4th Chemistry Race: Questions and Solutions



4th February 2023

Question A.1 (Anh Phung)

If you look at any modern periodic table, you will not find the element nipponium (Np). First characterised in 1908 by Japanese chemist Masataka Ogawa, he assigned it to the then-undiscovered element 43. However, an investigation in 1996 concluded that Ogawa's assignment was incorrect. In fact, unbeknownst to him, what Ogawa had found was not element 43, but another element which was also undiscovered at the time. Due to this misidentification, nipponium was officially re-assigned with a different name and chemical symbol. Using the modern periodic table, and knowing that its expanded electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^5 6s^2$, identify the element that Ogawa had assigned as Np.

Solution:

Rhenium (Re)

An easy way is to count the total number of electrons in the configuration, which is also equal to the number of protons and atomic number. This yields 75, pointing to Rhenium (Re) on the periodic table.

Ogawa had characterized element 75 instead of the then-wanted element 43 (now known as technetium). Because it is in the same group as technetium and just directly below it in the periodic table, they indeed share many similar chemical properties which might have misled Ogawa's assignment. Because of this mistake, his contribution was largely overlooked, and the name nipponium faded with time. Element 75 was officially reassigned as rhenium (Re), after the work of German chemists Walter Noddack and Ida Noddack in 1925, nearly 20 years after Ogawa's unfortunate discovery.

Question A.2 (Jiří Ledvinka)

Acid rain or acid snow? Igor, who lives in Yakutsk, woke up on a cold morning. The thermometer outside the window showed $-57\,^{\circ}\mathrm{C}$, so he quickly ran out of bed and put the local lignite in the stove. This coal naturally contains a high amount of sulphur and nitrogen, and its combustion produces sulphur dioxide and nitrogen dioxide in addition to carbon dioxide and water. If these gases escaped through the chimney, what kind of rain and snow would Igor observe falling from the sky above? You may find the following information useful:

H_2O: m.p. $0\,^{\circ}\mathrm{C}$, b.p. $100\,^{\circ}\mathrm{C}$

CO_2: s.p. $-78.5\,^\circ C$

NO_2: m.p. $-9.3\,^\circ C$, b.p. $21.2\,^\circ C$

SO_2: m.p. $-72\,^\circ C$, b.p. $-10\,^\circ C$

Consider all gases to be pure and not modified by any other reaction that might occur with air or between themselves.

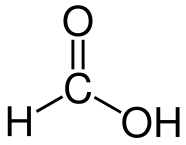
Solution:

It would snow snow and nitrogen dioxide, and it would rain sulphur dioxide. We can simply compare the melting point and boiling point (alternatively the sublimation point) to the ambient temperature, to find that sulphur dioxide would be a liquid ('sulphur dioxide rain'), whereas water and nitrogen dioxide would be solids ('snow of snow and nitrogen dioxide').

Question A.3 (Jiří Ledvinka)

Hydrogen vehicles have been talked about for some time, but they have been slow to enter the market. One reason for this is the difficulty of storing hydrogen: compressed hydrogen has major safety concerns, so you probably won't be seeing it at the pump in the near future. There has been a lot of work on the development of alternative hydrogen fuels which can be more easily handled and stored.

One solution to the problem is to react the hydrogen with carbon dioxide, to make formic acid. The formic acid can be handled more safely, and then catalytically converted back into H_2 and CO_2 again as you drive along. This process is carbon neutral because the formic acid fuel was made from CO_2. However, there is still a major drawback: the percentage by mass of hydrogen in formic acid is low. Work out the percentage by mass of hydrogen in the fuel. The structure of formic acid is given below.



Solution:

The formula of formic acid is CO_2H_2. So we have

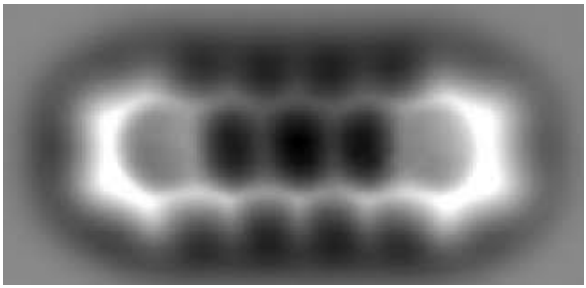
$$\frac{M_r(H_2)}{M_r(CO_2H_2)} = \frac{2}{12+16+16+2} \cdot 100\,\% = 4.35\,\%.$$

So we would need to carry around a lot of formic acid! Another problem is that formic acid is toxic and causes severe burns when it contacts the skin.

Question A.4 (Sam Holmes)

Atomic Force Microscopy (AFM) is an analytical technique that can be used to image surfaces at a sub-nanometre resolution. These microscopes have an atomically sharp tip which is scanned over the sample; the deflection of the tip is measured as it is attracted/repelled by the surface which allows its topology to be visualised. It is possible to adsorb organic molecules onto a surface, so they can be imaged at a very high resolution using AFM.

You are provided with an image of a hydrocarbon (the magnification is on the order of 10^7) that was recorded using AFM by Gross and collaborators in 2009. Work out its molecular formula.



Solution:

$C_{22}H_{14}$

Even the protons can be seen in this remarkable image – the molecule is pentacene, which has five benzene rings fused together in a straight chain. It may help to first draw the displayed formula – which will lead you to the solution $C_{22}H_{14}$.

More about this image can be found in DOI: 10.1126/science.1176210

Question A.5 (Sam Holmes)

For any given molecular formula, there are usually many possible structural formulas. Molecules with the same molecular formula but different arrangements of atoms can be constitutional isomers or stereoisomers. These molecules can have very different properties, so it is important that we can distinguish them.

Draw the structure of both of the stable isomers with the molecular formula C_3H_6.

Solution:

Cyclopropane and propene

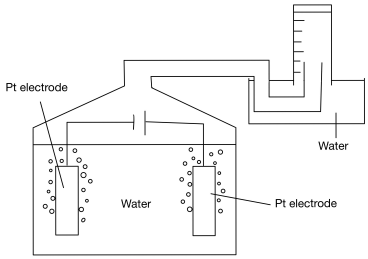
We have one degree of unsaturation, so that means one ring, or one double bond. The only stable possibilities are cyclopropane and propene. Other unstable species sharing the same summary formula are dimethylcarbene and ethylcarbene.

Question A.6 (Sam Holmes)

Electrolysis can be used to make 'green hydrogen', which is environmentally friendly because the electricity needed to drive the reaction comes from renewable sources. A student wishes to collect some green hydrogen using the apparatus shown. After first allowing all of the air in the system to be displaced, they begin collecting the gas produced by their setup.

Before they use it for any experiments, they want to confirm the purity of the hydrogen they have collected. They measure the density of the gas they collect and are surprised to find it is much greater than that of hydrogen. They hypothesise that there is another gas present in their sample.

Work out the identity of the other gas, and what percentage (by volume) of the gas they collect will be hydrogen.



Solution:

They have also collected oxygen. $^2/_3$ of the mixture will be hydrogen by volume (67%).

The student is also collecting oxygen, as the reduction of H^+ is coupled with the oxidation of O-II. The overall reaction is

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

so $^2/_3$ of the gas produced is hydrogen. Remembering that density is directly proportional to the number of moles, we don't need to do any calculation to determine the answer. The mixture they have collected is highly explosive: this is a very dangerous way to make green hydrogen!

Question B.1 (Sam Holmes)

The bifluoride anion, $[HF_2]^-$, is intriguing because its bonding is not well described using conventional ionic or covalent valence bond models. Draw the structure of the bifluoride anion, including the bond angle at the central atom.

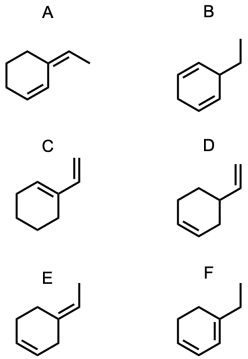
Solution:

F−H−F, bond angle 180 degrees.

The first question is whether we should draw H−F−F, or F−H−F (because of the lack of electrons in general, we quickly eliminate cyclic structures). If we think of the ion as H−F with another fluoride bound, we just need to decide which end the fluoride would bind to. Simple electrostatics would lead us to conclude that the structure should be F−H−F: it is sometimes said that bifluoride contains the strongest hydrogen bond known. Now we need the bond angle: there are definitely no lone pairs at hydrogen, so there are just two regions of electron density which will be 180 degrees apart.

Question B.2 (Sam Holmes)

There are many types of isomerism in chemistry, which must be controlled during chemical synthesis. Which of the following position isomers (if any) exhibit E/Z (previously called cis/trans) isomerism?

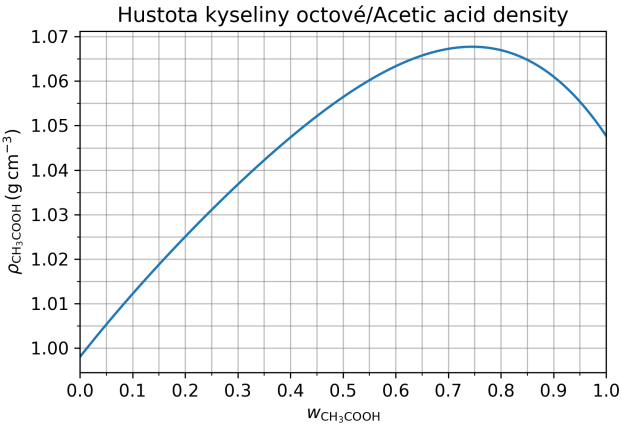


Solution:

A and E, if you reverse the geometry of the exocyclic double bond you get non-identical molecules. Double bonds in six-membered rings only have one stable configuration, or the ring would be too strained. D is chiral, so it does exhibit isomerism, but there are no E/Z isomers. C is a diene, which exists in two inter-convertible conformers (s-cis and s-trans), but these are not E/Z isomers.

Question B.3 (Jiří Ledvinka)

Pepík wanted to pickle some vegetables in vinegar at home to preserve them. Because he worked in a chemical laboratory and wanted to save money, he stole some acetic acid from the laboratory to make a pickling liquor. When he got home, he realised he had forgotten the concentration of the looted acid. As an experienced laboratory technician, he looked at the dependence of the density ρ of acetic acid on its mass fraction, w (see the graph in the appendix). He accurately measured 100 mℓ of this acid and found out it weighed 105.50 grams. He noticed that when he added a little water to this acid, its density increased. Pepík was confused by this observation, and could not work out the concentration of the acetic acid in the solution. Calculate for Pepík what % by mass of acetic acid this solution contains.



Solution:

We simply need to consult the graph to determine that the acetic acid with a density of $1.055\,\mathrm{g\,m}\ell^{-1}$ could have two different concentrations. Pepík noticed that adding water increased the density—i.e. the gradient of the graph must be negative around the concentration of interest (seeing as adding water decreases the concentration)—so we can constrain the solution to be the right hand side of the maximum point: a concentration of 95 %.

Question B.4 (Sam Holmes)

An entrepreneur is setting up an element shop which sells samples of all of the chemical elements with atomic numbers less than zinc to chemistry fans. As an opening promotion, they are selling all of the elements at £5 per gram. Excited to get my hands on some samples, I bought $1\,\ell$ balloons of all of the gases they sell. Which balloon will be the most expensive?

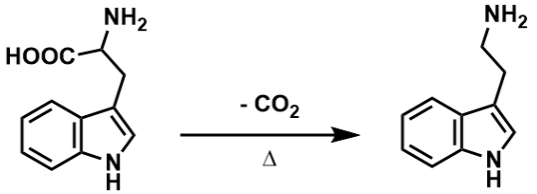
Solution:

The question is essentially asking for the densest of the gases in the first 30 elements, since we will be buying the most of this gas by weight. This is chlorine, as the ideal gas equation tells us the volume is independent of the identity of the chemical species – and the chemical species with the highest molecular weight is dichlorine Cl_2.

Question B.5 (Jiří Ledvinka)

At the beginning of autumn 2021, the price of emissions taxes in Czechia rose sharply to CZK 1,500 per metric ton (1000 kg) of CO_2 produced, resulting in an increase in energy prices. But increasing emissions taxes may be inconvenient for chemical companies too!

Imagine your small business wants to produce 1000 kg of tryptamine ($M = 160.216\,\mathrm{g\,mol^{-1}}$ by decarboxylating tryptophan ($M = 204.229\,\mathrm{g\,mol^{-1}}$, see the scheme below). How much will you pay in emissions tax, assuming a 100% reaction yield?



Solution:

We can see from the reaction scheme that the stoichiometric ratio between the reactant, the product, and the by-product (CO_2) is 1:1:1. We assume 100% reaction yield, the question text specifies the weight of the product ($m_{\mathrm{tryptamine}}$):

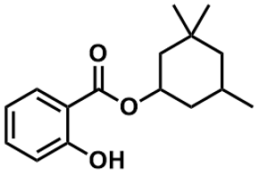
$$n_{\mathrm{CO_2}} = n_{\mathrm{tryptamine}} = \frac{m_{\mathrm{tryptamine}}}{M_{\mathrm{tryptamine}}},$$

$$m_{\mathrm{CO_2}} = M_{\mathrm{CO_2}}\, n_{\mathrm{CO_2}} = \frac{M_{\mathrm{CO_2}}}{M_{\mathrm{tryptamine}}}\, m_{\mathrm{tryptamine}} = \frac{44}{160.216} \times 1000 \doteq 274.16\,\mathrm{kg},$$

which corresponds to the CO_2 tax $\frac{274.63}{1000} \times 1500 \doteq 412$ CZK.

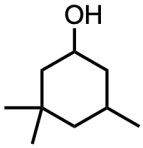
Question B.6 (Jiří Ledvinka)

Homosalate (see the image below) is an organic ester widely used in sunscreens. As an ester, it is produced by esterifying salicylic acid with the appropriate alcohol. The salicylic acid part is responsible for the absorption of UV radiation, while the alcohol part is responsible for the lipophilic character that prevents washing off with water. Draw the structure of this alcohol.



Solution:

We only need to identify the ester funcitonal group and correctly draw the alcohol connected to the salicylic acid (hence the 'salate' in the ester name).



Question C.1 (Lucie Peterková)

Fugu fish, of the family pufferfish (*Tetraodontidae*), is a staple of Japanese gastronomy. However, it may be considered a risky choice of meal: if not properly prepared, fugu may contain high doses of the lethal poison tetrodotoxin. Chefs who work with fugu are highly trained and the preparation of pufferfish is strictly controlled by law to avoid tetrodotoxin contamination. Tetrodotoxin is a neurotoxin of bacterial origin, with a fatal dose of $8.7\,\mu g\,kg^{-1}$ of body weight for humans. How many **whole** fugu fish would a sumo fighter weighing 160 kg have to eat to be fatally poisoned? Consider that every fish that eats contains 0.5 mg of tetrodotoxin.

Solution:

The deadly dose for this sumo fighter is $8.7 \times 160 = 1.392\,mg$. The number of fish is obtained by dividing the fatal dose of tetrodotoxin by the amount of tetrodotoxin in one fugu fish: $N = \frac{1.392}{0.5} \doteq 2.8$. One 160kg sumo fighter would therefore be killed if he ate 3 fish containing 0.5 mg of tetrodotoxin.

Note: In fact, there would be much more tetrodotoxin in a really badly prepared fish: one portion can be sufficient for a fatal dose.

Question C.2 (Adam Přáda)

Many people are wary of the chemicals in their food. Fewer people pay attention to the contents of another thing that they put in their mouth every day – toothpaste. The ingredients in a popular toothpaste of an unspecified brand are: Aqua, Hydrated Silica, Sorbitol, Glycerin, Sodium Lauryl Sulfate, Xanthan Gum, Aroma, Titanium Dioxide, PEG-6/PEG-8, Sodium Fluoride, Sodium Saccharin, Carrageenan, Limonene, CI 73360, and CI 74160.

There are plenty of ingredients! Do you know why they are there? Assign ingredients to their purpose (give your answer as six pairs of numbers and letters).

Example: hydrated silica—abrasive

1. sorbitol and sodium saccharine	a) aroma
2. sodium lauryl sulfate	b) enamel strengthener
3. xanthan gum and carrageenan	c) sweetener
4. titanium dioxide	d) thickener/stabiliser
5. sodium fluoride	e) colouring
6. limonene	f) detergent/foaming agent

Glycerin and PEGs are humectants, keeping moisture in the paste (sorbitol also helps with this). The mysteriously named CI 73360, CI 74160 are colourings for the red and blue stripes on the toothpaste.

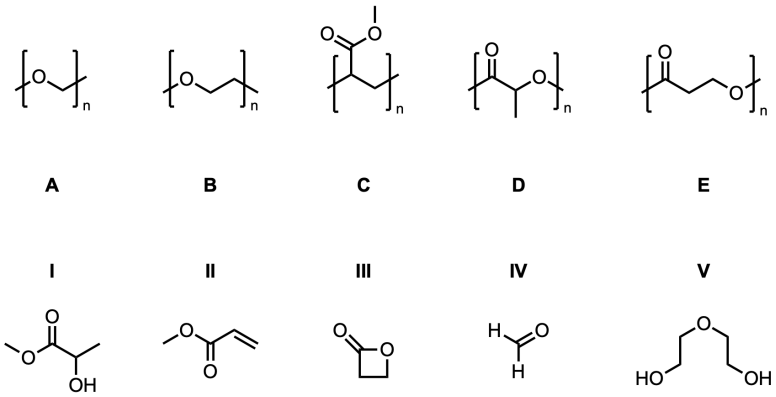
Solution:

Sorbitol and sodium saccharine are both well-known artificial sweeteners (1c). Limonene is a terpene responsible for the specific smell of all citrus fruits (6a). Titanium dioxide is a well-known white pigment (therefore colouring agent, 4e). We can then expect xanthan gum and carrageenan to thicken the structure of the toothpaste (3d). We know from various commercials that fluorides are added to strengthen our teeth (5b). Esters of long aliphatic alcohols and sulfuric acid are often used as detergents (which means 2f, see also e.g. sodium dodecyl sulfate).

Question C.3 (Sam Holmes)

Polymers are very important in our everyday lives: they are fantastically versatile and can be designed to have useful properties such as conductivity or biodegradability. The monomers can be complex, but for many commercial polymers, they are often rather simple molecules.

Match the following polymers to their monomer starting materials.



Solution:

A must be IV by the ratio of C to O. B is V because is is the only two-carbon repeat unit. C is II because we can see the result of addition polymerisation (the side chain was left intact). D is I by the connectivity of the three carbons. E is III again by connectivity – this is ring opening of the strained cyclic ester to make a polyester.

Question C.4 (Vojtěch Laitl)

Vojta, a shy inorganic chemistry student, has failed to explain to his examiner some basic properties of dichlorine hexoxide. This interesting compound is found to adopt a mixed anhydride structure in liquid phase, and ionic crystals in solid phase. In both forms, Cl_2O_6 readily reacts with water, forming a mixture of two chlorine oxoacids. Help Vojta by writing a balanced chemical equation for this reaction.

Hint: the two acids are created in the stoichiometric ratio 1:1.

Solution:

$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$

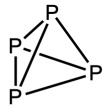
This is a disproportionation reaction: non-metal oxides in an oxidation state to which there is no corresponding stable oxoacid typically undergo this reaction. Knowing that the acids are created in a 1:1 ratio, we deduce that the number of electrons reducing one chlorine atom is equal to the number of electrons that caused the oxidation of the other chlorine atom. There is only one solution to this, $2\,Cl(VI) \longrightarrow Cl(V) + Cl(VII)$. Chloric and perchloric acids are created.

Question C.5 (Stanislav Chvíla)

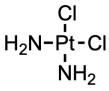
Chemists often find symmetry very satisfying: it is aesthetically pleasing, and can also be chemically useful. We have a natural ability to spot symmetry, but its mathematical definition is rather complex and it contains a lot of descriptions of various transformations (like rotating and mirroring).

Look at the following list of molecules and find three pairs among them that show exactly the same symmetry elements, which we would therefore classify in the same symmetry group (you could say that they are geometrically similar). One option will be left unused.

A White phosphorus
B Cisplatin
C Carbon dioxide
D Nitrogen
E Nickel tetracarbonyl
F Boron trifluoride
G 1,5-$C_2B_3H_5$



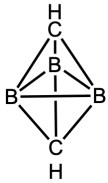
White phosphorus
A



Cisplatin
B



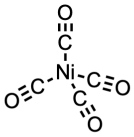
Carbon dioxide
C



1,5-$C_2B_3H_2$
G



Nitrogen
D



Nickel tetracarbonyl
E



Boron trifluoride
F

Solution:

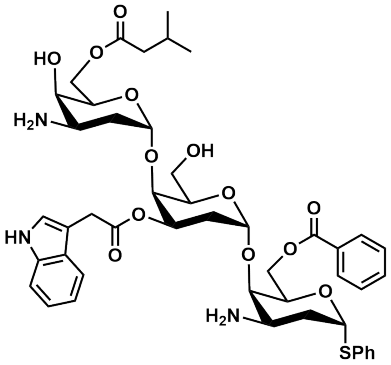
Both white phosphorus and nickel tetracarbonyl have tetrahedral symmetry (A–E). Carbon dioxide and dinitrogen are both linear and have a centre of symmetry (C–D). The carborane 1,5-$C_2B_3H_5$ is probably the most difficult to recognise, but we can see three boron atoms in the shape of an equilateral triangle and two C–H groups which

are perpendicular to this triangle and are placed above its centre. The molecule therefore has a three-fold main rotation axis (in which lie the two C–H groups),as well as a mirroring plane (in which lies the boron triangle). The same is true for boron trifluoride (F–G). Cisplatin is the molecule to be left out, being the least symmetrical of them all.

Question C.6 (Jiří Ledvinka)

The cellular tumour antigen p53 binds to the tumour protein MDM2, modulating the activity of this protein in the tumour. It may be beneficial to artificially stimulate this response by intravenously supplying more of the antigen p53, which is a peptide.

However, peptide-based drugs often suffer low enzymatic stability and are therefore not very potent. For this reason an analogue of the p53 peptide (called a peptidomimetic) based on a trisaccharide was developed. This molecule imitates the spatial arrangement of the p53 amino acid residues, which are responsible for its binding to MDM2. Identify the three amino acids responsible for the p53–MDM2 interaction.



Solution:

Phenylalanine (Phe, F), tryptophan (Trp, W) and leucine (Leu, L) – instead of leucine, valine (Val, V) can be accepted.

The amino acids responsible for the binding can be identified by comparison of the proteinogenic amino acid residues with the structure of the peptidomimetic.

Question D.1 (Vít Procházka)

Spectrophotometry is a technique for measuring absorbance, A. Absorbance is a function of concentration. Usually, this function is linear according to the Beer–Lambert law:

$$A = \varepsilon_\lambda c l,$$

where ε_λ is the absorption coefficient, c is the concentration, and l is the cuvette length.

Most proteins do not absorb visible light. However, we can use the biuret reaction to make peptide solutions which do absorb electromagnetic radiation with a wavelength in the visible region: peptides form a blue complex when an alkaline solution of copper(II) cations is added. A solution made by mixing $20\,\mu\ell$ of standard bovine serum albumin solution with concentration $70\,\mathrm{g}\,\ell^{-1}$ and $1\,\mathrm{m}\ell$ of biuret reagent had an absorbance of 0.256 at $\lambda = 544\,\mathrm{nm}$. What is the mass concentration of proteins in a sample of a bovine serum albumin prepared in this way which had an absorption 0.103 at the same wavelength when measured in a cuvette of the same dimensions?

Solution:

Since we work with the same protein at the same wavelength at the same conditions, the absorption coefficient ε_λ must be the same, as will the length of the cuvette, l. Expressing the absorption coefficient from the Beer–Lambert law, we get:

$$\frac{A_1}{c_1 l} = \frac{A_2}{c_2 l}.$$

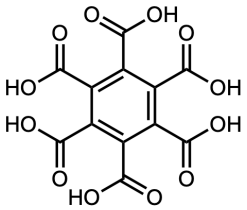
Clearly, the cuvette length will cancel out. We are interested in the second concentration, which means

$$c_2 = \frac{A_2}{A_1} \times c_1 = \frac{0.103}{0.256} \times 70 \doteq 28.16\,\mathrm{g}\,\ell^{-1}.$$

Question D.2 (Anh Phung)

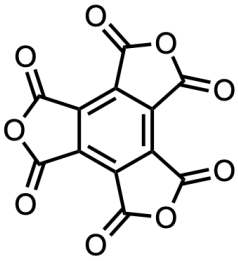
There are several stable oxides of carbon, including carbon dioxide (CO_2) and carbon monoxide (CO). Another stable oxide of carbon, mellitic anhydride, has the

molecular formula $C_{12}O_9$. It was first isolated by Friedrich Wöhler[1] from the mineral mellite (also called honeystone for its colour) in 1826, but it can also be prepared in the laboratory by fully dehydrating mellitic acid (see the structure below). Draw the structure of mellitic anhydride.



mellitic acid

Solution:



mellitic anhydride

Question D.3 (Petr Linhart)

Nucleic acids (DNA and RNA) code amino acids using codons, which are groups of nucleobases. There are 5 nucleobases: adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U).

Alexander, a biochemist, noticed something strange: there are only 20 proteinogenic amino acids that need to be distinguished, so doublet codons (consisting of just two nucleobases) should be satisfactory, because $5^2 = 25$ different combinations of letters (codes). Alexandr concluded from this that biology was inefficient, since

[1] Wöhler, F., Ueber die Honigsteinsäure. *Annalen der Physik* **1826**, *83* (7), 325-334

the genetic code uses triplet codons. Unfortunately for Alexander, nature always works efficiently and logically thanks to evolutionary pressure, and this case is no exception! Can you spot the error that Alexander has made? Calculate the actual number of codons that are possible in DNA.

Solution:

Alexandr forgot that in the coding process, only 4 bases are actually used: in DNA, it is adenine, guanine, cytosine and thymine, in RNA, thymine is replaced by uracil. The difference between thymine and uracil therefore bears no information, it is just the matter of different 'writing systems' for different 'media'. In reality, doublet codons would not suffice, since $42 = 16 < 20$. That's why we have triplet codons: $4^3 = 64$. This is an unnecessarily large number which leads to code degeneracy: more combinations code the same amino acid. This is a good thing, though, because it makes the genetic code less sensitive to point mutations (replacement of one amino acid by another).

Question D.4 (Sam Holmes)

The thermosphere is the layer of the atmosphere between 85 and 690 km above the surface of the earth. The gas molecules are so disperse at this altitude that our usual intuition about the behaviour of gases is not to be relied upon in the thermosphere!

The mean free path L_{mfp} of a molecule is the average distance a molecule travels before it collides with another. This quantity is important for determining the rate of reaction, as rate is dependent on collision frequency. Work out the mean free path of a gas molecule at the top of the thermosphere, given the following information (assume that all gas molecules in the thermosphere have the same collision diameter – that of dinitrogen).

Mean free path can be calculated as

$$L_{\text{mfp}} = \frac{1}{\sqrt{2}\pi d^2 N_v},$$

where N_v is number of molecules per unit volume and d is collision diameter.

In the thermosphere,
$P = 10 \times 10^{-10}$ atm,
$T = 1500$ K (on average),
and for dinitrogen, $d = 364$ pm.

Solution:

$$N_v = \frac{PN_A}{RT} = \frac{10 \times 10^{-5}\,\text{Pa} \times 6.02 \times 10^{-23}\,\text{mol}^{-1}}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1} \times 1500\,\text{K}} = 4.83 \times 10^{14}\,\text{particles m}^{-3}$$

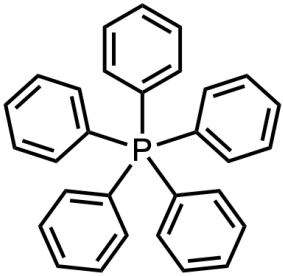
$$\begin{aligned} L_{\text{mfp}} &= \frac{1}{\sqrt{2} \times \pi \times d^2 \times N_v} \\ &= \frac{1}{\sqrt{2} \times \pi \times (3.64 \times 10^{-10}\,\text{m})^2 \times 4.83 \times 10^{14}\,\text{particles m}^{-3}} = 3.49\,\text{km} \end{aligned}$$

At sea level, the mean free path is about 100 nm (1000 molecular diameters). Each molecule undergoes 7×10^9 collisions per second (so imagine trying to bump into every human on earth in the space of one second). At this height in the thermosphere, the collision frequency is reduced to 0.3 collisions per second – but if you think about how far the molecules are travelling in that time, the molecules are moving incredibly quickly – around 1 km s^{-1}!

Question D.5 (Jiří Ledvinka)

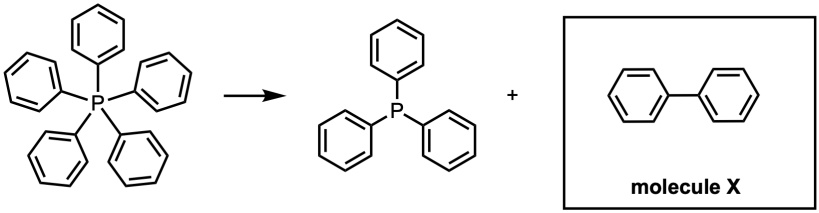
Previously in the Chemistry Race, we have asked several questions about the chemistry of nitrogen compounds. So as not to repeat ourselves this year, let us now look at the chemistry of phosphorus, which has much in common with that of nitrogen (and of course some important differences).

The phosphorus analogue of triphenylamine Ph_3N is triphenylphosphine Ph_3P. Like Ph_3N, Ph_3P can act as a nucleophile thanks to its lone pair. However, unlike Ph_3N, it willingly reacts to form pentavalent phosphorus compounds such as triphenylphosphine oxide ($Ph_3P{=}O$). Pentaphenylphsophorus, Ph_5P, can also be isolated (its structure is given below), which has no stable nitrogen analogue. When heated, Ph_5P decomposes into triphenylphosphine Ph_3P and substance X. Draw the structure of substance X.



Solution:

The solution is biphenyle.

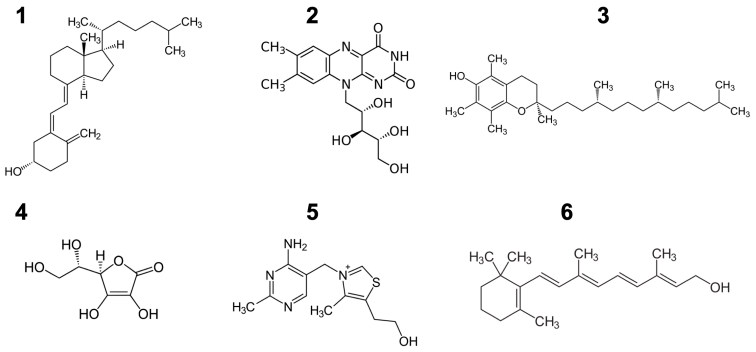


Question D.6 (Petr Linhart)

'*Similia similibus solvuntur*'

'Similar dissolves in similar' is an old saying used by alchemists, which turns out to be quite useful. We know from biochemistry that some vitamins are soluble only in fats—there is an acronym in Czech to remember which ones: (Z)**ADEK** (this means buttocks in Czech).

The solubility of a molecule in lipids or water can be well estimated based on its structure. Determine which three of the given molecules are 'more similar to fats' (lipophilic, soluble in fats) and which three are 'more similar to water' (hydrophilic, soluble in water)?

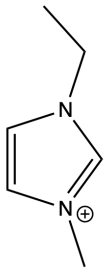


Solution:

Structures 1, 3 and 6 are similar. All have a polar OH group but also long, non-polar chains. We can judge from that that these vitamins are insoluble in water. They are (respectively): calciferol (vitamin D_3), α-tocopherol (one of the E vitamins) and retinol (vitamin A). The remaining structures have proportionally more polar groups (OH or NH_2), structure E even has a net charge. They are (2, 4, 5, respectively): riboflavin (vitamin B_2), ascorbic acid (vitamin C) and thiamine (vitamin B_1).

Question E.1 (Sam Holmes)

Ionic liquids are compounds which, despite being made up of ions, have a melting point below room temperature. They are a recent area of interest in chemical research, with applications in battery technology and large-scale chemical processing. One example of an ionic liquid is $[Emim]^+$ acetate (ethanoate). The structure of the $[Emim]^+$ cation is shown below.



1-ethyl-3-methyl-1*H*-imidazol-3-ium
[Emim]+

The conductivity of a liquid is dependent on the concentration of mobile charge carriers it contains. Calculate the concentration of $[Emim]^+$ cations in $[Emim]^+$ acetate. You are given that the density of $[Emim]^+$ acetate is $1090\,\mathrm{kg\ m^{-3}}$ at room temperature.

Solution:

Don't forget to include the acetate when you calculate the M_r, and don't be tempted to halve the answer at the end! The molecular weight of $[Emim]^+$ acetate is $M = 170.21\,\mathrm{g\,mol^{-1}}$.

$$c = \frac{n}{V},$$
$$N = \frac{m}{M},$$
$$\rho = \frac{m}{V}.$$

$$c = \frac{\rho}{M} = \frac{1090\,\mathrm{g\ dm^{-3}}}{170.21\,\mathrm{g\,mol^{-1}}} = 6.404\,\mathrm{mol\ dm^{-3}}.$$

Question E.2 (Jiří Ledvinka)

In a recent scientific paper, the reaction of 1,1-binapthyl with potassium was reported. The scientists who carried out the reaction noted that Teflon stirrers, which are often used to agitate reaction mixtures, should not be used in this case because

a side reaction can take place. The Teflon (PTFE, poly(tetrafluoroethene)) can react with potassium to produce potassium fluoride and a very fine black powder which is pyrophoric (meaning it spontaneously ignites when exposed to air). Write the chemical formula of this powder.

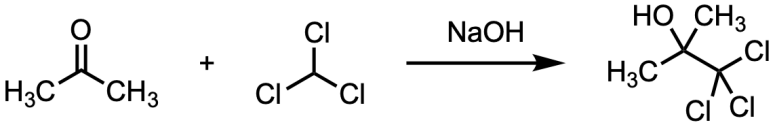
Solution:

The product is carbon, which results from complete deflourination of PTFE.

Question E.3 (Jiří Ledvinka)

One of the oldest known anaesthetics can be prepared from acetone (propanone) and chloroform (trichloromethane). Sodium hydroxide is added to a mixture of these liquids, which deprotonates the chloroform. The deprotonated chloroform then attacks the carbonyl of acetone, which, upon protonation, forms the product. Draw the structure of the anaesthetic prepared in this procedure.

Solution:



Question E.4 (Jakub Štěpánek)

White phosphorus fires are very dangerous, because they are almost impossible to extinguish. White phosphorus spontaneously ignites in air, so even if it is extinguished, it will relight back when oxygen is reintroduced. It is also very sticky, so if one was to get white phosphorus on their skin, the consequences could be very severe. The recommended first aid in this situation is intensive washing of the affected area with a solution of copper(II) sulfate, which can oxidise phosphorus to a water-soluble form in the +V oxidation state. The remaining white phosphorus is covered by an impermeable copper layer so it cannot continue to burn. Write a balanced chemical equation for the reaction that takes place when copper sulfate solution reacts with white phosphorus (P_4).

Solution:

$$P_4 + 10\,CuSO_4 + 16\,H_2O \longrightarrow 10\,Cu + 10\,H_2SO_4 + 4\,H_3PO_4$$

Copper ions are reduced to copper metal and phosphorus is oxidized. In this way, the phosphorous is covered by a copper layer and cannot continue to burn.

Question E.5 (Sam Holmes)

I have built a toy sailing boat that I want to show off to my friends. Sadly, my engineering skills leave a lot to be desired, so the boat doesn't float particularly well. Thankfully I can use my chemical cunning to trick my friends into thinking I am good at building model boats by altering the density of the water in which it is floating. I wish to fill the local pond with $3500\,\mathrm{m}^3$ of water with a density of $1.08\,\mathrm{g\,m}\ell^{-1}$, which is to be made by mixing H_2O and D_2O. I buy deuterium oxide from a well-known chemical company for £$1000\,\ell^{-1}$. How much will it cost to fill the pond? Assume that H_2O is free. Density of H_2O, $\rho_{H_2O} = 0.997\,\mathrm{g\,m}\ell^{-1}$.

Solution:

Heavy water has the same molecular density as regular water, its molar mass is heavier, though ($20\,\mathrm{g\,mol}^{-1}$ compared to the density of regular water, $18\,\mathrm{g\,mol}^{-1}$). Density of D_2O is therefore

$$\rho_{D_2O} = 0.997 \times \frac{20}{18} = 1.108\,\mathrm{g\,m}\ell^{-1}.$$

The overall volume is

$$V_{H_2O} + V_{D_2O} = 3\,500\,000\,\ell.$$

Balancing the mass, we get

$$\rho_{H_2O} \times V_{H_2O} + \rho_{D_2O} \times V_{D_2O} = \bar{\rho} \times V = 3\,780\,000\,\mathrm{kg}.$$

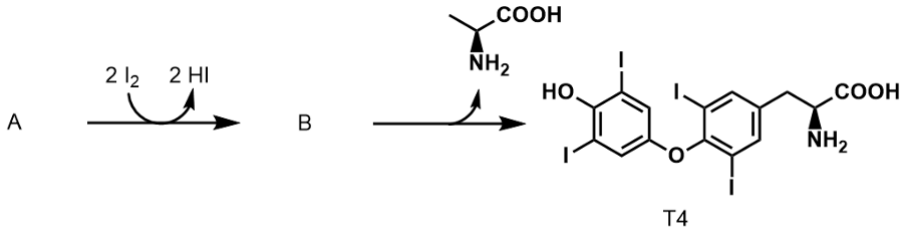
We need to solve two simultaneous equations, obtaining

$$V_{D_2O} = \frac{\bar{\rho} - \rho_{H_2O}}{\rho_{D_2O} - \rho_{H_2O}} \times V = 2\,622\,000\,\ell.$$

I'll need $2\,622\,000\,\ell$ D_2O, which costs about £2.62 billion. I'd be better off just buying a boat!

Question E.6 (Jiří Ledvinka)

Thyroxine T4 is one of the thyroid hormones that primarily regulates metabolism. Thyroxine T4 is synthesized by the thyroid gland from amino acid A, which first undergoes double aromatic iodination to form substance B. Two molecules of substance B then react to form the diaryl ether bond in T4, liberating L-alanine as a byproduct. Identify the proteinogenic amino acid A.



Solution:

Tyrosine.

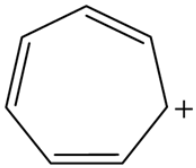
The amino acid is tyrosine. If you look at the right hand side of the molecule, you can see the full backbone of tyrosine. The left hand part of the molecule has been formed by removal of alanine from iodinated tyrosine in the second step.

Question F.1 (Petr Linhart)

Mass spectrometry is an analytical method in which molecules are ionised and accelerated through an electric or magnetic field. Depending on the ionisation technique used, the molecule under investigation may break up into smaller fragments which can also provide useful information about the structure of the parent molecule. The mass of the fragments can be characteristic of common chemical motifs: for example, aliphatic chains are usually split into the fragments CH_3^+ (rel. mol. wt. 15), $CH_3CH_2^+$ (rel. mol. wt. 29), etc.

In the mass spectrum of benzene we observe the fragment $C_6H_5^+$ (rel. mol. wt. 77). Neither methyl nor phenyl carbocations are observed in the mass spectrum of toluene (methylbenzene), though. However, a very intense peak at mass/charge 91 is observed. Draw the structure of this fragment, given that it is a cycle without side chains. Don't forget to include the charge.

Solution:



Tropylium carbocation.

Ionized toluene is stabilized by rearrangement to the tropylium cation, which is an aromatic structure and is therefore very stable.

Question F.2 (Michal Straka)

Phenolphthalein is an indicator which turns from transparent to vibrant purple in a basic environment. Jerry wants to use it in a magic trick – he will carefully fill a test tube with layers of three solutions, one containing phenolphthalein and one containing NaOH. After showing the transparent test tube to his friends, he will shake it while saying "Abracadabra" to mix the solutions and the test tube will turn purple.

Which three of the following solvents should he choose and in which order should he pour them into the test tube? Don't forget that each solution must be immiscible with the others it's touching.

Hint: NaOH is soluble in polar solvents and phenolphthalein in polar organic solvents and ether. Assume dissolving NaOH or phenolphthalein does not change the solution density.

Solvent	**Density** ($\mathrm{g\,cm^{-3}}$)	**Miscible with:**
Water	1	Ethanol
Mercury	13.53	None
Diethyl ether	0.71	All organics including oil
Silicone oil	0.95	None
Benzene	0.88	All organics including oil
Ethanol	0.79	Water, all organics except oil
Carbon tetrachloride	1.59	All organics except oil

Solution:

1) Water (+ NaOH), 2) Silicone oil, 3) Ethanol (+ Phenolphthalein)

NaOH is only soluble in water and ethanol. Phenolphthalein (PPH) is only soluble in ethanol and ether. To get two separate solutions, we could either use NaOH in water and PPH in ethanol or ether, or NaOH in ethanol and PPH in ether. However, there is no solvent with density between ethanol and ether which could form the separating layer. Therefore, we must choose water for NaOH and ethanol or ether for PPH. The possible separating layers are benzene and silicone oil, and since ethanol is miscible with benzene and ether is miscible with both, Jerry must choose the oil and ethanol. He has to pour in the solutions with the higher density first, so the answer is water (with NaOH), then silicone oil, then ethanol (with PPH).

Question F.3 (Vojtěch Laitl)

Methyl isocyanate, CH_3NCO, is a potential peptide bond precursor: this makes it interesting as a candidate for origins of life studies. Methyl isocyanate is made in regions of the interstellar medium known as molecular clouds, where new stars are formed. One of the possible reactions of its synthesis is a direct reaction between methane and isocyanic acid. The activation barrier of this reaction is too high to be overcome at typical conditions in the clouds. Nevertheless, the reaction can be catalysed by water-ice.

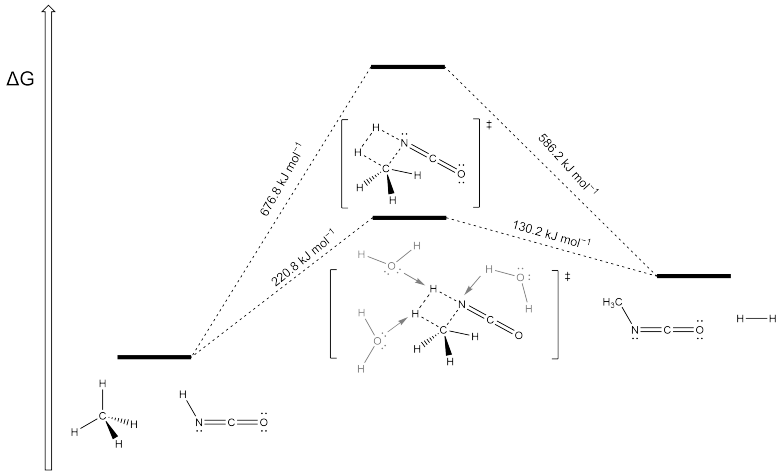
In the appendix to this question, you are provided with an energy level diagram showing the standard Gibbs free energy changes between reactants, transition states, and products for both the catalysed and uncatalysed reactions. Calculate:

i) the standard Gibbs energy change of the **uncatalysed** reaction;

ii) the equilibrium constant for the **catalysed** reaction.

The temperature of the interstellar medium is 20 K.

Hint: Gibbs energy is a state function, so Hess's Law can be used; you may find the equation $\Delta_r G^\ominus = -RT \ln K$ useful.



Solution:

1) $90.6\,\mathrm{kJ\,mol^{-1}}$; 2) 0

Activation energies of a forward and reverse reaction link the reactants and products, respectively, to the transition states. Their values correspond to the standard Gibbs reaction energies of the following processes:

$$\text{(R1): HNCO + CH}_4 \longrightarrow [\text{H}_3\text{C(H)}{-}{-}{-}\text{N(H)CO}]^{\ddagger},\ \Delta_r G_1^{\ominus} = 676.8\,\mathrm{kJ\,mol^{-1}}$$

$$\text{(R2): H}_3\text{CNCO + H}_2 \longrightarrow [\text{H}_3\text{C(H)}{-}{-}{-}\text{N(H)CO}]^{\ddagger},\ \Delta_r G_2^{\ominus} = 586.2\,\mathrm{kJ\,mol^{-1}}$$

The standard reaction energy is equal to the Gibbs energy of a reaction (R),

$$\text{(R): HNCO + CH}_4 \longrightarrow \text{H}_3\text{CNCO + H}_2,\ \Delta_r G^{\ominus}.$$

(R) may be understood as a formal combination of (R1) and (R2), i.e., (R) = (R1) − (R2). According to the Hess's law, the same relation holds for the reaction energies. Therefore

$$\Delta_r G^{\ominus} = \Delta_r G_1^{\ominus} - \Delta_r G_2^{\ominus} = 90.6\,\mathrm{kJ\,mol^{-1}}.$$

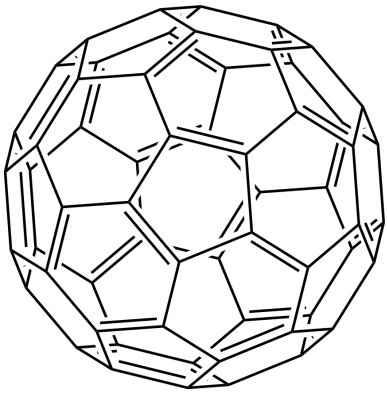
The same result is obtained by examining the catalysed process. Since the activation energy of both forward and reverse reaction is suppressed, the presence of a catalyst

does not affect the chemical equilibrium whatsoever. We may notice that the activation barrier decreased, though: catalysts have kinetic effects (they increase the reaction rate, which does not correlate with locating the chemical equilibrium).

In both cases, the equilibrium constant is equal to $K = \exp\left(-\frac{-90600}{20R}\right)$, which is almost zero (enumerating it gives $e^{-544} \sim 10^{-236}$, which is far smaller than the smallest number pocket calculators operate with). Despite that, the reaction is feasible. Molecular clouds represent an open system and find themselves very far from chemical equilibrium. Therefore, the synthesis may occur in an excess of reactants and may be initiated by a number of stochastic processes taking place in the universe.

Question F.4 (Sam Holmes)

How many sigma bonds are there in the C_{60} fullerene (a fullerene containing 60 carbon atoms)?



Solution:

90. Each carbon makes three sigma bonds, and each sigma bond is connected to 2 carbon atoms – so the ratio of bonds to carbon atoms is 1.5:1. $60 \times 1.5 = 90$ sigma bonds.

Question F.5 (Vojtěch Laitl)

The Planck constant's value has recently been fixed to precisely $h = 6.62607015 \times 10^{-34}\,\mathrm{J\,s}$. Let's look at the accuracy of the value obtained from the following (real) experiment.

A laser pulse was used to irradiate a silicon monocrystal, evaporating 3.5×10^{17} silicon atoms (estimated by spectroscopic measurements). The laser beam has a wavelength of 200 nm and delivers 2×10^{17} photons in a single short pulse. Work out the value of the Planck constant which would result from this experiment.

The enthalpy of evaporation of silicon is $300\,\mathrm{kJ\,mol^{-1}}$.

Hint: Balance the total energy to get an equation for the unknown h value. You may like to use the following values: $c = 3 \times 10^8\,\mathrm{m\,s^{-1}}$, $N_\mathrm{A} = 6.022 \times 10^{23}\,\mathrm{mol^{-1}}$.

Solution:

$5.816 \times 10^{-34}\,\mathrm{J\,s}$

Assuming that the energy of 2×10^{17} photons is converted to the heat of evaporating 3.5×10^{17} silicon atoms gives the following energy balance:

$$2 \times 10^{17} \times \frac{hc}{\lambda} = \frac{3.5 \times 10^{17}}{N_\mathrm{A}} \times \Delta_\mathrm{vap} H^\ominus$$

We attempt to get the Planck constant's value (remaining variables are given). Rearranging and enumerating gives

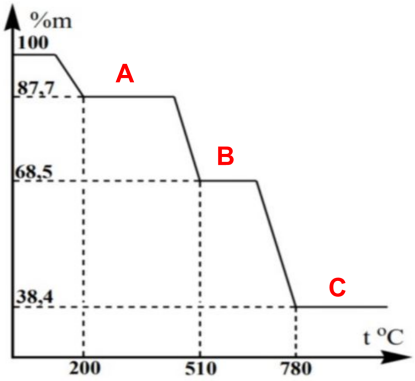
$$h = \frac{3.5 \times 10^{17}}{6.022 \times 10^{23} \times 300\,000} \times \frac{200 \times 10^{-9}}{3 \times 10^8} = 5.816 \times 10^{-34}\,\mathrm{J\,s}.$$

Such a value is biased by a remarkable error, which is due to neglecting the entropic contributions to the above energy balance. In our case, the total energy is not only given by heat but also by the pressure-volume changes invoked by the rapid evaporation.

Question F.6 (Anh Phung)

Thermogravimetric analysis (TGA) is an analytical method for investigating temperature-dependent phase transitions and chemical reactions of solid compounds. In this protocol, the mass of the sample is measured as the percentage of original mass over time as the temperature changes.

Consider the oxalate salt of metal M. Its monohydrate salt ($MC_2O_4 \cdot H_2O$) was analyzed using TGA and the result is shown in the following thermogram, showing three stages of reactions, where A, B and C are solid products of each stage. By deducing the identity of M, give the molecular formulae for A, B and C.



Solution:

A: CaC_2O_4, B: $CaCO_3$, C: CaO

The first drop must correspond to loss of H_2O ($18\,\mathrm{g\,mol^{-1}}$), which according to the diagram corresponds to $(100-87.7) = 12.3\%$ of the total molar mass. Knowing this, we can calculate the total molar mass of the monohydrate $M(MC_2O_4 \cdot H_2O) = 18/0.123 = 146\,\mathrm{g\,mol^{-1}}$. The molar mass of the metal M is $146 - 18 - 2 \times 12 - 4 \times 16 = 40\,\mathrm{g\,mol^{-1}}$. There is only one metal in the periodic table with this molar mass, calcium, the compound A is therefore anhydrous calcium oxalate CaC_2O_4, a compound well-known for its significance in kidney stone formation.

Similarly, we can determine what molecules were cleaved off the oxalate in the next steps: the compound B is $CaCO_3$ (one CO_2 from the oxalate is cleaved) and the compound C is CaO (another CO_2 is cleaved).

Question G.1 (Sam Holmes)

The term 'chirality' is derived from the Greek word χειρ ('kheir'), meaning palm. Like your hands, chiral molecules are molecules which have non-superimposable mirror images. They usually (but not always) contain chiral centres, which are often defined as carbon atoms with four different groups attached. However, some

molecules which contain multiple chiral centres are not chiral. Find the **three** achiral molecules from the list below.

Hint: molecules which contain a mirror plane cannot be chiral.



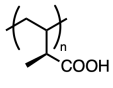
A



B



C



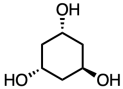
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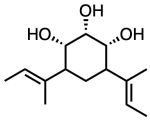
E



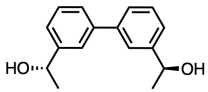
F



G



H



I

Solution:

B, G and H

All of these molecules contain a mirror plane.

Question G.2 (Jiří Ledvinka)

With the rising cost of energy, a warm bath is becoming an unaffordable luxury. As a chemist, you can rarely boast of employee benefits, but imagine that you are employed in an unnamed chemical company in Neratovice. You don't have a huge salary, but you do have access to an almost unlimited amount of caustic soda and hydrochloric acid. How about taking a pleasantly warm sea bath?

Help this exemplary employee by calculating how many kilograms of solid sodium hydroxide and how many kilograms of 31% hydrochloric acid he needs to bring home from work to prepare a 150-litre bath at 35 °C from 10°C tap water.

Assume the heat capacity of the bath is that of water ($4.2\,\mathrm{kJ\,kg^{-1}\,K^{-1}}$), and the density of the bath to be $1\,\mathrm{kg\,dm^{-3}}$. The dissolution enthalpy of sodium hydroxide is $-44.51\,\mathrm{kJ\,mol^{-1}}$, the dissolution enthalpy of hydrogen chloride is $-78.4\,\mathrm{kJ\,mol^{-1}}$, the neutralization enthalpy of NaOH and HCl is $-55.84\,\mathrm{kJ\,mol^{-1}}$. The molar mass of NaOH is $40\,\mathrm{g\,mol^{-1}}$, HCl is $36\,\mathrm{g\,mol^{-1}}$.

Solution:

6.278 kg NaOH and 18.226 kg 31% HCl

To heat the bath, we need heat $Q = m \times c \times \mathrm{d}T = 150 \times 4200 \times 25 = 15.75\,\mathrm{MJ}$. This heat will be supplied either by the exothermic dissolution of sodium hydroxide in water and then by neutralization with hydrochloric acid to form "sea" salt. Since it is most pleasant to bathe in a completely neutral bath, we will neutralize all dissolved hydroxide. The substance amount will then be

$$\begin{aligned} n &= \frac{Q}{\mathrm{d}H(\text{NaOH solution}) + \mathrm{d}H(\text{neutralization})} \\ &= \frac{15.75 \times 10^6}{44.51 \times 10^3 + 55.84 \times 10^3} \\ &= 156.95\,\mathrm{mol}. \end{aligned}$$

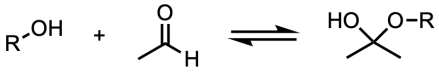
The weight of the reactants is obtained as follows:

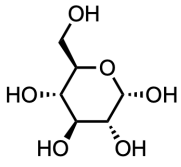
$$\begin{aligned} m(\mathrm{NaOH}) &= n \times M(\mathrm{NaOH}) \\ &= 156.95 \times 0.04 \\ &= 6.278\,\mathrm{kg}, \\ m(\mathrm{HCl}) &= \frac{n \times M(\mathrm{HCl})}{w} \\ &= \frac{156.95 \times 0.036}{0.31} \\ &= 18.226\,\mathrm{kg}. \end{aligned}$$

Question G.3 (Jiří Ledvinka)

Inorganic cyanides are perhaps the most infamous of poisons, known even to those who do not know the chemical formula of the cyanide ion. We often hear about cyanides in the context of ecological disasters, or read about their misuse in detective stories. When cyanide poisoning occurs in humans, intravenous administration of methylene blue followed by sodium thiosulfate is recommended. However, these are not common household items, so intravenous administration of glucose is used as an alternative, which reversibly binds blood hydrogen cyanide. Draw the product of the reaction of glucose with cyanide. You do not need to show the stereochemistry.

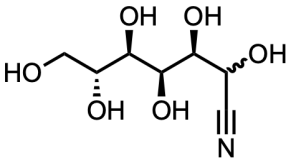
Hint: In the presence of an alcohol, aldehydes and ketones usually exist in equilibrium with an hemiacetal form:





D-Glucose

Solution:



Question G.4 (Sam Holmes)

I wish to fill 4 party balloons with helium to mark the UK Chemistry Race's 4^{th} birthday. I obtain the helium from the decay of my Po-210 stock, which decays into stable Pb-206 with a half-life of 138 days. As in the earth's crust, the alpha particles released can strip electrons from other molecules to form helium. Estimate how long I would need to wait (in days) to generate enough helium from 1 kg of Po-210 to fill the four party balloons. The volume of a party balloon is 10 ℓ and the pressure inside the balloon is 1.003 atm at room temperature (25 °C).

Solution:

84 days.

Using ideal gas equation of state, we get that we need

$$n_{\text{He}} = \frac{pV}{RT} = \frac{1.003 \times 101\,325 \times 4 \times 10 \times 10^{-3}}{8.314 \times 298.15} \doteq 1.64\,\text{mol}$$

of helium which corresponds to the amount of polonium that needs to decay.

Radioactive decay follows the equation

$$n_{\mathrm{Po}}(t) = n_{\mathrm{Po},0} \times 2^{-t/t_{1/2}},$$

from which

$$t = -\log_2 \frac{n_{\mathrm{Po}}(t)}{n_{\mathrm{Po},0}} \times t_{1/2}.$$

At the beginning, we have

$$n_{\mathrm{Po},0} = \frac{m}{M} = \frac{1000}{210}\,\mathrm{mol},$$

of polonium, after we have waited sufficient amount of time, there will be

$$n_{\mathrm{Po}}(t) = n_{\mathrm{Po},0} - n_{\mathrm{He}} = \frac{1000}{210} - 1.64 \doteq 3.12\,\mathrm{mol}$$

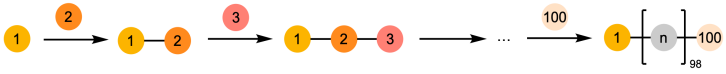
of polonium remaining.

We substitute back to the relation for time and get

$$t = -\log_2 \frac{3.12}{\frac{1000}{210}} \times 138 \doteq 84.06\,\mathrm{days}.$$

Question G.5 (Anh Phung)

Artificial peptide synthesis has received considerable attention in the last few decades. In this process, each amino acid is linked together by a peptide bond during a coupling reaction. This is performed one-by-one, as shown in the following reaction scheme:



Though very promising, the major difficulty of this synthetic step stems from its low overall yield and efficiency. One difficulty is that nineteen out of the twenty naturally occurring amino acids (all except glycine) are chiral and thus can exist in a mixture of L- and D- isomers. However, to make a biologically functional protein, all of the amino acids must be L-isomers.

Consider a quantitative synthetic pathway to make an L-polypeptide that is 100 amino acids long. The polypeptide should contain a glycine at the 1st, 10th, 23th and 58th place.

If each step is performed without purification and diastereoisomer separation, what is the maximum allowed percentage of D-enantiomer 'contaminating' the amino acids added at each step, if we require that there is at least 30% of the right L-polypeptide after the last step?

Solution:

1.12 %

The chain consists of 100 amino acids. The question text is a bit tricky in specifying particular positions for glycine residues but in fact, it is only the amount of them that is pertinent here. There are therefore $99 - 3 = 96$ coupling steps (excluding the first step and all other glycine residues) where some percentage of the wrong enantiomer is introduced to the polypeptide. Like with compound interest, we are losing the fraction x of the enantiomerically pure protein at each step, retaining $(1 - x)$ of it, and we repeat it 96 times, thus we can formulate an expression for the yield of the L-polypeptide:

$$\begin{aligned}(1-x)^{96} &= 0.30,\\ 1-x &= 0.30^{1/96},\\ \implies x &= 1.12\,\%.\end{aligned}$$

The maximal D-enantiomer contamination is therefore 1.12 % in each chiral coupling step.

Question G.6 (Petr Linhart)

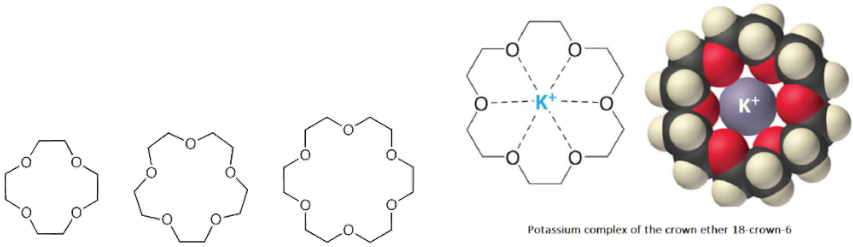
Crown ethers are cyclic molecules with interesting properties: their interior always fits one alkali metal ion. This way, 12-crown-4-ether complexes Li^+ ions, 15-crown-5-ether complexes Na^+ ions, 18-crown-6-ether complexes K^+ ions and 21-crown-7-ether complexes Cs^+ ions (interestingly not Rb^+ ions!), as shown in the attached figures.

In actuality, they are not planar (all atoms in the ring have sp^3 hybridisation and therefore are tetrahedral), but we will consider them so for the sake of this question. Inside the following table, you have ionic radii of alkali metal ions, but a few of them are missing:

Metal ion	Li^+	Na^+	K^+	Rb^+	Cs^+
Ionic radius (pm)	74.5	?	?	148	168

The covalent radius of oxygen is $r_O = 74\,\text{pm}$. Estimate the remaining ionic radii from the geometry of crown ethers. Assume that the complexes are planar, and that the atoms can be modelled as hard spheres (according to the figure).

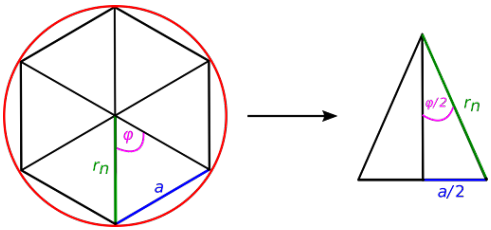
Hint: There is a relation between the radius of a circumscribed circle of a regular polygon, its side length, and the number of its sides.



Potassium complex of the crown ether 18-crown-6

Solution:

Let's start by deriving the formula for the radius r_n of a circumscribed circle of a polygon with n sides. We divide the polygon to isosceles triangles with a shared vertex at its centre. Because of its symmetry, the radius of the circumscribed circle is equal to the length of the leg of the isosceles triangle. Since crown ethers are always composed of the same patterns (ethylene group with two oxygen atoms at its ends), we assume that every polygon has the same side length a (in the case of hexagon depicted in the picture below, the triangles are equilateral, meaning $a = r_n$).



We extract one of the isosceles triangles and find that we will use the sine function:

$$\sin\frac{\varphi}{2} = \frac{\frac{a}{2}}{r_n} = \frac{a}{2r_n} \implies r_n = \frac{a}{2\sin\frac{\varphi}{2}},$$

where

$$\varphi = \frac{360}{n} \implies r_n = \frac{a}{2\sin\frac{180}{n}}.$$

Now we can use either the ionic radius of Li^+ or Cs^+ (careful, Rb^+ doesn't fit into any of the discussed crown ethers!) to work out the polygon side length, a. We must realise that the radius length is equal to the sum of radii of oxygen and alkali metal ion, $r_n = r_O + r_{\text{alk. met.}}$. We obtain

$$a = (r_O + r_{\text{alk. met.}}) \times 2\sin\frac{180}{n} = 210\,\text{pm}.$$

Using the derived formula, we get $r_5 \doteq 178.6\,\text{pm} \implies r_{Na^+} \doteq 104.6\,\text{pm}$; $r_6 = 210\,\text{pm} \implies r_{K^+} = 136\,\text{pm}$.

Note: Actual ionic radii of alkali metals slightly deviate from the values stated in this question. The deviation is not big, though (always just a few pm) and is caused mainly by the fact that the ion-crown ether complex is actually not planar.

Question H.1 (Petr Linhart)

Chaotic analytical chemist Matěj has the task of determining the content of magnesium ions in some bottled water. He planned to use a complexometric titration. In a complexometric titration, an indicator is added to the solution which changes colour when bound to a metal ion. This solution is then titrated with a complexing agent of known concentration which will bind to the metal ion, displacing the indicator and resulting in a colour change.

Matěj plans to use a solution of EDTA as the chelating agent. Unfortunately, he has forgotten the concentration of the EDTA solution he prepared! However, he realises he can still perform the experiment without this information. He first added 0.4 g of magnesium sulfate to 1 ℓ of the bottled water. Then he took equal volumes of the stock and modified samples and performed the titration. He used 13.7 mℓ of titrant for a sample of unmodified bottled water; he used 19.8 mℓ of titrant for the sample enriched with magnesium sulfate. What is the concentration of magnesium ions in water? Report the result in units of $\text{mg}\,\text{dm}^{-3}$. For simplicity, neglect the interference of other ions (e.g. calcium).

Solution:

$181\,\text{mg}\,\text{dm}^{-3}$

Although at first glance it may seem that it is impossible to solve the problem without knowing any of the concentrations, the problem is actually quite simple to solve. A 'specific' figure supplies a known amount of added magnesium sulfate. This method is often used in analytical chemistry and is called the standard addition method. Let's denote by c_A and V_A the concentration and volume of the analyte, V_1 and V_2 the volumes of the first (without addition) and the second titration (with addition), c_T the concentration of the titrant and c_E the concentration of the magnesium ions supplied to the water. We can calculate c_E using the molar mass of magnesium sulfate as

$$c_E = \frac{m_{\mathrm{MgSO_4}}}{M_{\mathrm{MgSO_4}} \times 1\,\ell}.$$

Chelaton 3 binds to all ions in a 1:1 stoichiometric ratio, therefore

$$n_{\mathrm{Mg}} = n_{\mathrm{chelaton}}.$$

Specifically for the first and second titration

$$c_A V_A = c_T V_1,$$

$$c_A V_A + c_E V_A = c_T V_2.$$

The ratio of the second and first equation (2)/(1) is

$$\frac{c_A + c_E}{c_A} = \frac{V_2}{V_1},$$

which is an expression with only one unknown – the titrant concentration c_A. After a simple rearrangement

$$c_A = \frac{V_1 c_E}{V_2 - V_1} = \frac{13.7 \times 0.4}{(19.8 - 13.7) \times 120.4} \doteq 7.46 \times 10^{-3}\,\mathrm{mol\,dm^{-3}},$$

which corresponds to $181\,\mathrm{mg\,dm^{-3}}$ $\mathrm{Mg^{2+}}$.

Question H.2 (Sam Holmes)

You are provided with the chemical structures of a series of common laboratory reagents. Match the reagents to their uses.

i. strong acid

ii. reducing agent

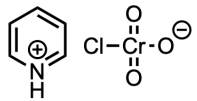
iii. oxidising agent

iv. strong base

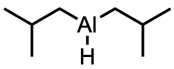
v. halogenating agent

vi. dehydrating agent

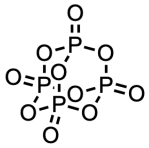
vii. solvent



A



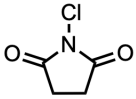
B



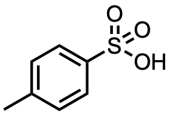
C



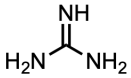
D



E



F



G

Solution:

A – iii, B – ii, C – vi, D – vii, E – v, F – i, G – iv

Perhaps the easiest to spot is the oxidising agent – students will probably know that Cr(VII) can oxidise organic molecules. They will also have seen that phosphorus pentoxide (like phosphoric acid) can be used to dehydrate alcohols, so this must be vi. There are only two molecules left containing halogens – NCS and chloroform. The C−Cl bond is much stronger than the N−Cl bond, so we should conclude that chloroform is relatively inert (a solvent), whereas NCS can be used as an electrophilic source of chlorine. The acid can be identified by analogy with sulfuric acid, in which the hydroxide group is replaced with a tolyl group to make it more soluble in organic solvents and, as a crystalline solid, easier to handle. We are left with the base and the reducing agent to identify. The base is guanidine, which is structurally similar to urea. Many amines, including urea, are bases because they have many lone pairs which can bind to a proton. The reducing agent, DIBAL, has an electron deficient aluminium centre which has only 6 electrons in its valence shell. It is a Lewis acid,

and it can lose the indicated hydride during a reaction with Lewis bases (such as esters), thus acting as a reducing agent. While students will not know how DIBAL functions, they can make the assignment via a process of elimination.

Question H.3 (Stanislav Chvíla)

During inorganic chemistry labs, one of the students lost the lid for the bottle of ferrous sulfate heptahydrate. They tried to hide the container in a cabinet, but it was later discovered by a laboratory technician during an inventory. Knowing that the green powder reacts slowly with air, they endeavoured to find out the extent of the damage.

They weighed out 1.022 g of green shale of unknown purity from the upper layer, dissolved it in 20 ml of diluted sulfuric acid and, after heating, titrated with a potassium permanganate solution of concentration $0.0192\,\mathrm{mol}\,\ell^{-1}$. The mean titre during this experiment was $31.6\,\mathrm{m}\ell$. The laboratory technician repeated the titration for a rock sample from the bottom of the dustpan weighing 1.054 g, where the mean titre was $39.1\,\mathrm{m}\ell$. Based on these titrations, determine the percentage of the ferrous iron which has reacted with air in the upper layer of the open dust box.

Solution:

16.65 %

The reaction is

$$5\,\mathrm{Fe^{2+}} + \mathrm{MnO_4^-} + 8\,\mathrm{H_3O^+} \longrightarrow 5\,\mathrm{Fe^{3+}} + \mathrm{Mn^{2+}} + 12\,\mathrm{H_2O}\ .$$

Top layer:

$$n(\mathrm{MnO_4^-}) = 0.0192\,\mathrm{mol}\,\ell^{-1} \cdot 31.6\,\mathrm{m}\ell = 6.0672 \times 10^{-4}\,\mathrm{mol}$$

$$n(\mathrm{Fe^{2+}}) = 3.0336 \times 10^{-3}\,\mathrm{mol}$$

$$c(\mathrm{Fe^{3+}}) = 2.968 \times 10^{-3}\,\mathrm{mol\,g^{-1}}$$

Bottom layer:

$$n(\mathrm{MnO_4^-}) = 0.0192\,\mathrm{mol}\,\ell^{-1} \cdot 39.1\,\mathrm{m}\ell = 7.5072 \times 10^{-4}\,\mathrm{mol}$$

$$n(\mathrm{Fe^{2+}}) = 3.7536 \times 10^{-3}\,\mathrm{mol}$$

$$c(\mathrm{Fe^{3+}}) = 3.561 \times 10^{-3}\,\mathrm{mol\,g^{-1}}$$

The difference is thus

$$c(\text{bottom}) - c(\text{top}) = 5.93 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$$

and the percentage of reacted $\mathrm{Fe^{2+}}$ reads

$$\frac{5.93 \times 10^{-4}}{3.561 \times 10^{-3}} \cdot 100\,\% \doteq 16.65\,\%.$$

Question H.4 (Sam Holmes)

The death of Queen Elizabeth II in September 2022 was a historic and poignant occasion, involving some interesting chemistry. The body must have been preserved using an embalming fluid, which prevented it from deteriorating during the long ceremonies which marked the occasion. Embalming fluids usually contain formaldehyde, which 'fixes' the proteins in the body by linking nearby amino acid groups together.

Work out which residues in protein fragment A may react with formaldehyde to form cross-links.

Protein fragment A:

...—Gly–Lys–Val–Met–Phe–Gly–Ala–Pro–Lys–Tyr–Leu–Phe–Gly–Ala–Cys—...

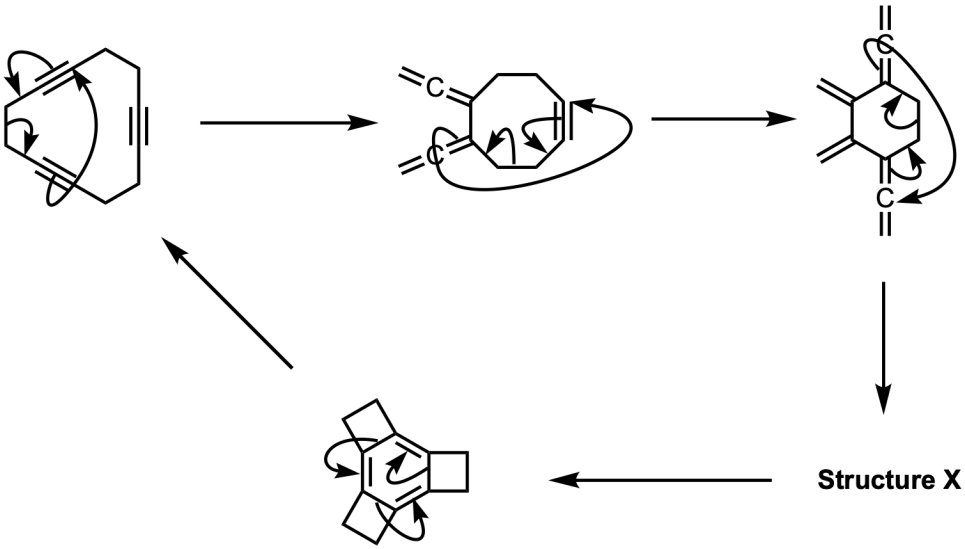
Solution:

Lys, Cys and Tyr

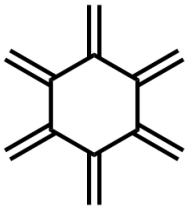
Formaldehyde is an aldehyde – and students should know that aldehydes react with nucleophiles in addition reactions. So the task is to identify the nucleophilic residues which can form a bond to formaldehyde: consulting a list of the amino acids will reveal that these are Lys, Cys and Tyr. Met is not a correct answer, because (like ethers) thioethers can not react with electrophiles – there is no proton on sulfur which can be removed to quench the positively charged intermediate.

Question H.5 (Sam Holmes)

Some valence isomers of $\mathrm{C_{12}H_{12}}$ may interconvert by a series of rearrangements. By following the curly arrows provided, give the *skeletal formula* of structure X.



Solution:



All you need to do is follow the arrows – but this might be harder than it sounds! Where an arrow starts at a double bond, this becomes a single bond; where an arrow starts at a single bond, this bond is broken. When an arrow passes through one carbon atom and arrives at another, a new bond is formed between these atoms; when an arrow ends on a single bond, this becomes a double bond. If you follow these rules judiciously, and then redraw the molecule carefully, the structure of hexaradialene (which is very unstable) can be determined.

Question H.6 (Vojtěch Laitl)

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

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

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

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

with $K_H = 115\,\text{MPa mol}^{-1}\,\text{dm}^3$. Above the diatoms-containing marine water, there is air of atmospheric pressure 101 325 Pa with the amount of nitrogen yielding 79 mol. %. The correlation between reaction half-time $\tau_{1/2}$ and its rate coefficient k is given as

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

Solution:

$0.025\,\text{mol dm}^{-3}$

N_2 partial pressure held above the marine water reads $p(N_2) = 0.79 \cdot 101325$ Pa. This identification and the correlation between reaction half-life and rate coefficient help us to rearrange the stationary rate equation to the form

$$c(NH_4^+) = \frac{p(N_2)}{K_H} \cdot \frac{\tau_{1/2,2}}{\tau_{1/2,1}}.$$

Factoring out the unknown $c(NH_4^+)$ gives

$$c(NH_4^+) = \frac{p(N_2)}{K_H} \cdot \frac{\tau_{1/2,2}}{\tau_{1/2,1}}.$$

Reaction half-lifes and pressure need to be enumerated in consistent units, for instance in min and Pa, respectively, which yields

$$c(NH_4^+) = \frac{0.79 \cdot 101325}{115 \times 10^6} \cdot \frac{1.5 \cdot 60}{2.5} \doteq 0.025\,\text{mol dm}^{-3}.$$

Question K.1 (Vojtěch Laitl)

Electrochemical reduction of carbon dioxide is a promising way to turn this waste product into a useful chemical feedstock. Thermodynamically, the reduction of carbon dioxide is possible, even though current attempts have been failing to overcome its activation barriers.

Consider the complete reduction of CO2 to form methane in an electrochemical cell as follows:

$$\mathrm{CO_2(g)} + 2\,\mathrm{H_2O(l)} \longrightarrow \mathrm{CH_4(g)} + \mathrm{O_2(g)}\ .$$

The total cell pressure is 1 bar. The partial pressures of methane, oxygen, and carbon dioxide are 200 mbar each; the rest of the gas phase is buffered with an inert component.
The redox potential of such a reaction is equal to

$$E = E^{\ominus} - \frac{RT}{8F} \ln\Big(\frac{a(\mathrm{CH_4})a^2(\mathrm{O_2})}{a(\mathrm{CO_2})a(\mathrm{H_2O})}\Big).$$

$E^{\ominus}$ denotes the standard redox potential and $a(\cdot)$ are thermodynamic activities. Let us assume water to be a pure liquid of $a = 1$. For gaseous compounds, dimensionless pressures are to be used, i.e.,

$$a(\cdot) = \frac{p(\cdot)}{1\,\mathrm{bar}}.$$

The reaction proceeds at 298 K, for which the standard Gibbs free energies of formation are known. Calculate the value of the redox potential E.

Compound	$\Delta G^{\ominus}(298\,\mathrm{K})$ $(\mathrm{kJ\,mol^{-1}})$
$\mathrm{CO_2(g)}$	-394.4
$\mathrm{H_2O(l)}$	-237.2
$\mathrm{CH_4(g)}$	-50.6
$\mathrm{O_2(g)}$	0

Hint: If you do not know the relation between the standard reaction Gibbs energy and the standard redox potential (or do not have it to your disposal), you may like to consult the definition of $\Delta_r G$

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln\Big(\frac{a(\mathrm{CH_4})a^2(\mathrm{O_2})}{a(\mathrm{CO_2})a(\mathrm{H_2O})}\Big).$$

Solution:

$-1.05\,\mathrm{V}$

The standard reaction Gibbs energy for the balanced equation is equal to

$$\begin{aligned}\Delta_r G^\ominus &= 2\Delta G^\ominus(\mathrm{O_2}) + \Delta G^\ominus(\mathrm{CH_4}) - \Delta G^\ominus(\mathrm{CO_2}) - 2\Delta G^\ominus(\mathrm{H_2O}) \\ &= -50.6 - 2\cdot 0 + 394.4 + 2\cdot 237.2 = 818.2\,\mathrm{kJ\,mol^{-1}}.\end{aligned}$$

The standard redox potential thereof is given by scaling the value as follows:

$$E^\ominus = -\frac{\Delta_r G^\ominus}{8F} = \frac{-818200}{8F} \doteq -1.06\,\mathrm{V}.$$

If we happen not to know the above relation, we may obtain in by comparing the defining formulae:

$$\Delta_r G = \Delta_r G^\ominus + RT\ln\Big(\frac{a(\mathrm{CH_4})a^2(\mathrm{O_2})}{a(\mathrm{CO_2})a(\mathrm{H_2O})}\Big).$$

$$E = E^\ominus - \frac{RT}{8F}\ln\Big(\frac{a(\mathrm{CH_4})a^2(\mathrm{O_2})}{a(\mathrm{CO_2})a(\mathrm{H_2O})}\Big).$$

Both right-hand sides involve two terms corresponding to the Gibbs energy and the redox potential, respectively. The latter two are related by the factor of $-1/8F$; such scaling must therefore hold for the former two as well. Hence

$$E^\ominus = \frac{-1}{8F}\cdot\Delta_r G^\ominus$$

In our case, the thermodynamic activities of gaseous compounds are directly equal to their pressures (in the multiples of 1 bar); $a(\mathrm{CO_2}) = a(\mathrm{O_2}) = a(\mathrm{CH_4}) = 0.2$. Then, the final enumerating gives

$$E = -\frac{\Delta_r G^\ominus}{8F} - \frac{RT}{8F}\ln\Big(\frac{a(\mathrm{CH_4})a^2(\mathrm{O_2})}{a(\mathrm{CO_2})a(\mathrm{H_2O})}\Big) = -\frac{818200}{8F} - \frac{298R}{8F}\ln\Big(\frac{0.2^2\cdot 0.2}{0.2\cdot 1}\Big) = -1.05\,\mathrm{V}.$$

Since $E < 0$, the reaction is not spontaneous. The magnitude of the resultant potential corresponds to the voltage which we must apply on the system (similarly to, e.g., electrolysis). However, $U = 1.05\,\mathrm{V}$ is definitely not an unfeasibly high voltage value.

Question K.2 (Petr Linhart)

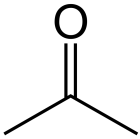
Martin, an analytical chemist, was assigned a task of determining the identity of a pure liquid substance. As a consequence of the increase in energy prices, his boss decided to cut their expenses dramatically and remove all the power cords from Martin's precious spectrometers. Martin had no other choice than to approach the task using old-school techniques.

Firstly, he tried to mix the substance with polar and nonpolar solvents. It was miscible with water, methanol, hexane and even benzene. Its odour led him to speculate it was an organic compound. That's why he then performed a Lassaigne's test to detect the presence of heteroatoms in the molecule. In the test, the sample is melted with sodium and the resulting products are tested for the presence of sodium sulfide, halogenides, thiocyanate, and cyanide. All these tests were negative. In order to determine the mass fraction of carbon and hydrogen in the liquid, Martin burned 0.5000 g of the compound and collected the gases that were released by absorbing it, using magnesium perchlorate (which is hygroscopic) and asbestos (which absorbed the remaining gaseous products). The magnesium perchlorate increased in mass by 0.465 g, and the asbestos increased in mass by 1.1866 g. He determined the molar mass using the Viktor Meyer method: he vapourised 0.5192 g of the liquid in a small furnace. The detected volume difference, measured at a pressure of 101.0 kPa and temperature of 19 °C (they decided to cut their gas bill as well), was $\Delta V = 215\,\mathrm{cm}^3$.

Determine the molecular formula of the compound and provide its structural formula, knowing that reaction of the compound with excess of iodine in basic solution yields yellow crystals of iodoform (triiodomethane).

Solution:

acetone



The solubility information does not tell much since the compound dissolves in both polar and non-polar solvents. We can estimate that the compound has both polar and non-polar parts.

We also know that it is an organic compound. Lassaigne's test excluded the presence of sulfur, nitrogen and halogens. The compound therefore includes only carbon,

hydrogen and possibly oxygen atoms. The necessity of polarity of the molecule confirms the presence of oxygen in it. The compound has a molecular formula $C_xH_yO_z$. Upon burning, carbon dioxide and water are formed:

$$C_xH_yO_z + \frac{2x + y - z}{2} O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$$

Next, let's determine the molar mass via the Viktor Meyer method. We will use the ideal gas equation of state:

$$pV = \frac{m}{M_m}RT \implies M_m = \frac{mRT}{pV} = \frac{0.5192 \times 8.314 \times (19 + 273.15)}{101.0 \times 10^3 \times 215 \times 10^{-6}} \doteq 58.075\,\mathrm{g\,mol^{-1}}.$$

Molar masses of water and carbon dioxide are $M_m(CO_2) = 46\,\mathrm{g\,mol^{-1}}$ a $M_m(H_2O) = 18\,\mathrm{g\,mol^{-1}}$.

We can work out the amounts of substance of reactants (compound A) and products:

$$n(\mathrm{A}) = \frac{m(\mathrm{A})}{M_m(\mathrm{A})} = \frac{0.5}{58.075} \doteq 0.00861\,\mathrm{mol},$$

$$n(H_2O) = \frac{m(H_2O)}{M_m(H_2O)} = \frac{0.465}{18} \doteq 0.0258\,\mathrm{mol},$$

$$n(CO_2) = \frac{m(CO_2)}{M_m(CO_2)} = \frac{1.1866}{46} \doteq 0.0258\,\mathrm{mol}.$$

From that we can see that the ratio of amounts of substance is

$$n(\mathrm{A}) : n(H_2O) : n(CO_2) = 0.00861 : 0.0258 : 0.0258 \doteq 1 : 3 : 3,$$

comparing this with the equation, we obtain $x = 3$ and $y = 2 \times 3 = 6$. The compound has the molecular formula $C_3H_6O_z$. Since we know the total molar mass, we know that we are $58.075 - 3 \times 12 - 6 \times 1 \doteq 16.08\,\mathrm{g\,mol^{-1}}$ shy, this corresponds to 1 oxygen atom.

The molecular formula therefore is C_3H_6O.

The reaction with iodine is a substitution at α-carbonyl atom (Lieben haloform reaction) which yields triiodomethane and acetic acid.

The molecule therefore needs to have a methyl group next to the carbonyl group. There is just one possible structure satisfying everything: acetone.

Question K.3 (Sam Holmes)

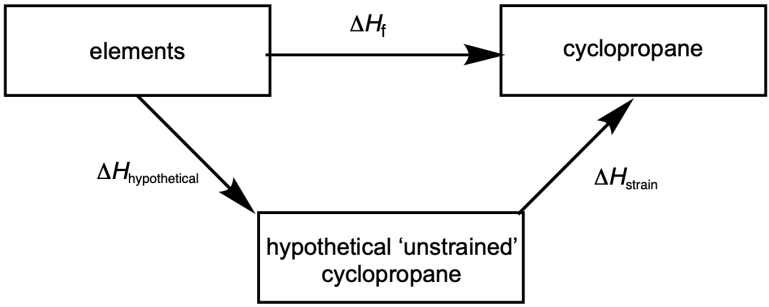
When the bond angles in a molecule differ from the ideal angle, the molecule is said to be strained. For strained molecules, we can calculate the 'strain energy', which is the increase in chemical potential energy of a molecule compared to a theoretical unstrained molecule with exactly the same type and number of bonds.

By way of example, the strain energy of cyclopropane would be calculated by finding the difference between the enthalpy of formation of cyclopropane and that of the non-existent molecule containing 3 C−C single bonds and 6 C−H bonds but no ring strain. We can calculate the 'theoretical' enthalpy of formation of this non-existent molecule using the average C-C and C-H bond enthalpies, via a Hess cycle as shown below.

Cubane is one of the most strained molecules to have been synthesised on a large scale. Work out the strain energy of cubane using the thermodynamic data given. Note that the bond dissociation enthalpy and strain energy are measured in the gas phase. The melting point of cubane is $t_m = 133.5\,^{\circ}\mathrm{C}$.

Bond dissociation enthalpies:
C−C = 348 kJ mol^{-1}; C−H = 414 kJ mol^{-1}; H−H = 431 kJ mol^{-1}

Enthalpies of formation and vapourisation: $\Delta_{\mathrm{f}}H(\mathrm{cubane}) = 542\,\mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{vap}}H(\mathrm{C}) = 720\,\mathrm{kJ\,mol^{-1}}$; $\Delta_{\mathrm{vap}}H(\mathrm{cubane}) = 55.2\,\mathrm{kJ\,mol^{-1}}$.

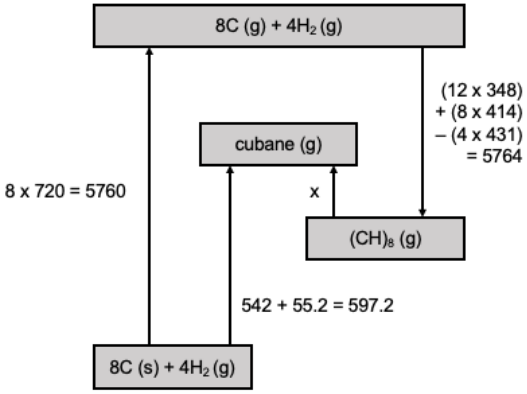


Hess's Law:

$$\Delta H_{\mathrm{f}} = \Delta H_{\mathrm{hypothetical}} + \Delta H_{\mathrm{strain}}$$

Solution:

$601\,\mathrm{kJ\,mol^{-1}}$. See attached diagram.



Question K.4 (Vojtěch Laitl)

Plug-flow reactors (PFR) are a useful model used to describe a number of chemical processes. The reactants are passed through a PFR (typically a long pipe) with a constant velocity in one direction and are ideally mixed in all remaining directions. The reaction kinetics can then be described using basic kinetic formulae, despite having a spatial component.

In the chemical industry, PFRs can be used to oxidise cyclohexane with airborne oxygen, which is the first step in polyamide fabrications, according to the following equation:

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

Cyclohexane is both a reactant and the solvent. This means we have a pseudo-first order reaction, where the concentration of oxygen is given by

$$[\mathrm{O_2}] = [\mathrm{O_2}]_0 \exp(-k\tau),$$

where 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). Consider a tubular reactor of length 10 m, filled with cyclohexane. Oxygen flows through the reactor at a temperature of 300 K, for which the rate coefficient is $3.05\,\mathrm{s}^{-1}$. If the stream velocity is $6.6\,\mathrm{m\,s}^{-1}$, 99 % of the O_2 is converted ($[O_2] = 0.01\ [O_2]_0$). Calculate the stream velocity which would result in 95% conversion of O_2.

Solution:

$10.2\,\mathrm{m\,s}^{-1}$

The residence time is directly given by $\tau = \frac{l}{v}$, as to describe the steady flow. That gives

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

and, after rearranging

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

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

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

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.5 (Anh Phung)

Fullerenes are a group of well-known carbon allotropes with hollow spherical structure. These novel nanomaterials are of great research interest in the field of material science and nanotechnology. Fullerenes with n carbon atoms have 12 pentagonal and $(\frac{n}{2}–10)$ hexagonal arrangements, where n must be an even number and $n > 20$.

One (purely hypothetical) application of large fullerenes ($n \geq 1000$) is making a 'molecular balloon' that can float in air. To achieve this, the density of the fullerene molecule must be lower than that of air. You can take the density of air at 298 K and 1 atm to be $1.18\,\mathrm{kg\,m^{-3}}$. Calculate the minimum number of carbon atoms, n, required to satisfy this condition. Assume the carbon-carbon length in fullerene is uniformly 0.14 nm, the molecule can be treated as a perfect sphere and is rigid enough to retain its structure under air pressure.

Hint: The area of a regular pentagon is:

$$S_{\text{pentagon}} = \frac{5a^2}{4\,\tan(36°)},$$

and the area of a regular hexagon is:

$$S_{\text{hexagon}} = \frac{3\sqrt{3}}{2}a^2,$$

where a is the side length of the polygon.

Solution:

1.96×10^9

The surface areas of a pentagon and hexagon in a fullerene molecule, respectively, are:

$$S_5 = \frac{5 \times 0.14^2}{4\tan(36°)} = 0.0337\,\mathrm{nm^2},$$

$$S_6 = \left(\frac{3 \times \sqrt{3}}{2}\right) \times 0.14^2 = 0.0509\,\mathrm{nm^2}.$$

Hence, the total surface area of the entire molecule is:

$$S_{\text{tot}} = S_5 \times 12 + S_6 \times \left(\frac{n}{2} - 10\right) = 0.0337 \times 12 + 0.0509 \times \left(\frac{n}{2} - 10\right) = 0.0255n - 0.1046\,\mathrm{nm^2}.$$

Since we assume the fullerene is a perfect sphere, the surface area is also equal to:

$$S_{\text{tot}} = 4\pi r^2.$$

Equating and rearranging, we obtain the expression for the radius, in terms of n:

$$r = \sqrt{\left(\frac{0.0255n - 0.1046}{4\pi}\right)}.$$

The mass of one fullerene molecule with n carbon atoms is:

$$m = Mr(\mathrm{C}) \times \frac{n}{\mathrm{N_A}}.$$

The volume of a sphere (and hence the fullerene) is:

$$V = \frac{4}{3}\pi r^3.$$

Hence, we obtain an expression for the density of one fullerene molecule, with respect to variable n:

$$\rho_{\text{fullerene}} = \frac{m}{V} = \frac{\frac{12.01n}{\mathrm{N_A}}}{\frac{4}{3}\pi \times \left(\frac{0.0255n - 0.1046}{4\pi}\right)^{\frac{3}{2}}}\ \mathrm{g\ nm^{-3}}.$$

For the fullerene molecule to float, $\rho_{\text{air}} > \rho_{\text{fullerene}}$. Hence, we obtain the inequality:

$$1.18 \times 10^{-24}\,\mathrm{g\,nm^{-3}} > \frac{\frac{12.01n}{\mathrm{N_A}}}{\frac{4}{3}\pi \times \left(\frac{0.0255n - 0.1046}{4\pi}\right)^{\frac{3}{2}}}\ \mathrm{g\ nm^{-3}}.$$

This can be solved for n, using a calculator, which gives:

$$n > 1.96 \times 10^9.$$

Hence, the minimum number of carbon atoms needed for a fullerene molecule to float on air is 1.96×10^9, or $\mathrm{C}_{1960000000}$. Of course, this structure is entirely hypothetical. Even as $n > 1000$, the molecule quickly deviates from a perfect sphere.

Question K.6 (Sam Holmes)

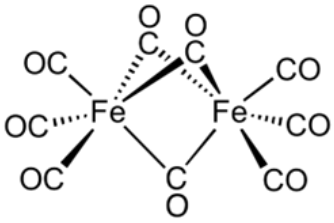
The 18-electron rule is used to predict the bonding and properties of metal complexes. If a metal centre has 18 electrons in its valence (bonding) orbitals, the arrangement is often stable. Electrons are counted by adding up the valence electrons of the metal and any valence electrons donated to it by its ligands, to give the "electron count".

Diiron nonacarbonyl, $\mathrm{Fe_2(CO)_9}$, is a molecular species containing two metal centres, both of which have their ligands arranged in an octahedral geometry. Draw the structure of the molecule. Also, give the electron count at each metal centre in the presence and absence of a metal-metal bond between the two iron centres: does the 18 electron rule predict such a bond to be electronically favourable?

Solution:

Structure, 17 electrons without the metal–metal bond, 18 electrons with the metal–metal bond.

We can work out that for each metal to have six ligands (octahedral geometry), then three must be shared between them. Therefore the CO ligands bridge the two metal centres.



To work out if there is a metal-metal bond, use the 18 electron rule:

- Fe has 8 valence electrons.
- Each terminal CO donates a lone pair $\implies 3 \times 2 = 6$ electrons.
- Each bridging CO only has 2 electrons to donate, so one goes to each centre $\implies$ 3 electrons.
- **So 17 electrons without a metal-metal bond.**

If we add a metal-metal bond, we have shared another electron: electron count increases by 1 and we have **18 electrons with a metal-metal (single) bond**.

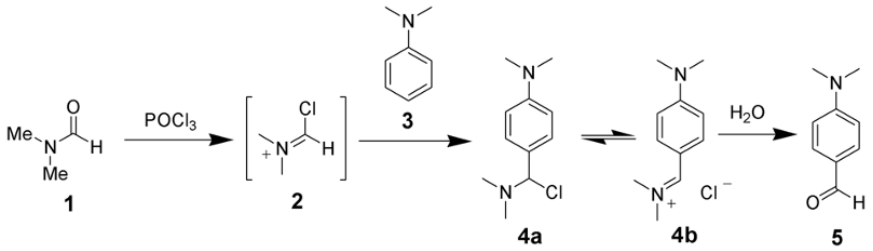
So we would predict a Fe-Fe bond to be present using this rule. From the X-ray structure, we can see that in fact the two Fe centres are too far apart to interact significantly, presumably due to sterics. **(structure and points in bold sufficient for the answer)**

Question L.1 (Ondřej Daněk)

Before the discovery of modern methods, the CHO group could only be introduced to the aromatic nucleus using toxic reagents such as HCN/HCl (Gattermann reaction) or CO/HCl (Gattermann–Koch reaction) in the presence of a Lewis acid catalyst.

In Vilsmeier–Haack formylation, we avoid the use of poisonous gases and instead use hepatotoxic but at least liquid DMF (N,N-dimethylformamide) and phosphoryl chloride ($POCl_3$).

You are provided with a mechanism for the Vilsmeier–Haack reaction demonstrated on a scheme of the formylation of dimethylaniline, which forms 4-(N,N-dimethylamino)benzaldehyde. $POCl_3$ reacts with DMF to generate an iminium cation, which then undergoes an electrophilic aromatic substitution reaction with dimethylaniline, forming an iminium chloride. Hydrolysis of the iminium cation then generates the aldehyde product.



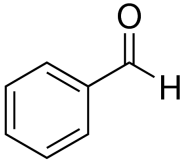
Draw the product of the Vilsmeier–Haack formylation of benzene where heavy water (D_2O) is used for the hydrolysis in the final step instead of normal water.

Solution:

In order to solve this question, we need to realise how the last step of Vilsmeier–Haack reaction (the imine hydrolysis) proceeds:



It is apparent that the solvent hydrogen (or deuterium atoms) do not end up in the product, hence the answer is just benzaldehyde (with no deuterium incorporation).

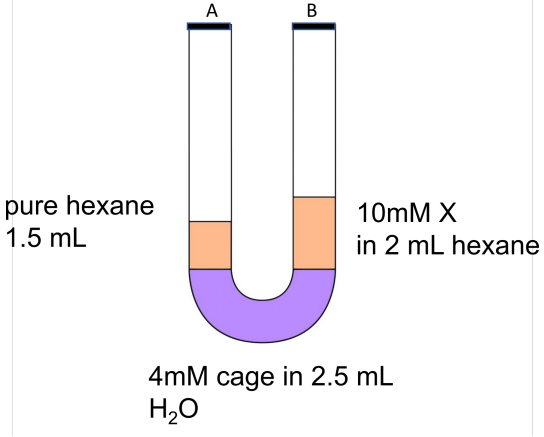


Question L.2 (Mirka Novoveská)

Metal-organic cages are large molecules made up of metal ions and organic ligands, forming a cage structure with one (or more) cavities. They are of interest in chemical research both for their unique topologies and properties, and because of their potential applications in (for example) chemical separation.

For example, it is possible to use a solution of a metal-organic cage as a liquid membrane. Consider the system illustrated in the figure - at the start, there is 1.5 mℓ of hexane in arm A of the U-tube and 2 mℓ of 10mM solution of X in hexane in arm B. The liquid membrane separating them consists of 2.5 mℓ of 4mM cage solution in water. Both of the arms are sealed and there is a slightly higher pressure in arm A to keep the level of the liquid lower than in arm B. Compound X can be readily encapsulated by the cage at the interface between hexane and the membrane and transported between the arms, the equilibrium constant K for the encapsulation of X into cage is $K = 0.1$. Assume X is insoluble in water, and that the cage is insoluble in hexane.

What will be the concentration of X in arm A, arm B, and in the liquid membrane (encapsulated in the cage) when equilibrium is reached? Give answers in mM and to 3 decimal places.



Solution:

[X(arm A)] = [X(arm B)] = 4.789 mM, [X(cage)] = 1.295 mM

The equilibrium constant for encapsulation can be expressed as $K = \frac{[\mathrm{X(cage)}]}{[\mathrm{X}][\mathrm{cage}]}$. Since we know the total concentration of the cage is $C(\mathrm{cage}) = 4\,\mathrm{mM} = [\mathrm{cage}] + [\mathrm{X(cage)}]$, we can express K as

$$K = \frac{[\mathrm{X(cage)}]}{[\mathrm{X}](C(\mathrm{cage}) - [\mathrm{X(cage)}])},$$

and hence get

$$[\mathrm{X(cage)}] = K \times C(\mathrm{cage}) \times \frac{[\mathrm{X}]}{1 + K \times [\mathrm{X}]}.$$

Now we need to write an equation for the total amount of X. Since the layers have different volumes, we have to use: number of moles (n) = concentration × volume. At the beginning, X is only in arm B: $n(\mathrm{tot}) = 2\,\mathrm{m}\ell \times 10\,\mathrm{mM} = 20\,\mu\mathrm{mol}$. At the end, X has the same concentration in both arms since the transport is driven by concentration gradient only, but the concentration of encapsulated X is different and depends on K:

$$\begin{aligned} n(\mathrm{tot}) &= (1.5\,\mathrm{m}\ell + 2\,\mathrm{m}\ell) \times [\mathrm{X}] + 2.5\,\mathrm{m}\ell \times [\mathrm{X(cage)}] \\ &= 3.5\,\mathrm{m}\ell \times [\mathrm{X}] + 2.5\,\mathrm{m}\ell \times K \times C(\mathrm{cage}) \times \frac{[\mathrm{X}]}{1 + K \times [\mathrm{X}]}. \end{aligned}$$

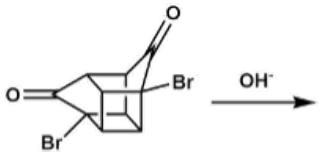
Equating $n(\mathrm{tot})$ at the beginning and at equilibrium and multiplying both sides by $1 + K \times [\mathrm{X}]$ will yield a quadratic equation with **one positive (the answer)** and one negative **solution** (unphysical) for [X]. Substituting this value into the expression for [X(cage)] will give us the concentration of X encapsulated in the cage.

The values are: [X(arm A)] = [X(arm B)] = 4.789 mM, [X(cage)] = 1.295 mM.

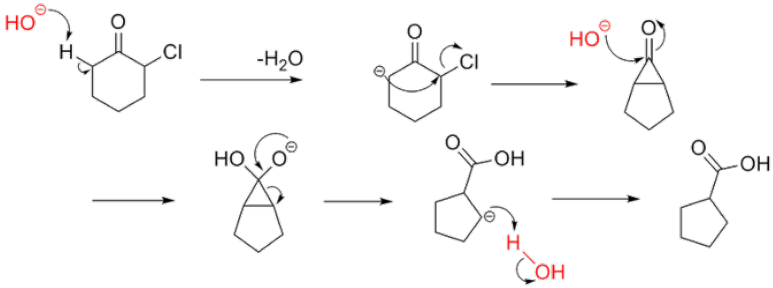
Question L.3 (Ondřej Daněk)

The Favorskii rearrangement is a reaction which converts cyclic alpha-haloketones into exocyclic carboxylic acids with the cycle being reduced in size by one carbon. The mechanism of the Favorskii rearrangement is shown in the appendix.

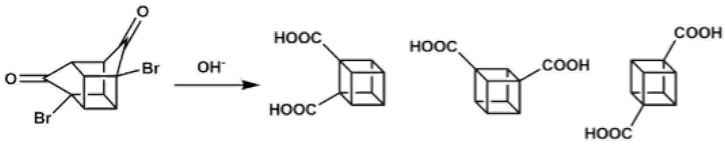
Draw structures of all possible products of the following reaction, in which the Favorskii rearrangement proceeds twice.



The Favorskii rearrangement:



Solution:



Question L.4 (Peter Rukovanský)

One mole of a solid oxide B is formed during the thermal decomposition of one mole of a salt A. The mass of the vessel contents decreases by 39.7 % during the decomposition. Apart from B, there are also two other products formed: one mole of a gas C and ν_D moles of gas D. The gas C has a density $\rho_C = 1.2506\,\mathrm{g}\,\ell^{-1}$ at atmospheric pressure and at 0 °C.

When the gases produced from the decomposition are passed through a tube filled with white copper sulphate powder, parts of the white powder turn blue. The conditions are set so that all reactions in the tube occur quantitatively (to the full extent). After the decomposition of 1.000 g of A, the mass of copper sulphate powder

increased by 286 mg. At the tube entreace, the gases were tested with a wet universal *p*H indicator paper and showed no reaction.

Electrolysis of an aqueous solution of A produces a metal on the cathode, due to a reduction of a component of the anion. When the metal was carefully collected and weighed, it was found to be 41.27 % of the mass of A that had been electrolysed. This element was also found to make up 68.42 % of oxide B by mass.

Identify compounds A to D and write down the balanced chemical equation for the thermal decomposition of A, including state symbols.

Solution:

We first need to identify products C and D. We can identify product C as follows: We can calculate the molar mass of C using the ideal gas equation of state:

$$pV = nRT,$$

From which we derive:

$$pM = \rho RT \implies M = \frac{\rho RT}{p},$$

where M is the molar mass and ρ is the density of the gas.

Substitute in quantities for product C:

$$M_{\mathrm{C}} = \frac{1.2506 \times 10^3 \times 8.314 \times 273.15}{101325} = 28\,\mathrm{g\,mol^{-1}}.$$

Using the fact that C is an inert gas and its mass, we deduce that C is nitrogen N_2. We deduce that D is water H_2O based on the facts that it dyes copper sulphate blue and is neutral (not ammonia).

Mass of B is $w_{\mathrm{B}} = 100\,\% - 39.7\,\% = 60.3\,\%$ of the mass of A. Mass of water produced is $w_{\mathrm{D}} = \frac{0.286\,\mathrm{g}}{1.000\,\mathrm{g}} = 28.6\,\%$ of the mass of A. Mass of nitrogen produced is then $w_{\mathrm{C}} = 100\,\% - 60.3\,\% - 28.6\,\% = 11.1\,\%$ of the mass of A.

We can use this to calculate the stoichiometric coefficient for water ν_D and the molar masses of A and B, M_{A} and M_{B} respectively

$$M_{\mathrm{A}} = \frac{M_{\mathrm{C}}}{w_{\mathrm{C}}} = \frac{28\,\mathrm{g\,mol^{-1}}}{0.111} = 252\,\mathrm{g\,mol^{-1}};$$

$$M_{\mathrm{B}} = M_{\mathrm{C}}\frac{w_{\mathrm{B}}}{w_{\mathrm{C}}} = 28\,\mathrm{g\,mol^{-1}} \times \frac{0.603}{0.111} = 152\,\mathrm{g\,mol^{-1}}.$$

$$\nu_{\mathrm{D}} = w_{\mathrm{D}} \frac{M_{\mathrm{A}}}{M_{\mathrm{D}}} = 0.286 \times \frac{252\,\mathrm{g\,mol^{-1}}}{18\,\mathrm{g\,mol^{-1}}} = 4.$$

We can use whatever metal mass percentage information to work out the remaining unknown atoms. We can notice that the metal accounts for $M_{\mathrm{metal}} = 252 \times 0.4127 = 104\,\mathrm{g\,mol^{-1}}$. Therefore, in A, we have

$$M_{\text{unaccounted for}} = M_{\mathrm{A}} - M_{\mathrm{C}} - 4 \times M_{\mathrm{D}} - M_{\mathrm{metal}} = 252 - 28 - 4 \times 18 - 104 = 48\,\mathrm{g\,mol^{-1}}.$$

Since B is an oxide, these atoms are oxygen atoms. B contains $\frac{48}{16} = 3$ oxygen atoms.

Overall, we have $4 + 3 = 7$ oxygen atoms in A. This is a high number for a salt of a simple acid, the anion probably contains 2 atoms of a metal with molar mass $\frac{104}{2} = 52\,\mathrm{g\,mol^{-1}}$. This corresponds to chromium. We could also work this out differently because there is no metal with the molar mass $104\,\mathrm{g\,mol^{-1}}$.

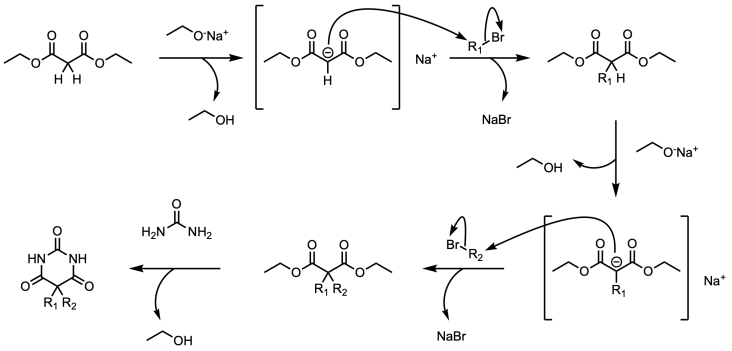
The formula of A therefore is $(\mathrm{NH_4})_2\mathrm{Cr_2O_7}$, it is ammonium dichromate.

The decomposition reaction is

$$(\mathrm{NH_4})_2\mathrm{Cr_2O_7\,(s)} \longrightarrow \mathrm{Cr_2O_3\,(s)} + \mathrm{N_2\,(g)} + 4\,\mathrm{H_2O\,(g)}\ .$$

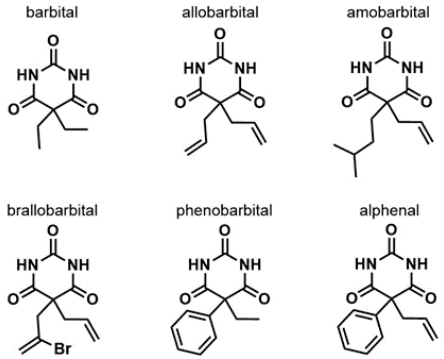
Question L.5 (Jiří Ledvinka)

Barbiturates can be considered the first modern anaesthetics: they largely replaced chloroform, chlorobutanol and chloral hydrate in healthcare settings. Barbituric acid itself, which is not biologically active, was synthesized by Adolf von Baeyer as early as 1864 by condensation of diethyl malonate and urea. A similar synthesis is still used today for the synthesis of a number of barbiturates:



Diethyl malonate is first deprotonated with sodium ethoxide and the resulting carbanion is alkylated with an appropriate alkylating agent. This sequence is repeated once more with another alkylating agent (which may or may not be the same as the first), and the product of the second alkylation is subsequently subjected to condensation with urea to form the corresponding barbiturate.

Which of the following barbiturates cannot be prepared by the above sequence?



Solution:

Alphenal and phenobarbital: we can't get nucleophilic substitution on an (unfunctionalized) aromatic ring.

Question L.6 (Terezie Císařová)

Muscular irradiation

Sources of radioactive radiation are not only well-known emitters and radioactive ores, we ourselves are also a source of radiation. One of the sources of radioactive radiation in the human body is the potassium isotope $^{40}_{19}\mathrm{K}$. This constitutes 0.0117 % of the total occurrence of potassium. The most is accumulated in the muscles, where there are 2 g of potassium per 1 kg of muscle mass. Potassium does not accumulate in human fat. The isotope $^{40}_{19}\mathrm{K}$ decays by β^- decay into $^{40}_{20}\mathrm{Ca}$ and an antineutrino, the energy of the β^- particle is 1.31 MeV. The decay constant λ of potassium $^{40}_{19}\mathrm{K}$ is $5.54\,\mathrm{y}^{-1}$.

Let us assume a 60 kg girl who may spend every night (8 hours) of her entire life (60 years) accompanying either a 100 kg muscular man (89 % of muscle mass) or a

person of the same weight but higher fat percentage. The latter has 54 % muscle in his body, and the radiation from it is shielded by another 4 cm thick layer of fat whose half-thickness is 25 cm (the definition of half-thickness is similar to the definition of half-life). Give the ratio of radioactive dosages to which the girl is exposed in both cases (i.e., the dosage corresponding to accompanying an athlete divided by that inflicted by a fat man). The molecular weight of $^{40}_{19}\mathrm{K}$ is $39.96\,\mathrm{g\,mol^{-1}}$.

Solution:

MM – muscular man
BB – bulky boi

The radioactive dosage is defined as $\frac{E}{m}$, for the total energy E of all β^- particles absorbed by a body of mass m. The number of β–particles is equal to the number of decayed $^{40}_{19}\mathrm{K}$ nuclei. The total amounts of potassium borne by either of the boys read

$$N_\mathrm{K} = n_\mathrm{K} \times \mathrm{N_A} = \frac{m_\mathrm{K}}{M_\mathrm{K}} \times \mathrm{N_A} = \frac{m_\mathrm{body} w_\mathrm{muscle} w_\mathrm{K} m_\mathrm{K\text{–}muscle}}{M_\mathrm{K}} \times \mathrm{N_A},$$

for m_body being the total body mass w_muscle the percentage of muscle masses, w_K the $^{40}_{19}\mathrm{K}$ occurrence, and $m_\mathrm{K\text{–}muscle}$ the mass of potassium given per 1 kg of muscle weight.

$^{40}_{19}\mathrm{K}$ decays in accordance with the decay law, stating the number of intact nuclei to be $N = N_0 \exp(-\lambda t)$ with N_0 corresponding to the total N_K content. The number of decay nuclei and hence the β^- particles emitted then reads

$$N_{\beta^-} = N_0 - N = N_0(1 - \exp(-\lambda t)).$$

As opposed to the athlete, the lady sleeping next to a fat boy is moreover only exposed to a certain fraction of β^- particles emitted. Due to the fat tissue shielding, the effective energy absorbed yields

$$E = E_0 \exp\Big(-\frac{\ln(2)}{\mu} l\Big).$$

where μ is the half-thickness of the fat tissue and l the actual thickness thereof. Coupling the above formulae into the definiton of radioactive dosage gives

$$\begin{aligned} D &= \frac{E}{m_\mathrm{girl}} \\ &= \frac{E_{\beta^-} N_{\beta^-}}{m_\mathrm{girl}} = \frac{\frac{m_\mathrm{body} w_\mathrm{muscle} w_\mathrm{K} m_\mathrm{K\text{–}muscle}}{M_\mathrm{K}} \times \mathrm{N_A} \times (1 - \exp(-\lambda t)) \times \exp(-\frac{\ln(2)}{\mu} l)}{m_\mathrm{girl}}, \end{aligned}$$

(for an athlete, $l_{\mathrm{MM}} = 0$).

Absolute dosages may be calculated over the given period of time; however, factoring out the desired ratio introduces the following simplification

$$\begin{aligned}\frac{D_{\mathrm{MM}}}{D_{\mathrm{BB}}} &= \frac{\frac{E_{\beta^-} N_{\beta^-;\mathrm{MM}}}{m_{\mathrm{girl}}}}{\frac{E_{\beta^-} N_{\beta^-;\mathrm{BB}}}{m_{\mathrm{girl}}}} \\ &= \frac{\frac{m_{\mathrm{body}} w_{\mathrm{muscle;MM}} w_{\mathrm{K}} m_{\mathrm{K-muscle}}}{M_{\mathrm{K}}} \times \mathrm{N_A} \times (1 - \exp(-\lambda t)) \times \exp(-\frac{\ln(2)}{\mu} l_{\mathrm{MM}})}{\frac{m_{\mathrm{body}} w_{\mathrm{muscle;BB}} w_{\mathrm{K}} m_{\mathrm{K-muscle}}}{M_{\mathrm{K}}} \times \mathrm{N_A} \times (1 - \exp(-\lambda t)) \times \exp(-\frac{\ln(2)}{\mu} l_{\mathrm{BB}})} \\ &= \frac{w_{\mathrm{muscle;MM}}}{w_{\mathrm{muscle;BB}} \times \exp(-\frac{\ln(2)}{\mu} l_{\mathrm{BB}})}.\end{aligned}$$

By enumerating, we get

$$\frac{D_{\mathrm{MM}}}{D_{\mathrm{BB}}} = \frac{0.89}{0.54 \times \exp(-\frac{\ln(2)}{25 \times 10^{-2}} \times 4 \times 10^{-2})} \doteq 1.84.$$

The lady accompanying the athlete is thus exposed to 1.84-times higher radioactive dosage.

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