6th Chemistry Race: Questions and Solutions



1st February 2025

Question A.1 (Jiří Ledvinka, Zuzana Hybnerová): Wholesome

How many Hemistry Races make up one Chemistry Race?

Solution:

The *hemi-* prefix denotes one half. Therefore, one Chemistry Race consists of two Hemistry Races.

Question A.2 (Nathaniel Loh): Simple molecule

In recent times, there has been increasing discussion about non-binary identities. However, you might be surprised to learn that in chemistry, we can also find compounds referred to as binary. As the root of the word suggests, these are substances that contain only two types of atoms. A typical example of a binary compound includes compounds with monovalent hydrogen, which bonds with another atom as many times as needed: with monovalent halogens, it forms acids HX, with trivalent nitrogen, it forms ammonia NH_3, and with tetravalent carbon, it forms methane CH_4. Slightly more complex binary compounds can be obtained if we consider two elements with higher valency.

What is the structure of the simplest (lowest molecular mass) molecule containing both carbon and nitrogen with no other elements, which is stable at room temperature and pressure? All atoms in your molecule should be neutral (no formal charge).

Hint: The molecule contains two triple bonds.

Solution:

As all electrons should be in pairs (whether in bonds or lone pairs) for the molecule to be stable, there must be an even total number of electrons in the molecule. As N has 5 valence electrons and C has 4 valence electrons, there must be an even number of N atoms for the total to be even. CN_2 would have to take a cyclic structure with two double bonds in a three membered ring, which would obviously not be stable due to ring strain. The next simplest possible molecule is C_2N_2, and the structure of cyanogen, N≡C−C≡N, is found to be the only one that is clearly stable.

Question A.3 (Daniel Čičovský): Ibuprofen

Some of the most popular painkillers contain ibuprofen. In this task, we will take a look at light yellow tablets produced in Prague. Besides the active ingredient, the tablet also contains excipients that ensure its proper function. The chemical substances listed below represent selected components of the tablet. Match each of them to its function:

1. Microcrystalline cellulose (approx. 70 % of the tablet)
2. Sodium croscarmellose salt (approx. 3 % of the tablet)
3. Titanium dioxide
4. Iron(III) oxide

a. Disintegrant (a substance facilitating tablet dissolution)
b. Yellow dye
c. Filler
d. White dye

Solution:

Based on the knowledge of the colours of oxides, we can immediately determine that titanium dioxide is a white pigment and iron(III) oxide is a yellow pigment. Microcrystalline cellulose is commonly used as a filler. The remaining compound, sodium croscarmellose, must therefore be the disintegrant, facilitating the dissolution of the tablet.

Question A.4 (Jiří Ledvinka): ACAB, wait, BCAA

Football hooligans often use the abbreviation ACAB to demonstrate their love of police. As we are not interested in such inappropriate behaviour, let's look at BCAA (branched-chain amino acids) instead.

BCAA is a group of amino acids containing a branched side chain. These amino acids are a popular dietary supplement for athletes. Although this group also includes some non-proteinogenic amino acids, most preparations for athletes contain only proteinogenic amino acids.

State three proteinogenic amino acids we should find in a BCAA dietary supplement.

Solution:

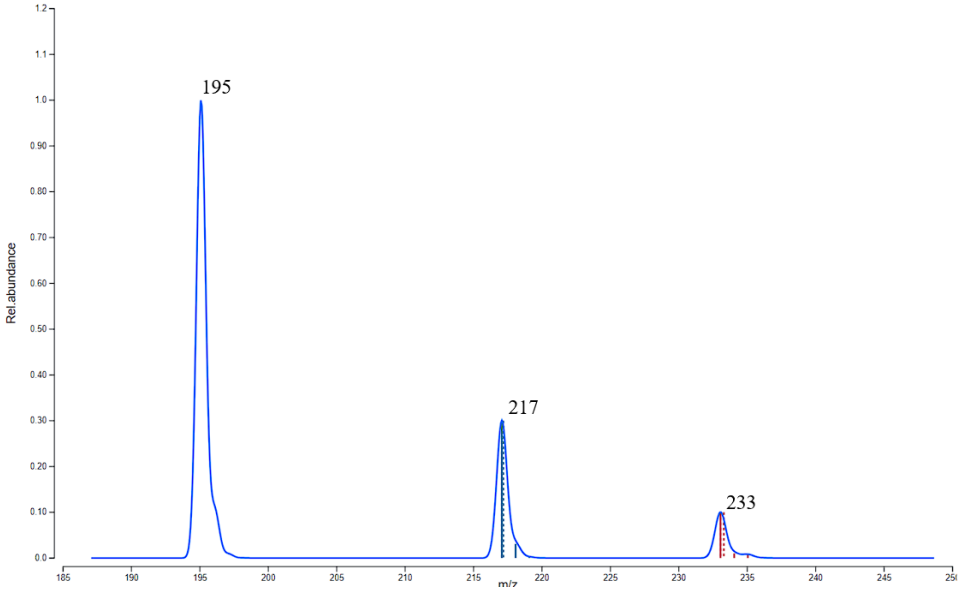
If we look at the overview of proteinogenic amino acids, in the subgroup of amino acids with hydrophobic chains we find three with a branched side chain: valine, leucine and isoleucine.

Question A.5 (Tadeáš Grabic): Mass spectrometry

Mass spectrometry is an instrumental method used in the analysis of mainly organic substances. The output of an analysis is a spectrum presenting the intensities of individual m/z (mass-to-charge) ratios. One of the most widely used ionization techniques is the so-called ESI ionization, in which molecular adducts are formed and thus the m/z of the whole molecule with the adduct is recorded. In the positive mode, i.e. ESI+, adducts of the analyte are formed with protons $[M+H]^+$, sodium $[M+Na]^+$, potassium $[M+K]^+$ or, for example, ammonium cations $[M+NH_4]^+$.

Chemist Thaddeus examined the spectrum of one bioactive substance. The spectrum of this substance was obtained at ESI+ ionization, with the dominant peak located at m/z 195. Other peaks (albeit of lesser intensity) were observed at m/z 217 and 233.

Determine the molar mass of the substance that Thaddeus was investigating, assuming that the charge of each ion (z) is +1.



Solution:

Due to the ionization technique used, the formation of adducts can be expected. The

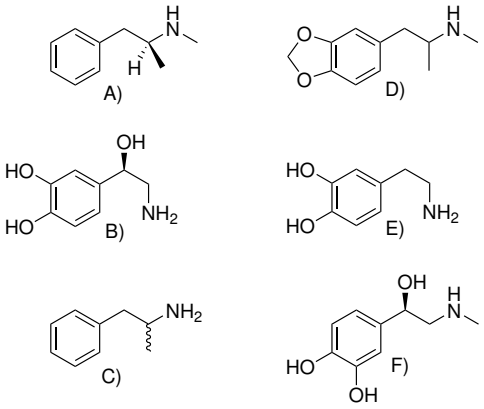
lightest peak has an m/z of 195, which corresponds to the $[M+H]^+$ adduct. Given the unit charges, the mass differences to the other peaks are 22 and 38, corresponding to the $[M+Na]^+$ and $[M+K]^+$ adducts, respectively. We have to remember that the mass of the molecule does not appear in the spectrum, only that of its adducts, so that the mass of one proton must be subtracted. The right mass is 194.

Question A.6 (Pavlína Muchová): Nymphetamine

In 2004, the British band *Cradle of Filth* released their album titled *Nymphetamine*. The name is derived from nymphomania and amphetamine. The latter is a highly addictive substance with a stimulant effect that is also used in treatment of ADHD. **Amphetamine** is the abbreviated name of the molecule alpha–methylphenethylamine (or (*RS*)-1-phenylpropan-2-amine).

Now you have a simple task: Identify the molecule of **amphetamine**.

In addition to this addictive substance, you have the choice among:
norepinephrine (4-[(1*R*)-2-amino-1-hydroxyethyl]benzene-1,2-diol), the levels of which amphetamine increases,
adrenaline ((*R*)-4-(1-hydroxy-2-(methylamino)ethyl)benzene-1,2-diol).
Amphetamines also stimulate **dopamine** (3,4-dihydroxyphenethylamine) receptors.
Other examples of amphetamine include:
MDMA or ecstasy (3,4-methylenedioxymethamphetamine),
and **methamphetamine** or pervitin (1-phenyl-*N*-methylpropan-2-amine).



Solution:

While molecules **B**, **D**, **E** and **F** are easily eliminated by the mere presence of oxygen in their names (-diol, dihydroxy-, and -dioxy-, respectively), in the case of molecule **A** we need to notice the *N*-methyl. This leaves us with molecule **C**.

Question B.1 (Supatpong Juntarawatt): Jelly Babies

People often believe that the most energy-rich substances are explosives. However, that's not necessarily true! Consider how much energy is stored in one small gummy bear. And when you throw it into molten potassium chlorate ($KClO_3$), that energy is released with hellish speed: it smells, it glows, and sometimes the test tube in which the reaction takes place bends significantly from the heat. This glowing gummy bear is a typical demonstration of the strong oxidizing effects of chlorates.

One of the reactions occurring in the reaction mixture is disproportionation, the decomposition of potassium chlorate into other potassium salts **A** and **B**, in which the chlorine atom has oxidation states of -1 and $+7$, respectively. No additional products are formed during this reaction.
Write the balanced equation for the disproportionation of potassium chlorate.

Solution:

As $KClO_3$ disproportionates into salts **A** and **B**, both compounds contain potassium, chlorine, and possibly oxygen. Based on the given the oxidation numbers of chlorine, **A** is KCl and **B** is $KClO_4$.

As the oxidation number of chlorine in $KClO_3$ is $+5$, the balanced disproportionation equation is then:

$$4\,KClO_3 \longrightarrow KCl + 3\,KClO_4$$

Question B.2 (Rostislav Huňa): Air in the air

What is the molar concentration of air in an ordinary auditorium where Chemistry Race is held, in $\mathrm{mol\,dm^{-3}}$? Consider ideal behavior, a temperature of 20 °C, a pressure of 100 000 Pa.

Solution:

Ideal gas law:

$$p \cdot V = n \cdot R \cdot T$$

Determine the concentration:

$$c = \frac{n}{V} = \frac{p}{R \cdot T} = \frac{100\,000}{8.314 \cdot (20 + 273.15)} \frac{\text{mol}}{\text{m}^3}$$

To obtain a result in the specified units, we need to convert in the denominator, which means dividing by 1000.
The result is $0.04103\,\text{mol}\,\text{dm}^{-3}$.

Question B.3 (Jiří Ledvinka): Taurine

Taurine (from Latin *taurus* – after the first isolation from ox bile) is a small non-proteinogenic amino acid. Its systematic name is 2-aminoethanesulfonic acid. Being a sulfonic acid, it has no carboxyl group, which is an integral part of all proteinogenic amino acids. Taurine is a common ingredient in energy drinks (up to 46 grains per 100 teaspoons), although it is not an essential nutrient for humans, as our bodies synthesise it in the liver by oxidation and decarboxylation of one proteinogenic amino acid. What proteinogenic amino acid does the body get taurine from?

Solution:

Only two proteinogenic amino acids contain sulfur: cysteine and methionine. While methionine can be oxidized to sulfone (R−S(=O)$_2$−R'), cysteine as a thiol can be easily oxidized to sulfonic acid. At the same time, methionine has a longer chain by one carbon, while only two carbons remain from cysteine after decarboxylation.

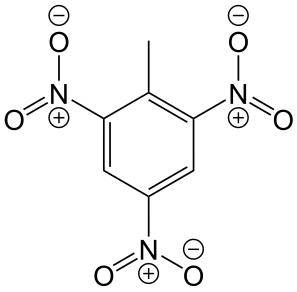
Question B.4 (Tadeáš Grabic): T. N. T.

"Cause I'm T. N. T., I'm dynamite
T. N. T., and I'll win the fight
T. N. T., I'm a power load
T. N. T., watch me explode!"

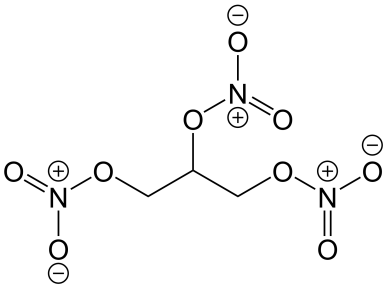
In the lyrics of the song *AC/DC* by the Australian band *AC/DC*, the lead singer compares himself to an explosive. The lyrics suggest that the explosive used in dynamite is the aforementioned trinitrotoluene, but this is not the case. The explosive used in it is nitroglycerine, which has slightly different properties. Among other things, it differs in the energy released on detonation. The detonation energy of trinitrotoluene is $950\,\text{kJ}\,\text{mol}^{-1}$ and that of nitroglycerine is $1414\,\text{kJ}\,\text{mol}^{-1}$.

Blasting charges need to be designed such that they release only the desired amount of energy. For example, during blasting operations in mines, excessive energy could not only cause undesired crumbling of waste rock surrounding the ore but also potentially cause collapse of the mine tunnel itself. Calculate how big this problem could be if blasters misunderstood the words of *AC/DC*'s lead singer, Brian Johnson, who weighs 85 kg. How much more energy would be released if the singer were made up of nitroglycerin instead of trinitrotoluene?

The structures of the substances mentioned are given below.



Trinitrotoluene



Nitroglycerin

Solution:

First, we obtaining each compound's molar mass from its structure. Then, from the singer's mass, we determine the molar quantity of the explosives. Multiplying this by the molar detonation energy of each compound, we determine the energy released in an explosion. Finally, the difference in question is found by subtracting the energy released in the explosion of trinitrotoluene from the energy released in the explosion of nitroglycerin.

$$\begin{aligned} n(\mathrm{TNT}) &= m/M = 85\,000/227.13 \\ &= 374.235\,\mathrm{mol} \\ n(\mathrm{TNG}) &= m/M = 85\,000/227.09 \\ &= 374.3\,\mathrm{mol} \\ E(\mathrm{TNT}) &= n(\mathrm{TNT}) \cdot E_{\mathrm{mol}}(\mathrm{TNT}) = 374.235 \cdot 950 \\ &= 355\,523.25\,\mathrm{kJ} \end{aligned}$$

$$
\begin{aligned}
E(\mathrm{TNG}) &= n(\mathrm{TNG}) \cdot E_{\mathrm{mol}}(\mathrm{TNG}) = 374.3 \cdot 1414 \\
&= 529\,260.20\,\mathrm{kJ} \\
\Delta E &= E(\mathrm{TNG}) - E(\mathrm{TNT}) = 529\,260.20 - 355\,523.25 \\
&= 173\,736.95\,\mathrm{kJ} \\
&= 173.736\,\mathrm{MJ}
\end{aligned}
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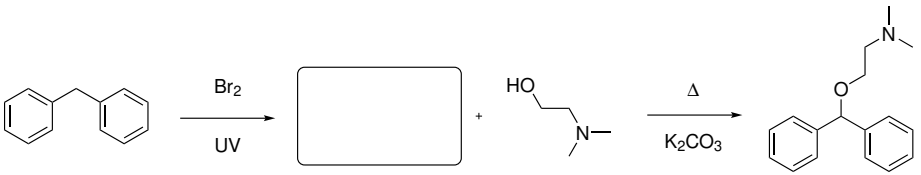
Question B.5 (Tatiana Nemirovich): Dramamine

After months of planning, you and your colleague have just carried out an attack on a Mexican drug cartel. Adrenaline rushes through your veins as you leap over concrete barriers and hear the shouts of furious gangsters behind you. Bullets whistle past as you finally reach the harbour. A fast boat is waiting there –- your only ticket to freedom. Without hesitation, you jump into the boat and start the engine. Your colleague, gun in hand, prepares to defend you from the enemies who are already dangerously close.

But then it happens. His face turns pale, and his hand begins to tremble. "The sea... spinning... my head..." he mutters, and the gun slips from his grasp. Seasickness. And at the worst possible moment?! Your survival plan begins to fall apart. Without a capable shooter, you're doomed.

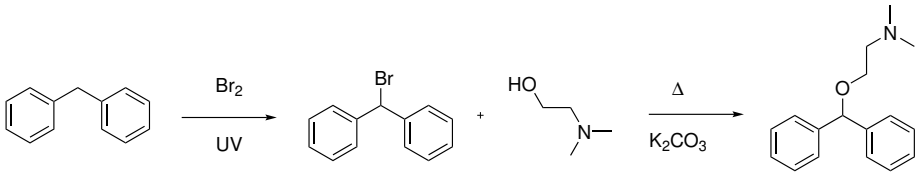
Fortunately, you're a skilled chemist, and the boat is equipped with a chemistry lab. You remember the commercially available anti-nausea drug, Dramamine, the synthesis procedure of which you've just found in a pile of old papers. However, you quickly notice that the instructions are incomplete –- the structure of an intermediate is missing. The gangsters are almost on board...

Complete the missing structure of intermediate **A** so that you can finish synthesizing the drug and escape safely from the Mexican gangsters. The synthesis scheme is below.



Dramamine

Solution:



Dramamine

Question B.6 (Adam Tywoniak): Sunset on the ocean

Content warning: Alcohol consumption, Swedish poetry.

Below you will find an excerpt from a poem by August Strindberg. Originally found in his work *Från Havet - Här och där*, written 1873-1876, translated into English by Markus Hartsmar[1].

Regardless of your level of Swedish language proficiency, you most likely noticed the mentions of magnesium chloride, sodium chloride, and potassium iodide. Let's ignore those inorganic salts for now, and focus on the last verse in the excerpt instead.

Absinthe is an alcoholic beverage derived from various plants including *Artemisia absinthium* ("grand wormwood"), that has become associated with the late 19th-century decadent movement in literature and arts. It was reputed for its alleged hallucinogenic effects and considered dangerously addictive at its time. These properties were attributed to the compound thujone, naturally occurring in the Artemisia plant.

Somewhat surprisingly, thujone itself was later found neither psychoactive nor particularly harmful – the health risks posed by consumption of absinthe are essentially those caused by ingestion of ethanol (45–74 % by volume when undiluted). Nowadays, food safety legislation in the EU permits alcoholic beverages prepared with artemisia species to have a thujone content of up to $35\,\mathrm{mg\,kg^{-1}}$. What molar concentration of thujone does this limit correspond to?

Thujone is a monoterpene ketone, its formula being $C_{10}H_{16}O$.
Assume a density of absinthe of $0.89\,\mathrm{g\,m\ell^{-1}}$.

[1]Source: http://www.absinthe.se/absinthe-poetry#august_strindberg

Solnedgång på havet
Jag ligger på kabelgattet
rökande “Fem blå bröder”
och tänker på intet.
Havet är grönt,
så dunkelt absintgrönt;
det är bittert som chlormagnesium
och saltare än chlornatrium;
det är kyskt som jodkalium;
och glömska, glömska
av stora synder och stora sorger
det ger endast havet,
och absint!

Sunset on the ocean
I’m lying on the boatswain’s locker
smoking “Fem Blå Bröder”
thinking of nothing
The sea is green
dark absinthe green
it is bitter like magnesium chloride
and saltier than sodium chloride
it is chaste like potassium iodide
and oblivion, oblivion
from major sins and great sorrows
you find only in the ocean,
and absinthe!

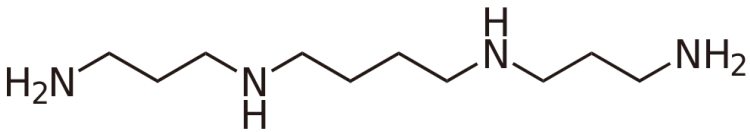
Solution:

Based on the chemical formula of thujone, we determine its molar mass to be $152\,\mathrm{g\,mol^{-1}}$ (precisely $152.237\,\mathrm{g\,mol^{-1}}$). Its molar concentration can be calculated from its mass fraction in the mixture w, the density of the beverage ρ, and thujone’s molar mass M:

$$\begin{aligned} c &= w \cdot \rho / M \\ &= 35 \times 10^{-6} \cdot 890 / 152.237 \\ &= 2.046 \times 10^{-4}\,\mathrm{mol\,dm^{-3}} \\ &= 0.205\,\mathrm{mmol\,dm^{-3}} \end{aligned}$$

Question C.1 (Jiří Ledvinka): Spermine

Spermine (shown below) is one of the polyamines found in semen, which make it basic.



For this exercise, imagine that spermine enters an acidic environment. What will be the charge of this molecule? The dissociation of the conjugated acids is described by these acidity constants:
$\mathrm{p}K_{\mathrm{a},1} = 7.96$, $\mathrm{p}K_{\mathrm{a},2} = 8.85$, $\mathrm{p}K_{\mathrm{a},3} = 10.02$, $\mathrm{p}K_{\mathrm{a},4} = 10.80$

Solution:

The $\mathrm{p}K_{\mathrm{a}}$ value defines the dissociation of the acid, in this case the conjugate acid – i.e. the protonated amine. It is defined as the negative decimal logarithm of the equilibrium constant K_{a} :

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

From this constant's definition, we can derived the Henderson–Hasselbalch equation:

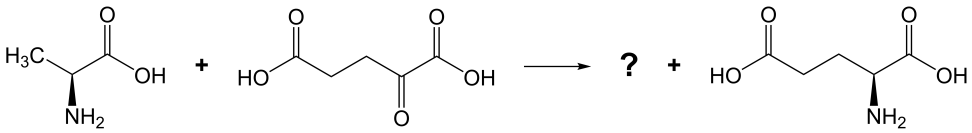
$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

Here, without any calculations, we can see what is commonly taught about acids – if the pH is higher than $\mathrm{p}K_{\mathrm{a}}$, the deprotonated form predominates, and at $\mathrm{pH} < \mathrm{p}K_{\mathrm{a}}$, the protonated form predominates. Spermine, as a basic amine, undergoes complete protonation occurs in an acidic environment, so that its form with a charge of +4 will predominate.

Question C.2 (Zuzana Zápotocká): Liver tests

After a series of exhausting life's trials, experienced chemist Ondřej's dream came true as he started working in his dream lab. But before he could fully immerse himself in his work, he faced one last challenge – tests to verify whether he met the level required by the institution. Despite having a lot of experience, these tests turned out to be the hardest trial of his life. When he finally received the test results, he broke out in a cold sweat. He had not passed. The reason for his failure were two words now glowing red on the results paper: ALT and AST.

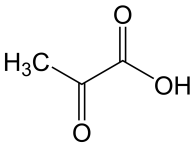
As you may have already understood, Ondřej's failed test was a liver test. Some of the markers that we monitor include the enzymes ALT (alanine aminotransferase) and AST (aspartate aminotransferase), which tend to be elevated in liver damage. Your task is to draw the structure of the product of the reaction below, catalyzed by ALT enzyme.



Fortunately, Ondřej was given a second chance. Let's hope he will study for his next round of liver tests properly.

Solution:

The reaction is a transamination, producing pyruvic acid (or its anion, pyruvate).



Question C.3 (Neil Waterson): An unnameable mess

$AuXe_4(Sb_2F_{11})_2$ is an unusual compound containing a bond between a noble gas and a noble metal. Give the oxidation states of Au, Xe and F. Assume that all the elements have integer oxidation states, the oxidation state of Sb is +V and all atoms of one element have the same oxidation state.

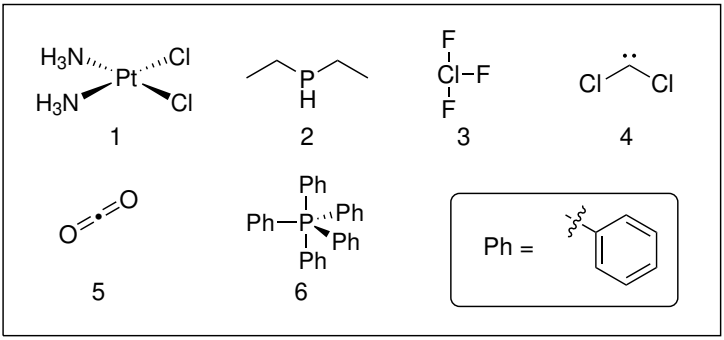
Solution:

Fluorine must have an oxidation state of −I. The whole anion will then have a charge of 1−. The $AuXe_4$ ion must have a 2+ charge, which means gold must have an oxidation state of II and xenon has 0.

Question C.4 (Štěpán Novák): VSEPR

Valence shell electron pair repulsion theory is a model used for predict the geometry of molecules. Match the molecules with their corresponding shapes:

1) *cis*−$[Pt(NH_3)_2Cl_2]$ (cisplatin)	a) square planar
2) diethylphosphine	b) trigonal pyramid
3) ClF_3	c) T-shape
4) Dichlorocarbene	d) bent
5) CO_2	e) linear
6) PPh_5	f) trigonal bipyramid



Solution:

cis−$[Pt(NH_3)_2Cl_2]$ has a central platinum atom with four ligands, and therefore has a square planar geometry. Tetrahedral geometry is not in the list, and furthermore, platinum has a d^8 configuration, which causes it to prefer ligand arrangement in one plane (the so-called square planar geometry).

In diethylphosphine, the central atom is phosphorus, bonded to two ethyl groups and one hydrogen atom. Due to the lone pair of electrons on phosphorus, the molecule has a trigonal pyramidal shape.

In ClF_3, the central atom is chlorine, surrounded by three fluorine atoms and two lone pairs of electrons. This arrangement creates a T-shape.

Dichlorocarbene (CCl_2) has a carbon atom bonded to two atoms of chlorine. Due to the lone pair of electrons on the carbon atom, the molecule has a bent shape.

Carbon dioxide is a linear molecule because carbon is bonded to two oxygens by double bonds and has no lone pairs itself.

In PPh_5, the central atom is phosphorus bonded to five phenyl groups. This leads to a trigonal bipyramidal shape.

Question C.5 (Supatpong Juntarawatt): Mexican

Traditionally, Mexicans enhance the nutritional values of corn kernels harvested by nixtamalisation. The process is done by cooking the kernels in an alkaline medium (such as limewater, $Ca(OH)_2$). At the end, corn dough or nixtamalized corn flour is obtained, which is the basis of many Mexican foods.

Agent FE0000 would like to discard the leftover limewater solution called nejayote; however, he is aware that pouring Ca^{2+} to water sources increases the hardness of water. Thus, he is determined to determine the concentration of Ca^{2+} in the nejayote via titration with a standardised ethylenediaminetetraacetic acid (EDTA) solution under Eriochrome black T (EBT) indicator.

It is known that the complexation reaction between Ca^{2+} and EDTA proceeds in a 1:1 mole ratio. Calculate the concentration of Ca^{2+} in $\mathrm{g}\,\ell^{-1}$ if $42.50\,\mathrm{m}\ell$ of EDTA solution of concentration $0.10\,\mathrm{mol\,dm^{-3}}$ is used to titrate $25.00\,\mathrm{m}\ell$ of nejayote.

Solution:

The amount of substance of EDTA used for the titration corresponds to the amount of substance of Ca^{2+} in $25.00\,\mathrm{m}\ell$ of nejayote. The concentration of Ca^{2+} is then

$$c_{\mathrm{Ca^{2+}}} = \frac{c_{\mathrm{EDTA}} \cdot V_{\mathrm{EDTA}}}{V_{\mathrm{Ca^{2+}}}} = \frac{42.50\,\mathrm{m}\ell \times 0.10\,\mathrm{mol\,dm^{-3}}}{25.00\,\mathrm{m}\ell} = 0.170\,\mathrm{mol\,dm^{-3}}$$

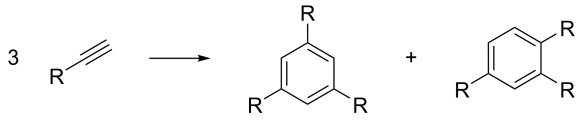
Mass concentration Ca^{2+} in nejayote is then

$$\rho = c \cdot M = 0.170\,\mathrm{mol\,dm^{-3}} \times 40.08\,\mathrm{g\,mol^{-1}} = 6.81\,\mathrm{g}\,\ell^{-1}$$

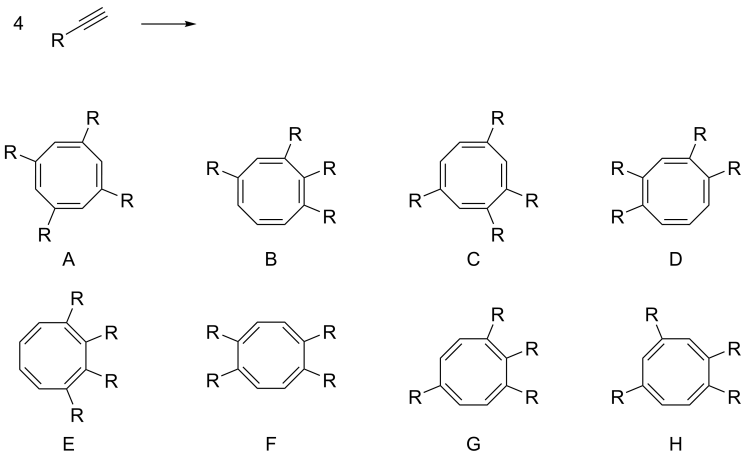
Question C.6 (Jan Hrubeš): Mechanochemistry

Mechanochemistry is a young, developing branch of chemistry. Mechanochemical reactions take place in dry conditions (sometimes called neat), without the presence of solvents. The powdered reactants are then ground together using metal beads, such as zinc or nickel. This way, unexpected products are formed - some of the products that are formed in mechanochemical reactions would not be formed at all in solution. At the same time, mechanochemistry is environmentally friendly - there is no need to use toxic solvents with a high environmental footprint. This is why many research teams are currently working on mechanochemistry. One such reaction is the pericyclic condensation of alkynes. In solution, its known product is

a benzene nucleus formed by cyclization of three triple bonds. Below are examples of two products that can be formed by cyclization of three terminal alkynes.



Mechanochemically, however, the cyclization of four triple bonds produces an eight-membered antiaromatic ring. From the following eight molecules (see the image), select those that could be formed by mechanochemical condensation of the four terminal alkyne units.



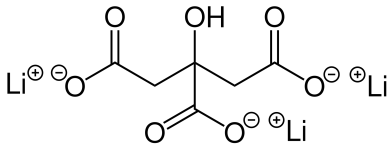
Solution:

A, **C**, **F**, **H**

When considering which products are realistic, we must base our reasoning on how the starting terminal alkynes can be oriented. The formation of a 1,2,3,4- or 1,3,4,5-tetrasubstituted ring is therefore not feasible, as there is no way to orient four alkynes in such a way that the desired product could be formed through cyclization. For the same reason, no product containing a $-(CH)_3-$ motif can be formed either. On the other hand, for example, a 1,2,5,6-tetrasubstituted ring can be formed by cyclization of suitably oriented alkynes.

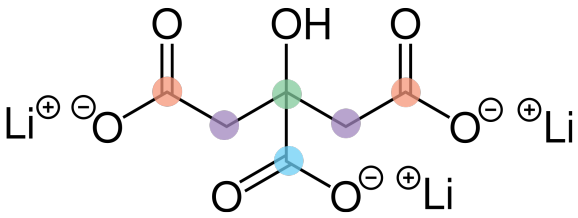
Question D.1 (Tatiana Nemirovich): Bipolar

Just like cocaine in Coca-Cola, lithium was widely marketed as one of many patent medicines popular in the late 19th and early 20th centuries and was a medicinal ingredient in a refreshing beverage. Charles Leiper Grigg, founder of *The Howdy Corporation*, invented a formula for a lemon-lime soft drink in 1920. The product, originally called "Bib-Label Lithiated Lemon-Lime Soda", was introduced in 1929 and contained the mood stabilizer lithium citrate. Its name was soon changed to 7 Up. The drink was a patent medicine promoted as a hangover cure. Lithium citrate was removed from 7 Up in 1948 after being banned by the U.S. Food and Drug Administration. How many peaks are found in the carbon NMR spectrum of lithium citrate? Each chemically non-equivalent nucleus will give a distinct signal.



Solution:

The molecule contains a total of six carbon atoms; however, due to symmetry, two pairs of them are equivalent. This leaves four non-equivalent carbon nuclei, which give rise to four signals in the molecule's carbon nuclear magnetic resonance spectrum. The non-equivalent carbons are highlighted in colour in the diagram.



Question D.2 (Štěpán Novák): Victor Meyer

The label on one of the bottles in your lab's chemical cabinet, has fallen apart after being stored for a long time, and now you don't know what substance is in it. Unfortunately, you have been underfunded for a long time and therefore do

not have access to NMR or GC-MS/LC-MS analysis. However, you have found an older apparatus in your laboratory for determining molar mass by the Victor Meyer method. The method involves evaporating a known amount of sample in a gas-tight apparatus with a pressure equaliser. The resulting vapour is then forced out of the apparatus into an attached gas burette where, after equilibrating the pressures, you read off the vapour volume of the substance. The sample is loaded into the apparatus in a sealed, bubble-free ampoule, which is then dropped into an oven, where the ampoule ruptures and releases the sample. You have made three measurements, which are recorded in the table. Assume the validity of the ideal gas law. Determine the molar mass of the unknown substance.

	$T = 23.5\,°\mathrm{C}$	$p = 101\,325\,\mathrm{Pa}$	$R = 8.314\,\mathrm{J/K/mol}$
Sample	Mass of the empty ampoule	Mass of the full ampoule	Volume in the burette
1	84.6 mg	204.6 mg	31.7 mℓ
2	96.2 mg	205.6 mg	28.9 mℓ
3	136.5 mg	308.4 mg	45.4 mℓ

Solution:

Using

$$pV = nRT \text{ and formula } n = \frac{m}{M}$$

we obtain the formula:

$$M = \frac{mRT}{pV}$$

The mass of the sample is obtained by subtracting the mass of the empty vial from the mass of the full vial. Thus, for the calculation we have:

$$M = \frac{(m_2 - m_1)RT}{pV}$$

By substituting the data from the table of values, we get the solution. There should be no rounding errors in the solution.

Sample	Molar mass	Average
1	92.142	92.149
2	92.142	Standard deviation
3	92.163	0.01

Question D.3 (Alexandros Terzopoulos): Eutectic

Sodium and potassium, which are both solid at room temperature, if combined at the correct ratio famously form a highly reactive liquid alloy known as "NaK". This is an example of a eutectic system, i.e. a homogeneous mixture possessing a melting point lower than the individual components. A lesser known alkali metal eutectic alloy with a very low melting point of $-37.5\,°C$ has the formula $Cs_{77}K_{23}$.

Caesium metal has been obtained historically by the electrolysis of caesium cyanide:

$$2\,CsCN + 2\,e^- \longrightarrow 2\,Cs + C_2N_2$$

Calculate how long (in hours) the electrolysis using 10 A current must run to produce enough cesium metal to form the aforementioned eutectic alloy upon reaction with 250 g of potassium. Assume that the reaction proceeds with 100 % efficiency.

Solution:

This is essentially a stoichiometric calculation question, deliberately obfuscated with additional information so that you have to extract what is pertinent.

We have 250 g of potassium metal, which constitutes a molar quantity of $\frac{250}{39.1} = 6.40\,mol$. This will react to give $\frac{6.40}{23} = 0.278\,mol$ of the eutectic.

The preparation requires $77 \times 0.278 = 21.4\,mol$ of caesium and therefore also 21.4 mol of CsCN precursor.

Using the Faraday law with 21.4 mol and a current of 10 A, we find the time required to be 57.37 h.

Question D.4 (Jiří Ledvinka): Sour Coke

Classic Coca-Cola has a pH of 2.37, in comparison 8 % vinegar has a pH of approximately 2.6. Coca-Cola is therefore more acidic than the vinegar commonly used for descaling. The pH of Coca-Cola is due solely to phosphoric acid, which is a tri-saturated acid with $pK_{a,1} = 2.14$, $pK_{a,2} = 7.20$, and $pK_{a,3} = 12.37$. Calculate the mass concentration of this acid in Coca-Cola.

Solution:

Definition of acidity constant:

$$K_{\mathrm{a},1} = [\mathrm{H^+}] \times \frac{[\mathrm{H_2PO_4^-}]}{[\mathrm{H_3PO_4}]}$$

Mass balance:

$$c = [\mathrm{H_2PO_4^-}] + [\mathrm{H_3PO_4}]$$

Ionic balance:

$$[\mathrm{H^+}] = [\mathrm{H_2PO_4^-}]$$

Then

$$c = [\mathrm{H^+}] + \frac{[\mathrm{H^+}]^2}{K_{\mathrm{a},1}} = 10^{-2.37} + \frac{(10^{-2.37})^2}{10^{-2.14}} = 0.0068\,\mathrm{mol/l}$$

$$\rho = c \cdot M = 0.0068 \times 98 = 0.66\,\mathrm{g/l}$$

The next degree of dissociation can be neglected as the corresponding constant is 5 orders of magnitude smaller.

Question D.5 (Neil Waterson): Electrides

Electrides are compounds where an electron acts as an anion, called a solvated electron. An example of one is $[\mathrm{Na(NH_3)_6}] + \mathrm{e^-}$. This species can decompose via a redox reaction into three products. Write the full equation of the decomposition of $[\mathrm{Na(NH_3)_6}]^+\mathrm{e^-}$.

Solution:

$$2\,[\mathrm{Na(NH_3)_6}]^+\mathrm{e^-} \longrightarrow 2\,\mathrm{NaNH_2} + 10\,\mathrm{NH_3} + \mathrm{H_2}$$

The solvated electron can reduce the ammonia, forming sodium amide. Therefore hydrogen must also be produced.

Question D.6 (Jiří Ledvinka): Angela

At the beginning of September 2024, there were complications in local transport in Lower Saxony as the hydrogen trains, newly introduced in line with *Energiewende*, ran out of hydrogen. The supplier promised to remedy the situation within a week. In order to prevent an ADAC-iniciated Gerexit, the local government sought to quickly address the situation. With all the German fathers of industrial chemistry like Fritz Haber, Carl Bosch and Carl von Linde already six feet (183 cm) under, it was necessary to call in someone younger. And so it was the turn of Berlin's famous retired chemist, Angela Merkel. Before her political career, she had been a theoretical chemist, so unfortunately she could only remember how they prepared hydrogen by dissolving zinc in hydrochloric acid at grammar school.
Let's consider the task Angela faces. She needs to cover the weekly hydrogen consumption of 14 *iLint* units, running on electricity generated by a hydrogen fuel cell. Each unit has a 1800 kg hydrogen tank with a range of approximately 1175 km. The weekly range of each unit is approximately 5000 km, their top speed 140 km/h. How many tonnes of zinc will Angela need? Since Angela is a theoretical chemist, assume that her reaction yield is 100 %.

Solution:

First hint:

$$\text{Consumption} = \frac{\text{tank volume}}{\text{range}} [\text{kg km}^{-1}]$$

First we calculate how much hydrogen will be needed. The consumption of one unit is 1800 kg(H_2)/1175 km. So in a week, one unit will consume

$$m(H_2) = \frac{5000}{1175} \times 1800\,\text{kg} = 7659.57\,\text{kg}$$

Therefore, all fourteen units will use up 107.2 tonnes of hydrogen.

Angela will produce this hydrogen according to the following reaction equation:

$$\text{Zn} + 2\,\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2$$

The amount of zinc needed is therefore:

$$m(\text{Zn}) = \frac{M(\text{Zn})}{M(\text{H}_2)} \times m(\text{H}_2) = \frac{65.38}{2.02} \times 107.2\,\text{t} = 3470\,\text{t}$$

Question E.1 (Tatiana Nemirovich): Truffle flavoured

Sulfur compounds belong to a group of substances with a highly characteristic and unpleasant odor, detectable by humans at concentrations as low as 10 ppb (by molar amount).

While walking home from the lab, chemist Š. accidentally spilled a small amount of dithiapentane (IUPAC name: bis(methylsulfanyl)methane; density = $1.059\,\mathrm{g/cm^3}$) in a residential room with dimensions $3 \times 4 \times 2.5\,\mathrm{m}$. Assuming the spilled substance formed a puddle, which can be approximated as a circle with a thickness of 100 µm, and subsequently evaporated completely into the air, calculate the maximum radius of the puddle (in cm) such that its evaporation would not be detected by the occupants of the room.

Assume air behaves as an ideal gas with a temperature of 25 °C and pressure of 101 325 Pa.

Solution:

The volume of the room is $3 \times 4 \times 2.5 = 30\,\mathrm{m^3}$. We use the ideal gas law:

$$pV = nRT \quad \Rightarrow \quad n_{\mathrm{air}} = \frac{pV}{RT}$$

Substituting values:

$$n_{\mathrm{air}} = \frac{101325 \times 30}{8.314 \times 298} \approx 1225.5\,\mathrm{mol}.$$

The maximum concentration of dithiapentane:

$$n_{\mathrm{dithiapentane}} = \frac{10}{10^9} \times 1225.5 = 1.2255 \times 10^{-5}\,\mathrm{mol}.$$

The mass of dithiapentane:

$$m_{\mathrm{dithiapentane}} = 1.2255 \times 10^{-5} \times 108 \approx 1.326 \times 10^{-3}\,\mathrm{g}.$$

The volume of the substance is determined from its density:

$$V_{\mathrm{dithiapentane}} = \frac{1.326 \times 10^{-3}}{1.059} \approx 1.25 \times 10^{-3}\,\mathrm{cm^3}.$$

The volume of a circular puddle is given by the equation:

$$V_{\mathrm{puddle}} = \pi r^2 d,$$

where $d = 0.01\,\text{cm}$. Expressing the radius r:

$$r = \sqrt{\frac{V_{\text{puddle}}}{\pi d}}.$$

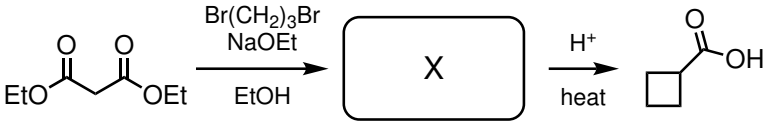
Substituting values we obtain:

$$r = \sqrt{\frac{1.25 \times 10^{-3}}{\pi \times 0.01}} \approx 0.2\,\text{cm}.$$

The maximum radius of the puddle at which the odour will not be detected is approximately 0.2 cm.

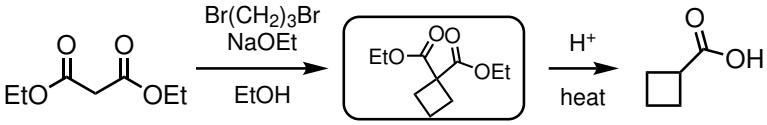
Question E.2 (Štěpán Novák): An acid outside the box

Since the synthesis of barbiturates was deemed too difficult for this competition according to other authors (but students could certainly do it, right?) we decided to look at the synthesis of cyclobutanecarboxylic acid. It uses the same key reaction, which a knowledgeable chemist will recognise, as the malonic ester synthesis. This reaction takes advantage of the relative acidity of the alpha hydrogens of diethylmalonate, which have a pK_a of about 13.5. This allows the use of weaker bases for deprotonation and subsequent substitution. Your task will be to draw a cyclic substance **X** which, after acid hydrolysis, is thermally decarboxylated to give our target cyclobutanecarboxylic acid.



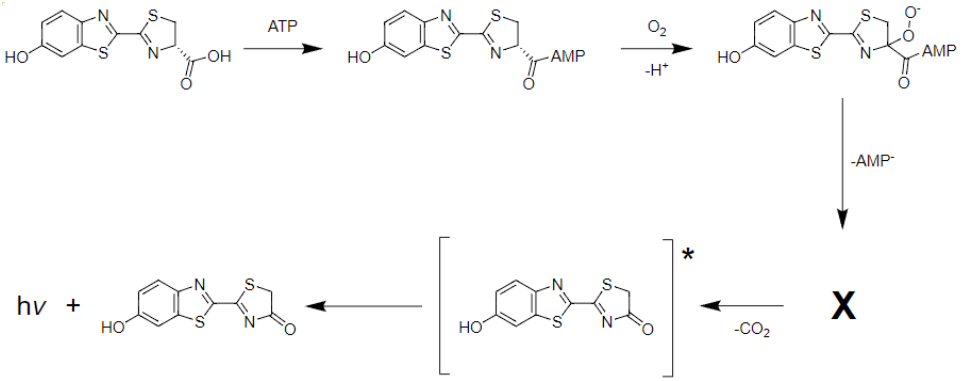
Solution:

A twofold nucleophilic substitution yields diethyl cyclobutane-1,1-dicarboxylate.



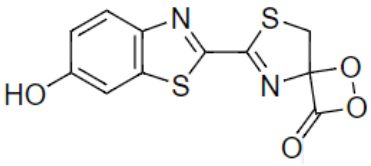
Question E.3 (Jakub Sochor): Luciferins

Luciferins are a group of compounds enabling bioluminescence. These are small molecules that, in the presence of enzymes from the luciferase class, undergo oxidation by atmospheric oxygen and subsequently release chemical energy in the form of light. The scheme illustrates the principle of luminescence in firefly luciferin. The first step is the phosphorylation of a carboxylic acid, followed by oxidation at the α-carbon by molecular oxygen, and an intramolecular acyl substitution leading to intermediate **X**. This intermediate loses carbon dioxide and transitions to an excited product, which emits a photon upon returning to the ground state. Draw the structure of compound **X**, knowing that it contains a four-membered ring.



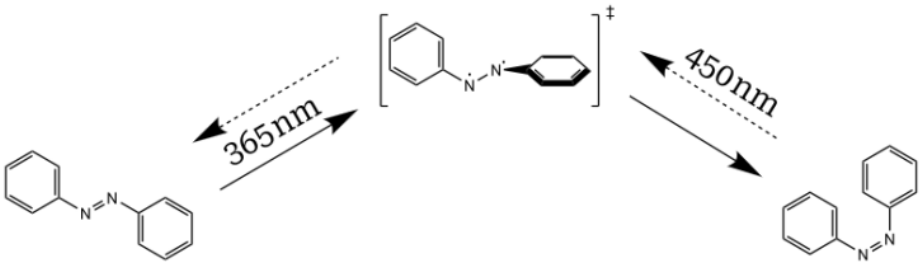
Solution:

An unstable 1,2-dioxetane is formed.



Question E.4 (Jakub Sochor): Azobenzene

Azobenzene is a well-known molecule and the parent structure of various molecular switches. The switching mechanism consists of a photochemically induced change in the double bond conformation from *E*- to Z- and vice versa. The wavelength of light necessary for the transformation of *E*-azobenzene to *Z*-azobenzene is 365 nm. The reverse process occurs under visible light (450 nm). Using the formula for the energy of photons $E = h \cdot \frac{c}{\lambda}$, calculate the approximate change of Gibbs free energy for the isomerization of *E*-azobenzene to *Z*-azobenzene in $\mathrm{kJ\,mol^{-1}}$. Assume no energy is lost during the switching.



Solution:

First, we substitute the relevant values into the energy equations:

$$E_{E\to Z} = \frac{h \cdot c}{365 \times 10^{-9}} \approx 5.4426 \times 10^{-19}\,\mathrm{J},$$

$$E_{Z\to E} = \frac{h \cdot c}{450 \times 10^{-9}} \approx 4.4143 \times 10^{-19}\,\mathrm{J}.$$

Then we subtract the energies of the given processes to obtain the Gibbs free energy:

$$\Delta G = E_{E\to Z} - E_{Z\to E} \approx 1.02799 \times 10^{-19}\,\mathrm{J}.$$

Finally we need to get the result in requested units:

$$\Delta G(\mathrm{kJ\,mol^{-1}}) = \Delta G(\mathrm{J}) \cdot N_A \cdot 10^{-3} = 1.0280 \times 10^{-19} \times 6.0221 \times 10^{23} \times 10^{-3} \approx 61.91\,\mathrm{kJ\,mol^{-1}}.$$

The approximate change of Gibbs free energy for the isomerization of *E*-azobenzene to *Z*-azobenzene is $61.91\,\mathrm{kJ\,mol^{-1}}$.

Question E.5 (Nathaniel Loh): Boranes

The octet rule is an empirical tool that helps us determine which molecules are likely to exist and which are not. According to the octet rule, a molecule is considered stable if all its atoms have eight electrons (or two, in the case of hydrogen) in their extended vicinity. But what does "extended vicinity" mean? It includes all the electrons found in both atomic and molecular orbitals associated with the given atom.

However, for some molecules, the octet rule is somewhat inapplicable. A typical example is boranes, compounds of hydrogen and boron. Since boron has only three valence electrons, it should, according to classical valence bond theory, be only trivalent. Yet the widely accepted theory that a chemical bond forms by pairing two unpaired electrons from two different atoms is simply not entirely true.

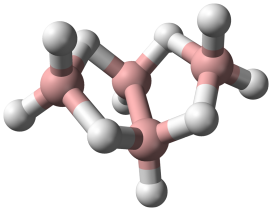
In boranes, there are three-center two-electron (3c-2e) bonds between two boron atoms and one hydrogen atom. These bonds arise from the combination of atomic orbitals on all three atoms, but only two electrons are shared among them. This economizes on electrons, allowing boron to participate in additional bonding interactions. Its extended vicinity, which includes both electrons from the three-center two-electron bond, will contain eight electrons, precisely fulfilling the octet rule as we imagine it.

Determine how many 3c-2e B−H−B bonds there are in the molecule with formula B_4H_{10}.

Solution:

Boron has 3 valence electrons and hydrogen has 1, so the total number of valence electrons in the molecule is $3 \times 4 + 1 \times 10 = 22$. Boron needs 8 electrons to have a full valence shell and hydrogen needs 2, so the total number of effective valence electrons required is $8 \times 4 + 2 \times 10 = 52$.

If the 22 available electrons are shared between 2 atoms each in (2c-2e) bonds, we get that there would be 44 effective valence electrons, 8 fewer than required. Therefore 8 electrons must be shared between 3 atoms in (3c-2e) bonds, meaning that there are 4 of these bonds in B_4H_{10}. The structure of B_4H_{10}, called tetraborane(10), is shown in the image.



Question E.6 (Stanislav Chvíla): Kaolin

At the kaolin clay plant, the leak tightness of the filtering equipment for capturing impurities is tested on Monday morning before the line starts up. From the previous test, 180 litres of kaolin suspension with a density of $1.025\,\mathrm{g\,cm^{-3}}$ and a kaolin mass fraction of 0.053 remained in the storage tank. To this, $50\,\ell$ of water and 2 kg of dry kaolin were added with vigorous stirring, mixed thoroughly, and then one third of the volume of the suspension was filtered through a cloth. After filtration, the wet filter cake was weighed and its weight was 5.374 kg and the solids content of the cake was 71.1 wt%.

Determine the filtration efficiency of the cloth in the device, or the fraction of solids that the cloth captured. (In engineering terms, consider the volumes to be completely additive.)

Solution:

Before the leakage test is started, kaolin from the previous test is present in the load with a mass of

$$m_{\mathrm{old}} = \rho_{\mathrm{old}} V_{\mathrm{old}} w_{\mathrm{old}} = 1.025 \times 180 \times 0.053 = 9.7785\,\mathrm{kg}$$

After the addition and homogenization of the deposit, one third of the mass is filtered:

$$m_{\mathrm{pumped}} = \frac{1}{3} \times (m_{\mathrm{old}} + m_{\mathrm{added}}) = \frac{1}{3} \times (9.7785 + 2) = 3.9216\,\mathrm{kg}$$

The filter cake contains

$$m_{\mathrm{captured}} = m_{\mathrm{cake}} \cdot w_{\mathrm{cake}} = 5.374 \times 0.711 = 3.8209\,\mathrm{kg}$$

And thus the filtration efficiency is

$$\phi = \frac{m_{\mathrm{captured}}}{m_{\mathrm{pumped}}} \times 100\,\% = \frac{3.8209}{3.9216} \times 100\,\% = 97.32\,\%$$

Question F.1 (Vojtěch Laitl): Photochemistry

Photochemistry employs radiation to catalyse or initiate several chemical reactions. A well-known example of such a process is the synthesis of hydrogen chloride from its elements. Reactions which may be involved in the synthesis, together with their standard enthalpies, are given below.

(R1): $\frac{1}{2}\,\mathrm{H_2(g)} + \frac{1}{2}\,\mathrm{Cl_2(g)} \longrightarrow \mathrm{HCl(g)},\ \Delta_r H = -92\,\mathrm{kJ\,mol^{-1}}$

(R2): $\mathrm{Cl_2(g)} + h\nu \longrightarrow 2\,\mathrm{Cl(g)},\ \Delta_r H = 242\,\mathrm{kJ\,mol^{-1}}$

(R3): $\mathrm{H_2(g)} + h\nu \longrightarrow 2\,\mathrm{H(g)},\ \Delta_r H = 434\,\mathrm{kJ\,mol^{-1}}$

(R4): $\mathrm{H(g)} + \mathrm{Cl_2(g)} \longrightarrow \mathrm{HCl(g)} + \mathrm{Cl(g)},\ \Delta_r H = -188\,\mathrm{kJ\,mol^{-1}}$

(R5): $\mathrm{Cl(g)} + \mathrm{H_2(g)} \longrightarrow \mathrm{HCl(g)} + \mathrm{H(g)},\ \Delta_r H = 4\,\mathrm{kJ\,mol^{-1}}$

The synthesis consists of three elementary steps, i.e., the photoinitiation and consecutive formation of two HCl molecules. Select such steps from within (R1)–(R5) and give them in the correct order. The reaction is initiated with blue light, which corresponds to the wavelength of 450 nm.

Solution:

Energy carried by blue light corresponds to the enthalpy of

$$\Delta H = N_\mathrm{A}\frac{hc}{\lambda} = 6.022\times10^{23}\times\frac{6.626\times10^{-34}\times3\times10^{8}}{450\times10^{-9}} \doteq 265\,800\,\mathrm{J\,mol^{-1}}.$$

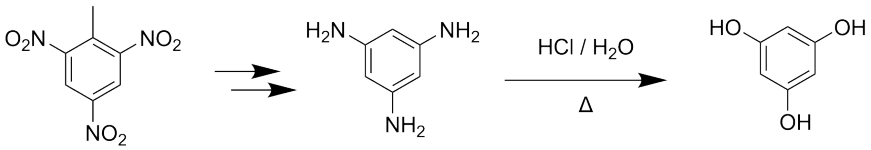
Such energy is not sufficient for the H–H bond cleavage (R3); the synthesis is therefore initiated by the photodissociation of $\mathrm{Cl_2}$. The resultant Cl· radical is unstable and proceeds to attack molecular hydrogen, yielding the first HCl molecule (R5). Hydrogen radical is released as a side product and recombines with another $\mathrm{Cl_2}$ molecule to give the second product equivalent (R4).

The reaction (R1) is not an elementary reaction. It is a mere rephrasing of the summary equation and as such, it is not needed to solve this problem.

Question F.2 (Jakub Sochor): Phloroglucinol

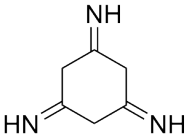
Phloroglucinol, also known as benzene-1,3,5-triol, is an organic compound widely used in the synthesis of drugs and explosives. Its structure can be found in nature in various tannins. Phloroglucinol exhibits spasmolytic properties and is used to treat renal colic and gastrointestinal spasms.

The reaction scheme below shows one of the possible preparations of this compound, starting from the readily available 2,4,6-trinitrotoluene (TNT). The last step of this synthesis is an acidic hydrolysis of benzene-1,3,5-triamine, which can at first seem as a rather uncharacteristic reaction for anilines. Draw the tautomeric structure of benzene-1,3,5-triamine explaining this observed reactivity.



Solution:

Benzene-1,3,5-triamine is in equilibrium with the imine tautomer (see the structure below) which undergoes the hydrolysis.



Question F.3 (Jiří Ledvinka): Titration

Amino acids, as the name suggests, contain an amino group in addition to the carboxylic acid. Thus, in a normal alkalimetric titration, we would not obtain usable consumptions. One relatively old method of acid-base determination of amino acids is the use of formalin (aqueous formaldehyde), which reacts with the amino group to form the corresponding imine, which is no longer as basic and does not interfere with the carboxyl groups in the titration. In the reverse acidimetric titration of the same titrated sample, the imine is broken down back into free amine and formaldehyde by successive acidification, and the consumption per methyl red corresponds to the neutralisation of the amino group itself.

You have dissolved 232.9 mg of pure free (i.e., not its salt) proteinogenic amino acid in distilled water at boiling, added ethanol and titrated with 0.1 M NaOH to phenolphthalein. The consumption was 25.55 mℓ and with the addition of 50 mℓ of 25% formaldehyde, the consumption of the titration reagent increased to 35.00 mℓ. This solution is back titrated with 0.1M HCl to methyl red. The consumption is 17.50 mℓ.

Which proteinogenic amino acid is involved?

Solution:

As we know from the assignment, the addition of formaldehyde produces an imine that does not interfere with the titration. Therefore, the hydroxide consumption under these conditions corresponds only to the carboxyl group(s):

$$n(\mathrm{COOH}) = V(\mathrm{NaOH}) \cdot c(\mathrm{NaOH}) = 35 \times 10^{-3} \cdot 0.1 = 3.5\,\mathrm{mmol}$$

In contrast, back titration with HCl corresponds only to the amino group:

$$n(\mathrm{NH_2}) = V(\mathrm{HCl}) \cdot c(\mathrm{HCl}) = 17.5 \times 10^{-3} \cdot 0.1 = 1.75\,\mathrm{mmol}$$

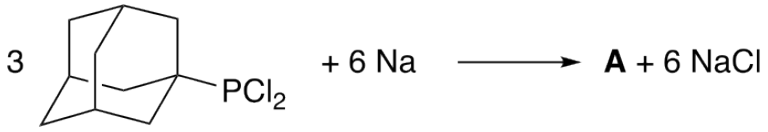
From the ratio of these two amounts, we see that this is a dibasic amino acid. Its molar mass is

$$M = \frac{m}{n} = \frac{0.2329}{0.00175} = 133.1\,\mathrm{g\,mol^{-1}},$$

which corresponds to aspartic acid.

Question F.4 (Alexandros Terzopoulos): Cyclophosphine

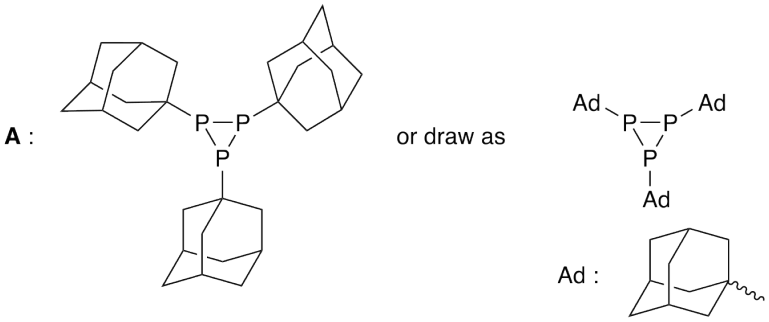
The Wurtz reaction is a classic reductive coupling reaction which involves treating two alkyl halides with an alkali metal to form a longer alkane. Although of diminished utility to modern organic chemistry, this type of reaction is still widely used in the field of main-group chemistry to construct p-block element rings from the coupling of their dihalides. As an example, dichloro(1-adamantyl)phosphine reacts with sodium to afford one equivalent of cyclophosphine (**A**):



From the reaction scheme above, sketch the structure of the product **A**.

Solution:

The compound **A** is a three-membered cyclophosphine $(PAd)_3$ (this ring size is obtained due to the steric bulk of the adamantyl group and is clear from the stoichiometry of the reaction).



Question F.5 (Filip Hůlek): Fat Man

Oppenheimer, a film depicting the story of the leading team designing the atomic bomb, recently became one of the two worldwide ticket box-office hits as well as the winner of seven Oscars. Robert Oppenheimer can be seen in discussions with Albert Einstein on multiple occasions in the film. And it is one of the most famous equations of Albert Einstein that you will need in this question.

The explosion of the *Fat Man* atomic bomb released 21 kilotons of TNT equivalent. But this falls far short of the energy that would have been released if all the plutonium-239 atoms in the bomb succumbed to nuclear fission.

Calculate how many times more energy would have been released if that had happened. For the bomb's construction, 6.4 kg of plutonium-239 was used, which underwent the following reaction:

$$^{1}\mathrm{n} + {}^{239}\mathrm{Pu} \longrightarrow {}^{134}\mathrm{Xe} + {}^{103}\mathrm{Zr} + 3\,{}^{1}\mathrm{n}$$

The energy of 1 metric tonne of TNT equivalent is equal to 4.184 GJ.

Relative masses of particles:

$A_\mathrm{r}(^{1}\mathrm{n}) = 1.0087$; $A_\mathrm{r}(^{239}\mathrm{Pu}) = 239.0522$; $A_\mathrm{r}(^{134}\mathrm{Xe}) = 133.9054$; $A_\mathrm{r}(^{103}\mathrm{Zr}) = 102.9266$

Solution:

Einstein's formula hinted at in the question text is obviously the well-known $E = m \cdot c^2$ which sets the relation between total energy of matter and its mass. Indeed, when we subtract the sum of relative atomic masses of the left-hand side of the equation from the right-hand side, we obtain a number different from zero:

$$\Delta A_\mathrm{r} = \left(A_\mathrm{r}(^{134}\mathrm{Xe}) + A_\mathrm{r}(^{103}\mathrm{Zr}) + 3\,A_\mathrm{r}(^{1}\mathrm{n})\right) - \left(A_\mathrm{r}(^{239}\mathrm{Pu}) + A_\mathrm{r}(^{1}\mathrm{n})\right) = -0.2028.$$

This difference corresponds to energy, in this case released, since the difference has a negative sign. We first need to convert the relative atomic mass to actual mass by multiplying it by the atomic mass constant u, then we substitute into the Einstein's formula, and then multiply by Avogadro's constant N_A to obtain energy relative to 1 mole of reactants (molar reaction energy):

$$E_r = \Delta E\, N_\mathrm{A} = \Delta m\, c^2\, N_\mathrm{A} = \Delta A_\mathrm{r}\, u\, c^2\, N_\mathrm{A} \doteq -18\,226.755\,\mathrm{GJ\,mol^{-1}}.$$

From now on, we will ignore the negative sign, since it only indicates that the reaction is exergonic, i.e., energy is released in its course.

According to the question text, the bomb contained 6.4 kg of plutonium-239, which corresponds to

$$n = \frac{m}{M} = \frac{6.4 \times 10^3}{239.0522} \doteq 26.7724\,\mathrm{mol}$$

of plutonium-239. Therefore, the theoretical maximum amount of released energy E_THEOR is

$$E_\mathrm{THEOR} = E_r\, n \doteq 487\,973.79\,\mathrm{GJ}.$$

But we know from the question text that in reality, energy equivalent to 21 metric kilotonnes of TNT was released, and we need to convert this number to GJ:

$$E_\mathrm{REAL} = 21\,000 \times 4.184 = 87\,864\,\mathrm{GJ}.$$

The only thing left to do is to determine the ratio k between the theoretical and real amounts of energy:

$$k = \frac{E_{\mathrm{TEOR}}}{E_{\mathrm{REAL}}} = \frac{487\,973.79}{87\,864} \doteq 5.55.$$

If all plutonium-239 atoms had undergone the fission reaction, 5.55times more energy would have been released.

Question F.6 (Martin Balouch): Analytical

Why doesn't anyone want to write analytical chemistry questions?

It's such a beautiful part of chemistry. For example, titrations. One might say it's an outdated and long outmoded method, but it can still be useful at times.

For pharmaceutical preparations containing adrenaline, sodium disulfite is used as an antioxidant to prevent the adrenaline from deteriorating. For its determination in the formulation, one of the easiest solutions is titration, namely iodometric titration, where the disulfite in the formulation is titrated with an excess of iodine solution. This reaction takes place in an acidic environment. The excess iodine is then titrated with sodium thiosulfate, which reacts to tetrathionate.

The latter reaction is interesting in itself, but you will find it in any good textbook, so we will not ask you about it. Also, an assignment with lots of volumes and concentrations could now follow, but no, that is not the point of this assignment. The equation for the titration of sodium disulfite with iodine (it can be in ionic form) will suffice.

To make it easier for our reviewers, we only take as the correct solution stoichiometric coefficients that are natural numbers and also not all divisible by a natural number other than one.

Solution:

The disulfite is oxidised by iodine to hydrogen sulfate / sulfate (oxidation state of +VI, simply). The reaction can be written as

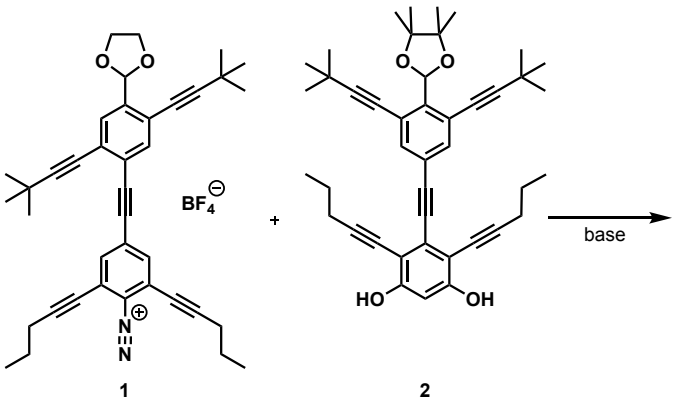
$1\,Na_2S_2O_5 + 2\,I_2 + 3\,H_2O \longrightarrow 2\,NaHSO_4 + 4\,HI$ or

$1\,S_2O_5^{-2} + 2\,I_2 + 3\,H_2O \longrightarrow 2\,HSO_4^{-1} + 4\,H^+ + 4\,I^-$ or

$1\,S_2O_5^{-2} + 2\,I_2 + 3\,H_2O \longrightarrow 2\,SO_4^{-2} + 6\,H^+ + 4\,I^-$.

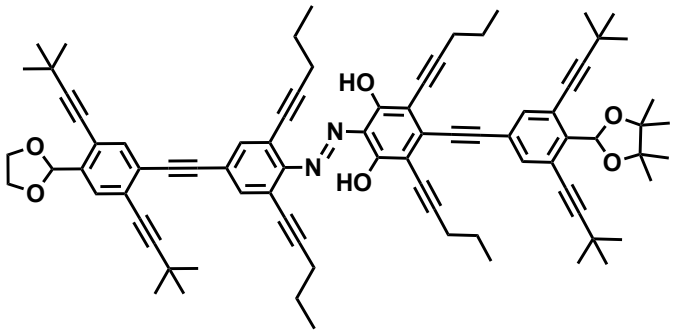
Question G.1 (Tomáš Marný): A different kind of coupling

While diazotation is a term you encounter only in chemistry, you can run into coupling in various other contexts as well. Just as diazonium salts react violently with phenols to form azo compounds, in biology the product of passionate copulation is usually another organism. Nanoputians are molecules that resemble the shape of a figure. Draw the product of the coupling of diazonium salt **1** with molecule **2**.



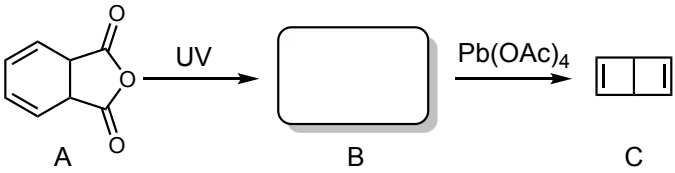
Solution:

The product is an azo compound with a N=N bond formed between the aromatic nuclei of the diazonium salt and the electron-rich phenol. The diazonium salt, being a strong electrophile, will only react with the more electron-rich nucleus.

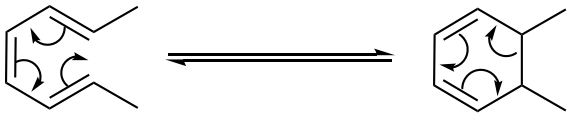


Question G.2 (Štěpán Novák): Benzene as you don't know it

Every chemist and quite a few non-chemists know benzene and its structure. However, there have been several theories about the possible structures of benzene throughout history. One of those structures was the so-called Dewar's benzene. Dewar published this structure in 1869 as part of a list of possible isomers with the structure C_6H_6. However, he did not claim that this was the structure of benzene, Dewar supported the benzene structure proposed by Kekulé. Almost a century later in 1963, Eugene van Tamelen succeeded in synthesizing unsubstituted Dewar's benzene. In this assignment, we look at his synthesis. The synthesis starts from the *cis*-1,2-dihydro derivative of phthalic anhydride, which is first photochemically converted to the tricyclic compound **B** via electrocyclic reaction. Which, after oxidation, gives the desired Dewar's benzene. Give the structure of compound **B**.

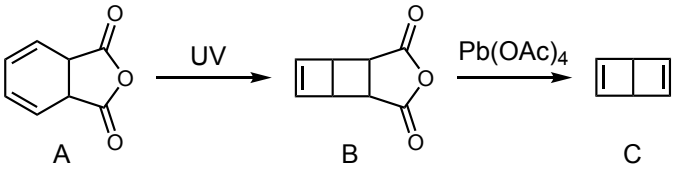


The general scheme of an electrocyclic reaction can be found below.



Solution:

In the first step, a photochemical electrocyclic ring-closing occurs, which generates the tricyclic product **B**.



Question G.3 (Štěpán Novák): Biotechnological

Citric acid is produced industrially by a biotechnological process using the fungus *Aspergillus niger*, which produces one molecule of citric acid (citrate) from one molecule of glucose. This conversion takes place under aerobic conditions, i.e. the fungus uses mitochondria. Using the attached metabolic pathways, calculate how many molecules of ATP the fungus gets from one molecule of glucose. For simplicity, consider that it gets three molecules of ATP from the reoxidation of the reduced NADH cofactor. Some of the cycles are redundant. Aim for the highest possible ATP yield. See the metabolic map available on `https://doi.org/10.5281/zenodo.14217367`.

Solution:

Glycolysis yields 2 ATP and 2 NADH (6 ATP from reoxidation), yielding a total of 8 ATP. The pyruvate to AcSCoA pathway yields 3 ATP. The carboxylation of pyruvate to oxalacetate requires one ATP unit. Thus, from a single glucose, the fungus gains 10 ATP units.

Question G.4 (Supatpong Juntarawatt): Complexed

Agent FE0000 has two solutions of different isomers, sharing the same empirical formula $BrCoH_{15}N_5O_4S$. However the colour of each solution is different from one another. His qualitative analysis by addition of aqueous solutions of $BaCl_2$ and $AgNO_3$ yields results as shown:

Solution	Colour of the aqueous solution	$BaCl_2$	$AgNO_3$
A	Red	White solid forms	No solid forms
B	Red-violet	No solid forms	Off-white solid forms

Identify the formula of the cobalt-containing cationic complex of each solution.

Solution:

First, we have to identify the possible ligands in both complexes. As there are off-white AgBr and white $BaSO_4$ forms during the experiment, the ligands involved include Br^- and SO_4^{2-}. Thus, we are left with 5 nitrogen atoms and 15 hydrogen ones. As the colours of the solutions are different, the ligands in the complexes are different. The 5 remaining ligands containing N and H should be NH_3. The anions involved in precipitation are anionic counter-ions, not the ligands themselves.

Question G.5 (Zev Armour-Garb): Charles Darwin

Charles Darwin is known for pioneering the evolutionary theory of natural selection. He is also known to have fallen ill after eating dairy products. This is likely because Charles Darwin lacked the enzyme lactase—a common condition known as lactose intolerance. Lactase hydrolyses the β-glycosidic bond in lactose at a 1:1 enzyme:substrate ratio, yielding D-glucose and β-D-galactose. Thankfully, lactose intolerance was not sufficient selective pressure, and Darwin has many descendants alive today—even evolution has a soft spot for our love of dairy!

The rate of enzymatic reactions can be described with the Michaelis–Menten equation:

$$v = \frac{V_{\max} \cdot [\mathrm{S}]}{K_{\mathrm{M}} + [\mathrm{S}]}$$

In an enzymatic reaction, the concentration of substrate at half of the maximum reaction velocity can be described by its Michaelis constant, K_{M}. For lactase-phlorizin hydrolase, the lactase enzyme in humans, $K_{\mathrm{M}} = 21\,\mathrm{mM}$. If a person consumes enough lactose such that its reaction velocity, v, with lactase-phlorizin hydrolase is exactly two-thirds of the maximum, $V_{\max}$, what concentration of lactose [S] was digested, in mM?

Solution:

To solve this problem, we can apply the Michaelis–Menten equation:

$$v = \frac{V_{\max} \cdot [\mathrm{S}]}{K_{\mathrm{M}} + [\mathrm{S}]}$$

We are given that $K_{\mathrm{M}} = 21\,\mathrm{mM}$ and $v = \frac{2}{3}V_{\max}$. Plugging these values into the above equation, we obtain the following relation:

$$\frac{2}{3}V_{\max} = \frac{V_{\max} \cdot [\mathrm{S}]}{21\,\mathrm{mM} + [\mathrm{S}]}$$

From here, we can simplify the equation to obtain:

$$21\,\mathrm{mM} + [\mathrm{S}] = \frac{3 \times [\mathrm{S}]}{2}$$

Finally, we can easily solve for [S] to get $[\mathrm{S}] = 42\,\mathrm{mM}$

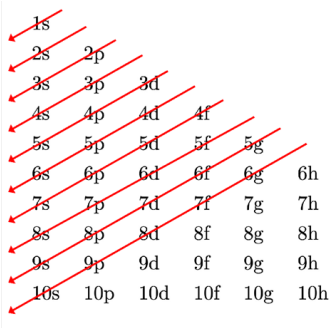
Question G.6 (Petr Linhart): Periodic

Chemistry Race celebrates its 10th anniversary. That is a cause not just for celebrations but also for a philosophical contemplation. What is the future of the periodic table? Will we ever see its 10th period? It has been with us for more than 150 years, yet we have still "only" discovered elements of its first 7 periods and even the currently heaviest among them are already extremely unstable (e.g., the half-life of the isotope ^{294}Og, the currently heaviest known element, is only 0.7 ms).

The present relativistic quantum theory sets the limit to the atomic number at $Z = 172$. This is because for higher values ($Z \geq 173$), the energy level of 1s orbital would fall into the positron continuum region. But what does this imply for the present outlooks of the 10th period? Determine the atomic number of the hypothetical first element of the 10th period. We assume that the Aufbau principle is valid even for high atomic numbers, as well as the Madelung rule, where energy increases with $n + l$. Do not forget that the g orbitals will come into play for the higher periods of the table. The g orbitals are a logical continuation of the sequence s, p, d, f, and have hence degeneracy 9 (azimuthal quantum number $l = 4$).

Solution:

According to the Aufbau principle, orbitals with the lowest energy are filled first. Madelung rule $n+l$ states that the orbital with lower energy has a lower sum of the principal quantum number n and the azimuthal quantum number l. Both rules are combined and summarised in the following diagram, where the orbital order can be found when going diagonally in the direction of the red arrows.



If we realise that every period starts with an orbital s and ends with an orbital p, it is obvious from the diagram that the last element of the 9th period would have 9 fully

filled orbitals s ($9\times1\times2 = 18$ electrons), 8 sets of orbitals p ($8\times3\times2 = 48$ electrons), 6 sets of orbitals d ($6\times5\times2 = 60$ electrons), 4 sets of orbitals f ($4\times7\times2 = 56$ electrons) a 2 sets of orbitals g ($2\times9\times2 = 36$ electrons), together $18+48+60+56+36 = 218$ electrons. The first element of the 10th period would therefore have the atomic number $Z = 219$. According to the present quantum theory, we will never see the 10th period of the periodic table.

Question H.1 (Alexandr Zaykov): Pizza kinetics

Chemist Popeye wanted to quickly bake his favourite Neapolitan pizza to celebrate the 10$^{\text{th}}$ anniversary of Chemistry Race. So he took his sourdough starter (150 g of plain flour, 150 g of water, 2.5 g of honey and 5 g of fresh yeast — 2.5 g of dried yeast can be substituted) and mixed it in 350 g of water, then added 20 g of salt. He then stirred in half of the 625 g of flour, let the dough stand for a while, and immediately incorporated the other half of the flour. He then left the dough to rise for 30 minutes. He then shaped the dough into loaves, which he then rolled into pancakes. To prevent the dough from sticking to his hands, he always greased them carefully with olive oil. In the meantime, because he multitasks like a good chemist, he preheated his oven to 220 °C. And lo and behold! When he put all the ingredients he wanted on the raw pizza, he found that he had to bake it for 13 minutes at 200 °C. However, he also knows from his own experience that when he made the pizza in Jardik's oven, which could only heat up to 180 °C, it took him exactly 20 minutes and 50 seconds. The chemist Pepik, however, is no dummy and follows the scientific trio of Zanoni, Peri and Bruno closely.[2] He knows that the speed of browning of the crust corresponds to first-order kinetics. So he doesn't dawdle and puts the pizza in the oven. In 6 minutes, Pepi has managed to calculate how long it will take him to cook the pizza. How long from the completion of the calculation must he take the pizza out? What is the activation barrier for browning the pizza?[3]

Solution:

Using the Arrhenius equation and two known times, we calculate the activation barrier to browning.

$$k(T) = A \cdot \exp\left(-\frac{E_{\text{A}}}{R \cdot T}\right)$$

We also consider that we always keep the browning of the pizza to the same level

[2] B. Zanoni; C. Peri; D. Bruno. (1995). Modelling of browning kinetics of bread crust during baking. LWT, 28(6), 604–609. 10.1016/0023-6438(95)90008-x

[3] It is reasonable to assume that the activation barrier is INDEPENDENT of temperature over such a narrow temperature range.

(pizzas are equally cooked):

$$k = \frac{\text{const.}}{t}$$

And thus we write:

$$\ln\left(\frac{t_2}{t_1}\right) \cdot \frac{R \cdot T_1 \cdot T_2}{T_1 - T_2} = E_\text{A}$$
$$= (42000 \pm 200)\,\text{J}\,\text{mol}^{-1}$$

We then calculate the required time:

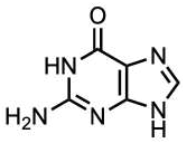
$$t_3 = t_1 \cdot \exp\left[\frac{E_\text{A}}{R} \cdot \left(\frac{T_1 - T_3}{T_1 \cdot T_3}\right)\right]$$
$$= 8\,\text{min}\,(26 \pm 10)\,\text{s}$$

Popeye has 2 minutes and (26 ± 10) seconds left, so he still has time to brew some real Italian coffee.

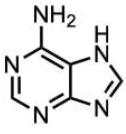
Question H.2 (Sam Holmes): Mutations

There are many ways that mutations are introduced to the genetic code. One possible cause of mutation is deamination, in which one nuclear base is converted to another by reaction with water, releasing ammonia as a byproduct. A fragment of RNA undergoes a deamination event before it is translated into protein by the ribosome. The fragment includes the code CCU, which codes for the amino acid proline (see the table).

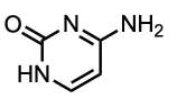
Which two amino acids may be coded by this triplet after undergoing one mutation?



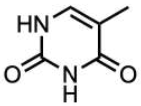
guanine



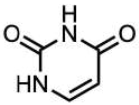
adenine



cytosine



thymine



uracil

UUU	Phe	UCU	Ser	UAU	Tyr	UGU	Cys
UUC		UCC		UAC		UGA	
UUA	Leu	UCA		UAA	Stop	UGC	Stop
UUG		UCG		UAG		UGG	Trp

CUU	Leu	CCU	Pro	CAU	His	CGU	Arg
CUC		CCC		CAC		CGA	
CUA		CCA		CAA	Gln	CGC	
CUG		CCG		CAG		CGG	

AUU	Ile	ACU	Thr	AAU	Asn	AGU	Ser
AUC		ACC		AAC		AGC	
AUA		ACA		AAA	Lys	AGA	Arg
AUG	Met/Start	ACG		AAG		AGG	

GUU	Val	GCU	Ala	GAU	Asp	GGU	Gly
GUC		GCC		GAC		GGC	
GUA		GCA		GAA	Gly	GGA	
GUG		GCG		GAG		GGG	

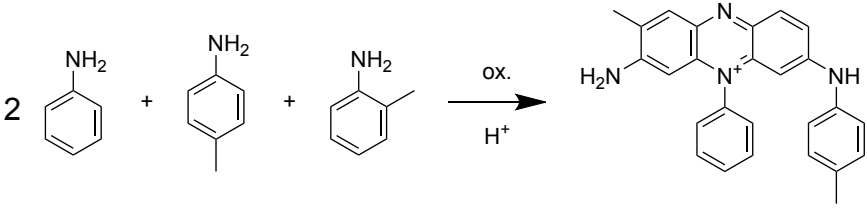
Solution:

Deamination converts C to U – so we could have CUU or UCU. These are leucine and serine respectively.

Question H.3 (Jakub Sochor): Mauveine

There are a vast number of serendipitous discoveries throughout the history of life sciences, including, of course, chemistry. Most of you are likely familiar with the discovery of penicillin or the drug Viagra. The focus of this question is a lesser-known compound with great historical significance called Mauveine – the first commercially produced synthetic organic dye. This intensely violet material was accidentally prepared and then patented by William Henry Perkin at the age of 18. The synthesis of Mauveine consisted of one mere step – the oxidation of aniline containing *ortho*- and *para*-toluidine as impurities. Depending on the stoichiometry of this reaction, a series of related compounds can be formed, the reaction scheme depicts Mauveine A. Unlike 19$^{\text{th}}$ century chemists, we are now familiar with the exact structure of the product, which gives us a nice edge – we can now calculate the precise amount of oxidant needed for the reaction.

Your task is to determine how many electrons the starting materials have to lose during the formation of one molecule of Mauveine A. (The answer is an integer).

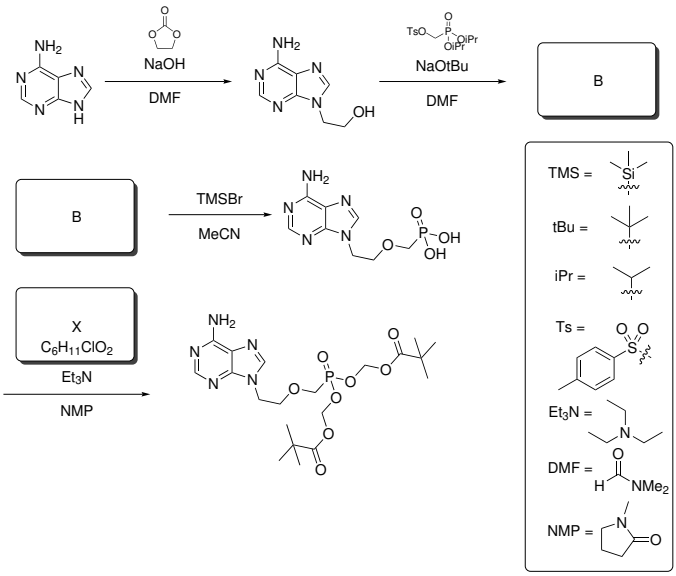


Solution:

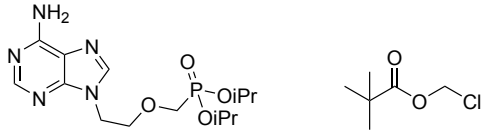
We can work from the changes in the oxidation numbers of individual C atoms, or by comparing the total formulas of the reactants and the product.
Equation of the oxidation reaction: $2\,C_6H_7N + 2\,C_7H_9N \longrightarrow C_{26}H_{23}N_4^+ + 10\,e^- + 9\,H^+$.

Question H.4 (Štěpán Novák): Antivirals

Antiviral drugs developed by prof. Antonín Holý and his team at the Institute of Organic Chemistry and Biochemistry of the CAS brought prestige to Czech science and billions of dollars in royalty income to the Institute. In this assignment we will look at the synthesis of Adefovir, more specifically its prodrug adefovir dipivoxil. This is an acyclic nucleotide used for the treatment of hepatitis B. Adefovir acts as an inhibitor of viral reverse transcriptase, thereby preventing the virus from replicating in the cell. Complete the diagram with substance **B** and give the structure of reagent **X**.



Solution:



B X

In the first reaction related to the question, the hydroxyl group is first deprotonated. The resulting alkoxide then attacks the methylene carbon of the phosphonate, kicking off the para-toluenesulfonyl group. The second step is very similar: the phosphonic acid undergoes double deprotonation, after which it attacks the chloromethyl group of reagent **X**. The structure of reagent **X** can be easily deduced from the knowledge of the structure of adefovir dipivoxil and its molecular formula.

Question H.5 (Tatiana Nemirovich): TikTok Units (TT Units)

The world has long moved past caring about boring kilograms, cringe-worthy seconds, and irrelevant Kelvins. Who needs to know how much a kilo weighs or how long a second lasts these days? We present a new system of units designed to elevate physics to a level that aligns perfectly with your TikTok feed.

- **Blockproud (bp)** – A unit of electric current derived from the energy needed to mine a single virtual block in Minecraft. 1 bp corresponds to a current of 0.55 A, which is approximately the power consumption of a laptop running the game on low graphics settings.
- **TikTok-Pause (tp)** – The amount of time you can resist opening TikTok before succumbing to the urge. $1\,\text{tp} = 3.2\,\text{s}$.
- **Beerless Distance (bd)** – The distance someone walks at a festival or concert before finally getting another beer. $1\,\text{bd} = 15\,\text{m}$.
- **Energy Can (ec)** – The mass of an empty Monster energy drink can. $1\,\text{ec} = 0.106\,\text{kg}$.
- **Crop-Kelvin (ck)** – A unit of temperature corresponding to the point at which it becomes too cold to wear a crop top. $1\,\text{ck} = 288\,\text{K}$.
- **Litre-mole (lm)** – The amount of alcohol equivalent to a blood alcohol content of one promille (0.1 %) in an average adult, 0.8 moles of ethanol.
- **Feedlight (fl)** – A unit of luminance for a phone screen while scrolling Instagram in complete darkness, making you question why you are still awake. A typical phone in dark mode and low brightness has a screen luminance of about 4.2 cd.

Your task will be to calculate the value of Planck's constant using the fundamental TikTok units.

Solution:

The most important thing to understand is that 1 J is defined as $\text{kg} \cdot \text{m}^2/\text{s}^2$, meaning that Planck's constant has the unit $\text{kg} \cdot \text{m}^2/\text{s}$. Then we simply substitute:

$$\begin{aligned} h &= 6.626 \times 10^{-34} / [\text{ec} \cdot \text{bd}^2 \cdot \text{tp}^{-1}] \\ &= 6.626 \times 10^{-34} / [0.106 \cdot 15^2 \cdot 3,2^{-1}] \\ &= 8.89 \times 10^{-35} \end{aligned}$$

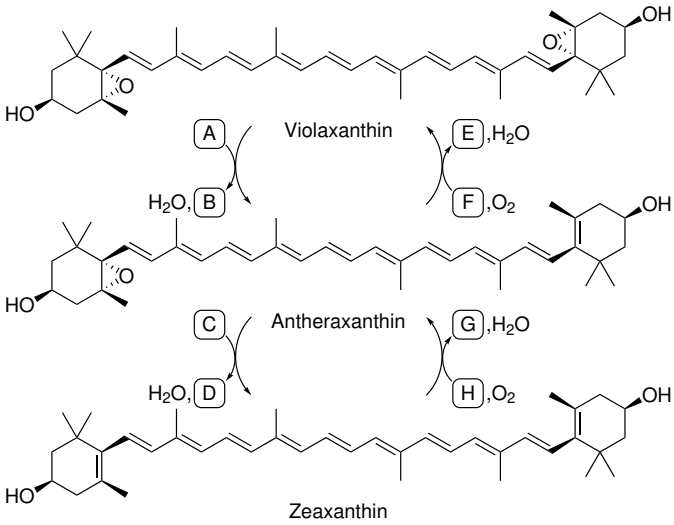
Question H.6 (Vojtěch Laitl): Diatoms

Diatoms (*Bacillariophyceae*) are an interesting group of marine microalgae whose cells contain several β-carotene-based organic dyes. Three of them, violaxanthin (orange), antheraxanthin (orange-yellow) and zeaxanthin (yellow) may undergo enzymatic redox reactions to form one another as shown in the following scheme: In the one direction, the conversion is driven by a NADPH$-H_3O^+$ coenzyme while in the other, docosahexaenoic acid (DHA, long-chain fatty acid) is used. Complete the scheme below by assigning the letters **A**–**H** to the following compounds:

- NADPH–H_3O^+
- $NADP^+$ (oxidised coenzyme)

- DHA
- $DHAH_2$ (reduced docosahexaenoic acid)

Make use of oxidation numbers/states and the fact that the reduced NADPH coenzyme is a very strong reducing agent, capable of direct reduction of O_2. You may need to assign either compound multiple times.



Solution:

A and C: $DHAH_2$
B and D: DHA
E and G: $NADP^+$
F and H: $NADPH{-}H_3O^+$

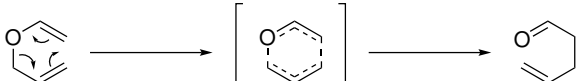
The right-hand side arrows are drawn bottom to top and both depict a double bond epoxidation by O_2. This process only consumes 1 O atom out of the O_2 molecule, while the other is reduced to H_2O. Only the $NADPH{-}H_3O^+$ is capable of this reduction and is itself oxidised onto $NADP^+$. By exclusion, the left-hand side arrows therefore include the docosahexaenoic acid derivatives. Written top to bottom, they follow a reduction of the given dyes, and must therefore always begin with the reduced $DHAH_2$ agent.

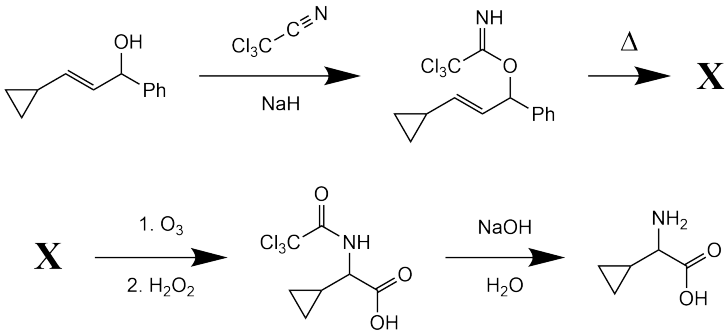
Question K.1 (Jakub Sochor): Pericyclic

The Overman rearrangement is a reaction used for the preparation of allylic amines and amino acid derivatives. The image below shows the scheme for the synthesis of cyclopropylglycine.

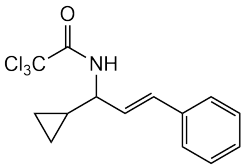
First, allyl alcohol reacts with trichloroacetonitrile in the presence of a base to form a trichloroacetimidate. Upon heating, it undergoes a [3,3]-sigmatropic rearrangement to intermediate **X**. Ozonolysis with oxidative workup followed by basic hydrolysis of intermediate **X** yields cyclopropylglycine. Draw the structure of intermediate **X**.

An example of a [3,3]-sigmatropic rearrangement (Claisen rearrangement) is shown below.





Solution:



The Overman rearrangement is a variation of the hetero-Claisen rearrangement.

Question K.2 (Vojtěch Laitl): PFR

Plug-flow reactors (PFR) are a useful model used to describe a number of chemical processes. The model assumes that the chemical reactants pass through the PFR (typically a long pipe) with a constant velocity in one direction and are ideally mixed in perpendicular directions. The reaction kinetics is then similar to the basic kinetic formulae despite containing a spatial component. In industry, such reactors are used for instance to oxidise cyclohexane with airborne oxygen, which is the first step in polyamide manufacturing.

The reaction

$$2\,C_6H_{12} + O_2 \longrightarrow 2\,C_6H_{12}O$$

employs cyclohexane both as a reactant and as a solvent. Therefore, it is a pseudo-first order reaction and the concentration of oxygen is given by

$$[O_2] = [O_2]_0 \times e^{-k\cdot\tau},$$

τ is the residence time spent by oxygen in the reactor and k is the rate coefficient. In industry, high conversions of oxygen are needed for safety reasons (oxygen would compromise the following high-temperature processes). Let us have a tubular reactor of 10 m length filled with cyclohexane. When oxygen is supplied from the air at T = 300 K, the rate coefficient then reads $k = 3.05\,s^{-1}$. If the stream velocity is $6.6\,m\,s^{-1}$, we reach 99 % conversion of O_2 ($[O_2] = 0.01[O_2]_0$). Give the velocity that corresponds to 95 % conversion.

Solution:

The residence time is directly given by

$$\tau = \frac{l}{v},$$

as to describe the steady flow. That gives

$$\ln\left(\frac{[O_2]}{[O_2]_0}\right) = -k \times \frac{l}{v}$$

and, after rearranging

$$v = -\frac{k \times l}{\ln\left(\frac{[O_2]}{[O_2]_0}\right)}.$$

We may fill in the 99 % conversion data to make sure our assumptions are aligned with the assignment, i.e.,

$$v = -\frac{3.05 \times 10}{\ln(0.01)} = 6.6\,m\,s^{-1}.$$

For the 95 % conversion, the stream velocity reads

$$v = -\frac{3.05 \times 10}{\ln(0.05)} = 10.2\,\mathrm{m\,s^{-1}}.$$

The higher the flow velocity, the lower the conversion. With lower residence times experienced, lesser amounts of reactants are generally converted.

Question K.3 (Jiří Ledvinka): Czechs like their beer cold

Pepa bought a cold beer at the store, but on the way home he realised that he had mistakenly bought non-alcoholic beer. So he decided to fix it by adding 20 g of ethanol for UV-VIS spectroscopy (purity min. 99.99%), which he stores in a refrigerator at 4 °C. But as an educated chemist, he knew that mixing water with ethanol would heat up the mixture. That's why he made a calculation to check if the beer would warm up to an uncomfortable temperature. Let's approximate the beer with 500 g of water at the original temperature of 4 °C and let's calculate with Pepa. The molar masses of water and ethanol are respectively $18.02\,\mathrm{g\,mol^{-1}}$ and $46.07\,\mathrm{g\,mol^{-1}}$. The heat capacity of the mixture in this temperature range can be assumed to be equal to $75.35\,\mathrm{J\,mol^{-1}\,K^{-1}}$. The additional enthalpy of the ethanol–water mixture (that is, the enthalpy resulting from the preparation of one mole of the mixture with a given molar fraction of ethanol x from pure components) for this temperature is described by the following polynomials:

$$hE\ [\mathrm{J\,mol^{-1}}] = 34\,752x^2 - 10\,422x$$

for $0 \leq x < 0.157$, and

$$hE\ [\mathrm{J\,mol^{-1}}] = 659.53x^3 - 1455.3x^2 + 1794.8x - 1035.6$$

for $0.157 \leq x < 1$, where x is the mole fraction.

What was the resulting temperature of the fixed beer?

Solution:

While fixing his beer, Pepa mixes 20 g of ethanol with 500 g of water. The molar fraction of

$$\begin{aligned} x &= n(\mathrm{EtOH})/[n(\mathrm{EtOH}) + n(\mathrm{H_2O})] \\ &= \frac{m(\mathrm{EtOH})/M(\mathrm{EtOH})}{[m(\mathrm{EtOH})/M(\mathrm{EtOH})] + [m(\mathrm{H_2O})/M(\mathrm{H_2O})]} \\ &= \frac{20/46.07}{(20/46.07) + (500/18.02)} \\ &= 0.01540. \end{aligned}$$

To calculate the excess enthalpy, we substitute into the first equation and obtain:

$$hE = -152\,\mathrm{J\,mol^{-1}}.$$

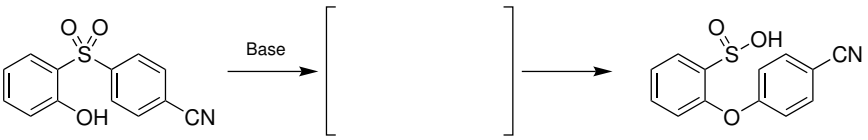
The mixture heats up by a temperature:

$$\begin{aligned} \Delta T = \frac{hE \cdot n}{C \cdot n} &= hE/C \\ &= 152/75.35 \\ &= 2.02\,\mathrm{K} \end{aligned}$$

The final temperature will then be $T_{\mathrm{final}} = 6.02\,^{\circ}\mathrm{C}$.

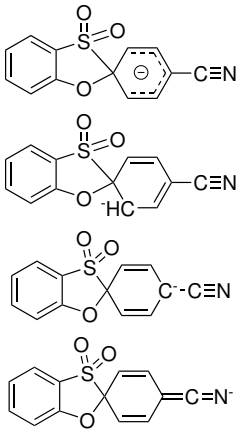
Question K.4 (Štěpán Novák): Time for smiles!

Time for smiles, more organic chemistry! The Smiles rearrangement is a reaction involving an intramolecular nucleophilic aromatic substitution forming a spirocyclic intermediate followed by a rearrangement of the aromatic system. Your task is to draw the reaction intermediate of the nucleophilic substitution.



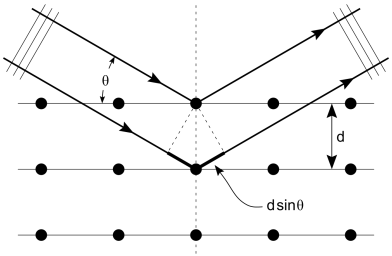
Solution:

It is the so-called Meisenheimer complex. First, deprotonation of the OH group occurs, which then attacks the carbon carrying the sulfonyl group. Through electron shifts, the negative charge is transferred to the nitrile nitrogen. (A correct answer is any valid resonance structure, as shown below) the electrons then move in the opposite direction and can either reform the starting material or move to the sulfone which leaves as sulfinic acid.



Question K.5 (Quyll Pavlakovic): Polonium

Andrey has a sample of isotopically-enriched polonium, with density $9.026\,\mathrm{g\,cm^{-3}}$. Polonium is unique as it is the only element to adopt a simple cubic structure. To determine the lattice parameter, Andrey asks for help from Dmitry's x-ray diffractometer. Dmitry's machine emits x-rays with a wavelength of 1.937 Å. If the path difference between reflections from adjacent layers in the polonium crystal is an integer multiple of the wavelength, the x-rays will constructively interfere and be reflected. If the path difference between adjacent layers is not an integer multiple of the wavelength, destructive interference occurs, and the x-ray is not reflected. This can be summarized by Bragg's equation



$$n\lambda = 2d \cdot \sin\ \theta.$$

In a simple cubic structure, the distance between adjacent atoms, the lattice parameter, and d (the spacing between planes), are all equal.

The first order ($n = 1$) reflection is at a deflection angle of 33.516°, corresponding to 2θ on the diagram. Determine which isotope of polonium Andrey's sample contains.

Solution:

As we are looking at the first order reflection, $n = 1$, rearrangement of the Bragg equation gives

$$d = \frac{\lambda}{2\sin\,\theta} = \frac{1.937\,\text{Å}}{2\sin(16.758°)} = 3.359\,\text{Å}.$$

Molar mass can be then obtained using the density and Avogadro's constant

$$M = \rho{\cdot}d^3{\cdot}N_\text{A} = 9.026\,\text{g cm}^{-3}{\times}(3.359{\times}10^{-8}\,\text{cm})^3{\times}6.022{\times}10^{23}\,\text{mol}^{-1} = 206.00\,\text{g mol}^{-1}$$

This molar mass corresponds to isotope ^{206}Po.

Question K.6 (Ondřej Daněk): Photoaffinity labelling

Photoaffinity labelling (PAL) is an approach used in medicinal chemistry and chemical biology to identify protein targets of small molecules. For example, when a new natural product which exhibits some interesting biological activity is isolated, it is not easy to figure out which enzyme or receptor in the cell it interacts with to induce those effects. The small molecule which is being studied can be synthetically modified to incorporate a group that is stable under normal physiological conditions, but upon irradiation with (usually UV) light converts into a highly reactive intermediate that can covalently bind to amino acid residues in the binding pocket of the target protein. Other synthetic modifications of the small molecule can be used to incorporate a terminal alkyne which can be later used for a copper catalysed alkyne azide cycloaddition reaction (CuAAC) with fluorophore bearing azides or biotin azides for example, making it possible to identify the target protein on electrophoresis gel (fluorophore example) or directly isolate it from the cell lysate by bioaffinity chromatography (biotin example using streptavidin pulldown). These synthetic modifications are shown below.

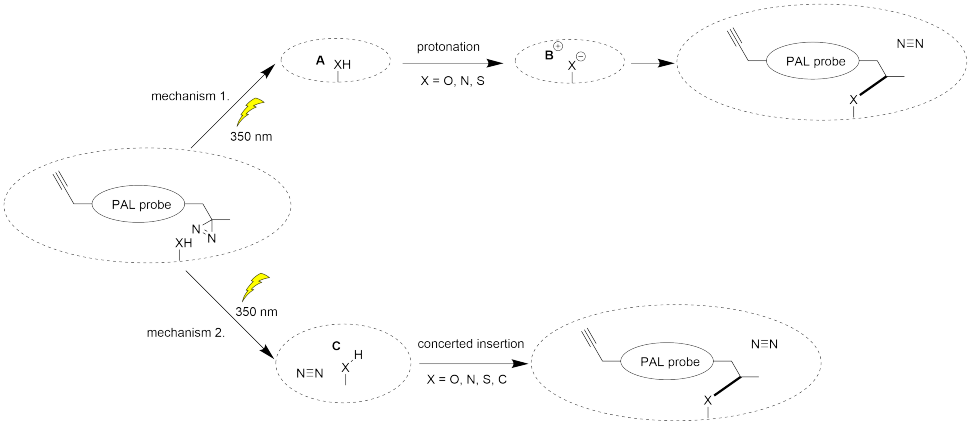
One of the photolabile groups frequently incorporated into PAL probes is a diazirine ring, which is nearly isosteric (similarly sized) to a methyl group, and which upon ir-

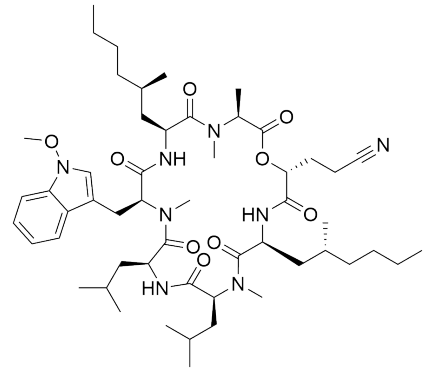
radiation with UV light (350 nm) can generate two different reactive species through two different mechanisms. Binding of the PAL probes to heteroatoms in the amino acid residues of the target protein can be explained by both of these mechanisms, but binding to carbon atoms in the side chains of aliphatic amino acids such as alanine or valine can be explained only by the second mechanism.

In the first mechanism, the diazirine bearing PAL probe first generates intermediate **A** (which is an isomer of the original probe) after irradiation. This intermediate can be protonated by an OH, NH_2 or SH groups in the amino acid side chains leading to the formation of cation **B**. Cationic intermediate **B** can be then attacked by the deprotonated heteroatom in a nucleophilic substitution leading to the covalent attachment of the PAL probe and expulsion of molecular nitrogen (N_2).

The second mechanism, which occurs less frequently compared to the first one, generates a reactive intermediate **C** after irradiation of the PAL probe, and in this case, nitrogen is formed directly in this step. Then, the reactive intermediate **C** can undergo a one-step reaction (proceeding by a concerted mechanism) with any amino acid residue leading to the insertion of the carbon atom from the diazirine into a O−H, N−H, S−H or even a C−H bond (see below).

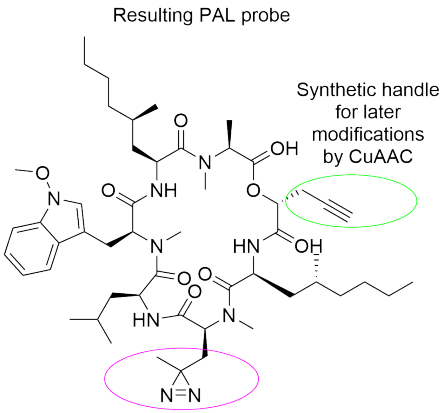
Draw the Lewis electronic structures of the reactive intermediates **A**, **B** and **C** using the simplified structure given in the reaction schemes.





HUN-7293
A natural product, inhibitor of cell adhesion

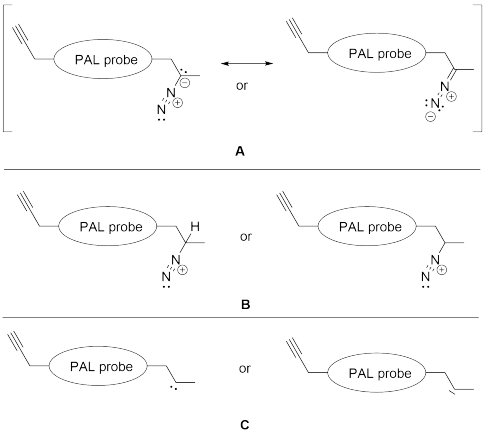
Resulting PAL probe



Solution:

Substance **A** must be an isomer of the original PAL probe that can be readily protonated and later release nitrogen as a leaving group in a nucleophilic substitution. The most reasonable option is therefore the corresponding diazomethane derivative which can be drawn in several resonance structures. For the purposes of this problem, the resonance structure with the negative charge localized on carbon is the most important, but all correct resonance structures were marked as correct answers. The cationic intermediate **B** is then the product of the protonation of **A** on the carbon (the corresponding alkyldiazonium). As the electroneutral and also very reactive substance **C** which is formed by the liberation of a nitrogen molecule from the original PAL probe must then be the corresponding carbene.

The reaction itself produces a singlet carbene, but by intersystem crossing, it can then change to a triplet carbene which, instead of synchronous insertion into the X-H bond, reacts by a series of radical reactions. To simplify the text of the problem, this information was omitted in the question text, and both possible structures of the singlet (with a dash symbolizing the electron pair) and triplet (with two dots symbolizing unpaired electrons) carbene were marked as correct answers.



You can read more about the workflow of photoaffinity labelling used for target protein identification here: `https://doi.org/10.1002/9780470559277.ch090167`

Question L.1 (Martin Balouch): "Should you see me, weep!"

This famous inscription from the "Hunger Stone" in Děčín can also apply to this task–especially if you're not a fan of classical analytical chemistry.

In the analysis of an unknown double oxalate, you proceeded as follows: First, you weighed 0.242 g of the unknown oxalate, dissolved it in 250 mℓ of distilled water acidified with sulfuric acid in a volumetric flask, and filled it up to the mark, creating a stock solution.

Then, you pipetted 10 mℓ from the stock solution, added a small amount of sulfuric acid, heated it, and titrated it hot with a standard solution of potassium permanganate ($c = 0.002\,\text{mol}\,\ell^{-1}$) until a pale pink color appeared. The average titration volume was 10.6 mℓ.

Subsequently, you took another 10 mℓ from the stock solution, added 15 mℓ of ammonia solution, which formed a light green precipitate of ferrous hydroxide and soluble tetrahydroxozincate ions in the solution. The precipitate was filtered, and the filtrate was transferred to a 100 mℓ volumetric flask and diluted to the mark. From this 100 mℓ flask, you pipetted 10 mℓ three times and titrated each sample with an EDTA solution ($0.002\,\text{mol}\,\ell^{-1}$) using a small amount of indicator, obtaining an average titration volume of 2.4 mℓ. Determine the empirical formula of the double oxalate. Assume it may be a hydrate.

Solution:

The text provides information about the ions forming the double oxalate: ferrous and zinc ions. Since both are divalent cations, the empirical formula can be written as:

$$\mathrm{Zn}_x\mathrm{Fe}_{(1-x)}\mathrm{C_2O_4} \cdot y\mathrm{H_2O}$$

We now only need to determine the values of x and y.

Start with zinc, which is the only metal complexed by EDTA after filtering out ferrous hydroxide. EDTA complexes metals in a 1:1 ratio, so from the consumption of EDTA, we directly obtain the molar amount of zinc ions. Considering the sampling and dilution steps, we recalculate this for the entire sample:

$$n_{\mathrm{Zn}} = 0.002\,\mathrm{mol}\,\ell^{-1} \times 0.0024\,\ell \times 250 \doteq 1.20 \times 10^{-3}\,\mathrm{mol}$$

Now for iron. The key is the balanced equations of the oxidation reaction with potassium permanganate. In acidic conditions, manganous ions are produced. Both iron and oxalate are oxidized according to these reactions:

$$5\,\mathrm{Fe^{2+}} + 1\,\mathrm{MnO_4^-} + 8\,\mathrm{H^+} \longrightarrow 5\,\mathrm{Fe^{3+}} + 1\,\mathrm{Mn^{2+}} + 4\,\mathrm{H_2O}$$

$$5\,(\mathrm{C_2O_4})^{2-} + 2\,\mathrm{MnO_4^-} + 16\,\mathrm{H^+} \longrightarrow 10\,\mathrm{CO_2} + 2\,\mathrm{Mn^{2+}} + 8\,\mathrm{H_2O}$$

The total permanganate consumption can thus be split into molar amounts corresponding to oxalate and ferrous ions. (Pay attention to the stoichiometric coefficients!) We have:

$$n_{\mathrm{KMnO_4}} = \frac{1}{5} \times n_{\mathrm{Fe}} + \frac{2}{5} \times n_{\mathrm{C_2O_4}}$$

The total amount of potassium permanganate for the entire sample is:

$$n_{\mathrm{KMnO_4}} = 0.002\,\mathrm{mol}\,\ell^{-1} \times 0.0106\,\ell \times 25 = 5.30 \times 10^{-4}\,\mathrm{mol}$$

Now use the known molar amount of zinc ions and the fact that the molar amount of oxalate must equal the sum of zinc and ferrous ions:

$$n_{\mathrm{C_2O_4}} = n_{\mathrm{Fe}} + 1.20 \times 10^{-3}\,\mathrm{mol}$$

We now have two equations with two unknowns, which we solve, for example, by substituting the molar amount of oxalate into the first equation:

$$n_{\mathrm{KMnO_4}} = 5.30 \times 10^{-4}\,\mathrm{mol} = \frac{1}{5} \times n_{\mathrm{Fe}} + \frac{2}{5} \times (n_{\mathrm{Fe}} + 1.20 \times 10^{-3}\,\mathrm{mol})$$

$$5.30 \times 10^{-4}\,\text{mol} = \frac{1}{5} \times n_{\text{Fe}} + \frac{2}{5} \times n_{\text{Fe}} + 4.80 \times 10^{-4}\,\text{mol}$$

$$n_{\text{Fe}} = 0.0833 \times 10^{-3}\,\text{mol}$$

Thus:

$$n_{\text{C}_2\text{O}_4} = 1.2833 \times 10^{-3}\,\text{mol}$$

Since we have been working with actual molar amounts for the entire sample, we can calculate the mass of the anhydrous double oxalate:

$$m_{\text{anhydrous}} = n_{\text{C}_2\text{O}_4} \times M_{\text{C}_2\text{O}_4} + n_{\text{Fe}} \times M_{\text{Fe}} + n_{\text{Zn}} \times M_{\text{Zn}}$$

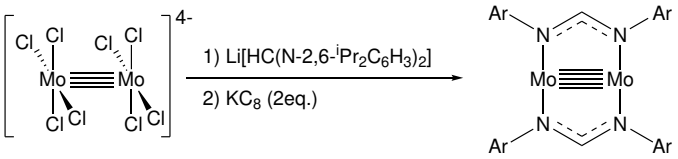
$m_{\text{anhydrous}} = 1.2833{\times}10^{-3}\,\text{mol} \times 88\,\text{g mol}^{-1} + 0.0833{\times}10^{-3}\,\text{mol} \times 55.845\,\text{g mol}^{-1} + 1.2{\times}10^{-}$

The remaining mass is due to water, calculated as: $m_{\text{water}} = 0.242\,\text{g} - 0.196\,\text{g} = 0.046\,\text{g}$, corresponding to $2.555{\times}10^{-3}$ mol of water. Finally, divide all molar amounts by the molar amount of oxalate anions to obtain the empirical formula:

$$\text{Zn}_{0.935}\text{Fe}_{0.065}\text{C}_2\text{O}_4 \cdot 2\,\text{H}_2\text{O}$$

Question L.2 (Supatpong Juntarawatt): Bonding

Question text: Chemists have successfully made multiple bonds between 2 transition metal atoms for many years. Owing to the five d-orbitals involved in the bond formation, quadruple (4-fold) and quintuple (5-fold) bonds can be observed. The reaction below (Tsai et al., **2009**) shows the synthesis of quintuple Mo−Mo bonding in **E** from a compound **A** with quadruple Mo−Mo bonding. Note that Ar in **E** is the 2,6-diisopropyl phenyl group. It is discovered that quadruple and quintuple bonds follow the trend of properties of single, double, and triple C-C bonds in organic chemistry. Indicate whether these statements are true or false.



A **E**

(i) The Mo−Mo distance in **E** is longer than in **A**.

(ii) Energy required to stretch Mo−Mo bond in **E** is greater than in **A**, ignoring the effects of the ligands.

(iii) The formal oxidation state of Mo in **A** is +4.

(iv) The formal oxidation state of Mo in **E** is +1.

(v) From the reaction scheme, KC_8 in step 2) is an oxidising agent.

Solution:

(i) The bond order of the Mo−Mo bond in **E** is greater than in **A**. The bond length is longer when the bond order drops. Therefore, the Mo−Mo distance in **E** is shorter than in **A**, making the statement false.

(ii) Since the bond strength is weaker when the bond order decreases, the Mo−Mo bond in **E** is much stronger. Akin to a stiff spring, the energy needed to vibrate the metal-metal bond in **E** is greater, making the statement true.

(iii) Each Cl anion contributes –1 charge, so the 'total' charge on both Mo is $-4-(8\times-1)=+4$. Since there are 2 Mo per complex anion, the formal oxidation state of Mo is $+\frac{4}{2}=+2$, making the statement false.

(iv) The source of amidinate (the new ligand) has only one Li cation per formula unit. Thus, it can be deduced that the amidinate has a formal charge of −1. Hence, the 'total' charge on both Mo is $-(-2)=+2$. Since there are 2 Mo per complex anion, the formal oxidation state of Mo is $+\frac{2}{2}=+1$, making the statement true.

(v) As the oxidation state of Mo decreases from +2 to +1, Mo is reduced. Hence, KC_8 is a reducing agent, making the statement false.

Question L.3 (Ondřej Daněk): Thermal dehydrogenation

Thermal dehydrogenation is a reaction used in industry for production of alkenes from alkanes. Alkanes are heated to very high temperatures and through a radical mechanism shown below, hydrogen and corresponding alkenes are formed. You have already seen that bananas produce ethylene in miniscule quantities in last year's Chemistry Race. However, harvesting this gas from bananas is not feasible for industrial use.

In this question, we will take a look at the pyrolysis of ethane which is used for large scale production of ethylene – a very important chemical used for production of polyethylene plastics. Each of the following reactions can be described with a rate constant k_1–k_5:

$$CH_3{-}CH_3 \longrightarrow 2\,CH_3\bullet \quad (k_1)$$

$$\mathrm{CH_3\bullet} + \mathrm{CH_3{-}CH_3} \longrightarrow \mathrm{C_2H_5\bullet} + \mathrm{CH_4}\,(k_2)$$
$$\mathrm{C_2H_5\bullet} \longrightarrow \mathrm{C_2H_4} + \mathrm{H\bullet}\,(k_3)$$
$$\mathrm{H\bullet} + \mathrm{CH_3{-}CH_3} \longrightarrow \mathrm{C_2H_5\bullet} + \mathrm{H_2}\,(k_4)$$
$$\mathrm{H\bullet} + \mathrm{C_2H_5\bullet} \longrightarrow \mathrm{C_2H_6}\,(k_5)$$

Using these constants and the steady state approximation for the concentrations of reactive radical species, derive the formula for the rate of formation of ethylene. Simplify the formula by assuming that k_1/k_3 is negligible in comparison to $(k_1\,k_4)/(k_3\,k_5)$.

Solution:

From the propagation steps we can easily see that the rate of formation of ethylene must be:

$$v = k_3\,[\mathrm{C_2H_5\bullet}].$$

The concentration of the ethyl radical can be then derived from the steady state approximation (assumption that the concentration of the radical species does not change in time). First, steady state approximation of the concentrations of reactive radical species can be formulated as follows:

$$\frac{\mathrm{d}[\mathrm{CH_3\bullet}]}{\mathrm{d}t} = 2\,k_1\,[\mathrm{C_2H_6}] - k_2\,[\mathrm{CH_3\bullet}]\,[\mathrm{C_2H_6}] = 0.$$

Which can be rearranged to:

$$[\mathrm{CH_3\bullet}] = 2\,\frac{k_1}{k_2},$$

$$\frac{\mathrm{d}[\mathrm{H\bullet}]}{\mathrm{d}t} = k_3\,[\mathrm{C_2H_5\bullet}] - k_4\,[\mathrm{H\bullet}]\,[\mathrm{C_2H_6}] - k_5\,[\mathrm{H\bullet}]\,[\mathrm{C_2H_5\bullet}] = 0.$$

Which can be rearranged to:

$$[\mathrm{H\bullet}] = \frac{k_3\,[\mathrm{C_2H_5\bullet}]}{k_4\,[\mathrm{C_2H_6}] + k_5\,[\mathrm{C_2H_5\bullet}]}.$$

These two concentrations can be then used directly in the steady state approximation of the concentration of the ethyl radical:

$$\frac{\mathrm{d}[\mathrm{C_2H_5\bullet}]}{\mathrm{d}t} = k_2\,[\mathrm{CH_3\bullet}]\,[\mathrm{C_2H_6}] - k_3\,[\mathrm{C_2H_5\bullet}] + k_4\,[\mathrm{H\bullet}]\,[\mathrm{C_2H_6}] - k_5\,[\mathrm{H\bullet}]\,[\mathrm{C_2H_5\bullet}] = 0,$$

$$k_2\left(2\,\frac{k_1}{k_2}\right)[\mathrm{C_2H_6}] - k_3[\mathrm{C_2H_5\bullet}] + k_4\,\frac{k_3[\mathrm{C_2H_5\bullet}]}{k_4[\mathrm{C_2H_6}] + k_5[\mathrm{C_2H_5\bullet}]}[\mathrm{C_2H_6}] - k_5\,\frac{k_3[\mathrm{C_2H_5\bullet}]}{k_4[\mathrm{C_2H_6}] + k_5[\mathrm{C_2H_5\bullet}]}[\mathrm{C_2H_5\bullet}] = 0.$$

Which can be rearranged to:

$$[\mathrm{C_2H_5\bullet}] = \frac{2\,k_1[\mathrm{C_2H_6}] + k_4[\mathrm{C_2H_6}]\,\frac{k_3[\mathrm{C_2H_5\bullet}]}{k_4[\mathrm{C_2H_6}]+k_5[\mathrm{C_2H_5\bullet}]}}{k_3 + k_5\,\frac{k_3[\mathrm{C_2H_5\bullet}]}{k_4[\mathrm{C_2H_6}]+k_5[\mathrm{C_2H_5\bullet}]}}$$

$$[\mathrm{C_2H_5\bullet}] = \frac{\frac{2\,k_1\,k_4[\mathrm{C_2H_6}]^2+2\,k_1\,k_5[\mathrm{C_2H_5\bullet}][\mathrm{C_2H_6}]+k_3\,k_4[\mathrm{C_2H_5\bullet}][\mathrm{C_2H_6}]}{k_4[\mathrm{C_2H_6}]+k_5[\mathrm{C_2H_5\bullet}]}}{\frac{k_3\,k_4[\mathrm{C_2H_6}]+2\,k_3\,k_5[\mathrm{C_2H_5\bullet}]}{k_4[\mathrm{C_2H_6}]+k_5[\mathrm{C_2H_5\bullet}]}}$$

$$[\mathrm{C_2H_5\bullet}] = \frac{2\,k_1\,k_4[\mathrm{C_2H_6}]^2 + 2\,k_1\,k_5[\mathrm{C_2H_5\bullet}][\mathrm{C_2H_6}] + k_3\,k_4[\mathrm{C_2H_5\bullet}][\mathrm{C_2H_6}]}{k_3\,k_4[\mathrm{C_2H_6}] + 2\,k_3\,k_5[\mathrm{C_2H_5\bullet}]}$$

$$0 = \Big(2\,k_1\,k_4[\mathrm{C_2H_6}]^2 + 2\,k_1\,k_5[\mathrm{C_2H_5\bullet}][\mathrm{C_2H_6}] + k_3\,k_4[\mathrm{C_2H_5\bullet}][\mathrm{C_2H_6}] - k_3\,k_4[\mathrm{C_2H_5\bullet}][\mathrm{C_2H_6}] - 2\,k_3\,k_5[\mathrm{C_2H_5\bullet}]^2\Big) / \Big(k_3\,k_4[\mathrm{C_2H_6}] + k_3\,k_5[\mathrm{C_2H_5\bullet}]\Big)$$

Multiplying both sides by the denominator and rearranging gives:

$$2\,k_1\,k_4[\mathrm{C_2H_6}]^2 + 2\,k_1\,k_5[\mathrm{C_2H_5\bullet}][\mathrm{C_2H_6}] + k_3\,k_4[\mathrm{C_2H_5\bullet}][\mathrm{C_2H_6}] - k_3\,k_4[\mathrm{C_2H_5\bullet}][\mathrm{C_2H_6}] - 2\,k_3\,k_5[\mathrm{C_2H_5\bullet}]^2 = 0.$$

Multiplying this equation by $\frac{1}{-k_3\,k_5}$, we get

$$0 = -\frac{2\,k_1\,k_4}{k_3\,k_5}[\mathrm{C_2H_6}]^2 - \frac{2\,k_1}{k_3}[\mathrm{C_2H_6}][\mathrm{C_2H_5\bullet}] + 2[\mathrm{C_2H_5\bullet}]^2.$$

Here we can use the assumption that k_1/k_3 is negligible in comparison to $(k_1\,k_4)/(k_3\,k_5)$ given in the question text which simplifies the equation to:

$$0 = -\frac{2\,k_1\,k_4}{k_3\,k_5}\,[\mathrm{C_2H_6}]^2 + 2\,[\mathrm{C_2H_5}\bullet]^2 \iff [\mathrm{C_2H_5}\bullet]^2 = \frac{k_1\,k_4}{k_3\,k_5}\,[\mathrm{C_2H_6}]^2$$

$$\implies [\mathrm{C_2H_5}\bullet] = \sqrt{\frac{k_1\,k_4}{k_3\,k_5}}\,[\mathrm{C_2H_6}].$$

Finally, we can put this formula for the stationary concentration of ethyl radical into the rate formula that we devised at the beginning of the solution to get the final answer:

$$v = k_3 \sqrt{\frac{k_1\,k_4}{k_3\,k_5}}\,[\mathrm{C_2H_6}].$$

Question L.4 (Nathaniel Loh): Boron clusters

Boron forms cluster compounds with hydrogen containing a skeleton of boron atoms bonded together in a polyhedral structure based on a convex deltahedron. A deltahedron is a polyhedron where all faces are equilateral triangles, and there exists one deltahedron only for every number of vertices from 4 through to 10, as well as one for 12.

closo-$\mathrm{B_n}$ clusters are arranged in the shape of the deltahedra with n vertices, a boron at each vertex with the edges being B-B bonds. *nido*-$\mathrm{B_n}$ clusters have the same geometry as the *closo*-$\mathrm{B_{n+1}}$ cluster, but with one vertex removed. *arachno*-$\mathrm{B_n}$ clusters are equivalent to the *nido*-$\mathrm{B_{n+1}}$ cluster but with one vertex removed again.

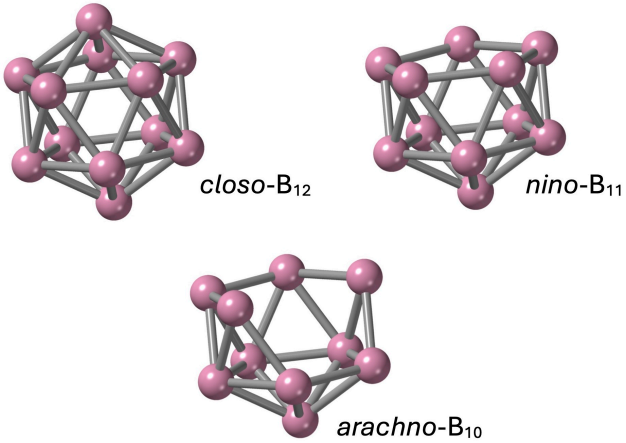
Generally, the boron with the highest number of bonds in the *closo*- structure is removed to form the nido- structure, and an adjacent boron to the one already removed is removed to form the geometry of the *arachno*- structure. As an example, the *closo*-$\mathrm{B_{12}}$ structure is an icosahedron, the *nido*-$\mathrm{B_{11}}$ structure is an icosahedron with a vertex removed, and the *arachno*-$\mathrm{B_{10}}$ structure is an icosahedron with two adjacent vertices removed (see the image).

Find the number of different boron environments (symmetrically non-equivalent positions) in

a) *closo*-$\mathrm{B_5}$, b) *nido*-$\mathrm{B_5}$, and c) *arachno*-$\mathrm{B_5}$ structures.

As the hydrogens in boranes do not affect the symmetry of the molecule, this is the number of different boron environments in the given compounds. Give **only the**

number of different position/environments as an answer, you **do not need to provide the structures**.



Solution:

a) *closo*-B_5: The structure is a triangular bipyramid. The three equatorial borons shared by both pyramids are equivalent, and the two borons at the apexes of the pyramids (axial atoms) are equivalent.

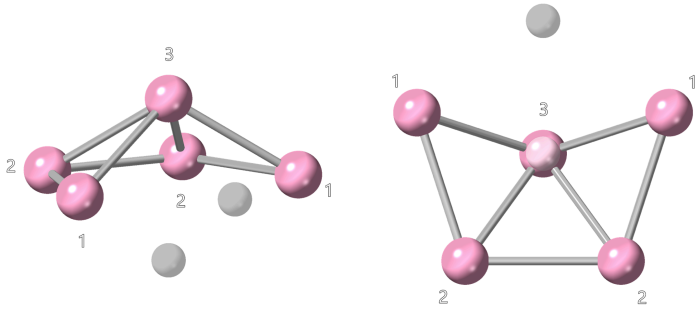
In total, there are 2 **different environments** (non-equivalent positions).

b) *nido*-B_5: The structure is an octahedron (equivalent to a square bipyramid) with one vertex removed, making it a square pyramid. The four borons at its base are equivalent, and the boron at its apex is in another environment.

In total, there are 2 **different environments** (non-equivalent positions).

c) *arachno*-B_5: The structure is a pentagonal bipyramid with one apex vertex and one equatorial vertex removed as per the rules described in the question. The resulting figure has a plane of symmetry through the two apexes (one now removed) and the removed equatorial vertex. The two equatorial borons adjacent to the removed equatorial boron are equivalent, and the remaining two equatorial borons are also equivalent (see the picture below where the structure is shown from the front and from below).

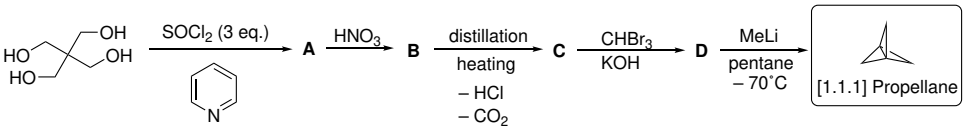
In total, there are 3 **different environments** (non-equivalent positions).



Question L.5 (Ondra Daněk): A tiny propeller

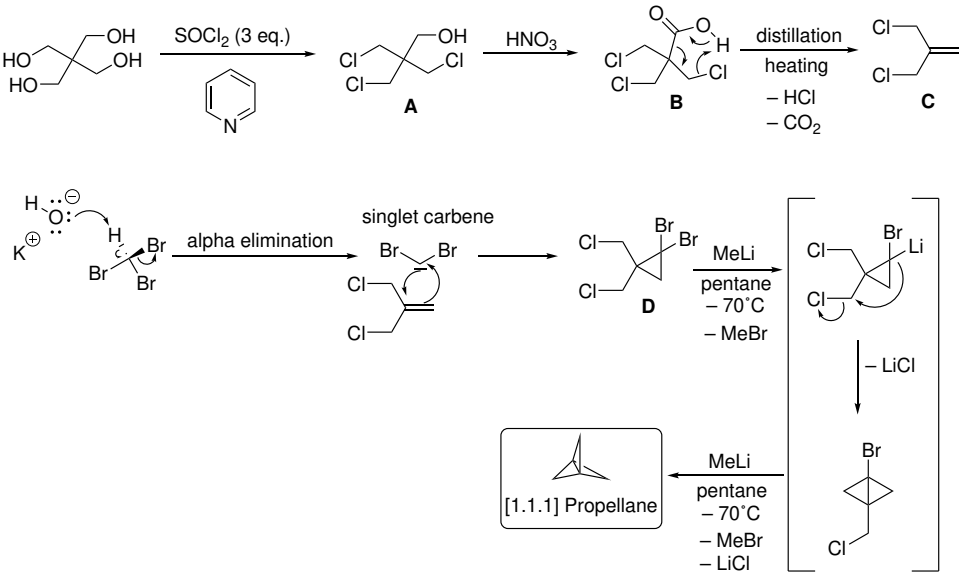
[1.1.1]Propellane is a highly strained hydrocarbon which is interesting in many ways, one of which being its potential use for introduction of [1.1.1]bicyclopentane (BCP) motif into drug like compounds, where the BCP can act as a bioisostere of para substituted benzene ring.

The synthesis of [1.1.1]propellane starting from pentaerythritol is described in the scheme below. First, pentaerythritol is treated with three equivalents of thionyl chloride and pyridine as a base. Major product of this reaction, **A**, is then oxidised with nitric acid and the resulting product **B** decomposes into product **C**, CO_2 and HCl during distillation. Isolated product **C** is then treated with bromoform and a concentrated aqueous solution of KOH to give a dark tar in the flask, from which product **D** can be isolated. Finally, **D** can be converted into [1.1.1]propellane by a reaction with methyllithium in pentane at −70 °C. Draw the structures of intermediates **A**–**D**.



Solution:

For the rest of the synthesis to make sense, only three of the four OH groups in the pentaerythritol must be exchanged for chlorine, which is also deduced from the three equivalents of thionyl chloride. The single leftover OH group in **A** can be then oxidised to the corresponding carboxylic acid **B** with nitric acid which is a strong oxidising agent. The decomposition of **B** to **C** can be explained by the pericyclic mechanism drawn in the solution. The double bond in **C** can be then cyclopropanated by in-situ generated dibromocarbene and the last step is halogen-metal exchange between methyllithium and **D** generating the alkyllithium species shown in square brackets, which quickly cyclyses via intramolecular S_N2 substitution with chloride as the leaving group. This sequence then proceeds once again with the second bromine to form the final propellane.

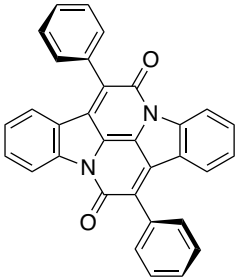


You can see this whole synthesis as well as one extra reaction of the final propellane being carried out in this youtube video: `https://www.youtube.com/watch?v=iTlRvQuIyqE`

Question L.6 (Saša Zaykov): Colourful

Chemist Anička decided to synthesize a red fluorescent dye. In some rather old literature, she found a mention of "Cibalackrot", first created by Gadient Engi for the Swiss company Ciba. Since the dye was once used to paint racing cars, the synthesis seemed relatively simple—it could be created from indigo in two steps.

However, chemist Jardík doubted that this substance would be red. He said, "Indigo is blue-violet. And here we've just added two twisted phenyl paddles, which don't even contribute to the conjugation. That can't make such a difference!"



Anička, well-versed in the dark corners of quantum chemistry, had her eyes light up and decided to test Jardík's hypothesis. She knew that the electrons absorbing light would move relatively freely across the π-system of the dye. However, she agreed with Jardík that the phenyl groups would not participate in the conjugation.

She continued her analysis: "Each double bond in the π-system contributes 2 electrons, and the nitrogen atoms contribute 2 each as well. We'll ignore the phenyl groups. And since the molecule is otherwise planar, the free movement of the electrons can be approximated using a two-dimensional rectangular infinite potential well."

"A well? And how big is it?" Jardík asked, confused.

"This length here", Anička said, pointing on the diagram to the longer side of the molecule running from left to right through the central double bond, "I'll call it x. I'd estimate it using the known bond length between carbons in benzene, 1.4 Å. The distance between the edge of the benzene ring and the top of the adjacent pyrrolidine cycle is roughly 1.5 times the length of the benzene bond."

She continued, "And, well, the central double bond is equivalent to the benzene bond, so 1.4 Å, as it's definitely delocalized."

Jardík was starting to catch on and added another question, "And what about the second dimension?"

Anička waved her hand and said, "That will be about half of the longer side, and I'll call it y. And just to be safe, I'd extend both sides by about 5%. After all, the electron won't just stop at the end of the molecule."

Anička cheerfully sketched out the solution to Schrödinger's equation for a particle of mass m trapped in a 2D well and wrote out the energy of the electron states:

$$E(n_x, n_y) = \frac{h^2}{8m} \times \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

where L are the dimensions of the well, and n are the quantum numbers of the states, analogous to atomic orbitals.

By solving this problem, Anička obtained a sequence of states, which she plotted in a diagram and populated with electrons according to known principles. She didn't forget that an electron has two possible spin states. Absorption of light refers to the transition of an electron from one state to another via energy supplied by a photon, a packet of light. The difference in energy between these electronic states corresponds to the absorbed wavelength. In this model, during the transition (excitation), only one quantum number is allowed to change.

At what wavelength **[nm]** of *visible light* will the molecule Cibalackrot absorb, according to this model?

Solution:

The easiest solution begins with recognizing that the equation for the energies of the electron wavefunctions can be simplified to:

$$E(n_x, n_y) = \text{Constant} \times \left(n_x^2 + 4n_y^2 \right) \tag{1}$$

From this, we derive a simple proportionality of energy to the quantum numbers.

To calculate the constant, we begin by calculating the length of the Cibalackrot molecule along the x-axis:

$$\begin{aligned} L_x &= 1.05 \times (4 \times \cos(\frac{\pi}{6}) \times 1.4 + 4 \times 1.4) \\ &= 1.05 \times (4.84 + 5.6) \\ &= 10.97\,\text{Å} \end{aligned}$$

The second length is therefore 5.486 Å. The constant can thus be calculated as:

$$\frac{h^2}{8mL_x^2} = \frac{(6.626 \times 10^{-34}\,\text{Js})^2}{8 \times 9.109 \times 10^{-31}\,\text{kg} \times (10.97 \times 10^{-10}\,\text{m})^2} = 5.004 \times 10^{-20}\,\text{J} \qquad (2)$$

Use of

$$\Delta E = \frac{hc}{\lambda}$$

for visible light gives a range of energy difference of

$$\frac{6.626 \times 10^{-34}\,\text{Js} \times 2.998 \times 10^{8}\,\text{ms}^{-1}}{750 \times 10^{-9}\,\text{m}} = 26.49 \times 10^{-20}\,\text{J} \qquad (3)$$

$$\frac{6.626 \times 10^{-34}\,\text{Js} \times 2.998 \times 10^{8}\,\text{ms}^{-1}}{380 \times 10^{-9}\,\text{m}} = 52.28 \times 10^{-20}\,\text{J} \qquad (4)$$

Comparison between (1), (2), (3), and (4) finds that the change in quantum numbers, $n_x^2 + 4n_y^2$, must be between 6 and 10 inclusive.

A table can be constructed to find the energy levels corresponding to each pair of quantum numbers:

	$L_x = 1$	$L_x = 2$	$L_x = 3$	$L_x = 4$	$L_x = 5$	$L_x = 6$	$L_x = 7$
$L_y = 1$	5*	8*	13*	20*	29*	40*	53
$L_y = 2$	17*	20*	25*	32*	41*	52	65
$L_y = 3$	37*	40*	45	52	61	72	85
$L_y = 4$	65	68	73	80	89	100	113

We also know that the central part of Cibalackrot (the section without phenyl groups) contains 13 pairs of π-electrons. As each "orbital" can contain one pair of electrons, the 13 lowest energy "orbitals" are occupied in the ground state, marked with an asterisk. From examination of the table, it can be found that the only transition from an occupied to unoccupied "orbital", such that $6 \leqslant \Delta(n_x^2 + 4n_y^2) \leqslant 10$ is satisfied, is (1,3) to (3,3)

The corresponding wavelength can then be calculated:

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34}\,\text{J s} \times 2.998 \times 10^{8}\,\text{ms}^{-1}}{8 \times 5.004 \times 10^{-20}\,\text{J}} = 496\,\text{nm}$$

The author acknowledges that this solution involves significant oversimplification. The result, which aligns surprisingly well with experimental values given the standards of theoretical chemistry[4], is not due to the accuracy or correctness of the theory. It is merely the result of the "tuning of constants" and a great deal of luck.

[4]Ryerson, Joseph L., et al. "Structure and photophysics of indigoids for singlet fission: Cibalackrot." *The Journal of chemical physics 151.18* (2019). https://doi.org/10.1063/1.5121863

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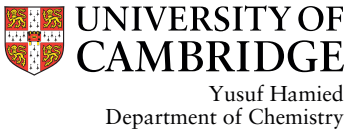
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