wasn't also an androgen antagonist – a compound that blocks the effects of testosterone.

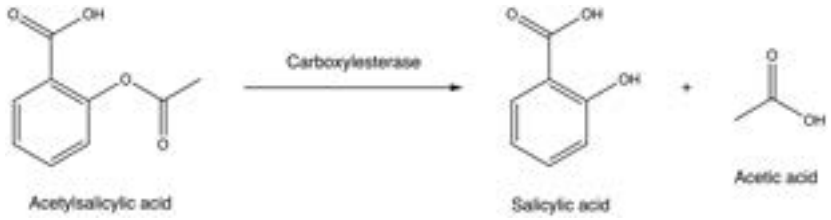
This small chemical detail means that spironolactone has another, equally fascinating field of use – it is one of the key substances used in feminizing hormone therapy for trans women, where it helps shift the body's hormonal balance toward the female spectrum.

So if the rumors about Trump's Aldactone use happened to be true, it might not just be a fight against heart failure – but also the greatest threat to his masculinity, which, chemically speaking, is rather unstable.

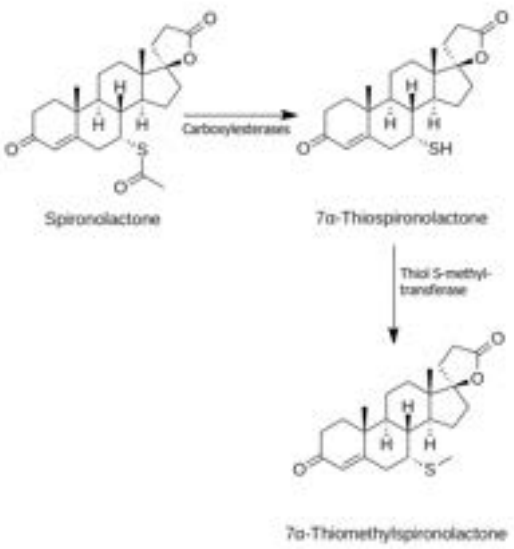
Spironolactone also belongs to the group of prodrugs – compounds that are not active themselves but are metabolically converted in the body into their active form. In the case of spironolactone, this conversion is carried out by two enzymes – first carboxylesterase, and then thiol-*S*-methyltransferase (in this particular case hydrolysis of lactone by carboxylesterase is not happening).

In the second figure, you are given the structure of spironolactone and the general reaction catalyzed by carboxylesterases.

Draw the structure of the active form of spironolactone.



Solution:



Question F.4 (Nathaniel Loh): An uncalibrated scale

Toby is trying to find out the identity of a metal M through some mass measurements. Unfortunately, he forgot to check the units on his scale, or to tare it at any point during the entire measurement!

He has two samples of the metal M, each giving a mass reading of 294.516 on the scale.

The first sample is oxidised with nitric acid to form an oxide of M, which was collected and weighed, giving a mass reading of 403.240.

The second sample is burnt in air to give a different oxide of M, which was weighed on the scale giving a reading of 359.751.

Just enough sodium borohydride ($NaBH_4$) was added to react completely with this second oxide, forming the hydride of the metal, which escaped as a gas, with the other products of the reaction being sodium oxide (Na_2O) and boric oxide (B_2O_3), both in the solid phase. The solid products of the reaction were weighed with the scale giving a reading of 97.683.

Identify the metal M. The oxidation state of the metal does not change in the final reaction. Assume that all reactions proceed to completion and the yield is 100 %.

Solution:

Let us call the number of moles of metal in each sample n, and the unknown units of the scale u. In forming the oxides of M, $\frac{xn}{2}$ moles of oxygen has been added in each case, where x is the oxidation state of the metal in the oxide. By finding the ratio of the extra mass of oxygen added between both oxides we get:

$$\frac{403.240\,\text{u} - 294.516\,\text{u}}{359.751\,\text{u} - 294.516\,\text{u}} = 1.66668 \approx \frac{5}{3}$$

Therefore the oxidation states of M in these oxides must be +5 and +3, as an oxidation state of +10 from doubling the ratio is unrealistic.

$$\text{Mass of } n \text{ moles of O} = \frac{359.751\,\text{u} - 294.516\,\text{u}}{\frac{3}{2}} = 43.490\,\text{u}$$

Therefore the conversion factor that we can use for relative atomic masses to scale weights is:

$$\frac{40.390\,\text{u per } n \text{ moles}}{15.999\,\text{g mol}^{-1}} = \frac{2.7183}{n}\,\text{u g}^{-1}$$

The second oxide is M_2O_3, so after some balancing we find that the equation for the last reaction is:

$$4\,M_2O_3 + 6\,NaBH_4 \longrightarrow 8\,MH_3 + 3\,Na_2O + 3\,B_2O_3$$

As only $\frac{n}{2}$ moles of M_2O_3 are produced from the n moles of M, the solid products remaining after this reaction are $\frac{3n}{8}$ moles of Na_2O and $\frac{3n}{8}$ moles of B_2O_3.

$$M_\text{r}(Na_2O) = 22.990 \times 2 + 15.999 = 61.979\,\text{g mol}^{-1}$$

$$M_\text{r}(B_2O_3) = 10.811 \times 2 + 15.999 \times 3 = 69.619\,\text{g mol}^{-1}$$

Therefore the exact mass of solid that should be left over from this reaction can be calculated as:

$$\left(\frac{3n}{8}\text{mol} \cdot 61.979\,\text{g mol}^{-1} + \frac{3n}{8}\text{mol} \cdot 69.619\,\text{g mol}^{-1}\right) \cdot \frac{2.7183}{n}\,\text{u g}^{-1} = 134.146\,\text{u}$$

Comparing this to the mass reading actually shown on the scale:

$$97.683\,\text{u} - 134.146\,\text{u} = -36.463\,\text{u}$$

So the balance always shows a mass 36.463 u too small due to the zeroing error. We can now finally calculate the relative atomic mass of M from its mass reading as follows:

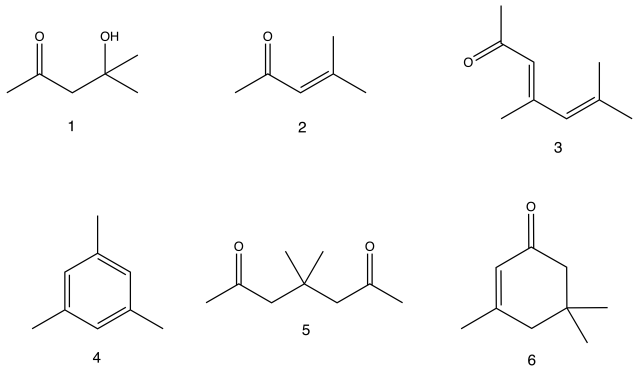
$$M_{\mathrm{r}}(\mathrm{M}) = \frac{(294.516\,\mathrm{u} + 36.463\,\mathrm{u})\ \text{per } n \text{ moles}}{\frac{2.7183}{n}\,\mathrm{u\ g^{-1}}} = 121.760\,\mathrm{g\,mol^{-1}}$$

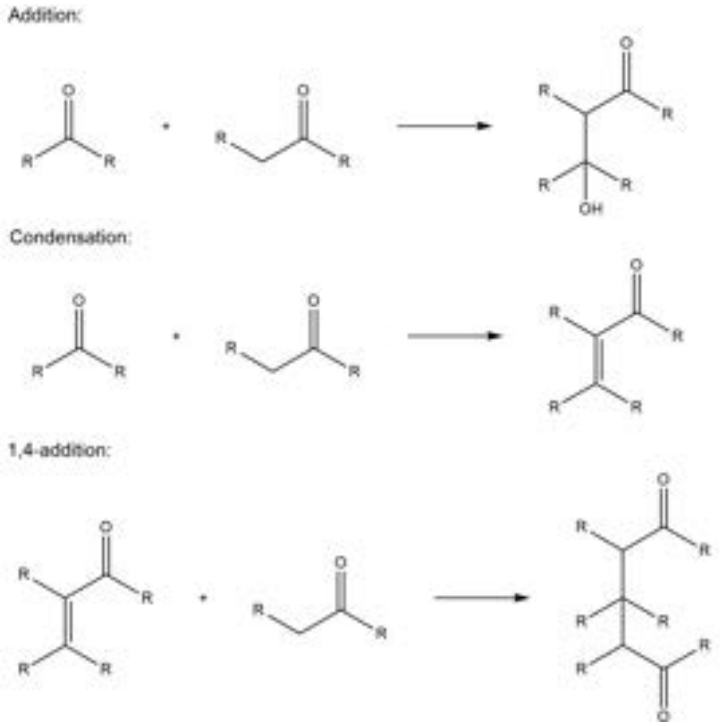
This matches exactly with Antimony (Sb), which has a relative atomic mass of 121.760 to 3 decimal places. Antimony does most commonly take the +3 and +5 oxidation states, and has a gaseous hydride at room temperature and pressure. The exact unit scaling factor used was the number e, and the exact zeroing error was π^{π}.

Question F.5 (Václav Verner): Bizarre acetone adventures

Apart from nail polish remover, acetone is also an organic solvent, and sometimes even an organic reactant! its capability of condensation with itself gives it the great possibility of creating many (sometimes weird) organic compounds!

Your task is to circle which of the bottom six compounds can be formed by reacting exclusively acetone with itself. The reactions that might come in handy are aldol addition, aldol condensation and 1,4-additions (these general reactions are provided to you as pictures).





Solution:

All of these compounds can be created just from acetone.
1 is a product of aldol addition,
2 is dehydrated 1.
3 is the product of aldol condensation between 2 and acetone.
4 is the product of intramolecular aldol condensation of *Z*-isomer of 3.
5 is the product of 1,4-addition of acetone to 2
6 is the product of intramolecular aldol condensation of 5.

Question F.6 (Quyll Pavlakovic): Don't follow the instructions

Participants of this contest should understand that, according to exam mark schemes, when heating under reflux, it is important that water flows bottom-in, and out from

the top (BITO). Proponents of this technique claim that this method is superior to water in from the top, as this more efficiently evacuates errant air bubbles from the condenser. However, a competent chemist would have the skill to hold a condenser upside down for a short period of time (with water flowing), to evacuate any air bubbles, before installation on top of the round-bottom flask. If the hose remains connected to the water tap, there will not be any viable method for air to enter the condenser, thus allowing continued efficient operation of the apparatus.

Proponents of the top-in bottom-out (TIBO) method are acutely aware of the need to save water, and the increased efficiency of this method. Say, for instance, you are refluxing a solution of ethanol, boiling point 78 °C. To avoid excessive solvent loss, your laboratory guide suggests that the top of the condenser does not exceed 40 °C.

With the BITO method, this means that the water flow rate through the condenser must be high enough such that the water leaving the top of the condenser does not exceed 40 °C. However, with the TIBO method, the top of the condenser can quite easily be maintained at 20 °C (the temperature of incoming water), despite the water exiting the condenser (the bottom) being able to approach the boiling point of the solvent. This allows for much more efficient use of water.

Kim is heating an ethanolic solution under reflux, with 400 W of heat transferred to the solution. At £1.39 per cubic meter, how much money a day would be saved by switching from BITO to TIBO? Assume that the condenser acts as a perfect heat exchanger, no heat is transferred through other mechanisms, and that as an environmentally conscious chemist, Kim uses the minimum possible flow rate for both methods.

$c = 4.18\,\mathrm{J\,g^{-1}\,K^{-1}}$
$\rho = 1.00\,\mathrm{g\,cm^{-3}}$

Solution:

Kim heats an ethanolic solution under reflux with 400 W of heat. In the BITO setup, cooling water enters at 20 °C and leaves at 40 °C, while in TIBO it enters at 20 °C and leaves at 78 °C.

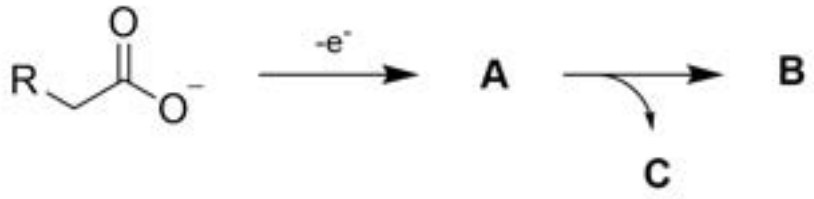
Using $P = m \times C_\mathrm{p} \times \Delta T$, with $C_p = 4.18\,\mathrm{J\,g^{-1}\,K^{-1}}$, the required flow rate is $0.0048\,\mathrm{kg\,s^{-1}}$ (BITO) and $0.0017\,\mathrm{kg\,s^{-1}}$ (TIBO).

This corresponds to $0.413\,\mathrm{m^3\,day^{-1}}$ and $0.143\,\mathrm{m^3\,day^{-1}}$ of water, respectively.

At £1.39 $\mathrm{m^3}$, the cost is £0.57 $\mathrm{day^{-1}}$ for BITO and £0.20 $\mathrm{day^{-1}}$ for TIBO. Switching saves about £0.37 $\mathrm{day^{-1}}$.

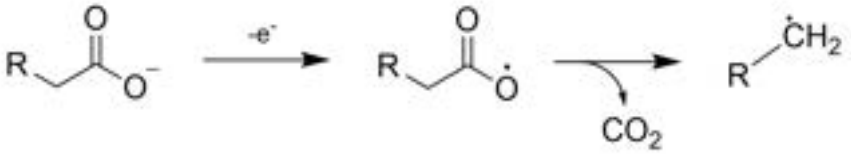
Question G.1 (Ondřej Michal): Electrolysis of carboxylates

In electrolytic reactions, carboxylates can behave like any other anions and can be oxidized at the anode. Propose a highly reactive intermediate (A) formed by one-electron oxidation of a carboxylate and also the products of its decomposition into another highly reactive molecule (B) and a gas (C) released during this decomposition. Assume the reaction involves only a single molecule, ignoring intermolecular products.



Solution:

One-electron oxidation of the carboxylate produces a carboxyl radical, which is unstable and undergoes decarboxylation to form an alkyl radical and carbon dioxide. The alkyl radical can, of course, dimerize or be further oxidized at the anode to a carbocation, but according to the problem statement, only a single molecule and a single oxidation are considered.

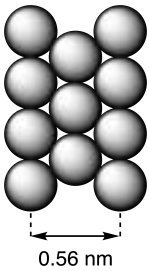


Question G.2 (Supatpong Juntarawatt): Gold leaf sheet

Nowadays, we can see gold leaf (gold hammered down into a thin sheet) in various applications. Kashiwaya and others have successfully synthesised a yellow solution of single-layered gold known as Goldene. It is formed by substituting Si in Ti_3SiC_2 with

Au, before selectively etching away the Ti_3C_2 host. They also analyse its structure via AIMD simulation, in which a part of its structure is depicted below.

Foop, CEO of Foopenshmirtz Devil Inc. tried to hide away the gold he stole from the National Bank of Sarkhan by turning it into a single sheet of Goldene. Suppose he has 42.2 g (around £2500 worth) of gold, what is the area of the Goldene sheet he synthesised in m^2? Assume that 45 % of gold is left unreacted with Ti_3SiC_2, while other steps have 100 % yield.

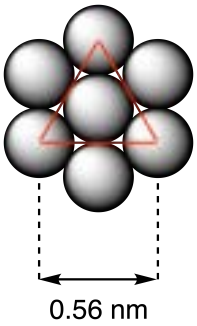


Solution:

Mass of gold reacted $= 0.55 \times 42.2\,\text{g} = 23.21\,\text{g}$

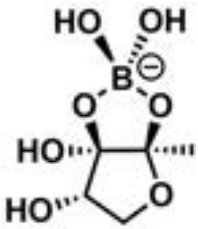
Number of Au in Goldene $= 23.21\,\text{g}/196.97\,\text{g mol}^{-1} \times (6.022 \times 10^{23}\ \text{atoms mol}^{-1}) = 7.096 \times 10^{22}$ atoms

From the red triangle in the repeating unit above, we found that $0.1358\,\text{nm}^2$ of Goldene consists of 1.5 gold atoms. Therefore, the area of Goldene formed is $6424\,\text{m}^2$.



Question G.3 (Jiří Ledvinka): Autoinducer-2

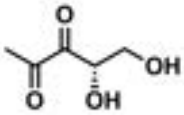
Autoinducer-2 (shown below) is a small signaling molecule that bacteria use in cell-to-cell communication of cell population density. It is also one of the few biomolecules containing boron. In cells, this substance is formed by condensation of boric acid and dicarbonyl compound **A**.



Draw the structure of compound **A** not including stereochemistry.

Solution:

If we view this substance as an ester of alcohol and boric acid, we can "disassemble" this ester back into reactants: boric acid and the corresponding alcohol. But this polyol contains one geminal diol and one hemiacetal, which are just masked carbonyls, which are mentioned in the task.



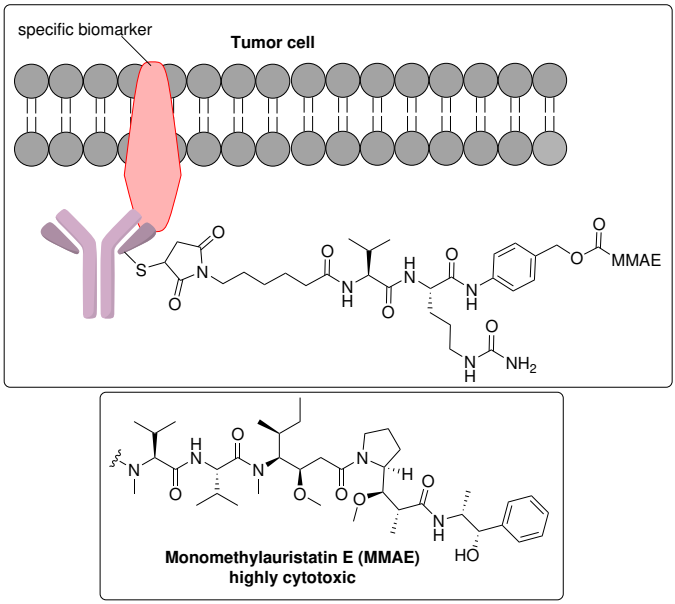
Question G.4 (Ondřej Daněk): Antibody-drug conjugates (ADCs)

Antibody-drug conjugates (ADCs) are a class of drugs that is nowadays frequently used for cancer therapy. ADCs consist of a monoclonal antibody and a cytotoxic payload connected by some type of linker. In the figure below, one of the most frequently used ADC designs (used for example in brentuximab vedotin (adcetris) to treat Hodgkin lymphoma) is depicted. Highly cytotoxic peptide monomethylauristatin E (MMAE) is connected to the monoclonal antibody by a so-called vc

linker containing the valine-citrulline motif, which is recognized by cathepsin B – one of the proteases overexpressed in tumor cells.

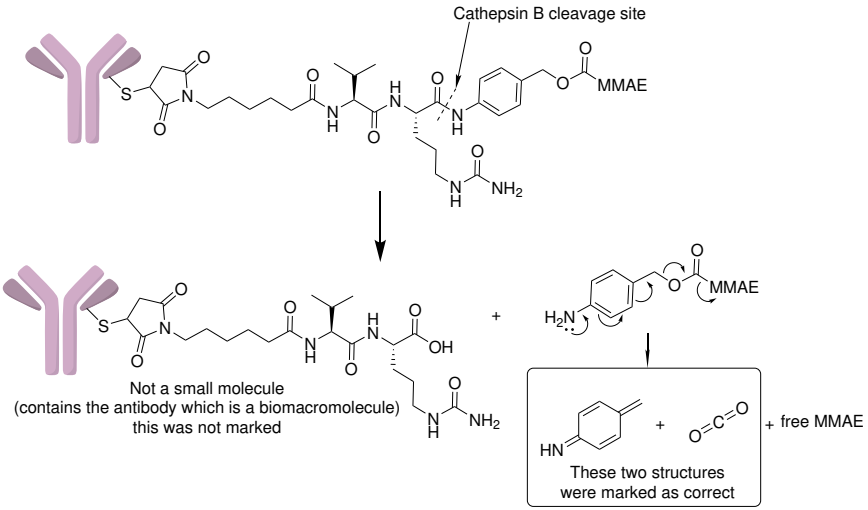
After the monoclonal antibody directs the ADC to the cancer cell by specifically binding to some biomarkers expressed only by tumor cells, the ADC is internalized in lysosomes where cathepsin B hydrolyses the peptide bond coming from the citrulline carboxyl group. That leads to further non-enzymatic reactions leading to the liberation of free MMAE (which kills the tumor cell) and two other small molecules.

Draw the structures of these two small molecules.



Solution:

The mechanism of the non-enzymatic reactions following the cleavage by cathepsin B is depicted below.



Question G.5 (Václav Verner): A twenty amino acid peptide

Imagine a 20 amino acid peptide with the structure ACDEFGHIKLMNPQRSTVWY. It contains every canonical amino acid (from the 20 commonly accepted ones) once.

How many optical isomers does it have?

Solution:

This compound contains $2^{21} = 2\,097\,152$ optical isomers. The number of optical isomers is given by $2^{(\text{number of chiral centres})}$, since this molecule does not have a center or a plane of symmetry. Since glycine possesses none, the other 19 contain one at the alpha-carbon and isoleucine and threonine contain an extra one at their beta-carbon, we are left with 21 chiral centres and 2^{21} optical isomers.

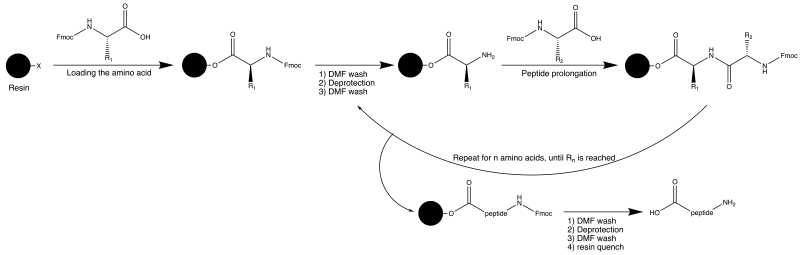
Question G.6 (Václav Verner): SPPS is a relative

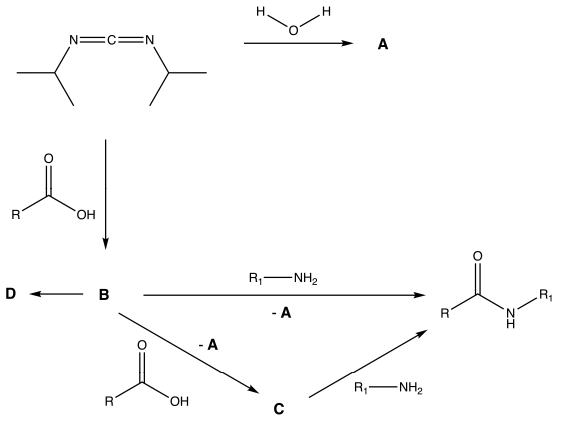
Solid phase peptide synthesis (SPPS) is a relatively modern way to obtain well-defined peptides of a precisely defined amino acid sequence. This is done by loading the wanted product onto resin, while everything else during this synthesis stays in solution.

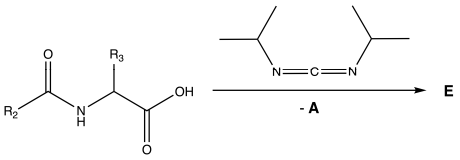
To be able to promote coupling between the carboxylate and amine within this reaction to prolong our peptide, we need to make the carboxylate more reactive. This is most often done by the use of substituted carbodiimides. In most machine-guided SPPS, diisopropylcarbodiimide (DIC) is used, because diisopropyl urea (A), to which it hydrolyses over time is solid (while DIC is a liquid) not soluble in DIC. That keeps DIC (supernatant of A) always fresh and ready to use.

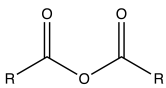
To obtain these activated esters, a carboxylate as a nucleophile attacks DIC and after protonation gives activated ester B. B reacts with the amine to give the amide product. The unfortunate thing is, activated esters can undergo many side-reactions to unwanted byproducts. Sometimes these can still react with the amine to give the desired amide product (C), while others (D) are stable and will not react with the amine to give the desired peptide bond. D is formed through acyl migration, which is driven forward by tautomerisation. This is not the case for SPPS, but when we have synthesis of peptides in solution, there is one more cyclic byproduct, which can still react with the amine to give the desired amide product (E).

Your task is to assign 1 through 5 to A–E.

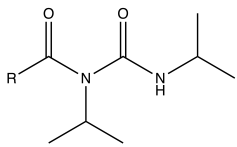








1



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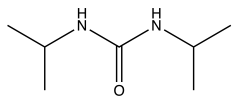

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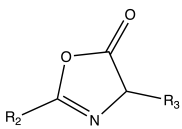

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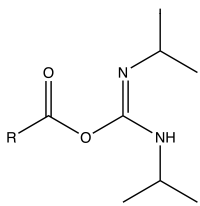


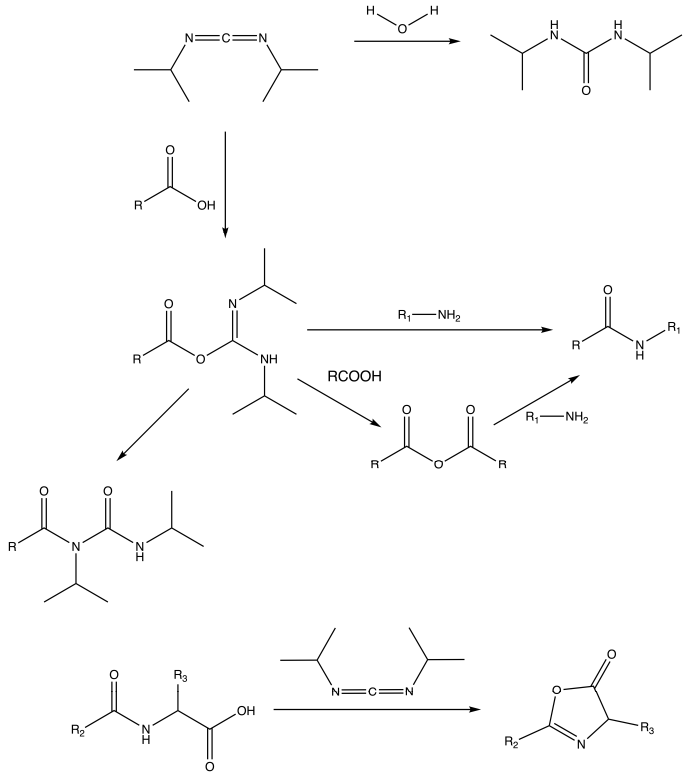
5

Solution:

From the task given,

- A is diisopropyl urea,
- B is the acid-DIC adduct,
- C is the anhydride of the acid (that was activated by DIC),
- D is the *N*-acyl urea,
- E is the oxazolone formed through cyclisation when the activated ester is more than one amino acid long.

So 1–C, 2–D, 3–A, 4–E, 5–B.



Question H.1 (Václav Verner): Unknown

Throughout this task, consider all molar masses to be integers.
The discovery of the element X was a very interesting one. The use of its oxide A is dated back to the first century AD. The discovery of the element itself is although fairly new, when in the eighteenth century an unnamed German chemist obtained B, a yellow solid, by dissolving A (a naturally occurring ore) in nitric acid and neutralising it with NaOH. B contains 68.39 % X. This chemist then heated B with charcoal, yielding A. He thought that A is an element, but that got disproved once an unnamed French chemist was able to convert A into C by reacting it with PCl_5. C is a binary compound containing 62.96 % X. He was able to get elemental X by reacting C with potassium.
Give us the element X and the formulae of A–C.

Solution:

This question, as many inorganic tricky ones, contains a lot of information we need to omit at first. We have to start with the information basically from the end: The French chemist reacted the oxide XO_y with PCl_5 and got a binary compound, that still contains X. XO_y needs to change, therefore the resulting compound must be XCl_z. We know that C contains 62.96 % X. That gives us the molar mass of X at $59.49 \cdot z$. Therefore C must be $SnCl_2$ or UCl_4. It may not be tin, since we know that This element has two oxidation states (in A < in B) and charcoal reduces B to A, not to X. SnO_2 gets reduced to Sn by charcoal. Therefore we have shown, that X is U and C is UCl_4. A must have uranium in the same oxidation state, because the reaction with PCl_5 is a simple exchange one (yielding $POCl_3$), therefore A must be UO_2. By dissolving UO_2 in nitric acid, $UO_2(NO_3)_2$ is obtained, yielding Na_2UO_4 upon neutralisation, which is B. This can be deduced from the molar mass of B, which we know to be $348\,\mathrm{g\,mol^{-1}}$ from the mass percentage of X in B.

Therefore: X = U, A = UO_2, B = Na_2UO_4, C = UCl_4

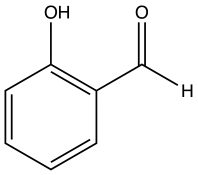
Question H.2 (Štěpán Novák): Reimer-Tiemann reaction

One of the reactions used to introduce an aldehyde (formyl) group onto an aromatic ring is the so-called Reimer-Tiemann reaction. It is specific for formylation in the ortho position relative to a phenolic OH group. This reaction involves chloroform, a strong base such as sodium hydroxide, and a phenolic compound. In the first step, alpha elimination occurs on chloroform, producing a carbene (a divalent carbon with a free electron pair), which is then attacked by electrons from the aromatic ring. The

desired aldehyde is then obtained via basic hydrolysis. Draw and name the product of the reaction of phenol if chloroform is replaced with its deuterated variant.

Solution:

Since alpha elimination involves deprotonation of chloroform, it does not matter whether the normal or deuterated variant is used (hydrolysis in heavy water from the environment would be negligible). Answers with deuterium accepted only if it is noted that it would appear in trace amounts.



Question H.3 (Filip Hůlek): Reaction equilibrium constant

In titrations in analytical chemistry, it is very important that the equilibrium of the reaction used to determine the concentration of the analyte is shifted as much as possible toward the products—that is, the reaction should be as irreversible as possible under the given conditions. If we titrate a solution of dilute sodium hydroxide with dilute nitric acid, what will be the equilibrium constant for the reaction between these two substances?

Hint: Write the reaction equation in ionic form.

Solution:

$10^{14}(10^{\mathrm{p}K_\mathrm{w}})$ or 5.0×10^{15} to 5.6×10^{16} or $\frac{1}{K_\mathrm{w}}$. This corresponds to the reverse reaction of water autoprotolysis, as nitrate and lithium ions do not participate in the reaction.

We have purposefully accepted multiple values to avoid arguments over the pKa of water.

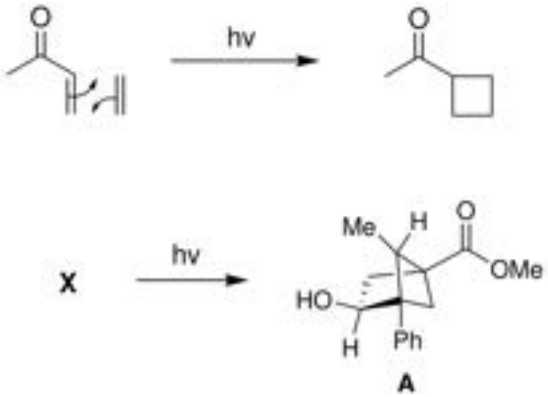
Question H.4 (Yejoon Park): Bicyclo[2.1.1]hexanes

Many of our current small molecule medicines are based heavily on substituted planar aromatic rings such as benzene (think aspirin for example). The compounds

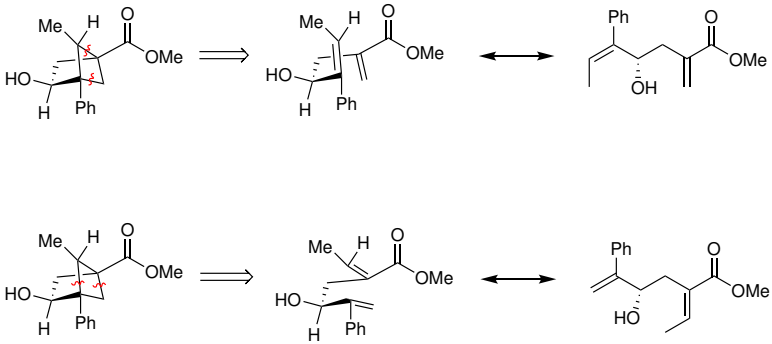
have been highly successful overall but overuse of aromatic groups have sometimes been the attributed cause of undesired effects such as metabolism to toxic substrates or poor uptake by cells.

The use of saturated polycyclic structures such as bicyclo[2.1.1]hexane has been proposed as alternative carbon frameworks to carry bioactive functional groups in place of aromatic rings. These bicyclo[2.1.1]hexanes can be obtained through a simple [2 + 2] cycloaddition reaction in the presence of visible light, an example mechanism of which is provided.

Give both possible structures of starting materials X that will produce **the given** bicyclo[2.1.1]hexane **A**. Ignore stereochemistry and steric effects.



Solution:

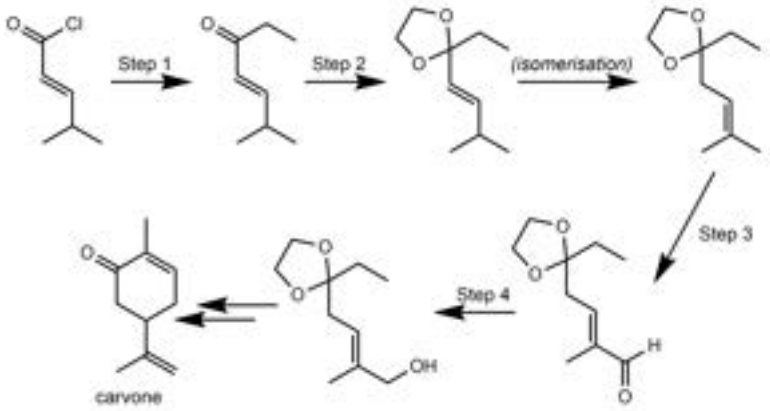


Question H.5 (Supatpong Juntarawatt): Carvone

Carvone is a naturally occurring organic compound found in mint and caraway seeds. The enantiomers smell differently: one smells like spearmint, while the other resembles caraway. Carvone is a terpene ketone, and its unique scent makes it useful in flavouring, perfumes, and essential oils.

In the image is the total synthesis of carvone based on a publication from 1966. Using the choices (from A to H) given, suggest which reagent(s) were being used in each step.

A) CH_3CH_2Br
B) $(CH_3CH_2)_2CuLi$
C) $(CH_3O)_2$, $HCl\,(aq)$
D) $(CH_2OH)_2$, $HCl\,(aq)$
E) SeO_2, H_2O
F) $NaBH_4$, $CeCl_3$
G) H_2, Pt/C
H) $KMnO_4$, reflux



Solution:

An ethyl group is added to the structure in Step 1 via nucleophilic substitution; thus, it should be either A) or B). Note that A) CH_3CH_2Br is an electrophile and therefore not fit, so step 1 -
B) $(CH_3CH_2)_2CuLi$.

In Step 2, a $(CH_2O)_2$ moiety is added in place of the carbonyl group via nucleophilic addition, so
D) $(CH_2OH)_2$, $HCl\,(aq)$, as it 'protects' carbonyl group whilst other reaction is occurring in later steps.

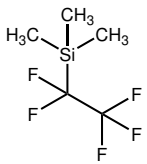
Steps 3 and 4 are oxidation and reduction respectively. It can be deduced that F) and G) are reducing agent, as they are hydride sources. However, as H_2 in G) would also reduce (i.e., hydrogenise) the C=C bond in an alkene group. Step 4 should be done via F) $NaBH_4$, $CeCl_3$.

Even though H) $KMnO_4$ is a strong oxidiser, it is too strong such that it would react directly with the C=C bond either into diols, or break the bonds to carboxylic acids. Hence, E) SeO_2, H_2O should be used for Step 3 by virtue of elimination. This step is known as Riley oxidation.

Question H.6 (Ondřej Michal): NMR titration

A clever chemist once prepared trimethylsilylpentafluoroethane (structure shown) and wanted to isolate it. However, he synthesized it in tetrahydrofuran (THF), which has almost the same boiling point as the target compound, making it difficult to separate by distillation. He thus distilled the mixture as best as possible and obtained a solution of TMS-pentafluoroethane in THF. For further reactions, he first needed to determine the concentration of the compound in solution, so he decided to use NMR titration.

Into an NMR tube, he pipetted 20 µL of trifluoromethylbenzene (standard, $\rho = 1.19\,\mathrm{g\,cm^{-3}}$), 100 µL of the TMS-pentafluoroethane solution, and filled the tube approximately to the appropriate volume with chloroform. From the ^{19}F NMR spectrum, calculate the molar concentration of TMS-pentafluoroethane in the solution (before he added the trifluoromethylbenzene). If the fluorine atoms in the molecule produce more than one signal in ^{19}F NMR, the fluorine atoms corresponding to a given signal are indicated. The integral under each peak (intensity) is shown in blue under the signal.





Solution:

$$\text{Volume of standard: } V(\mathrm{PhCF_3}) = 0.02\,\mathrm{mL}$$

$$n(\mathrm{PhCF_3}) = \frac{V(\mathrm{PhCF_3}) \cdot \rho(\mathrm{PhCF_3})}{M(\mathrm{PhCF_3})} = \frac{0.02 \cdot 1.19}{146.11} =$$

$$= 1.6289 \cdot 10^{-4}\,\mathrm{mol}$$

The NMR peak integrals show that the molar ratio of standard to compound = 10, so the compound is present at one-tenth the amount of standard:

$$n(\mathrm{TMSC_2F_5}) = \frac{n(\mathrm{PhCF_3})}{10} \approx 1.6289 \times 10^{-5}\,\mathrm{mol}$$

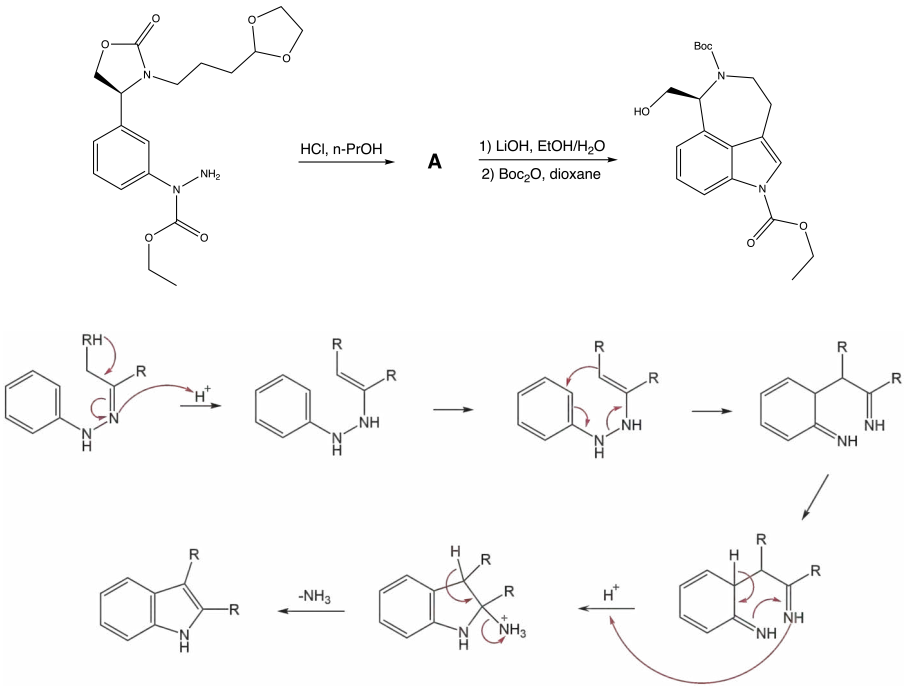
This is the number of moles in 100 µL of solution, so the molar concentration is:

$$c = 1.6289 \times 10^{-5} \times \frac{1000}{0.1\,\mathrm{mL}} \approx 0.163\,\mathrm{mol\,L^{-1}}$$

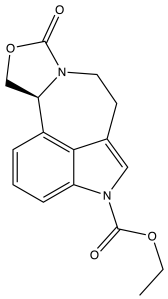
Question K.1 (Václav Verner): Intramolecular

The Fischer Indole synthesis is a useful synthesis pathway leading to a new heterocycle (indole) from benzene. This can be achieved through a pretty complex mechanism.

Use this knowledge to draw the structure of compound A in the total synthesis of (−)-aurantioclavine. Include stereochemistry.



Solution:



A

During the first reaction conditions, deprotection of ketal to ketone occurs, followed by intramolecular Fischer indole synthesis (the clue was given in the name of the task). The step going from compound A causes the carbamate to hydrolyse and then protection of the amine with Boc_2O occurs. Synthesis was inspired by J. Park, D.-H. Kim, T. Das and C.-G. Cho, "Intramolecular Fischer Indole Synthesis for the Direct Synthesis of 3,4-Fused Tricyclic Indole and Application to the Total Synthesis of (−)-Aurantioclavine", *Org. Lett.*, 2016, **18**, 5098–5101. DOI: 10.1021/acs.orglett.6b02541.

Question K.2 (Tatiana Nemirovich): Garfield

What do Garfield and galvanic corrosion have in common? Both of them have a plan for your cheesy and delicious dinner!

You might have never noticed, but when you're baking lasagna in the oven (180 °C), your kitchen can turn into a small electrochemical hell. All it takes is an ordinary steel baking tray, covered with aluminium foil, and a generous amount of tomato sauce-soaked lasagna. And you have a galvanic cell.

How did that happen? Steel and aluminium (two metals with different standard electrode potentials) are in direct contact, and between them is a properly acidic tomato mush that acts as an electrolyte.

The result? After baking, you might notice small holes and stains on the surface of the foil–a sign that galvanic corrosion has successfully been working on destroying your delicious and juicy dinner. Garfield definitely wouldn't be happy.

From a chemical perspective, in the lasagna cell, oxidation of aluminium occurs at

the anode ($E^{\ominus}_{\text{red}} = -1.66\,\text{V}$):

$$\text{Al} \longrightarrow \text{Al}^{3+} + 3\,\text{e}^-$$

While at the cathode, oxygen is reduced ($E^{\ominus}_{\text{red}} = 1.23\,\text{V}$):

$$\text{O}_2 + 4\,\text{H}^+ + 4\,\text{e}^- \longrightarrow 2\,\text{H}_2\text{O}$$

Using the Nernst equation, calculate the voltage of this tasty electrochemical cell, assuming that the lasagna pH is approximately 4 and that during baking, some aluminium has already dissolved, so the concentration of Al^{3+} ions is about $10^{-4}\,\text{mol}\,\ell^{-1}$. Consider the partial pressure of oxygen as 0.2 (normal dry air).

Solution:

Nernst equation: $E = E^{\ominus} - (RT/nF) \times \ln(Q)$
Temperature: $T = 180 + 273 = 453\,\text{K}$
Anode reaction (oxidation of aluminium, written as the reduction because we are presented a reduction potential) ($E^{\ominus}_{\text{red}} = -1.66\,\text{V}$):

$$\text{Al} \longrightarrow \text{Al}^{3+} + 3\,\text{e}^-$$

$Q = 1/[\text{Al}^{3+}] = 10^4$

Substitution into the Nernst equation:

$$\begin{aligned} E_{\text{anode}} &= -1.66 - \frac{8.314 \times 453}{3 \times 96485} \times \ln(10^4) \\ &= -1.66 - \frac{0.03899}{3} \times 9.21 \\ &= -1.66 - 0.1197 \\ &= -1.780\,\text{V} \end{aligned}$$

Cathode reaction (oxygen reduction) ($E^{\ominus}_{\text{red}} = 1.23\,\text{V}$):

$$\text{O}_2 + 4\,\text{H}^+ + 4\,\text{e}^- \longrightarrow 2\,\text{H}_2\text{O}$$

$Q = 1/([\text{H}^+]^4 \times p\text{O}_2) = 1/((10^{-4})^4 \times 0.2) = 5 \times 10^{16}$.

Substitution into the Nernst equation:

$$\begin{aligned} E_{\text{cathode}} &= 1.23 - \frac{8.314 \times 453}{4 \times 96485} \times \ln(5 \times 10^{16}) \\ &= 1.23 - \frac{0.03899}{4} \times 38.45 \\ &= 1.23 - 0.375 \\ &= 0.855\,\text{V} \end{aligned}$$

Resulting cell voltage: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.855 - (-1.780) = 2.635\,\text{V}$

Question K.3 (Supatpong Juntarawatt): A separatory funnel

A separatory funnel is normally used to extract one compound from one solvent into another. The logic behind this is a compound has a different solubility in different solvents. The quantitative value for the property is the octanol-water partition coefficient (K_{ow}), which is effectively an equilibrium constant for equilibrium

$$\text{X}\,(\text{aq}) \rightleftharpoons \text{X}(\text{octanol})$$

Doctor G. Stickyrice has 5.00 mg of N-acetylcysteine ($M_{\text{r}} = 163.20, \log K_{\text{ow}} = -0.66$) in 20 m$\ell$ of octanol, how many milligrams (in 3 significant figures) of N-acetylcysteine left in the octanol layer after being extracted three time, each with 20 mℓ of distilled water.

Solution:

The initial concentration of *N*-acetylcysteine is

$$c = \frac{m}{MV} = \frac{5}{20 \times 163.20} = 1.53 \times 10^{-3}\,\text{mol}\,\text{dm}^{-3}$$

Concentration of *N*-acetylcysteine in octanol after the first extraction can be calculated as

$$\begin{aligned} K_{\text{ow}} &= \frac{c - x}{x} \\ x &= \frac{1.53 \times 10^{-3}}{1 + 10^{-0.66}} = 1.26 \times 10^{-3}\,\text{mol}\,\text{dm}^{-3} \\ c(\text{after extraction}) &= c - x = 1.53 \times 10^{-3} - 1.26 \times 10^{-3} = 2.75 \times 10^{-4}\,\text{mol}\,\text{dm}^{-3} \end{aligned}$$

After we repeat the calculation twice, the concentration of *N*-acetylcysteine in octanol is $8.86 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}$. That means that the mass remaining in the solution is

$$m = c \times V \times M = 8.86 \times 10^{-6} \times 20 \times 163.20 = 0.0289\,\mathrm{mg}$$

Question K.4 (Vojtěch Laitl): Kinetics of metabolic crossroad

Microalgae diatoms (*Bacillariophyceae*) are capable of fixing nitrogen dissolved in marine water to produce NH_4^+ ion. Its excess is compensated by undergoing the urea cycle, as sketched by a simplified rate equation

$$v = k_1 c(N_2) - k_2 c(NH_4^+).$$

Biological half-life of nitrogen fixation reads $\tau_{1/2;1} = 2.5\,\mathrm{min}$, the half-life of the urea cycle equals $\tau_{1/2;2} = 1.5\,\mathrm{h}$. Both such processes are assumed to obey first-order kinetics. Estimate the stationary cellular concentration of NH_4^+, for which the overall reaction rate equals zero. Assume that the concentration of nitrogen is constant and may be determined by the Henry's law

$$p(N_2) = K_H c(N_2)$$

with $K_H = 115\,\mathrm{MPa\,mol^{-1}\,dm^3}$. Above the diatoms-containing marine water, there is air of atmospheric pressure 101 325 Pa with the amount of nitrogen yielding 79 mol%. The correlation between reaction half-life and its rate coefficient is given as

$$k = \frac{\ln(2)}{\tau_{1/2}}.$$

Solution:

Set $v = 0 \Rightarrow k_1 c(N_2) = k_2 c(NH_4^+)$, so

$$c(NH_4) = \frac{k_1}{k_2} c(N_2).$$

First get $c(N_2)$ from Henry's law. The partial pressure of N_2 in air is

$$p(N_2) = 0.79 \times 101\,325\,\mathrm{Pa} = 8.0047 \times 10^4\,\mathrm{Pa}.$$

With $K_H = 115\,\mathrm{MPa\,mol^{-1}\,dm^3} = 1.15 \times 10^8\,\mathrm{Pa\,mol^{-1}\,dm^3}$, Henry's law $p = K_H c$ gives

$$c(N_2) = \frac{p}{K_H} \approx \frac{8.0047 \times 10^4}{1.15 \times 10^8} \approx 6.96 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}.$$

Next, convert half-lives to first-order rate constants: $k = \frac{\ln(2)}{\tau_{1/2}}$. For nitrogen fixation, $\tau_{1/2;1} = 2.5\,\text{min} \Rightarrow k_1 = \frac{\ln(2)}{2.5}\text{min}$. For the urea cycle, $\tau_{1/2;2} = 1.5\,\text{h} = 90\,\text{min} \Rightarrow k_2 = \frac{\ln(2)}{90}\text{min}$. Their ratio is

$$\frac{k_1}{k_2} = \frac{\frac{\ln(2)}{2.5}}{\frac{\ln(2)}{90}} = \frac{90}{2.5} = 36.$$

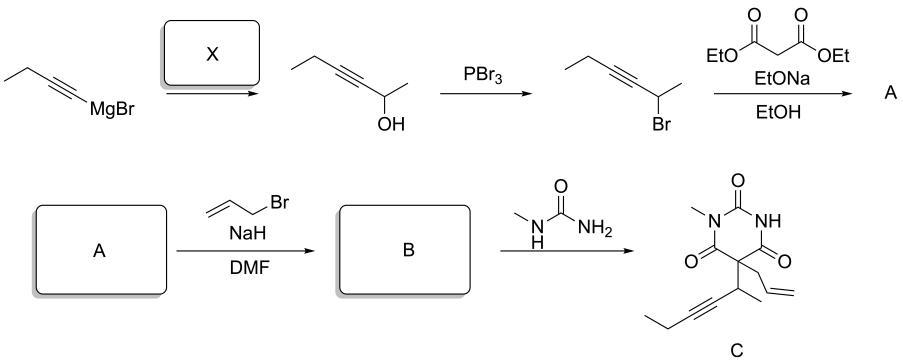
Therefore $c(\text{NH}_4^+) = 36 \times 6.96 \times 10^{-4}\,\text{mol}\,\text{dm}^{-3} \approx 2.51 \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}$, i.e. about $0.025\,\text{M} = 25\,\text{mM}$.

Question K.5 (Štěpán Novák): (Thio)barbiturates

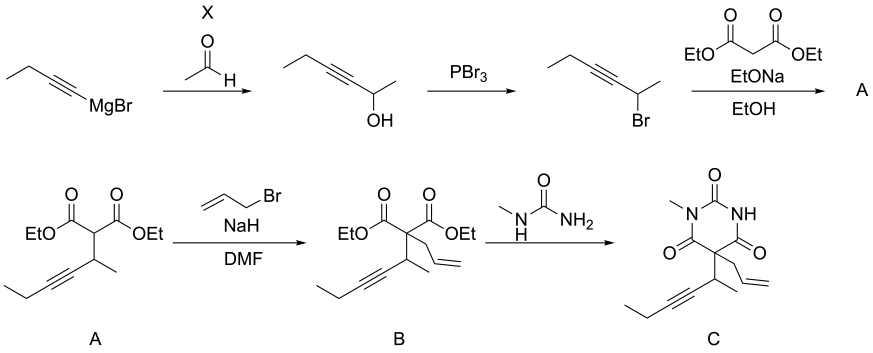
Derivatives of (thio)barbituric acid are widely used in medicine, for example to induce general anaesthesia (barbiturate induced coma). In this assignment, we will take a look at the synthesis of a barbiturate with ultrafast onset of action, methohexital, which is widely used in dentistry.

The synthesis is a classic example of the synthesis of barbituric acid derivatives by malonic ester synthesis. The synthesis starts from but-1-yn-1-ylmagnesium bromide, which is converted to 2-bromhex-3-yn in two steps. The latter reacts with diethyl malonate to give product A. A second alkylation with allyl bromide gives product B, which is subsequently condensed with N-methyl urea to give methohexital.

Draw the structure of reactant X and intermediates A and B.

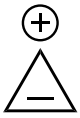


Solution:



Question K.6 (Alexandr Zaykov): The Tiniest Aromatic Molecule

While reading the name of this question, you may have inadvertently thought of benzene. Some of you may have decided to go smaller! Cyclopentadienyl anion cuts off one carbon moiety. With cyclobutadiene, you have surely calculated it to be actually anti aromatic, and you are frightened by the sight of "cyclobutadienyl anion". And then! Cyclopropenium (see the picture)! Surely, this must be the tiniest aromatic molecule!



What if I told you that that does not qualify as the "tiniest aromatic molecule" either. Perhaps, that confuses you a little. You recall the Hückel rules. "4n+2... for cyclopropenium, n = 0. It is the shortest possible cycle. Surely it cannot be smaller!" are perhaps your gedankargument against my gedankexperiment.

Meanwhile, I calculate all the electrons and paraphrase the greatest Czech that has never lived [1]: "And is it not a bit too many, dear competitor?" The tiniest possible, stable, and actually existing aromatic molecule is the hydrogenonium ion (H_3^+).

A molecule so extremely important that without it, life would not had had even the smallest chance of springing into existence. How does it look like? Well, just use the cyclopropenium picture and switch carbons for hydrogens. Rehash the bonds... and you suddenly realize, "Hold on a second! How can that be aromatic without any π electrons??" However, that does not matter in the slightest. Let's recall that

Hückel's rule uses π electrons, because the assumption is σ electrons contribute to the properties of the molecule very little. However, with our tiniest molecule, we have little choice.

How stable is the molecule? We will probe this using two metrics: (1) cyclization energy — the energy needed to be used (+) or released (−) by transforming linear geometry into the triangle one. (2) aromatization energy — that one is a wee bit ill-defined throughout the literature. We shall define aromatization energy as the energy consumed (+) or released (−) by transforming a diatomic molecule with a non-interacting cation (H_2 + H^+) into our tiniest aromatic molecule. To obtain the needed energies, use the known relationships for the energies of k-th molecular orbitals (k= $0, 1, ...$) from Hückel-approximated Ritz method [2], i.e.:

(1) For linear chains of N-atom lengths:

$$E_k^{\text{lin.}} = \alpha + 2\beta \cos\left(\frac{(k+1)\pi}{N+1}\right)$$

(2) For N-atomic cyclic molecules (except those with Möbius geometry):

$$E_k^{\text{cyc.}} = \alpha + 2\beta \cos\left(\frac{2k\pi}{N}\right)$$

Constant α is the energy of the electron in the atomic orbital that forms the molecular orbital. Constant β is the resonance energy. Author, eating the true Czech delicacy from Olomouc, estimated that the energy obtained by digesting one soy roll (CZ: sojový řez, [sohyovee rzhes]; E(s.ř.)= ∼200 kcal) would suffice for dearomatizing 2 moles of our tiniest aromatic molecule.

QUESTIONS:

1. What is the signed magnitude of constant β for our tiniest aromatic molecule in the units of soy rolls E(s.ř.) per mol?
2. What are the aromatization and cyclization energies in s.ř. per mol?
3. Will the molecule be linear or cyclic?

[1] Jára Cimrman Lying, Sleeping - (tinyurl.com/LeziciSpici)

[2] Assume that bond lengths of all geometries will be equivalent to 1.72 Bohr radius of hydrogen atom and that the atomic orbital overlap will be approximately the same.

Solution:

- $\beta = -1/4$ E(s.ř.)/mol $= -0.25$ E(s.ř.)/mol;
- E(aromatization) $= -1/2$ E(s.ř.)/mol [exactly];
- E(cyclization) $= -\left(1 - \frac{\sqrt{2}}{2}\right)$ E(s.ř.)/mol $= -0.293$ E(s.ř.)/mol (± 0.01);
- triangle is more stable

First, we realize that our hydrogenium molecule has exactly two electrons and three 1s atomic orbitals. To obtain the total electronic energies, we will therefore need exactly one molecular orbital where we place two electrons. The energies of the molecular orbitals are obtained from the given relationships:

For the cyclic molecule H_3^+ ($N = 3, k = 0$), we obtain the energy of the lowest orbital $\alpha + 2\beta$.

For the linear molecule H_3^+ ($N = 3, k = 0$), we obtain the energy of the lowest orbital $\alpha + \sqrt{2}\beta$.

For the linear hydrogen molecule H_2 ($N = 2, k = 0$), we obtain the energy of the lowest orbital $\alpha + \beta$.

Aromatization is defined in this problem as a "reaction" in which $H_2 + H^+$ transforms into H_3^+. The difference in energies of reactants and products will then be the aromatization energy. However, one of the reactants, H^+, has no electrons. Thus its contribution is 0. As there are two electrons in the lowest energy orbital, the difference in energy between H2 and H3+(cyc) is 2 β.

The constant β will then be equal to exactly $-1/4$ E(s.ř.)/mol.

Cyclization is then defined as the transition between H_3^+[lin.] to $H_3^+[\Delta]$, thus E(cyclization) $= (4 - 2\sqrt{2})\beta$.

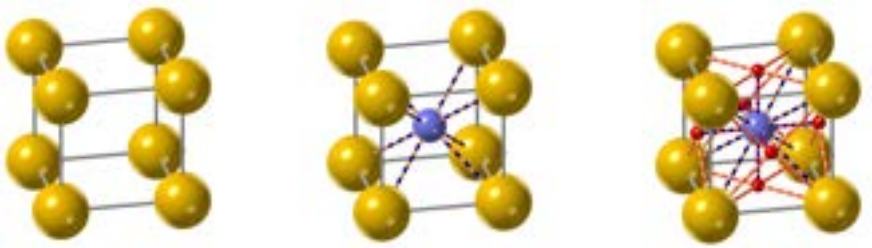
Footnote [2] is here for technical reasons. It only ensures that our approximation that beta is the same everywhere holds.

Question L.1 (Quyll Pavlakovic): Cubic Perovskite

Anyone who has ever experienced the morning rush hour in a tram knows the true meaning of "crystal density". The lucky ones who boarded first have taken the seats in the center, while the rest are squeezed into every available inch of space. While this daily ritual often ends in frustration, in chemistry, it leads to fascinating order. Crystals, like trams, are masterpieces of maximum density. Your task is to determine how efficiently these atoms can fit into the space — because it's not just people in trams, but also atoms in crystals, that need to know how to squeeze together.

To form a cubic perovskite, begin with atom A. Position atom A at the corners of a cubic lattice, to form a simple cubic structure. In our model perovskite, all A atoms are touching the 6 other A atoms which share an edge. Then, position a B atom in the centre of each cube, such that each B atom is touching 8 A atoms. C atoms are then placed in the centre of each face of the cube, such that the C atom is as large as possible without intersecting either A or B atoms. The C atom could be larger if it was offset slightly, however, this is not the structure adopted by real compounds, so we will not do this in our model perovskite. The image below shows this process for a single unit cell. Note that the atoms are not touching in this mockup, for reduced clutter.

By modelling the atoms as hard, solid spheres, find the packing density (volume of atoms/total volume) of our model perovskite. Give your answer as a decimal to (at least) 3 decimal places.



Solution:

Let a be the lattice parameter (side length of the cube) The radius of A atoms is $a/2$. The diagonal distance between opposite corners of each cube is $a\sqrt{3}$, which includes $2 \cdot r_{\mathrm{A}} + 2 \cdot r_{\mathrm{B}}$. Therefore, the radius of B atoms is $a(\sqrt{3}-1)/2$. Considering the diagonal across each face can be used to find the radius of C, assuming it only collides with A. As the diagonal is

$$a\sqrt{2} = 2 \cdot r_{\mathrm{A}} + 2 \cdot r_{\mathrm{C}}, \quad r_{\mathrm{C}} = a(\sqrt{2}-1)/2.$$

Considering a line between adjacent B atoms finds

$$a = 2 \cdot r_{\mathrm{B}} + 2 \cdot r_{\mathrm{C}}, \text{ giving } r_{\mathrm{C}} = a(2-\sqrt{3})/2.$$

As C collides with both A and B, the smaller of the two values $a(2-\sqrt{3})/2$ must be used. Each cubic unit cell contains 1 A atom ($8 \times 1/8$), 1 B atom, and 3 C atoms

$(6 \times 1/2)$. Using $V = (4\pi/3)\, r^3$, the total volume of atoms in each unit cell is

$$a^3(\pi/2)(23 - 13\sqrt{3}) = 0.7592279\, a^3.$$

As the volume of a cube is a^3, the packing density is 0.759.

Question L.2 (Václav Verner): Exploding phosphorus

It is commonly taught in high schools that phosphine (PH_3) is spontaneously flammable in air. However, this is not true. The reason why the gas evolved during phosphine production appears to ignite on its own is that it is highly flammable, but the truly self-igniting species is diphosphine (P_2H_4), which forms as a minor side product in most reactions producing phosphine. An example is the disproportionation of white phosphorus in hydroxides, where water is a reactant and the only side product is hypophosphite ($H_2PO_4^-$).

Imagine you have 1.0123 g of white phosphorus and 6.7815 g of potassium hydroxide, dissolved together in 121.1589 g of water in a 500 mℓ round-bottom flask. The entire apparatus is under argon, and the evolving gas is led out via a small tube into a beaker of water. After the reaction ends (observed when the gas exiting the beaker stops burning), argon is passed through the reaction mixture for 5 more minutes, and then everything is transferred quantitatively into a 1000 mℓ volumetric flask.

A 10 mℓ sample of this solution is titrated with 0.1026 mol dm^{-3} HCl using phenolphthalein, and the consumption was 9.40 mℓ. Calculate how many times larger the volume of phosphine produced is compared to diphosphine in this reaction in this setup. Round the result to the nearest whole number.

(Atomic masses: H=1, O=16, K=39.1, P=30.97)

Solution:

The problem seems complicated, but after balancing the reactions, we find that each reaction consumes a different amount of KOH (which is titrated because the pHis still too high to titrate KH_2PO_2 directly). Let P denote phosphorus for simplicity:

$$6\,P + 4\,KOH + 4\,H_2O \longrightarrow P_2H_4 + 4\,KH_2PO_2$$
$$4\,P + 3\,KOH + 3\,H_2O \longrightarrow PH_3 + 3\,KH_2PO_2$$

Back-calculating, 0.0244385 mol of KOH reacted with 0.03268647 mol of P in the flask. For these two data we can create an equation giving us an equality between

the P and KOH consumed in both reactions as:

$$\frac{3}{4 \times x} + \frac{4}{6} \times (0.03268647 - x) = 0.0244385,$$

where x denotes the molar amount of phosphorous consumed in the second equation. By solving this equation we get $x = 0.03177024$, which means that the first equation consumes $0.03268647 - 0.03177024 = 0.00091623$ moles of phosphorous and creates $\frac{1}{6} \times 0,00091623 = 0.00015271$ moles of P_2H_4.

From the second reaction we get $\frac{1}{4} \times 0.03177024 = 0.00794256\,\text{mol}$ of PH_3. That gives the molar ratio $PH_3 : P_2H_4 \approx 52$, which agrees with published data that the P_2H_4 impurity is about 2 % by volume in generated PH_3.

Question L.3 (Ondřej Daněk): Pictet-Spengler ligation

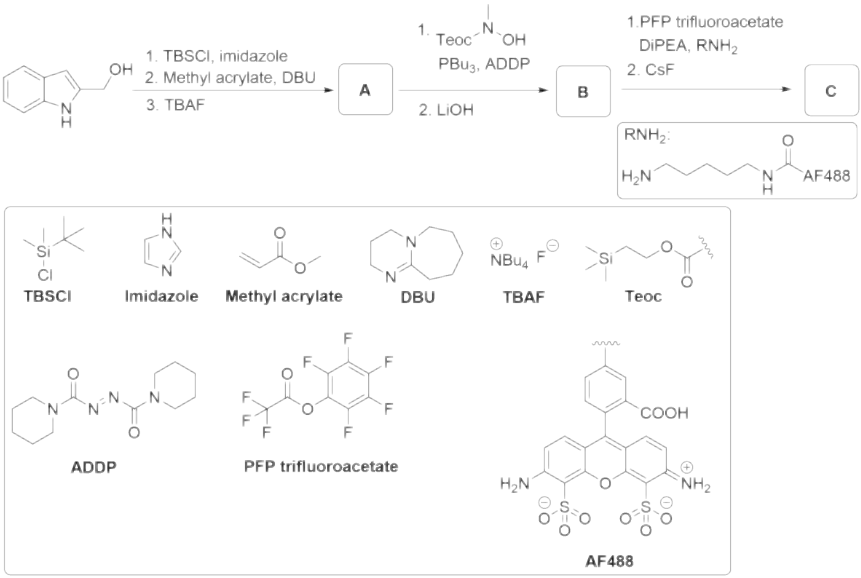
Oxime ligation is one of the frequently used reactions in bioorthogonal chemistry. It has been used for example for peptide cyclisation or protein bioconjugation of modified peptides and proteins bearing aldehyde/ketone containing sidechains in non-canonical amino acids such as *p*-acetylphenylalnine or formylglycine. Another notable use of oxime ligation is bioconjugation to aldehyde groups on cell surface polysaccharides which can be introduced by treating the cells with periodic acid.

The general scheme of oxime ligation is shown in the scheme below. Besides the relatively slow reaction kinetics compared to some more recent bioorthogonal click reactions, one of the main disadvantages of the oxime ligation is that it is reversible, and in the aqueous environment in biological systems, the oxime can get hydrolysed back into the corresponding hydroxylamine derivative and the aldehyde or ketone.



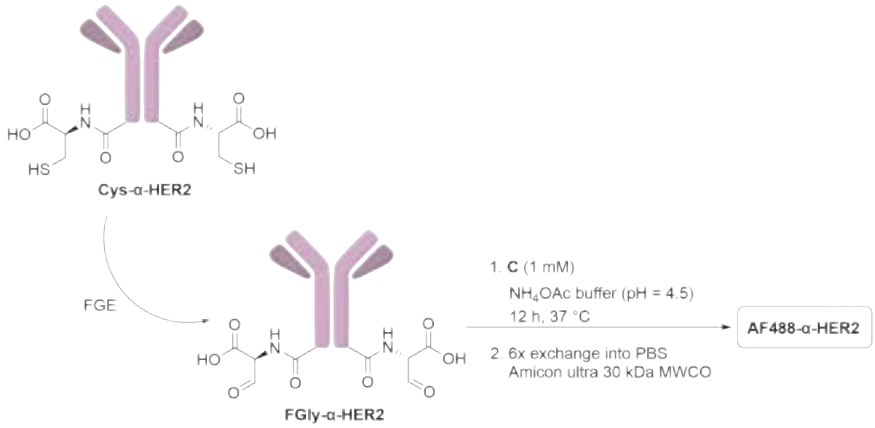
In 2012, a variation on the oxime ligation, which forms conjugates that are much more stable to hydrolysis was developed in the laboratory of Carolyn Bertozzi (who you might know as one of the 2022 chemistry Nobel prize winners for the development of bioorthogonal and click chemistry).

Synthesis of reagent C which can be used for this so called Pictet–Spengler ligation in place of the simple *O*-alkyl-hydroxylamine is shown in the scheme below.



To study the effectivity of the newly developed Pictet-Spengler ligation for preparation of so called antibody drug conjugates (ADCs), a green fluorophore Alexafluor 488 (AF488) was introduced into reagent C, and it's fluorescence signal was then used to quantify the labelling efficiency of the human α-HER2 human IgG Trastuzumab (monoclonal antibody targeting the Human Epidermal Receptor 2) modified on the C terminus of both of the heavy chains by treatment with formylglycine generating enzyme (FGE) which can transform the sulfhydryl sidechain of cysteine to an aldehyde sidechain of formylglycine.

From the fluorescence measurements of the modified AF488-α-HER2 it was calculated, that on average, each antibody is bearing 1.00±0.13 fluorophore moieties.



Draw the structures of compounds A–C and of the most abundant antibody modification in the isolated mixture of AF488-α-HER2. You can use the schematic representation of the antibody and abbreviations of protecting groups and of the fluorophore Alexafluor488.

Solution:

The first reaction sequence is a protection of the OH group of 2-hydroxymethylindole as a silylether. This protected intermediate is then used in an aza-Michael addition of the indole nitrogen to methyl acrylate. Last, the TBS group is deprotected by TBAF forming compound A.

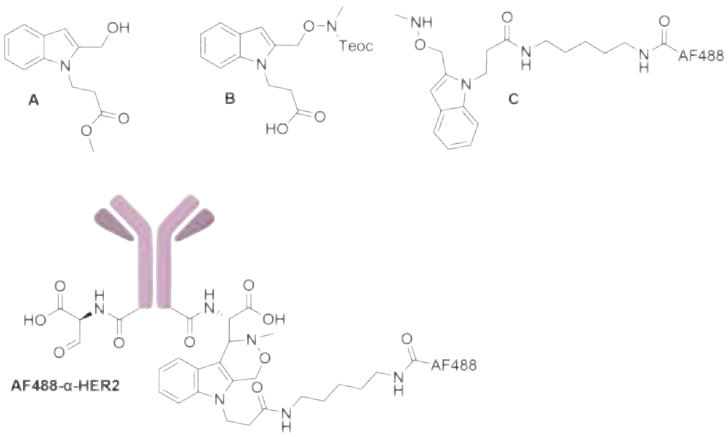
Second reaction sequence starts by a Mitsunobu reaction in which the OH group is first activated by tributylphosphine and 1,1'-(azodicarbonyl)dipiperidine (ADDP, which is used instead of the more common DiAD or DEAD) and then it can be substituted by the Teoc-protected N-methylhydroxylamine in a S_N2 fashion while tributylphosphine oxide leaves. Lithium hydroxide is then used for selective methyl-ester hydrolysis while leaving the Teoc group intact, forming B.

Free carboxylic acid is then activated by pentafluorophenyl trifluoroacetate under basic conditions, forming a mixed anhydride which then quickly reacts with the amine linker of the alexafluor derivative. Last, cesium fluoride is used for the Teoc deprotection to give C. Ethylene and carbon dioxide are formed during this step from the decomposition of the Teoc group.

As the name suggests, the product of the Pictet–Spengler ligation is very similar to beta carbolines which are formed by Pictet–Spengler reaction. The only difference here is the presence of oxygen in the six membered ring, so the newly formed hetero-

cyclic scaffold is called a oxacarboline which is formed by an intramolecular attack of the electron rich indole ring on the oxime that forms from the formylglycine and the hydroxylamine moiety. It is clear from the fluorescence measurement that the most abundant antibody conjugate in the mixture will be modified only on one of the heavy chains.

This question is based on this paper from Bertozzi lab: P. Agarwal,J. van der Weijden,E.M. Sletten,D. Rabuka, & C.R. Bertozzi, A Pictet-Spengler ligation for protein chemical modification, *Proc. Natl. Acad. Sci. U.S.A. 110* (1) 46-51, https://doi.org/10.1073/pnas.1213186110 (2013).



Question L.4 (Quyll Pavlakovic): A sh*t clock

Quyll, a talented chemist,[3] has a time management issue. They spend too much time doing their business in the lavatory. To prevent this endless procrastination, a plan is devised. A clock is installed in the bathroom. However, this is no ordinary clock. This innovative single use clock is activated by mixing and stirring the ingredients together. Shown below is the standard recipe for this cutting-edge technology:

- 20.00 cm^3 of 0.1000 M potassium persulfate
- 35.00 cm^3 of 0.1000 M sodium thiosulphate
- 0.200 g of potassium iodide in solution
- a small amount of starch solution
- then add sufficient deionised water to make the total volume up to 300 cm^3

[3]Citation needed.

This state-of-the-art timepiece relies on the following reactions:

$$\mathrm{S_2O_8^{2-}} + 2\,\mathrm{I^-} \longrightarrow 2\,\mathrm{SO_4^{2-}} + \mathrm{I_2} \quad \{1\}$$

$$2\,\mathrm{S_2O_3^{2-}} + \mathrm{I_2} \longrightarrow \mathrm{S_4O_6^{2-}} + 2\,\mathrm{I^-} \quad \{2\}$$

Thanks to alien-warp technology (chemical kinetics), the second reaction involving $\mathrm{S_2O_3^{2-}}$ happens at a sufficiently fast rate such that it can be modelled as instant. Analysis has also shown that the first reaction involving $\mathrm{S_2O_8^{2-}}$ obeys first-order kinetics towards the persulfate, in addition to the Arrhenius equation.

After some time has passed, the carefully calibrated chronograph will indicate that time is up for voiding the excrement, due to the new-found raven coloured iodine-starch complex.

However, disaster strikes at the last moment. The accuracy of this contraption relies on a temperature of exactly 20 °C. However, due to plumbing failure, this water closet was at a frigid 17 °C. Fortunately, Quyll knows the *solution* to this conundrum. Add more persulfate. They also remember from the pre air-conditioning days that at 35 °C, the reaction proceeds twice as fast as at 20 °C.

What volume of 0.1000 M persulfate solution should be added instead of 20.00 $\mathrm{cm^3}$, such that the clock remains calibrated to maintain consistent bowel movement timings at 17 °C? Give your answer to the nearest 0.01 $\mathrm{cm^3}$.

Solution:

The ratio of rate constants at temperatures T_1 and T_2 is given by the equation:

$$\frac{k_1}{k_2} = \frac{e^{-E_a/RT_1}}{e^{-E_a/RT_2}} = e^{E_a(\frac{1}{RT_2} - \frac{1}{RT_1})}$$

Rearrangement of this can be used to calculate activation energy for the reaction:

$$\ln\left(\frac{k_1}{k_2}\right) = E_a\left(\frac{1}{RT_2} - \frac{1}{RT_1}\right)$$

$$E_a = \ln\left(\frac{k_1}{k_2}\right)\left(\frac{1}{RT_2} - \frac{1}{RT_1}\right)^{-1} =$$

$$= \ln(2)\left(\frac{1}{R \times 293.15} - \frac{1}{R \times 308.15}\right)^{-1} = 34\,707\,\mathrm{J\,mol^{-1}}$$

Re-use of the first equation finds the number of times that the relative rate of reaction is slower at 17 °C compared to 20 °C

$$e^{34\,707\,\mathrm{J\,mol^{-1}}\left(\frac{1}{290.15\,\mathrm{k}\times 8.3145\,\mathrm{J\,mol^{-1}K^{-1}}}-\frac{1}{293.15\,\mathrm{k}\times 8.3145\,\mathrm{J\,mol^{-1}K^{-1}}}\right)}=1.1586$$

The reaction is indicated as completed once I_2 begins to complex with starch. This can only begin once $S_2O_3^{2-}$ is depleted, resulting in termination of the second reaction. During the reaction, I^- is immediately reformed by the second reaction after its consumption by the first reaction, therefore making $[I^-]$ constant. As the rate determining step is first order with respect to $S_2O_8^{2-}$, the integrated rate equation will be an exponential decay. This results in the following time requirement for the reaction of:

$$t=\frac{1}{k_{\text{eff}}}\times\ln\left(\frac{[S_2O_8^{2-}]_{\text{initial}}}{[S_2O_8^{2-}]_{\text{final}}}\right)=\frac{1}{k_{\text{eff}}}\times\ln\left(\frac{V_{[S_2O_8^{2-}]}}{V_{[S_2O_8^{2-}]}-\frac{1}{2}V_{[S_2O_3^{2-}]}}\right)$$

where k_{eff} is the rate constant (for a given temperature), times the concentration of the reactants whose concentration does change. As the total volume is always $300\,\mathrm{cm^3}$, the actual concentration will be ignored, and the relative amount of each reagent will be taken as the "concentration". Taking $V'_{[S_2O_8^{2-}]}$ as the new volume of persulfate, and k_{eff} at 17 °C as $\frac{1}{1.1583}$ (only the relative reaction rate is important), and equating the time:

$$t=\ln\left(\frac{20}{20-0.5\times 35}\right)=1.1586\times\ln\left(\frac{V'_{[S_2O_8^{2-}]}}{V'_{[S_2O_8^{2-}]}-(0.5\times 35)}\right)$$

$$\ln(8)=1.1586\times\ln\left(\frac{V'_{[S_2O_8^{2-}]}}{V'_{[S_2O_8^{2-}]}-17.5}\right)$$

$$8=\left(\frac{V'_{[S_2O_8^{2-}]}}{V'_{[S_2O_8^{2-}]}-17.5}\right)^{1.1586}$$

$$6.0182\times(V'_{[S_2O_8^{2-}]}-17.5)=V'_{[S_2O_8^{2-}]}$$

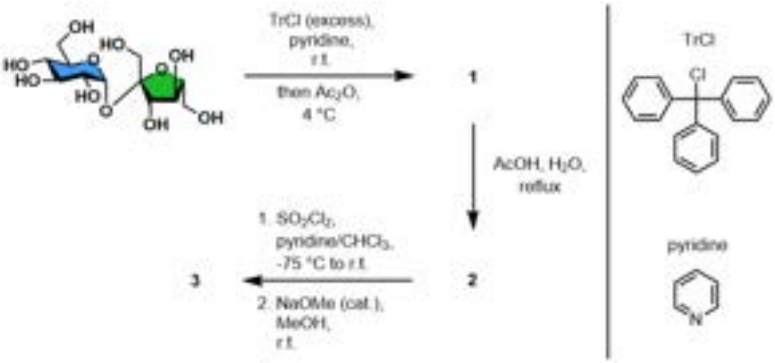
$$5.0182\times V'_{[S_2O_8^{2-}]}=105.32$$

$$V'_{[S_2O_8^{2-}]}=20.99\,\mathrm{cm^3}$$

Question L.5 (Jiří Ledvinka): The sweetest task

One of the most popular artificial sweateners used today is synthesized from table sugar (sucrose) but is undigestible, thus lowering the caloric intake. It is also so sweet, that tasting the pure sweetener completely saturates your taste buds for a significant time.

The synthesis starts by treatment of sucrose with excess of trityl chloride (TrCl) in pyridine followed by addition of excess acetic anhydride (Ac_2O), leading to protected intermediate 1. This intermediate is then boiled in diluted acetic acid, which leads to selective partial deprotection and subsequent protective group migration on the pyranose ring through a 6-membered transition state. The resulting intermediate 2 is then reacted with sulfuryl chloride in pyridine-chloroform mixture followed by reaction with methanol catalyzed by sodium methoxide. The sweetener (3) has the same number of carbons as sucrose.



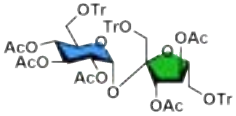
Solution:

The trityl chloride used in the first step is bulky and therefore reacts only with all primary hydroxyl groups, which are less stericaly hindered. The acetic anhydride then caps remaining hydroxyl groups with acetate, forming compound 1.

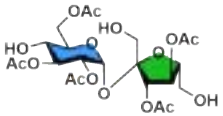
Heating of 1 in acetic acid deprotects the trityl groups selectively, because the leaving trityl cation is stabilized by conjugation with the phenyl rings. The rearrangment on the pyranose ring occurs on O-4, which can be approached by the now free O-6. The resulting migration of acetate from O-4 to O-6 is favored by minimization of the steric repulsion. Finaly, the intermediate 2 reacts with sulfuryl chloride, which first forms chlorosulfate esters with the three free hydroxyl groups, which are replaced

with chloride in an S_N2 fashion during the subsequent warm-up of the reaction mixture. The S_N2 mechanism leads to inversion of glucose O-4, forming a formal derivative of galactose.

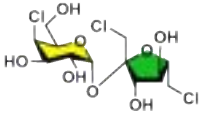
In the last step, the acetate groups are removed by base-catalysed transesterification using excess of methanol.



1



2



3

Question L.6 (Martin Balouch): Analytics goes evil

Teacher Martin was already utterly disgusted with his over-motivated student Vašek, so he decided to make his titration lab assignment unpleasant. The task was to titrate an unknown amount of citric acid with a 0.05 M NaOH solution using phenolphthalein as an indicator. At the moment when the students were about to start the titration, Teacher Martin quietly dropped 500 mg of crystalline citric acid (density $1.7\,\mathrm{g\,cm^{-3}}$) into Vašek's titration flask, which already contained citric acid dissolved in 100 mℓ of water — the amount all students were supposed to determine.

Vašek titrated 10.3 mℓ, quickly calculated the mass of citric acid in the sample, and, unaware of Martin's trick, was ready to hand in the result. Then he noticed that his titration flask had lost its color again. Confused, he titrated again, reaching a total consumption of 13.3 mℓ. By chance, he realized that he had finished the first titration 6 minutes after the task was assigned (and after the crystals were dropped in) and the second titration at the 12th minute. After watching for a while, the flask lost its color once more, and Vašek finally recognized Martin's betrayal. He waited another 3 minutes and titrated again to a total of 14.8 mℓ. He decided to approximate the solid citric acid as perfectly monodisperse cubes and submitted two values to the teacher: the mass of citric acid in the original solution and the edge length of the cubes of the added crystals.

Upon seeing the correct result, Teacher Martin burst with anger. Make Teacher Martin burst with anger too — by submitting the same correct answers as Vašek. Assume the following: the rate of dissolution is governed by the Noyes–Whitney equation:

$$\frac{\mathrm{d}m(t)}{\mathrm{d}t} = \frac{AD}{h}(c_\mathrm{S} - c(t))$$

where *c(t)* is the time-dependent concentration, m is the mass of dissolved substance, A the surface area from which the substance dissolves, D the diffusion coefficient ($10^{-10}\,\mathrm{m^2\,s^{-1}}$), h the thickness of the stagnant diffusion layer at the crystal surface ($1000\,\mu\mathrm{m}$), and c_S the solubility ($60\,\mathrm{g}/100\,\mathrm{mL}$).

Tip: Neglect everything you can.

Solution:

We begin by calculating the mass of dissolved citric acid in the flask. After getting over the initial shock from reading the problem, note that the titrated volumes are linearly dependent on time. The theoretical amount that Vašek would have titrated at time 0 can therefore be obtained easily, for example, from the times of the 2nd and 3rd titrations by similarity of triangles $(t_2, V_2), (t_3, V_2), (t_3, V_3)$ and $(t_0, V_0), (t_3, V_0), (t_3, V_3)$:

$$\frac{V_3 - V_2}{t_3 - t_2} = \frac{V_3 - V_0}{t_3 - t_0}$$

where V_2 is the volume at the 2nd titration ($13.3\,\mathrm{m}\ell$), V_3 is the volume at the 3rd titration ($14.8\,\mathrm{m}\ell$), t_3 is the time of the 3rd titration ($20\,\mathrm{min}$), and t_0 is the time the solid citric acid was dropped in ($0\,\mathrm{min}$).

$$\frac{1.5\,\mathrm{mL}}{3\,\mathrm{min}} = \frac{14.8 - V_0}{15\,\mathrm{min}}$$

$$V_0 = 14.8\,\mathrm{mL} - 1.5\,\mathrm{mL} \times \frac{15}{3} = 7.3\,\mathrm{mL\ NaOH}$$

From this result we can easily calculate the mass of the original citric acid, knowing that citric acid is neutralized to the 3rd stage and knowing its molar mass ($192\,\mathrm{g\,mol^{-1}}$).

$$m_\mathrm{citr} = n_\mathrm{citr} \times M_\mathrm{citr} = \frac{1}{3} \times n_\mathrm{NaOH} \times M_\mathrm{citr} = \\ = \frac{1}{3} \times c_\mathrm{NaOH} \times V_\mathrm{NaOH} \times M_\mathrm{citr} = 23.4\,\mathrm{mg}$$

Now let's move on to the more interesting part: the size of the cubes thrown into the titration flask. The much larger mass of the added material compared to what is already in the flask suggests that the whole dissolution process is at its very beginning. Therefore we can neglect the shrinking of the cubes over time. Another key simplification follows from this reasoning: the saturated concentration of citric acid is $60\,\mathrm{g}/100\,\mathrm{m}\ell$, while the flask contains something between 23 and $50\,\mathrm{mg}/100\,\mathrm{m}\ell$.

Thus the current concentration of citric acid is negligible compared to its saturated concentration. Therefore, the given Noyes–Whitney equation reduces to the following form:

$$\frac{\mathrm{d}m(t)}{\mathrm{d}t} = \frac{A \times D \times c_\mathrm{S}}{h}$$

Since this equation no longer contains a time-dependent concentration, we can readily replace the derivative with differences in mass and time and, for example, for the interval between t_2 and t_3 we solve:

$$\frac{m_{3,\mathrm{citr}} - m_{2,\mathrm{citr}}}{t_3 - t_2} = \frac{A \times D \times c_\mathrm{S}}{h}$$

The only slightly more complicated expression here is $m_{3,\mathrm{citr}} - m_{2,\mathrm{citr}}$:

$$m_{3,\mathrm{citr}} - m_{2,\mathrm{citr}} = \Delta n_{2,3,\mathrm{citr}} \times M_\mathrm{citr} = \frac{1}{3}\Delta V_{2,3,\mathrm{NaOH}} \times c_\mathrm{NaOH} \times M_\mathrm{citr}$$

Now we can substitute into the simplified equation and express the total area A:

$$\frac{\frac{1}{3}\Delta V_{2,3,\mathrm{NaOH}} \times c_\mathrm{NaOH} \times M_\mathrm{citr}}{t_3 - t_2} = \frac{A \times D \times c_\mathrm{S}}{h}$$

$$A = \frac{\frac{1}{3}\Delta V_{2,3,\mathrm{NaOH}} \times c_\mathrm{naoh} \times M_\mathrm{citr}}{t_3 - t_2} \times \frac{h}{D \times c_\mathrm{S}}$$

$$A = \frac{\frac{1}{3} \times 0.0015 \times 0.05 \times 192}{180} \times \frac{10^{-3}}{10^{-10} \times 600\,000} = 4.44 \times 10^{-4}\,\mathrm{m}^2$$

If you have made it this far, it should not be a challenge to calculate the total volume of the introduced crystals:

$$V = \frac{m}{\rho} = \frac{0.5}{1.7} = 0.294\,\mathrm{ml} = 2.94 \times 10^{-7}\,\mathrm{m}^3$$

Now only the grand finale remains, namely the relations for the volume and area of N identical cubes.

$$A = N \times 6a^2$$

$$V = N \times a^3$$

By dividing these equations we obtain directly the desired edge length of the cubes thrown into the titration flask and therefore the final solution:

$$\frac{V}{A} = \frac{a}{6}$$

$$a = \frac{6V}{A} = \frac{6 \times 2.94 \times 10^{-7}}{4.44 \times 10^{-4}} = 3.97\,\mathrm{mm}$$

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