3rd Cambridge Chemistry Race: Questions and Solutions



chemistryrace

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Online round

Question a.1 (Sam Holmes)

There are frequent fears of a helium crisis, as demand often exceeds supply. Helium is formed by radioactive decay of uranium in the crust and accumulates in pockets deep beneath the surface. This makes helium hard to find, and expensive to extract.

Helium is unusual because, if it is not recaptured after use, it has sufficiently low density to escape the Earth's gravity. Work out the density of helium at RTP (25 °C, 100 kPa).

Solution:

Into the definition of density, we plug in mass as the product of molar quantity and molar mass. Molar quantity can be determined from the ideal gas equation. Since density is an intensive quantity, volume is canceled out in the formula.

$$\rho = \frac{m}{V} = \frac{M \times n}{V} = \frac{M \times p \times V}{R \times T \times V} = \\ = \frac{M \times p}{R \times T} = \frac{4\,\mathrm{g\,mol^{-1}} \times 100\,\mathrm{kPa}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 298\,\mathrm{K}} = 0.1614\,\mathrm{g\,l^{-1}}$$

Question a.2 (Milada Peřinová)

Vitamin C is probably the most used supplement for boosting immunity. It is usually sold in the form of pills or gelatin capsules. However, in our task, we will take a look at the fizzy tablet Celaskon (for making into a beverage). It contains: ascorbic acid, citric acid, sorbitol, sodium bicarbonate, lactose, orange aroma, macrogol 6000, acesulfame potassium and Allura red AC. What gas is created and helps with pill disintegration upon contact with water during beverage preparation?

Solution:

After the fizzy tablet has been thrown into water, carbon dioxide (CO_2) is released because of an acid-base reaction between acids (citric and ascorbic) and a base (sodium bicarbonate).

Question a.3 (Sam Holmes)

How many O_2 molecules are needed to fully oxidise 1 molecule of propane-1,2-diol?

Solution:

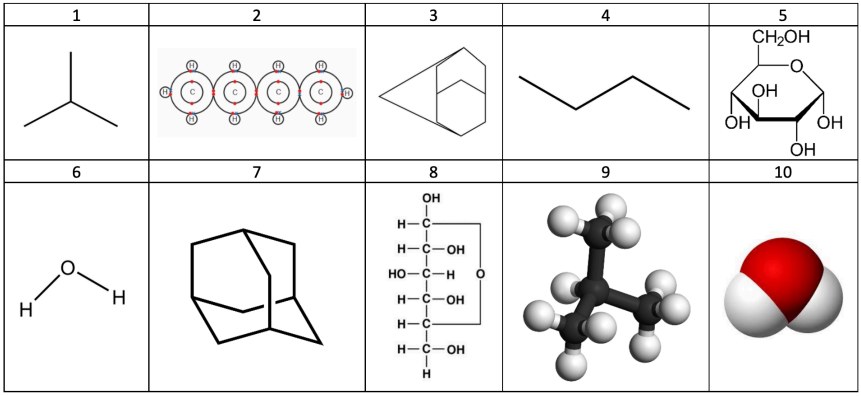
You might be tempted to stop at the ketone or carboxylic acid, but remember that the highest possible level of oxidation for carbon is CO_2, *i.e.* combustion. The reaction, therefore, is

$$C_3H_8O_2 + 4\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$$

and four oxygen molecules are needed.

Question a.4 (Richard Veselý)

Molecules can be represented in many ways and hence it is very useful to be able to make sense of different, not necessarily clear, representations of molecules. Here, you have an opportunity to practise that skill. Your task is to order images 1-10 into 5 pairs so that the images in each pair represent the same molecule.



Solution:

1–9, 2–4, 3–7, 5–8, 6–10. Structures 1, 3, 4, 5, 7 are drawn in such a way that each line band represents a carbon atom with that many hydrogens such that the carbon atom is tetravalent. In picture 2, the red dots represent electrons and the letters correspond to the nuclei of corresponding elements (black circles have no meaning). In images 9 and 10, white balls represent hydrogen atoms, black balls represent carbon atoms and red balls represent oxygen atoms.

Question a.5 (Bence Csakany)

The following experimental procedure was followed to synthesise phenol from Bromobenzene in a one to one reaction.

The Bromobenzene (1 mmol), *n*-$Bu_4NOH \cdot 5\,H_2O$ (544 mg, 3 mmol) an excess, and H_2O (0.6 ml) were added over 0.1 h to a stirred solution of CuI (19.0 mg, 10 mol%) and 8-hydroxyquinaldine (31.8 mg, 20 mol%, catalytic) in DMSO (0.4 ml), and the reaction mixture was stirred at 120 °C. The progress of the reaction was monitored by TLC (mobile phase EtOAc-hexane 1 : 9). After reaching full conversion the reaction mixture was cooled to r.t. and acidified with 0.5 M HCl (0.5 ml). The resulting mixture was extracted with EtOAc (30 ml) and dried (Na_2SO_4). Evaporation of the solvent gave a residue that was purified by column chromatography (short pad of silica gel, EtOAc-hexane) to yield phenol (0.0894 g). Calculate the yield of the reaction as a percentage. The molar mass of phenol is 94.11 g/mol.

Solution:

Stoichiometry of the reaction is 1 : 1 and the limiting reactant is bromobenzene (the other reactant is in excess), so the yield of the reaction can be calculated as

$$\text{yield} = \frac{n_{\text{phenol}}}{n_{\text{bromobenzene}}} = \frac{\frac{m_{\text{phenol}}}{M_{\text{phenol}}}}{n_{\text{bromobenzene}}} = \frac{\frac{0.0894}{94.11}}{0.001} \doteq 95\,\%.$$

The procedure followed is irrelevant for the calculation.

Question a.6 (Martin Balouch)

Biochemist Jarry was interested in the purity of a local brook. He was aware that one of the best ways to do this is to measure biochemical oxygen demand. Unfortunately, he did not have access to proper equipment. Therefore, he decided that chemical oxygen demand was the right choice, although this method also oxidizes inorganic compounds. Jarry did not want to work with dichromate, so he chose potassium permanganate. To accurately measure the concentration, Jarry decided to standardize the permanganate solution using oxalic acid. Balance the equation using the smallest possible integer coefficients.

$$\mathrm{KMnO_4 + (COOH)_2 + H_2SO_4 \longrightarrow MnSO_4 + K_2SO_4 + CO_2 + H_2O}$$

Solution:

There are 2 carbon atoms oxidized from +III to +IV, and 1 manganese atom reduced from +VII to +II. Thus, the ratio between permanganate and oxalic acid has to be 2:5. Then, it is easy to do the rest.

$$\mathrm{2\,KMnO_4 + 5\,(COOH)_2 + 3\,H_2SO_4 \longrightarrow 2\,MnSO_4 + 1\,K_2SO_4 + 10\,CO_2 + 8\,H_2O}$$

Question b.1 (Petr Linhart)

"This method is fast and accurate…" – guidelines for physical chemistry laboratories

Victor Meyer was a German chemist who developed an elegant and (in principle) simple method for determining molar masses of volatile liquids. His name is notoriously known to all students who have attended physical chemistry laboratories and have, using a burner, manufactured small glass ampoules containing a flammable liquid, praying that the ampoule wouldn't break and the liquid wouldn't just evaporate away or even burn.

If we look away from the challenging actual execution of this method, its principle really is simple, which is an advantage for you. A small glass ampoule containing a known amount of volatile liquid is inserted into a furnace, where it breaks and the liquid evaporates. This sudden volume change causes displacement of the (volumetrically) same amount of air out of the furnace. The volume of displaced air is measured at room temperature, i.e. 25 °C. The whole system is at atmospheric pressure, and the ampoule contains 1.12 g of unknown liquid. After the ampoule had broken, we measured that 595 ml of air had been displaced. Determine the molar mass of the unknown liquid.

Solution:

Although we don't know the temperature in the furnace and therefore the volume adopted by the volatile liquid, we can solve this task. We know that the volume of air that was displaced is the same as the volume of the evaporated volatile substance. By the definition of an ideal gas, the same volume of gas always corresponds to the same amount of substance. The volume of displaced air was given at 25 °C; the amount of substance of this volume of air is the same as the amount of substance of the liquid that was originally in the ampoule. We therefore apply the ideal gas equation of state,

$$pV = \frac{m}{M_\mathrm{m} RT},$$

and therefore

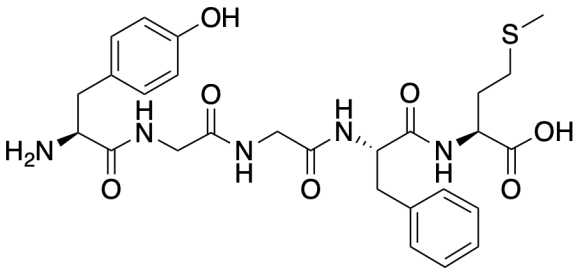
$$M_\mathrm{m} = \frac{mRT}{pV} = \frac{1.12 \times 8.314 \times 298.15}{101\,325 \times 595 \times 10^{-6}} \doteq 46\,\mathrm{g\,mol^{-1}}.$$

The volatile liquid was ethanol.

Question b.2 (Alena Budinská)

Met-enkephalin is an opioid neurotransmitter, which naturally occurs in the human nervous system. It binds to opioid receptors that are involved in the perception of chronic pain. Opium, morphine and codeine have a similar effect.

Write down the code of this peptide using the three-letter abbreviations of amino acids.



met-enkephalin

Alanine	Ala
Arginine	Arg
Asparagine	Asn
Aspartate	Asp
Cysteine	Cys
Glutamine	Gln
Glutamate	Glu
Glycine	Gly
Histidine	His
Isoleucine	Ile

Leucine	Leu
Lysine	Lys
Methionine	Met
Phenylalanine	Phe
Proline	Pro
Serine	Ser
Threonine	Thr
Tryptophan	Trp
Tyrosine	Tyr
Valine	Val

Solution:

Tyr-Gly-Gly-Phe-Met

Question b.3 (Alexandr Zaykov)

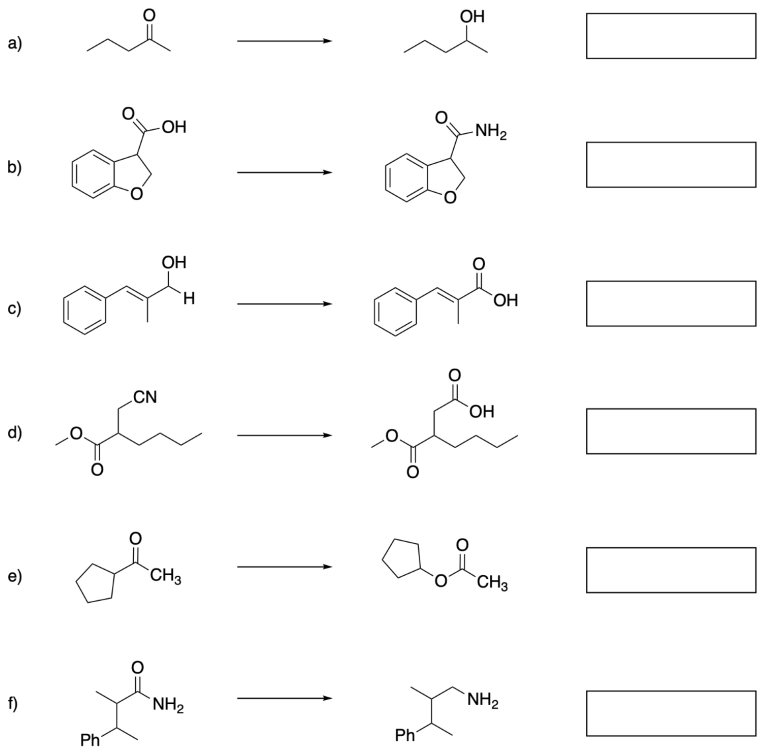
Chemistry enthusiast Ann decided to battle the world-wide, corporate-driven shortage of AdBlue additive by her wits. She knows that the commercial name 'AdBlue' hides a plain aqueous solution of urea with a mass concentration of 32.5 % and a density of 1088 $\mathrm{kg\,m^{-3}}$. Her idea is to obtain the suddenly-all-so-expensive solution by biological means - from one's urine.
How many whole days of urine collection and processing would it take for her to acquire enough AdBlue to embark on a trip from her hometown to Prague and back? The average distance to Prague from her hometown is 100 km. The human body expels 465 mmol/day of urea via urine. The average AdBlue consumption of her turbodiesel-powered car is 1 litre/1000 km.
According to Ann's research, the extraction of urea from urine should be 20 % efficient.

Solution:

It is a simple matter of unit-conversion. For the trip of 200 km, we require 0.2 litres of AdBlue, or 217.6 g of the solution. That is 70.72 g of urea. A human produces on average 27.93 g of urea each day. Using her special process, Ann can obtain 5.59 g of clean urea per day.
By dividing the total mass needed by the daily yield, we find out it would take 70.72 / 5.59 = 12.67 days, that is 13 whole days.

Question b.4 (Alena Budinská)

Determine whether the following reaction schemes represent an oxidation, a reduction or a redox-neutral reaction of the substrate.



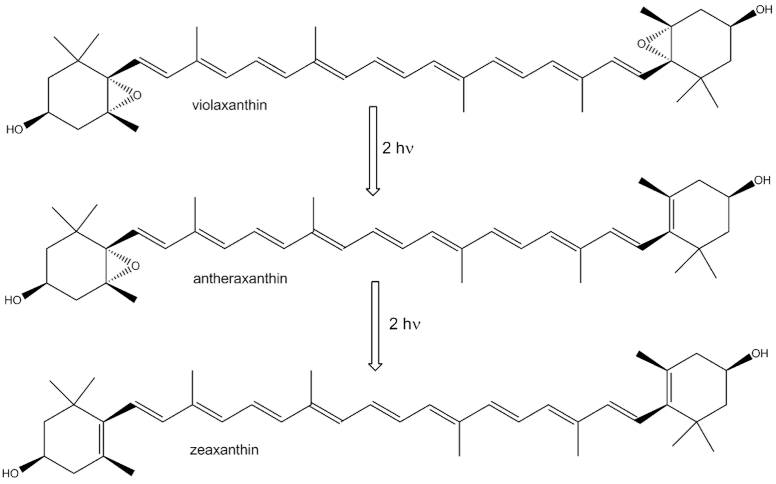
Solution:

A - reduction, B - neutral reaction, C - oxidation, D - neutral reaction, E - oxidation, F - reduction.

Question b.5 (Terezie Císařová)

Many interesting pigments can be found in diatoms (a type of algae, nothing to do with chemical atoms, apart from being made of them :-)). Three of these are shown in the figure, in a reaction where orange violaxanthin is changing to yellow zeaxanthin in two steps.

Apart from enzymatic reactions, this transition can proceed as light induced cleavage of first the epoxidic and then the hydroxylic bond. Write down the longest wavelength of the light source which is sufficient for both steps of the colour transition from orange to yellow. The bond disociation energy for the epoxidic bond is 2.36 eV and 4.5 eV for the hydroxylic bond. Then assign the wavelength to a region of the UV-VIS spectrum.



Solution:

From the Planck–Einstein relation $E = h\frac{c}{\lambda}$ we can see that the larger wavelengths correspond to lower energy, therefore we are searching for the minimum possible energy for bond fission of both types of the bonds. This energy is equal to the bond dissociation energy of hydroxylic bond, which is bigger. For this energy we can solve for the wavelength using the Einstein formula. It is important to remember to convert all units to SI units, thus

$$E[\mathrm{J}] = e \times E[\mathrm{eV}],$$

where e is the elementary charge. The whole solution is as follows:

$$\lambda = c \times \frac{h}{E[\mathrm{eV}] \times e} = 3 \times 10^8 \times \frac{6.626 \times 10^{-34}}{4.5 \times 1.602 \times 10^{-19}} \doteq 276\,\mathrm{nm},$$

which should be classified as UV light.

Question b.6 (Richard Veselý)

Sometimes chemistry can be too abstract which is the reason why it is useful to look for analogies wherever possible. That is something you can try in this task. It is possible to look for analogies between different reaction mechanisms and the dynamics of human relationships. Match mechanisms **1**–**6** with situations **I**–**VI**. The starting point for all situations is that Pepe and Ana form a couple and John is single.

Mechanisms:
1. S_N1, **2.** S_N2, **3.** E1, **4.** E2, **5.** Addition-elimination mechanism, **6.** Addition

Situations:

I Pepe, Ana and John agree on a polyamoric relationship where all three participate in that relationship.
II Pepe breaks up with Ana and nothing more happens.
III Ana and John start dating and after several months Ana breaks up with Pepe.
IV John tells Ana something about Pepe and as a result Ana breaks up with Pepe.
V John and Pepe would like to start dating each other so Pepe breaks up with Ana and starts dating John.
VI Ana breaks up with Pepe and after that she starts to like John and starts dating him.

Solution:

1. In a monomolecular nucleophilic substitution reaction (S_N1), one part of the molecule (the leaving group, here Ana) leaves, after which a new bond is formed with another molecule (here John). **1-VI**
2. On the other hand, in a S_N2 reaction, the incoming group (John) binds while the first group (Ana) leaves the molecule –- this happens via a single transition state (sort of a love triangle). **2-V**
3. In an E1 elimination reaction, just one molecule reacts, from which a part is cleaved off (Pepe from Ana). **3-II**
4. An E2 reaction occurs when one molecule binds a group leaving another molecule. Typically a base binds a proton leaving the molecule that is undergoing elimination. Here, John enters the reaction by initiating the breakup of Pepe and Ana. **4-IV**
5. In the addition-elimination mechanism, one molecule is first added (John in this case), then a small part leaves the original molecule (here Pepe). **5-III**
6. In a simple addition reaction, one molecule (John) joins a molecule with already existing bonds (Pepe and Ana). **6-I**

Offline round

Question c.1 (Ilija Srpak)

Inspired by the restless minds behind Cambridge Zero, Jesus has decided to reschedule his second coming to help the planet combat Global Warming. His plan is to absorb CO_2 from air and combine it with water to form alcohol (wine), possibly forming other byproducts.

Write the balanced equation for this reaction.

Solution:

$$2\,CO_2 + 3\,H_2O \longrightarrow C_2H_5OH + 3\,O_2$$

This is the opposite of the reaction for burning ethanol.

Question c.2 (Tatiana Nemirovich)

The energy value of a foodstuff is defined as the amount of energy the body gets when the food is digested. We can determine the energy value of a food by calorimetry, remembering to adjust for the efficiency of the digestive system. The energy value of a food is usually expressed in kilocalories (kcal), where $1\,\text{kcal} = 4.2\,\text{kJ}$.

The energy value of a 100g bar of chocolate is 530 kcal.

Another way of expressing energy is in tons (of TNT). 1 ton equals 4.184 GJ (the energy released when one ton of TNT is detonated). The nuclear bomb Little Boy that was dropped on Hiroshima on the 6th of August 1945 exploded with an estimated energy of 16 kilotons.

Calculate how many bars of chocolate you would need to eat to release an amount of energy comparable to that of the Little Boy explosion over Hiroshima.

Solution:

$$\frac{16 \times 10^3 \times 4.184 \times 10^9}{530 \times 4.2 \times 10^3} = 30 \times 10^6.$$

We would have to eat 30 million bars of chocolate.

Question c.3 (Vojtěch Laitl)

An ion lying on metabolic crossroads

Diatoms (*Bacillariophyceae*) are an interesting group of marine microalgae capable of direct fixation of N_2 dissolved in marine water. In the process, a certain inorganic ion is formed. At the same time, diatoms are able to decompose excess of this ion by the urea cycle, more commonly found in mammals' cells. Give the chemical formula of the ion discussed, making use of the following:

- it is a binary compound of nitrogen and hydrogen,
- it acts as a weak acid of $pK_a = 9.25$,
- it adopts a regular tetrahedral shape.

Solution:

A regular tetrahedral shape suggests that four equal binding partners should be placed around a central atom. Since it is impossible for hydrogen to adopt such connectivity, we must have a nitrogen central atom bearing four hydrogen atoms and hence a positive charge. Such a structure readily corresponds to the ammonium ion, NH_4^+. The ammonium ion indeed acts as a weak acid, being a conjugate acid to a weak base, NH_3.

Question c.4 (Sam Holmes)

Which d-block element has the lowest melting point at atmospheric pressure?

Solution:

Mercury. It is obvious from the fact that it is liquid.

Question c.5 (Richard Veselý)

Anthocyanins are naturally occurring colourful substances whose colour strongly depends on pH (a quantitative scale for measuring acidity). They are responsible, for example, for the red colour of red cabbage or the purple colour of purple potatoes. Although anthocyanin can have different colours, it is still the same molecule, just with a different number of hydrogen cations attached to it. These we call different forms of that molecule.

A strongly acidic anthocyanin sample has a red colour. By gradually adding hydroxide, one can observe a wide range of colours: red – pink – purple – blue – bluegreen – green – yellow. That is seven different colors, but does it mean that anthocyanins have seven different forms? No! There are only three forms: A (present in strongly acidic solution), B (present in neutral solution), C (present in strongly basic solution).

Your task is to determine the colours of these forms. You can choose only from this list: white, brown, red, yellow, orange, purple, green, pink, salmon, ochre, skin-color, blue, purple-pink.

Solution:

A – red, B – blue, C – yellow. Going from acidic to neutral pH, there is only the form A at the beginning, so that the solution has the colour of form A. Then, there is a mix of the forms A and B so the solution has the colour that is obtained by mixing the colour of A with the colour of B. At neutral pH, the solution has the colour of form B, as only that form is present and so on. From that we can conclude that the form present at strongly acidic pH (A) has a red colour and the form present at strongly basic pH (C) has a yellow colour. The form present in neutral pH (B) has to have such a colour that can explain the other observed colours. That means it can be mixed with yellow or red to give the other observed colours and it is one of the observed colours itself.

Question c.6 (Yizhe Lou)

The explosion in Beirut, Lebanon on 4 August, 2020, shocked the world, causing at least 218 deaths and 7000 injuries. A reddish brown mushroom cloud was spotted during the explosion. Later investigation pointed out that the cause of the explosion was a cargo of 2750 tonnes of ammonium nitrate. The reaction responsible for the explosion was:

$$4\,NH_4NO_3 \longrightarrow 3\,N_2 + 2\,NO_2 + 8\,H_2O$$

Calculate the volume of gas produced in the explosion in m^3 at 101 kPa and 700 K. Treat the gas produced as ideal gas and assume that all of the ammonium nitrate decomposed in the reaction above.

Solution:

First calculate the amount of substance of NH_4NO_3:

$$n_{NH_4NO_3} = \frac{m_{NH_4NO_3}}{Mr_{NH_4NO_3}} = \frac{2.75 \times 10^9\,\text{g}}{80\,\text{g mol}^{-1}} = 3.44 \times 10^7\,\text{mol}$$

By stoichiometric relationships, calculate the number of moles of gas produced in this reaction. Note that the temperature is 700 K, so the water will certainly be produced in gas form!

$$n_{gas} = n_{NH_4NO_3} \times \frac{3+2+8}{4} = 1.12 \times 10^8\,\text{mol}$$

Finally, apply the ideal gas equation to find out the volume:

$$V = \frac{n_{gas}RT}{p} = \frac{1.12 \times 10^8\,\text{mol} \times 8.3145\,\text{J K}^{-1}\,\text{mol}^{-1} \times 700\,\text{K}}{101\,\text{kPa}} = 6.45 \times 10^6\,\text{m}^3$$

Question d.1 (Richard Veselý)

Young chemist Martin took part in the Chemistry Olympiad and, in the practical part, he encountered a task too hard for his theoretical abilities. He was given 5 unknown substances: A, B, C, D and E, and he knew that they come from this list: sucrose, calcium carbonate, glucose, sodium chloride and starch. Using different chemicals, he was supposed to determine which compound is which.

However, Martin didn't give up. As he had no respect for laboratory safety and had noticed that there were no poisons among the compounds, he started tasting them. Compound A tasted salty. Compound B was tasteless and didn't dissolve in the mouth. Compounds C and D were sweet, while compound E was tasteless and he gnashed it between his teeth. For the next test, Martin tried dissolving the compounds in water. Compounds A, C and D dissolved in cold water, while compound B dissolved only in hot water and compound E didn't dissolve at all. Finally, Martin remembered the so-called Fehling test which he then used on compounds C and D and found out that C is most likely a monosaccharide, while D is a disaccharide.

Determine the identity of compounds A - E.

Solution:

Based on taste, the compounds can be categorised into 3 groups:

- salty: A – NaCl,
- sweet: C, D – glucose and sucrose,
- tasteless: B, E – starch and $CaCO_3$.

The information about solubility distinguishes B and E, of which starch dissolves in hot water, whereas $CaCO_3$ doesn't. C and D are distinguished using the hint about monosacharide and disacharide.
A - NaCl, B - starch, C - glucose, D - sucrose, E - $CaCO_3$.

Question d.2 (Adam Jaroš)

Compounds of antimony were used by the ancient Egyptians, mostly in cosmetics. Nowadays, antimony has many uses: it is often used as an alloying element with lead for use in some solders and batteries. In order to make such alloys, we first need to obtain antimony in its metallic form, which can be easily prepared in a laboratory. We first need to dissolve antimony(III) oxide in hydrochloric acid and then reduce the antimony(III) chloride solution with zinc filings. The process follows the reaction scheme:

$$\mathrm{Sb_2O_3 + HCl \longrightarrow SbCl_3 + H_2O}$$
$$\mathrm{SbCl_3 + Zn \longrightarrow Sb + ZnCl_2}$$

Calculate the mass of antimony obtained from 3g of Sb_2O_3. The overall yield is 70%. Do not forget to take the stoichiometry into account.

Solution:

The theoretical quantity of antimony produced can be determined as the product of the molar mass of antimony and twice the amount of antimony(III) oxide:

$$m_{\mathrm{theor}} = 2 \times n_{\mathrm{Sb_2O_3}} \times M_{\mathrm{Sb}} = 2 \times \frac{M_{\mathrm{Sb}}}{M_{\mathrm{Sb_2O_3}}} \times m_{\mathrm{Sb_2O_3}} = 2 \times \frac{121.76}{291.5} \times 3 = 2.506\,\mathrm{g}$$

The mass of antimony actually produced is limited by the 70 % yield:

$$m = \eta \times m_{\mathrm{theor}} = 0.70 \times 2.506\,\mathrm{g} = 1.754\,\mathrm{g}$$

Question d.3 (Terezie Císařová, Vojtěch Laitl)

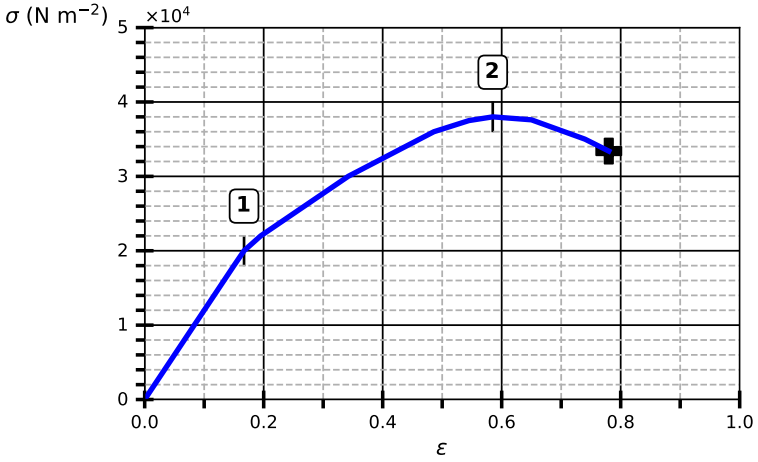
Stress-strain curves are a convenient tool for the estimation of material deformation parameters, relevant for process engineering. Such curves are obtained by measuring the relative axial elongation ε of a material sample under increasing mechanical stress σ. A typical stress-strain curve is depicted in the appendix.

The graph shows deformation behaviour of Gouda cheese (containing 60 % of fat in dry matter) that is used in various well-known fried cheese recipes.

If we apply only a moderate mechanical load to the cheese, without exceeding its yield strength (marked **1**), it returns into its original shape once the deforming force stops. That part of the function $\sigma(\varepsilon)$ is described by Hooke's law, i.e. $\sigma = E \times \varepsilon$ with the coefficient E called the Young's modulus and $\varepsilon = \Delta L / L_0$ is the relative axial extension.

Once the applied stress exceeds the yield strength, the deformation is not entirely reversible anymore and plastic deformation takes place. The cheese is no longer able to return to its original shape and its axial elongation grows spontaneously until the stress reaches the material's ultimate strength (**2**), leading to its ultimate failure by fracture (marked with a plus). A similar physical mechanism takes place when one separates a meal of fried cheese into pieces.

Estimate the Young's modulus E of Gouda cheese, making use of the graph provided.



Solution:

The first part of the stress-strain curve is described by a linear function and therefore corresponds to Hooke's law. The coordinates of any point on that segment form the pair $[\varepsilon; \sigma]$. From the graph, we can easily obtain the pair $[0.1; 1.2 \times 10^4]$.
From the formula of Hooke's law, Young's modulus equals the ratio

$$E = \frac{\sigma}{\varepsilon} = \frac{1.2 \times 10^4}{0.1} = 0.12\,\text{MPa}$$

Source of plotted data: Luyten, H. The rheological and fracture properties of Gouda cheese. Ph.D.Dissertation, 1219 *Proefschrift Wageningen*, 1988, 62. `https://edepot.wur.nl/201864`

Question d.4 (Yuxuan Li)

Aluminium is produced on an industrial scale from the mineral bauxite. Bauxite contains alumina, Al_2O_3, from which aluminium can be obtained by electrolysis. Bauxite also contains other metal salts such as $NaAlO_2$ and $Al(OH)_3$, which are present in much smaller amounts.

Electrolysis of molten alumina is complicated by the fact that the melting point of pure alumina is 2072 °C. This can be lowered by dissolving the alumina in molten cryolite (Na_3AlF_6, m.p. 1012 °C).

However, cryolite is scarce: an alternative method for lowering the melting point is to react the impure bauxite with HF, which forms cryolite in situ from the other metal salts present and Na_2O.

The unbalanced equations for the reactions of HF with the minerals in bauxite are shown below.

$$\text{HF} + \text{NaAlO}_2 \longrightarrow \text{Na}_3\text{AlF}_6 + \text{H}_2\text{O} + \text{Al}_2\text{O}_3$$

$$\text{HF} + \text{Al(OH)}_3 \longrightarrow \text{AlF}_3 + \text{H}_2\text{O}$$

$$\text{AlF}_3 + \text{Na}_2\text{O} \longrightarrow \text{Na}_3\text{AlF}_6 + \text{Al}_2\text{O}_3$$

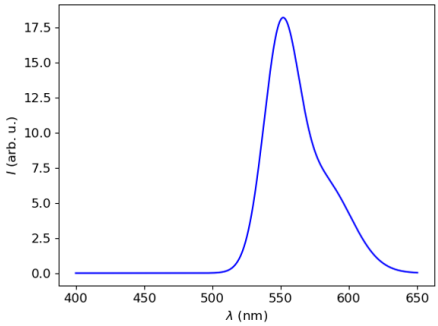
Balance the equations, using the smallest possible whole-number coefficients.

Solution:

$$6\,\mathrm{HF} + 3\,\mathrm{NaAlO_2} \longrightarrow \mathrm{Na_3AlF_6} + 3\,\mathrm{H_2O} + \mathrm{Al_2O_3}$$
$$3\,\mathrm{HF} + \mathrm{Al(OH)_3} \longrightarrow \mathrm{AlF_3} + 3\,\mathrm{H_2O}$$
$$4\,\mathrm{AlF_3} + 3\,\mathrm{Na_2O} \longrightarrow 2\,\mathrm{Na_3AlF_6} + \mathrm{Al_2O_3}$$

Question d.5 (Vojtěch Laitl)

Microalgae called diatoms (*Bacillariophyceae*) are capable of producing luminescent nanoparticles, which are formed in their cells upon metabolizing rhodamine-based organic dyes. The production of such particles may be conveniently observed by spectroscopic methods. After one diatom had digested rhodamine, its content was spilled into a 1L bioreactor and the following luminescent spectrum was recorded.



The area under its graph is proportional to the concentration of resultant nanoparticles. For its value expressed in $\mathrm{mol\,dm^{-3}}$, the following relation holds:

$$I = 3.4 \times 10^5 \times c.$$

Total integrated intensity recorded during the one-diatom experiment read $I = 850$. Estimate the number of diatoms necessary for producing 0.05 mol of nanoparticles in a 1 litre bioreactor. Assume that both experiments are conducted under the very same conditions and individual diatoms do not influence each other.

Solution:

The integral intensity obtained during a one-diatom experiment may be used for calculating the concentration and thereby molar amount of nanoparticles yielded in a 1 litre bioreactor:

$$n_1 = 1 \times \frac{850}{3.4 \times 10^5} = 2.5 \times 10^{-3}\,\text{mol}$$

Provided that individual diatoms do not influence each other, their amount desired for the preparation of $n = 0.05\,\text{mol}$ of nanoparticles is given as

$$N = \frac{n}{n_1} = \frac{0.050}{0.0025} = 20 \text{ diatoms.}$$

Question d.6 (Richard Veselý)

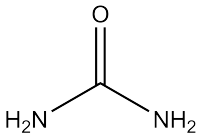
The main nitrogen metabolite in humans is a compound with molar mass $60\,\text{g mol}^{-1}$. Draw the structure of the compound.

Hint: It is derived from carbonic acid (H_2CO_3) and as a final metabolite it won't be very reactive. Derivates of carboxylic acids follow this trend: (Most reactive) chloride > anhydride > carboxylic acid > ester > amide.

Solution:

Urea. It can be thought of as diamide of carbonic acid which corresponds to the

1. hint about mass,
2. very low reactivity,
3. fact that it should contain nitrogen.



Question e.1 (Petr Linhart)

Sulfur is an element which has a tendency for chain formation, as is apparent from one of its allotropes, cyclo-octasulfur S_8. This tendency also shows up in its compounds. For example, if we oxidise thiosulfate anion with iodine, we get tetrathionate anion:

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

What are the average oxidation states of sulfur in thiosulfate and in tetrathionate anions?

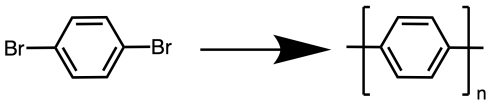
Solution:

Oxygen binding with sulfur has an oxidation state of −II, and the totals of the oxidation states must match the net charges of the molecules. Using this fact, we obtain +2 in case of thiosulfate and $+\frac{5}{2}$ in case of tetrathionate.

Question e.2 (Sam Holmes)

There are many ways to make polymers, but one of the more common methods is metal-catalysed coupling. This method can be used to prepare some very unusual materials, such as poly(*para*-phenylene), PPP. A simplified reaction scheme is shown below.

What mass of 1,4-dibromobenzene would be needed to create a PPP molecule which stretches around the equator? (Bond lengths: aromatic C−C 138 pm, C−C 148 pm; equator 40 075 km).



Solution:

37.0 µg. The length of a monomer is 424 pm (2× aromatic C−C bond, 1× C−C bond), dividing the length of the equator by this number gives the number of monomers:

$$N = \frac{40\,075 \times 10^3}{424 \times 10^{-12}} \doteq 9.45 \times 10^{16}.$$

This is easily turned into the mass via the $M = 235.9\,\mathrm{g\,mol^{-1}}$, which can be easily worked out from the structure:

$$m = Mn = \frac{MN}{N_\mathrm{A}} = \frac{235.9 \times 9.45 \times 10^{16}}{6.022 \times 10^{23}} \doteq 37.0\,\mu\mathrm{g}.$$

Question e.3 (Sam Holmes)

I have a solution of 5 M HCl, and add to it some 5 M acetic (ethanoic) acid. What will happen to the pH as I add the acetic acid?

1. It will stay the same.
2. Increase, reaching a limiting value.
3. Increase linearly.
4. Decrease linearly.
5. Decrease, reaching a limiting value.
6. Initially increase before decreasing to a limiting value.
7. Initially decrease before increasing to a limiting value.
8. Initially decrease before increasing indefinitely.
9. Initially increase before decreasing indefinitely.

Assume that the temperature is constant throughout.

Solution:

Increase to a limiting value (pH of 5M EtOOH). You are essentially just diluting the solution of HCl, which will stay almost completely dissociated. As you add more and more EtOOH, you will eventually end up with a solution which is essentially pure EtOOH (a weak acid, therefore the pH will be higher compared to strong HCl).

Question e.4 (Filip Hůlek)

One of your friends contacted you a couple days ago, telling you that he had ordered some magical pills from E-Bay. However, a few days after that, he read on the internet that they contained a lot of mercury. Therefore, he asked you to take a look at them. You, of course, did not hesitate at all and decided to determine the amount of mercury contained in the pills by yourself. You took one pill, which weighs $m = 0.53\,\mathrm{g}$, ground it and oxidised all the mercury that was present into mercury(II) ions. You then titrated a solution of them with a solution of potassium thiocyanate (KSCN) (concentration $c = 0.021\,\mathrm{mol\,dm^{-3}}$). Mercury(II) ions form a precipitate – mercury(II) thiocyanate ($Hg(SCN)_2$). Iron(III) ions were used as an indicator and a red colour prevailed after $V = 41.4\,\mathrm{ml}$ of KSCN had been added to the analysed solution. The limit for mercury content in these pills is 0.1 mg per kg of product. By what factor was the limit exceeded?

Solution:

The story of this question is based on a real event: it was truly possible for some time to buy these pills on E-Bay. If we look at the reaction stoichiometry, we can see that we need two molecules of titrant for one molecule of mercury(II) thiocyanate ($Hg(SCN)_2$) precipitate. Therefore, the amount of mercury in the pill is

$$n_{\mathrm{Hg}} = \frac{1}{2} \times n_{\mathrm{KSCN}} = \frac{1}{2} \times c \times V.$$

. The molar mass of mercury is $M_{\mathrm{Hg}} = 200.59\,\mathrm{g\,mol^{-1}}$; the mass of mercury present in one pill is therefore

$$m_{\mathrm{Hg}} = \frac{1}{2} \times c \times V \times M_{\mathrm{Hg}} = 0.5 \times 0.021 \times 41.4 \times 10^{-3} \times 200.89 \doteq 0.0873\,\mathrm{g} = 87.32\,\mathrm{mg}.$$

This amount is equal to $\frac{87{,}32}{530} \doteq 16.5$ mass per cent! A limit for mercury content is

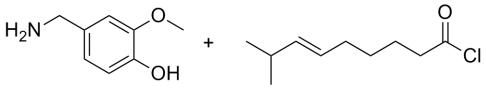
$$\frac{0.1\,\mathrm{mg}}{1\,\mathrm{kg}} = \frac{0.1 \times 10^{-6}}{1} = 1 \times 10^{-7},$$

so it was exceeded by a factor of $\dfrac{16.5 \times 10^{-2}}{1 \times 10^{-7}} = 1.65 \times 10^{6}$.

Question e.5 (Tatiana Nemirovich)

Organic molecules that contain nitrogen are sometimes called alkaloids. They may be naturally occuring, or synthesised by chemists in the laboratory.

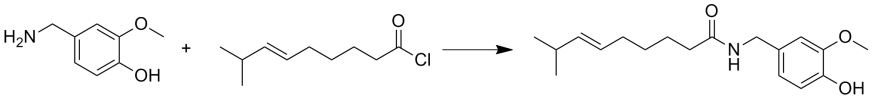
One naturally occuring alkaloid which is widely used in Indian cookery can also be prepared in the laboratory, by reacting 8-methylnon-6-enoyl chloride with 4-(aminomethyl)-2-methoxyphenol. The skeletal formuale of these molecules are shown below.



Draw the structure of the alkaloid product.

Solution:

See the figure:



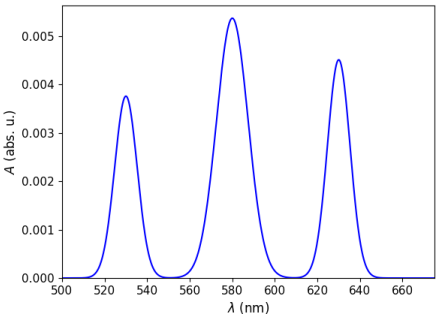
The desired alkaloid is capsaicin (active component of chilli peppers).

Question e.6 (Vojtěch Laitl)

Diatoms are unicellular microalgae known for producing shells of many different colours. Let us use this property for analysing their model population by well-known physical chemistry methods. According to the Bouguer-Beer-Lambert law, the intensity of a colour, expressed as absorbance, is given by

$$A_\lambda = \epsilon_\lambda c \ell,$$

where ϵ_λ is an absorption coefficient for a given wavelength, c is the concentration of the species investigated and ℓ is the length of the optical environment. Let us imagine a reservoir in which diatoms of three different colours, respectively blue, green and red, meet each other. A specimen of reservoir water adjusted into a cuvette of $\ell = 1\,\mathrm{dm}$ gave the following absorption spectrum:



λ (nm)	ϵ_λ (dm^3 cell^{-1} dm^{-1})	A_λ
530	5.00×10^{-4}	0.05
580	2.50×10^{-4}	0.10
630	1.20×10^{-4}	0.06

Give the percentage of blue, green and red diatoms in the model reservoir. Assume that each kind of diatom absorbs only in its region of the spectrum.

Solution:

The Bouguer–Beer–Lambert law gives a formula to calculate unknown concentrations expressed as nominal amounts in a unit volume:

$$c = \frac{A_\lambda}{\epsilon_\lambda \cdot 1}$$

The absorption of yellow colour around 580 nm corresponds to blue diatoms, green diatoms absorb red colour at 630 nm, and red ones are characterised by the absorption of green colour at 530 nm. Stepwise calculation gives the concentrations c(blue) = 400 cells dm^{-3}, c(green) = 500 cells dm^{-3}, and c(red) = 100 cells dm^{-3}. In total, there are 1000 diatoms in 1 litre of the reservoir. The fraction of particular concentrations over the total amount of 1000 cells dm^{-3} gives the corresponding percentages, *i.e.* 40% of blue diatoms, 50% of green diatoms, and 10% of red diatoms.

Question f.1 (Richard Veselý)

It is a known fact that hydrogen is the most abundant element in interstellar space. But what is the most abundant ion in interstellar space? It is a molecular ion with a charge to mass ratio of 1:3 and two electrons in total. (The charge is in units of elementary charge and the mass in atomic mass units.)

Give the formula of this ion, including charge.

Solution:

H_3^+. Out of all weird things with the given ratio of charge to mass, this one is the least weird. Furthermore, it is consistent with hydrogen being the most abundant element in the interstellar space.

Question f.2 (Petr Linhart)

Infrared spectroscopy is an analytical method used to obtain information about the bonds present in a molecule. By absorbing infrared radiation, chemical bonds can move to a higher mode of oscillation, meaning they vibrate with more energy. Only infrared radiation of particular frequencies is absorbed by any particular chemical bond, so by determining what frequencies the bond absorbs we can determine the type of bond present.

In spectroscopy, waves are commonly characterised by their wavenumber $\tilde{\nu}$, with units cm^{-1}: for example, the carbon-oxygen double bond in propanone is well-known to absorb radiation with wavenumber $1710\,\mathrm{cm}^{-1}$. What is the frequency of this radiation in Hz?

Solution:

Dimensional analysis tells us that wave number is the inverse value of wavelength, $\tilde{\nu} = 1/\lambda$. Infrared radiation is an electromagnetic radiation, its velocity is therefore equal to the speed of light. For light, the following relationship holds:

$$c = \frac{\lambda}{T} = \lambda\nu = \frac{\nu}{\tilde{\nu}} \implies \nu = c\tilde{\nu}.$$

We just need to substitute in base SI units, $1710\,\mathrm{cm}^{-1} = 171\,000\,\mathrm{m}^{-1}$. Therefore $\nu = 5.126 \times 10^{13}\,\mathrm{Hz}$.

Question f.3 (Sam Holmes)

Decide whether mixing the following pairs of chemicals would lead to a vigorous reaction (V), a slow reaction (S), or no reaction (N). Assume that all solutions are saturated.

$H_2O_2(l)$ + $KMnO_4(s)$

$CH_3COOH(aq)$ + $NaHCO_3(s)$

$Au(s)$ + $HF(g)$

$CsI(aq)$ + $H_2O(l)$

$Cu(s)$ + $O_2(aq)$

Solution:

$H_2O_2(l)$ + $KMnO_4(s)$: V - This is elephant's toothpaste

EtCOOH(aq) + $NaHCO_3(s)$: V - this is a common 'volcano' formulation

$Au(s)$ + $HF(g)$: N - HF is a strong acid but not an oxidiser

$CsI(aq)$ + $H_2O(l)$: N - Cs^+ is already solvated by water molecules (the clue is that it is already dissolved in water)

$Cu(s)$ + $O_2(aq)$: S - Though copper is fairly corrosion resistant, it will oxidise slowly over time.

Question f.4 (Petr Linhart)

Equilibrium is a key concept in all divisions of chemistry. We can characterise a particular chemical equilibrium via its equilibrium constant. In secondary school, however, it is often incorrectly defined. The terms in the formula are not concentrations, but thermodynamic activities (think of them as, for example, "improved concentrations"). Although we often approximate activities of solutes by their equilibrium concentrations $a_X \approx [X]$, the activity of pure substances (e.g. solvents and pure solids) is $a_X = 1$. Consider the following reaction

$$HCOOH\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + HCOO^-\,(aq)\ .$$

Calculate the equilibrium constant of this reaction, given that the solution of formic acid has pH = 1.88 when the concentration of formic acid is $1\,\mathrm{mol\,dm^{-3}}$. Neglect the self-ionisation of water (i.e. the only source of H_3O^+ ions is the reaction above).

Solution:

$$K = 1.76 \times 10^{-4}$$

If we neglect the self-ionisation of water, the only source of protons is the acid dissociation, therefore $[H^+] = [A^-]$. The concentration of protons can be determined from the given pH value: $[H^+] = 10^{-pH} \approx 0.013\,\mathrm{mol\,dm^{-3}}$. The given concentration (further denoted c_0) is the total concentration of acid, meaning that it regards all its forms in the solution! It is also obvious from the task text that the activity of water (a pure substance) is 1. Substituting into the definition of equilibrium constant, we obtain

$$K = \frac{a_{H^+} \times a_{HCOO^-}}{a_{HCOOH} \times a_{H_2O}} = \frac{[H^+][HCOO^-]}{(c_0 - [HCOO^-]) \times 1} = 1.76 \times 10^{-4}.$$

Question f.5 (Veronika Boguschová)

Caffeine, a xanthine derivative, is the best friend of many students because it stimulates their neural system: perfect for solving the tough problems in the Chemistry Race! If the problems prove down heartening, chocolate might be a good way to cheer up as it contains theobromine: another xanthine derivative which has been shown to affect mood.

The systematic name for caffeine is 1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione. Caffeine and theobromine molecules are identical except that the latter has no methyl group at position 1.

How many bromine atoms are there in one theobromine molecule?

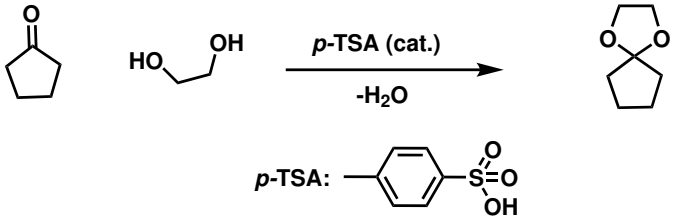
Solution:

Since there is no hint of bromine in the systematic name and, unlike the methyl group, it is not added to the molecule either, we can readily claim that there are no bromine atoms in theobromine.

Question f.6 (Ondřej Daněk)

During protection of a carbonyl group by an acid catalyzed acetal formation with ethylene glycol (as shown in the scheme), 12.5 ml of water was collected in the Dean-Stark trap after 4 hours. The reaction started from 100g of cyclopentanone. Calculate the conversion of cyclopentanone.

(Even though the reaction mixture in the flask is boiling, the water collected in the Dean Stark trap is at room temperature and the density can be assumed to be $998\,\mathrm{kg\,m^{-3}}$)



Solution:

The conversion can be calculated from the amount of water in the Dean-Stark trap (assuming that all of the water formed in the reaction is collected). The amount of water in the Dean Stark trap is the same as the amount of reacted cyclopentanone, and the conversion is then calculated as the amount that reacted divided by the initial amount.

$$\zeta = \frac{n - n_0}{n_0} = \frac{n(\mathrm{H_2O})}{n_0} = \frac{\frac{m(\mathrm{H_2O})}{M(\mathrm{H_2O})}}{n_0} = \frac{\frac{V(\mathrm{H_2O})\rho(\mathrm{H_2O})}{M(\mathrm{H_2O})}}{\frac{m_0(\mathrm{cyclopentanone})}{M(\mathrm{cyclopentanone})}} = \frac{\frac{12.5\times 0.998}{18}}{\frac{100}{84.12}} = 0.583$$

Question g.1 (Jakub Štěpánek)

Work out what mass of chalcanthite (copper(II) sulfate pentahydrate) should be added to 250 ml of water to make a 10 % solution (by weight) of copper sulfate.

Solution:

We were asked to prepare a 10% solution of copper sulfate ($M_{\mathrm{CuSO_4}} = 159.6\,\mathrm{g\,mol^{-1}}$), but we're adding it in the form of a pentahydrate ($M_{\mathrm{CuSO_4 \cdot 5\,H_2O}} = 249.7\,\mathrm{g\,mol^{-1}}$), a part of the mass added is therefore the water of crystallisation. The original amount of water — 250 ml, which is approximately $m_{\mathrm{H_2O},0} = 250\,\mathrm{g}$ — is therefore not the only water that will be present in the final solution. When calculating the mass fraction, we need to account for the water of crystallisation as well:

$$w_{\mathrm{CuSO_4}} = \frac{m_{\mathrm{CuSO_4}}}{m_{\mathrm{CuSO_4 \cdot 5\,H_2O}} + m_{\mathrm{H_2O},0}} = 0.1.$$

Since the amount of substance of copper sulfate is the same as that of its pentahydrate, we get

$$n_{\mathrm{CuSO_4 \cdot 5\,H_2O}} = n_{\mathrm{CuSO_4}} \implies m_{\mathrm{CuSO_4}} = m_{\mathrm{CuSO_4 \cdot 5\,H_2O}} \times \frac{M_{\mathrm{CuSO_4}}}{M_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}.$$

When we substitute this into the mass fraction formula, we obtain

$$w_{\mathrm{CuSO_4}} = \frac{m_{\mathrm{CuSO_4 \cdot 5\,H_2O}} \times \frac{M_{\mathrm{CuSO_4}}}{M_{\mathrm{CuSO_4 \cdot 5\,H_2O}}}}{m_{\mathrm{CuSO_4 \cdot 5\,H_2O}} + m_{\mathrm{H_2O},0}}$$

$$m_{\mathrm{CuSO_4 \cdot 5\,H_2O}} = \frac{w_{\mathrm{CuSO_4}} m_{\mathrm{H_2O},0}}{\frac{M_{\mathrm{CuSO_4}}}{M_{\mathrm{CuSO_4 \cdot 5\,H_2O}}} - w} = \frac{0.1 \times 250}{\frac{159.6}{249{,}7} - 0.1} \doteq 46.37\,\mathrm{g}.$$

Question g.2 (Vláďa Němec)

When manufactured, plastic granules need to be cooled down to prevent them from sticking together and forming large lumps. The granules are cooled as they flow through a pipe system with cold water. One of the important parameters for this process is how long each granule spends in the pipe system.

Calculate how long it will take for a granule to pass through a pipe system with the following parameters:

Inner diameter of the pipe: 52.5 mm
Length of the pipe system: 12 m
Flow rate of water with granules through the system: $10\,000\,\mathrm{dm^3\,h^{-1}}$
Water density: $1000\,\mathrm{kg\,m^{-3}}$
Granule density: $980\,\mathrm{kg\,m^{-3}}$

Assume that the granules flow with the water current and their speed is the same as the speed of the current.

Solution:

Since the granules flow with the water current, we must first determine its velocity, v. Water flows perpendicularly to the pipe cross-section A; therefore, its flow rate $\dot{Q}$ can be calculated using the following formula:

$$\dot{Q} = Av = \pi\frac{d^2}{4}v \implies v = \frac{4\dot{Q}}{\pi d^2}$$

(it is in fact a calculation of a volume of a cylinder). We need to pay attention to the units used; we want the velocity to have units of metres per second, so we convert everything to basic SI units:

$$\dot{Q} = 10\,000\,\mathrm{dm^3\,h^{-1}} = \frac{10000}{1000 \times 3600} = \frac{1}{360}\mathrm{m^3\,s^{-1}}$$
$$d = 52.5\,\mathrm{mm} = 0.0525\,\mathrm{m}$$

.

By substituting in the correct values, we obtain $v \doteq 1.283\,\mathrm{m\,s^{-1}}$. Since the length of the pipeline is $l = 12\,\mathrm{m}$, the time τ needed for a granule to pass through is

$$\tau = \frac{l}{v} \doteq 9.35\,\mathrm{s}.$$

Question g.3 (Anh Phung)

Element X and its compounds are infamous for its involvement in many historical incidents. One of these was the 1858 Bradford sweets poisoning in England, where more than 200 people were poisoned from consuming a type of sweet called a "humbug" sold in a local sweet shop. It was documented that 2.3 kg of humbugs was sold during the incident.

At the time, sugar was expensive, so some dishonest pharmacists—who were also sugar suppliers—mixed a cheaper white compound with regular sugar to sell to sweet makers. The adulterant was found to contain an oxide X_2O_3, which was the culprit of the poisoning. A highly sensitive test to detect X was developed around the time of the incident and continued to be used in forensic studies until recently. The original protocol involved reacting the oxide of X with zinc granules and nitric acid, generating a garlic-smelling gas whose molecules are trigonal pyramidal in shape.

Upon heating, this gas decomposes into elemental X and H_2 gas, which can then be collected for quantitative measurement. Suppose all the humbugs sold during the incident were analysed using this test, with the volume of H_2 collected totalling $405.72\,dm^3$ (at 25 °C and 101 325 Pa).

Deduce the identity of X and calculate the mass of elemental X in one humbug. Assume that one humbug weighs 2 g and no other side-reactions occur. Hint: Element X is monoisotopic and belongs to period 4.

Solution:

0.721 g

The element X is arsenic. Gas containing H and As is AsH_3 (group 15), which we can deduce from the fact that XH3 is trigonal pyramidal and has a garlic odour. $n_{H_2} = 405.72\,/24.47 = 16.58\,mol$ from reaction equation of AsH_3 thermal decompostion, $nAsH_3 = 11.06\,mol$ from reaction equation of the test (Marsh test) giving 11.27 mol of elemental As. 1 humbug contains 9.61×10^{-3} mol of As, which is 0.721 g.

Question g.4 (Ilija Srpak)

The ratio of the mass fractions of oxygen in the oxides MO and M_2O is about 1.8. Which metal could M be?

Solution:

Setting the ratio, we get

$$\frac{w_M(MO)}{w_M(M_2O)} = \frac{\frac{M_M}{M_M+16}}{\frac{M_M}{2\times M_M+16}} = \frac{2 \times M_M + 16}{M_M + 16} = 1.8,$$

from which we get that molar mass of the metal equals 64. This is close to the mass of copper (63.55), as well as reasonably close to zinc (65.4). However, while Cu_2O exists, Zn_2O does not. The unknown metal is copper.

Question g.5 (Kaijia Liu)

Even though we live on Earth, we have managed to determine the elemental composition of the Sun. In particular, we know that it is composed primarily of hydrogen. However, until around 100 years ago, people believed that the Sun had a similar composition to the Earth. Henry Norris Russell, an American astronomer who once worked at the Cambridge Observatory, has often been recognised for discovering through spectral analysis that the Sun is mostly hydrogen, although it is disputed whether he should actually receive the credit (Cecilia Payne-Gaposchkin made a similar discovery four years earlier).

The electronic energy levels of a hydrogen atom are given by the equation $E_n = -\mathrm{R}/n^2$, where n is the principal quantum number of the electron shell and R is the Rydberg unit of energy, equal to 13.6 eV. Find any two wavelengths of visible light waves that would be emitted from the Sun due to thermal excitations of hydrogen in its atmosphere. The visible region of the electromagnetic spectrum is 400 nm to 700 nm.

Solution:

Any two of 656 nm, 486 nm, 434 nm, 410 nm. Express the energy difference between the shells, and then equate that energy difference to the energy of a photon. By some trials the answer should be found without much difficulty.

Question g.6 (Yizhe Lou)

An alloy of aluminium and magnesium was discovered in a chemistry laboratory. To determine its composition, 2.56 g of sample was selected and fully dissolved in dilute HCl. The hydrogen generated was collected and the volume was measured as 2.80 litre at 0 °C and 1 atm. Determine the mass percentage of magnesium in the alloy. (1 mol of gas has a volume of 22.414 litre at 0 °C and 1 atm) Useful Reactions:

$$\mathrm{Mg} + 2\,\mathrm{HCl} \longrightarrow \mathrm{H_2} + \mathrm{MgCl_2}$$

$$\mathrm{Al} + 3\,\mathrm{HCl} \longrightarrow \frac{3}{2}\,\mathrm{H_2} + \mathrm{AlCl_3}$$

Solution:

The mass percentage is 46.99 %. At 0 °C and 1 atm, 1 g of aluminium can generate: $\frac{22.414\,\text{litre/mol}\times 1\,\text{g}}{26.98\,\text{g/mol}} \times 1.5 = 1.246\,\text{litre}$. 1 g of magnesium can generate: $\frac{22.414\,\text{litre/mol}\times 1\,\text{g}}{24.31\,\text{g/mol}\times 1} = 0.922\,\text{litre}$. Assume there are x grams of magnesium, then there are $(2.56 - x)$ grams of aluminium.

$$1.246(2.56 - x) + 0.922x = 2.80$$

$$x = 1.203\,\text{g}$$

The mass percentage is therefore

$$\frac{1.203}{2.56} \times 100\% = 46.99\%$$

Question h.1 (Kaijia Liu)

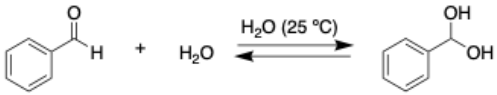
Glycogen is composed of α-glucose molecules linked by either α-1,4-glycosidic bonds or α-1,6-glycosidic bonds. A glycosidic bond is formed between two glucose molecules by the condensation of two alcohol groups to form an ether. Branches form at the connections of α-1,6-glycosidic bonds, allowing the glycogen molecule to adopt a more compact structure. Find the molar mass of a short glycogen molecule containing 11 branching points, formed by a condensation reaction between 100 glucose molecules.

Solution:

16 232 g mol^{-1}. Most of the question text is just red herring (distraction), as the α-1,4-glycosidic bonds and α-1,6-glycosidic bonds do not change the number of water molecules lost. For 100 glucose molecules, we expect 99 glycosidic bonds. The 100 glucose molecules together give $C_{600}H_{1200}O_{600}$, and subtracting 99 H_2O gives $C_{600}H_{1002}O_{501}$, giving 16 232 g mol^{-1} as molecular mass.

Question h.2 (Alena Budinská)

Benzaldehyde (C_6H_5CHO) is the simplest aromatic aldehyde. It is a colourless liquid, with a characteristic pleasant almond odour – it is indeed found in almond extracts and may be isolated from many natural feedstocks, e.g. from almonds or from apricot, cherry, or peach seeds. The following scheme describes a hydration of benzaldehyde in aqueous solution at 25 °C:



Estimate the equilibrium concentration of benzaldehyde hydrate, provided that the equilibrium concentration of benzaldehyde is 0.1 mM. The equilibrium constant is $K(\mathrm{H_2O}, 25\,^\circ\mathrm{C}) = 0.008$ and the activity of water can be assumed to be unitary.

Solution:

$$K = \frac{a(\text{hydrate})}{a(\text{aldehyde})a(\text{water})}$$

$$c(\text{hydrate}) = Kc(\text{aldehyde})a(\text{water}) = 0.1\,\text{mM} \times 0.008 \times 1 = 0.8\,\mu\text{M}$$

Question h.3 (Adam Přáda)

Chemist Adam wanted to be cool, so he put "all chemicals" in his home into identical chemical containers. However, in the humid bathroom, the front labels did not stick very well, and only the back labels with contents remain. Help Adam assign the front labels based on the ingredients:

1) shower gel
2) antiperspirant spray
3) toothpaste
4) hand cream
5) sun screen cream
6) shaving foam spray

a) Aqua, Triethanolamine, Palmitic Acid, Stearic Acid, Isobutane, Laureth-23, Sodium Lauryl Sulfate, Propane, Parfum, BHT, Limonene

b) Aqua, Sodium Myreth Sulfate, Cocamidopropyl Betaine, Sodium Laureth Sulfate, Glycol Distearate, Decyl Glucoside, Glycerin, Sodium Chloride, Citric Acid, Laureth-4 Tocopherol, Propylene Glycol, Butylene Glycol, Sodium Benzoate, Parfum

c) Aqua, Glycerin, Paraffinum Liquidum, Alcohol Denat., Cetyl Alcohol, Glyceryl Stearate, Hydrogenated Coco-Glycerides, Stearyl Alcohol, Cera Microcristallina, Palmitic Acid, Stearic Acid, Tocopheryl Acetate, Sodium carbomer, Myristic Acid, Arachidic Acid, Oleic Acid, Dimethicone, Phenoxyethanol, Methylparaben, Geraniol, Parfum

d) Aqua, Alcohol Denat., Octocrylene, Glycerin, C12-15 Alkyl Benzoate, Butyl Methoxydibenzoylmethane, Ethylhexyl Salicylate, Titanium Dioxide (nano), Dicapryl Carbonate, Tocopheryl Acetate, VP/Hexadecene Copolymer, Panthenol, Silica, Parfum, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Ethylhexylglycerine, Sodium Hydroxide, Carbomer, 1,2-hexanediol, Caprylyl Glycol, Xanthan Gum, Disodium EDTA, Dimethicone, Citral, Benzyl Alcohol, Linalool, Citronellol, Tocopherol

e) Butane, Isobutane, Propane, Cyclomethicone, Aluminium Chlorohydrate, C12-15 Alkyl Benzoate, Isopropyl Palmitoate, Palmitoamidopropyltrimonium Chloride, Octyldodecanol, Propylene Gllycol, Disteardimonium Hectorite, Propylene Carbonate, Dimethiconol, Linalool, Limonene, Geraniol, Parfum

f) 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, CI 74160

Solution:

1b, 2e, 3f, 4c, 5d, 6a

The best way to solve this problem is to look for ingredients that can only really occur in one or two of these products.

Propane and butane are gases, so they can be only found in sprays. Then we can distinguish the shaving foam from the antiperspirant e.g. by the presence of water in the foam or aluminium chlorohydrate, which is the active ingredient in the antiperspirant.

The toothpaste can be found in several ways. It contains sodium fluoride to strengthen enamel, saccharine to taste better, hydrated silica for its abrasive properties and titanium dioxide for its white colour.

To distinguish the shower gel from the two creams, we look for amphiphilic molecules, which are the active components of soaps. These usually have a long hydrocarbon tail and an ionic head. Sodium Myreth Sulfate, Cocamidopropyl Betaine and Sodium Laureth Sulfate are such compounds.

Finally, we need to distinguish the hand cream from the sun screen. Since both of these are creams, we expect the ingredients to be quite similar. The main difference between the two is the active ingredient in the sun screen that absorbs UV light. This is titanium dioxide in the form of nanoparticles.

Question h.4 (Vláďa Němec)

Flame retardants are compounds added to plastic products to decrease their flammability. Commonly used primary flame retardants are polybrominated aromatic compounds which release bromine radicals on thermal decomposition. These radicals then suppress the highly exothermic reactions of other organic radicals with oxygen in the initial phase of burning. Antimony (III) oxide is often used as a synergist that promotes the release of bromine radicals by first reacting with the primary flame retardant according to the equation:

$$\mathrm{Sb_2O_3} + \mathrm{C_{14}Br_{10}H_4} \longrightarrow \mathrm{SbBr_3} + \text{residue},$$

where the "residue" does not contain any bromine or antimony. Find the necessary mass percentage of $\mathrm{Sb_2O_3}$ that we need to add to the composition of a plastic product containing 20 mass percent of the brominated flame retardant, in order to achieve a stoichiometric reaction. $M_{\mathrm{Sb_2O_3}} = 291.52\,\mathrm{g\,mol^{-1}}$ $M_{\mathrm{C_{14}Br_{10}H_4}} = 971.2\,\mathrm{g\,mol^{-1}}$

Solution:

Although we don't know the exact chemical composition of the residue (it is probably a mixture of various organic compounds), the rest of the equation is possible to balance. The important fact is that the remainder doesn't contain any bromine atoms. The balanced equation (regarding bromine and antimony) is therefore:

$$5\,Sb_2O_3 + 3\,C_{14}Br_{10}H_4 \longrightarrow 10\,SbBr_3 + \text{residue}.$$

The mass of the retardant is represented by its mass fraction in the mixture, $w_{C_{14}Br_{10}H_4} = 20\%$. From the reaction above, we can see that the ratio of the stoichiometric coefficients of antimony(III) oxide and the retardant is 5:3. In other words,

$$\frac{n_{Sb_2O_3}}{n_{C_{14}Br_{10}H_4}} = \frac{5}{3},$$

therefore

$$m_{Sb_2O_3} = M_{Sb_2O_3} n_{Sb_2O_3} = M_{Sb_2O_3} \times \frac{5}{3} \times n_{C_{14}Br_{10}H_4} = m_{C_{14}Br_{10}H_4} \times \frac{5 \times M_{Sb_2O_3}}{3 \times M_{C_{14}Br_{10}H_4}}.$$

The same equation can be applied to mass fractions as well (we're in fact dividing both sides of the equation by the overall mass of the mixture), from which we obtain

$$w_{Sb_2O_3} = w_{C_{14}Br_{10}H_4} \times \frac{5 \times M_{Sb_2O_3}}{3 \times M_{C_{14}Br_{10}H_4}} \doteq 20\,\% \times 0.5 = 10\,\%.$$

Question h.5 (Richard Veselý)

Two beakers A and B containing solutions of Cu(II) ions are connected with a copper wire. Beaker A has volume $1.15\,dm^3$ and contains a solution of Cu(II) with a concentration $0.123\,M$. Beaker B has volume $3.55\,dm^3$ and contains a solution of Cu(II) with a concentration of $0.042\,M$. As a result of the difference between the concentrations, there is current through the wire. At one end, the wire dissolves, giving Cu(II) cations and electrons that flow through the wire to the other end, where they reduce the Cu(II) ions, increasing the size of the wire.

The current I that goes through the wire depends on the concentration c_A of ions in beaker A and the concentration c_B in beaker B based on this equation: $I = C \ln\left(\frac{c_A}{c_B}\right)$, where C is a positive constant. When the current stops going through the wire, the concentrations c_A and c_B will no longer change and they will satisfy the following equation: $c_A = c_B \times z$.

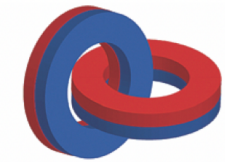
Determine the value of the constant z.

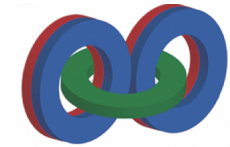
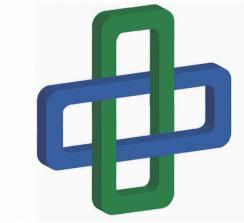
Solution:

The current won't be present once the system reaches equilibrium, which is when the concentrations in beakers A and B are the same. It can be also solved by taking $I = 0$ in the first equation, substituting $c_B z$ for c_A, and solving that equation. Therefore, $z = 1$.

Question h.6 (Sam Holmes)

Catenanes are molecules containing interlocked rings. These interlocking ring systems can be chiral. Decide if each of the following catenane structures is chiral. (You may wish to draw the mirror images.)

A)  B)  C) 

D)  E)  F) 

Solution:

A) No
B) Yes
C) Yes
D) No
E) Yes
F) Yes

Drawing the mirror images is one good way to approach this question, as is spotting the molecules which contain mirror planes. Note the images are taken from a paper, doi 10.1039/C8CS00097B.

Question k.1 (Martin Balouch)

The two most important parameters for drug bioavailability are its solubility in water and permeability. The concept of solubility is easy to understand as the maximum concentration that the drug can have without any crystallisation. The more complicated concept is the permeability coefficient P. It can be defined as follows:

$$j = P\Delta c$$

Where j is flux through the membrane — amount of substance which permeates through unit area per unit time [amount $\mathrm{m^{-2}\,s^{-1}}$] and Δc is the difference in concentration of the permeating substance between the donor and acceptor parts of the membrane.

Calculate the time of permeation for 1 mg of ibuprofen through the stomach wall, for a person who has taken enough ibuprofen to have a saturated solution in their stomach (21 mg/l). When any ibuprofen permeates, more instantly dissolves to return to a saturated solution in the stomach.

The permeation coefficient of ibuprofen is $P = 10^{-4.2}$ $\mathrm{cm\,s^{-1}}$. Approximate the stomach as a sphere of volume 900 ml full of water and assume that the concentration of ibuprofen outside of the stomach is zero.

Solution:

First we must calculate the surface of the spherical stomach from the knowledge of its volume.

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

$$r = \sqrt[3]{\frac{3}{4}V\pi}$$

$$S = 4\pi r^2 = 4\pi\sqrt[3]{\frac{3}{4}V\pi}^{\,2}$$

$$S = 2\pi\sqrt[3]{\frac{9V^2}{16\pi^2}} = \sqrt[3]{\frac{64\times 9(\pi^3 V)^2}{16\pi^2}} = \sqrt[3]{36(\pi V)^2} = 0.045\,\mathrm{m^2}$$

Now, all we have to do is to substitute into the equation that we have been given. However, we must know what the meaning of 'flux' is. We can devise this from the knowledge of its unit and the given definition. Since we have been given the concentration of the saturated solution is a mass concentration (rather than molar),

it is better to stay in the units of mass. $j = P\Delta c$

$$\frac{m}{St} = P(c_{\max} - 0)$$

$$t = \frac{m}{PSc_{\max}}$$

$$t = \frac{1\,\mathrm{mg}}{10^{-6.2}\,\mathrm{m\,s^{-1}} \times 0.045\,\mathrm{m^2} \times 21 \times 10^3\,\mathrm{mg\,m^{-3}}} = 1677\,\mathrm{s} = 28\,\mathrm{min}$$

This may seem like a long time, but stomach is not adapted to be permeated. Our bodies use permeation in their guts, which, therefore, have a large surface area.

Question k.2 (Petr Linhart)

Metal X has an atomic number x. It is a metal with rather interesting chemistry, the presence of its divalent cation can be shown in classic analytical chemistry by precipitation with sulfane in basic NH_3 solution.

Element Y has an atomic number y. At normal conditions, it is present in one of the (in the periodic table) less common states of matter. It is toxic both in its elemental form and in its compounds. Its neighbours, which are in the same group above and below it, are both biogenic. The same goes for its neighbour on the left, which is found in some rare amino acids. Don't expect much chemical activity from its neighbour on the right, though.

Determine the identities of elements X and Y. If you are unsure, here is a hint which may help you...

Permanganometry is a well-known analytical method which is used to determine the concentration of solutions of reducing agents. This is done by titrating the reducing solution against a solution of permanganate of known concentration. During the titration, permanganate is reduced to Mn(II) in the presence of acid.

In order to obtain accurate results, it is important that the concentration of the permanagate solution is known exactly. One method to obtain a precise concentration of the permanganate solution is to titrate it against oxalic acid, which is oxidised to CO_2. The equation for this process is shown below:

$$KMnO_4 + (COOH)_2 + H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + CO_2 + H_2O$$

The sum of the atomic numbers of X and Y is equal to one-eightieth of the product of the smallest whole number coefficients of the species in the balanced permanganometry standardisation equation above.

Solution:

Element Y is bromine, its two biogenic neighbours are chlorine and iodine, the element occuring in rare amino acids is selenium, the element with low reactivity is one of the noble gases, kryptonium.

Metal X is difficult to identify from the task text, in order to unveil its identity, we need to balance the permanganometry standardisation equation. The coefficients are (left to right) 2, 5, 3, 2, 1, 10, 8. Their product is 4800, one eightieth out of which equals $4800/80 = 60$. Since the atomic number of bromine is 35, we get that $60 - 35 = 25$, which is the atomic number of manganese. Metal X is therefore manganese, its compound was boldly given to you as a help directly in the task text.

Question k.3 (Raz Benson)

Tami is home after a long day in the lab and wants to get some dinner ready as soon as possible. Having decided on pasta, she starts by measuring out the recommended 500 ml water (for about 80 g dried pasta) and places it on the stovetop to boil.

Tami's flatmate, Gabi, enters the kitchen and notices the water boiling. He asks whether she has salted the water, to which she responds that she hasn't. Gabi suggests adding a pinch of salt to the saucepan, as this will raise the boiling temperature of the water, thereby reducing the cooking time for the pasta.

Calculate, to the nearest teaspoon, how much salt (sodium chloride) Tami would need to dissolve in the water to raise its boiling temperature by 1 °C. You may assume that dissolving n_{ions} moles of ions in n_{solvent} moles of a solvent causes the boiling temperature of the solvent to increase by

$$\Delta T_{\text{b}} = \frac{n_{\text{ions}} R T_{\text{b}}^2}{n_{\text{solvent}} \Delta H_{\text{v}}},$$

where R is the gas constant, T_{b} is the boiling temperature of the pure solvent (in Kelvin), and ΔH_{v} its enthalpy of vaporisation. Note that n_{ions} refers to the total number of moles of dissolved cations and anions.

Assume that one teaspoon of salt weighs 6 g. The enthalpy of vaporisation of water is $\Delta H_{\text{v}} = 40.657\,\text{kJ mol}^{-1}$.

Solution:

Explanation: $\Delta T_\mathrm{b} = 1\ \mathrm{K}$, $T_\mathrm{b} = 373.15\,\mathrm{K}$

$$n_\mathrm{solvent} = \frac{500}{18.0152} = 27.7543\,\mathrm{mol}$$

$$n_\mathrm{ions} = \frac{1 \times 27.7543 \times 40657}{8.3145 \times 373.15^2} = 0.9747\,\mathrm{mol}$$

$$m_\mathrm{NaCl} = \frac{0.9747}{2} \times (22.9897 + 35.453) = 28.481\,\mathrm{g}$$

Calculated mass corresponds to approximately 5 teaspoons.

Question k.4 (Kaijia Liu)

Compounds ABH_2 and AH are stable substances at room temperature and pressure that could be used to store and release hydrogen. When ABH_2 is heated, it releases a gas with a pungent smell, which could turn damp, red litmus paper blue. In the presence of a suitable catalyst, mixing ABH_2 with AH in the molar ratio $1 : 2$ causes all of the hydrogen to be released, resulting in a mass loss of 10.4 %. Identify elements A and B.

Solution:

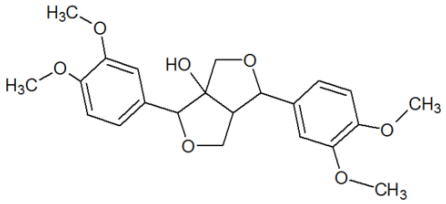
A is Li, B is N. Since the pungent gas could turn damp red litmus paper blue, it is probably ammonia. Ammonia gas contains nitrogen, so either A or B has to be nitrogen; however, since the compound NH is not stable in room conditions, nitrogen cannot be A and must be B. Then we can find what A is based on calculation. We know that $ANH_2 + 2\,AH \longrightarrow 2\,H_2 + A_3N$, and by conservation of mass we determine the relative atomic mass of A, which is 6.9. A is thus lithium.

Question k.5 (Sam Holmes)

Zeisel determination was developed by the Austrian-Czech chemist Zeisel, to determine the number of methoxy and ethoxy groups in a molecule before spectroscopic techniques became available. The method was as follows:

1. A known mass of the compound of interest is combined with an excess of hydrogen iodide.
2. This mixture is distilled at 50 °C and the distillate collected.
3. An excess of acidified silver nitrate solution is added to the distillate.
4. The precipitate is collected, dried, and weighed.

A scientist wishes to apply this method to determine the number of methoxy groups in gmelinol ($C_{22}H_{26}O_7$, see the structure below), an antifungal agent. They add 5 g of gmelinol to excess hydrogen iodide. What mass of solid will be collected? Consider that one mole of methyl or ethyl groups is cleaved off by one mole of hydrogen iodide.



Solution:

Precipitate mass is 11.68 g. From the given structure, we can see that there are 4 methoxy groups in gmelinol. We have to determine its molar mass: $M(C_{22}H_{26}O_7) = 402.17\,\mathrm{g\,mol^{-1}}$, therefore 5 g of gmelinol correspond to

$$n = \frac{n}{M} = \frac{5}{402.17} \doteq 0.0124\,\mathrm{mol}$$

of the compound. The task text gives a hint that methyl groups are cleaved off in the reaction, from which we can deduce that methyl iodide is formed. Since there is a precipitation with $AgNO_3$ occurring, the precipitate is probably silver iodide, AgI. The amount of substance of AgI is equal to the amount of substance of methoxy groups in gmelinol and its molar mass is $M(\mathrm{AgI}) = 234.77\,\mathrm{g\,mol^{-1}}$. Therefore the mass of precipitate collected is

$$m = 4nM(\mathrm{AgI}) = 4 \times 0.0124 \times 234.77 \doteq 11.68\,\mathrm{g}.$$

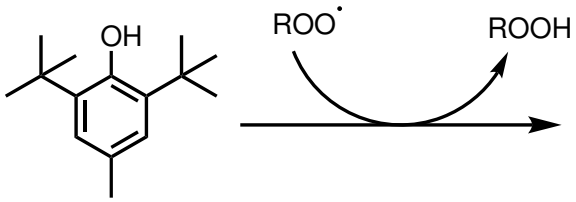
Question k.6 (Vladimír Němec)

Plastics undergo a relatively high oxidative load during production and in everyday use: high temperatures during processing, UV radiation during use, exposure to oxygen and atmospheric ozone. Unless an antioxidant is added to the formulation, these influences propagate into the material properties—over time, the plastic loses elasticity and strength, cracks, and in the most extreme cases, the plastic product crumbles to dust. These undesirable consequences of oxidation can be prevented by antioxidants. One group of antioxidants used in the polymer industry are sterically hindered phenols. Butylated hydroxytoluene (BHT) serves as a model.

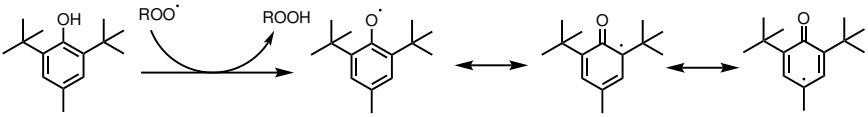
In the presence of oxygen, organic peroxoradicals are formed in the polymer material. These radicals are very reactive and cause chain scission of the polymer, which are macroscopically manifested as the defects mentioned above.

The BHT molecule reacts with the organic peroxoradical. The resulting molecule is less reactive than the organic peroxoradical. Due to steric hindrance, it is more difficult to attack the polymer chain and is also stabilised by electron delocalisation.

Write the product of the reaction below and draw at least one alternative resonance structure of the molecule that shows the delocalisation of electrons.



Solution:



Resonance forms are ways of drawing the same molecule with the electrons arranged differently. For BHT, which contains an aromatic ring, you should know that the Kekule structure of alternating double and single bonds is inappropriate because there is delocalisation of electrons. We can draw resonance forms that illustrate the

delocalisation in BHT by moving around the electrons as shown. Three acceptable resonance forms are drawn here, separated by resonance arrows (notice how they are different from equilibrium arrows!).

Note that the ability to draw resonance forms is the reason we often draw the Kekule structure rather than the delocalised "ring" representation: for the latter there would not be a satisfactory way to depict the delocalisation of the radical into the aromatic ring.

Question m.1 (Adam Přáda)

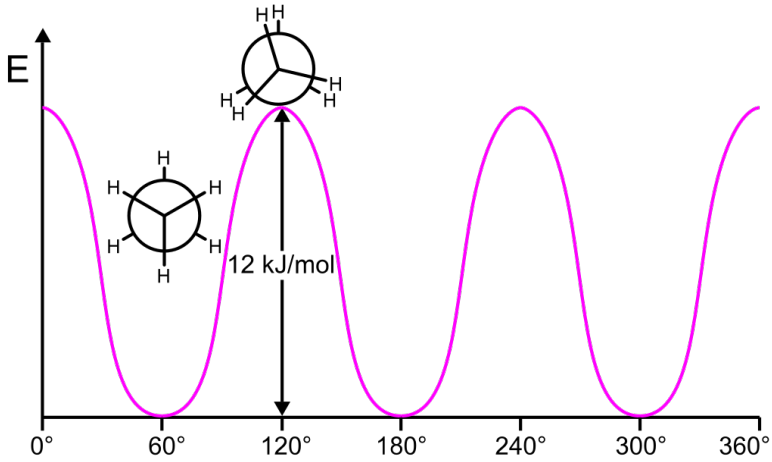
Much has been said about the world being designed for men. One of the everyday problems women face is opening Vacuum Lug Closures (VLCs). Studies have shown that the stereotype of women asking men for help with opening a jar of pickles is not unfounded, since the maximum torque that men can exert is on average around 6 Nm, while for women it is around 4 Nm. Pickles are usually found in jars with 85 mm lids, where the average torque required to open them is about 6 Nm. [1]

The question I asked myself is, what if we magnified the ethane molecule. Would people be able to twist ethane over its rotational barrier like the lid of a pickle jar? Calculate the required torque to twist an ethane molecule magnified to the size of a pickle jar (lid).

Assume that the force required to twist the molecule scales proportionally with its diameter. Also assume that you exert constant force on the hydrogens when going from the staggered conformation to the eclipsed conformation. (note that this is not the ideal torque spring behaviour) See the picture in the figure for illustration.

Required data:
The rotational barrier of ethane is 12 kJ/mol, the diameter of the ethane molecule is 204 pm. (i.e. the diameter of a cylinder circumscribed to ethane)

[1] `https://etheses.whiterose.ac.uk/14919/`



Note that the shape of the energy curve is in the figure is more realistic than the one described in the question, which you are expected to use.

Solution:

We first want to find out how large force we need to rotate ethane. Energy is force times distance, i.e. $E = FL$. The distance travelled by force rotating ethane by an angle θ is $L = R\theta$. Since we assume the force to be constant and we know the angle $\theta = 60°$ to get to the top of the barrier, we can express $F = E/(R\theta)$. Then we just scale the force linearly w.r.t. the diameter as given in the question.

$$
\begin{aligned}
E &= 12\,\mathrm{kJ/mol} = 1.99265 \times 10^{-20}\,\mathrm{J} \\
F &= \frac{1.99265 \times 10^{-20}\,\mathrm{J}}{102 \times 10^{-12}\,\mathrm{m} \times 60 \times 2\pi/360} = 1.8655269 \times 10^{-9}\,\mathrm{N} \\
F_1 &= F_2 \frac{D_1}{D_2} = 1.8655269 \times 10^{-9}\,\mathrm{N} \times \frac{85 \times 10^{-3}}{204 \times 10^{-12}} \\
F_1 &= 0.077732111225455\,\mathrm{N} \\
\tau &= F_1 R_1 = 0.00330\,\mathrm{Nm}
\end{aligned}
$$

We find that ethane scaled in this particular way would be rather easy to rotate around.

Question m.2 (Milada Peřinová)

In an earlier question, we mentioned the composition of a Celaskon effervescent vitamin C tablet. Match the ingredients (1–9) listed below to their functions (A–G). Note that there are two sweeteners and two gas-forming agents.

1 – ascorbic acid	A – binder
2 – citric acid	B – sweetener (×2)
3 – sorbitol	C – active ingredient
4 – sodium bicarbonate	D – flavour
5 – lactose	E – colour
6 – orange aroma	F – gas-forming agent (×2)
7 – macrogol 6000	G – filler
8 – acesulfame potassium	
9 – Allura Red AC	

Solution:

1C, 2F, 3B, 4F, 5G, 6D, 7A, 8B, 9E

Ascorbic acid (1), a.k.a. vitamin C, is the active ingredient (C) here. Citric acid (2) and sodium bicarbonate (4) are the two reagents of an acid-base reaction which is responsible for carbon dioxide production (both F), that causes disintegration of the tablet – because of CO2, the tablet fizzes and falls apart. Sorbitol (3) is a known for its use as a sweetener (B) for diabetics. Another sugar in the contents is lactose (5), however, it is not used as a sweetener here (in fact, its taste is only mildly sweet) – its function is to increase tablet volume, therefore it is a filler (G). Some drugs and excipients have an unpleasant taste, which must be hidden (D), for instance using an orange aroma (6). For the tablet to hold together (A), macrogol 6000 is added to the mixture (7), i.e. polyethylene glycol with the average molar mass of $6000\,\mathrm{g\,mol^{-1}}$. The second sweetener (B) is the acesulfame potassium (8), an artificial sweetener used e.g. in soft drinks. Last but not least is the Allura Red AC (9), whose function is to give the tablet a more attractive colour (E).

Question m.3 (Karolína Fárníková)

Substance A decomposes at 720 K with a rate constant $k_A = 0.422\,\text{mol}^{-0.25}\text{dm}^{0.75}\text{s}^{-1}$ while substance B decomposes at 642 K with a rate constant $k_B = 0.447\,\text{h}^{-1}$.

What is the difference in the orders of reaction between the decompositions of substances A and B?

Solution:

The order of reaction in case A is 1.25 and 1 in case B, thus their difference is 0.25. Both orders can be determined from the rate constants' units, based on the formula for reaction rate:

$$v = k \cdot c^n$$

with c the initial concentration, k the rate constant and n the order of reaction. The unit of reaction rate is mol $\text{dm}^{-3}\text{s}^{-1}$ and the unit of concentration is mol dm^{-3}.

Question m.4 (Yizhe Lou)

Radiometric dating is extremely significant in Earth sciences as it can be used to determine the absolute ages of igneous rocks. One important isotope for radiometric dating is ^{176}Lu, which decays into ^{176}Hf with a half-life of 3.716×10^{10} years, which is even greater than the age of the Earth. Measuring the amount of an isotope is extremely difficult, but fortunately measuring the ratio between isotopes is easy.

^{177}Hf's natural abundance stays constant through geological history, so the ratios between ^{176}Lu and ^{177}Hf and the ratio between ^{176}Hf and ^{177}Hf are usually measured. The formula used to determine the age is:

$$\frac{^{176}\text{Hf}}{^{177}\text{Hf}} = \frac{^{176}\text{Hf}_0}{^{177}\text{Hf}} + \frac{^{176}\text{Lu}}{^{177}\text{Hf}} \times (\text{e}^{\lambda t} - 1)$$

where $^{176}\text{Hf}_0$ is the original abundance of ^{176}Hf and λ is a constant that can be calculated from the half-life of the isotope by the relationship $\ln(c/c_0) = -\lambda t$, where c_0 is the original abundance. Several samples are collected from an igneous intrusion by a geologist for analysis. In the first sample, $^{176}\text{Hf}/^{177}\text{Hf} = 0.28630$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.42850$; in the second sample, $^{176}\text{Hf}/^{177}\text{Hf} = 0.28239$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.01470$. Determine the age of the igneous intrusion.

Solution:

The age of the intrusion is 5.04×10^8 years. A value between 4.8–5.2 $\times 10^8$ is acceptable.

The problem looks extremely difficult at the first glance but is not too complex. To solve the problem, first calculate the constant λ

$$\ln(0.5/1) = -\lambda(3.716 \times 10^{10})$$

$$\lambda = 1.8653 \times 10^{-11}$$

Then apply the relationship to calculate the age. You will find that there is a linear relationship between $^{176}Hf/^{177}Hf$ and $^{176}Lu/^{177}Hf$, with the slope $e^{\lambda t} - 1$ and the y-intercept $^{176}Hf_0/^{177}Hf$ (this is the $^{176}Hf/^{177}Hf$ ratio at the time of the igneous intrusion). Therefore

$$e^{\lambda t} - 1 = \frac{0.28239 - 0.28630}{0.01470 - 0.42850} = 9.4490 \times 10^{-3}$$

$$e^{\lambda t} = 1.009449$$

$$\lambda t = 9.4046 \times 10^{-3}$$

And use the value of λ calculated above to get

$$t = \frac{9.4046 \times 10^{-3}}{1.8653 \times 10^{-11}} = 5.0419 \times 10^8 \text{ years}$$

Then the geologists can decide that the intrusion took place in Cambrian. In real life, radiometric dating is for sure more complex. More data is required and a linear regression analysis is required to obtain a more accurate age.

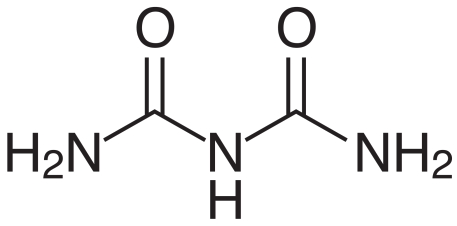
Question m.5 (Petr Linhart)

An unknown compound of molar mass 103 g mol^{-1} is composed of four elements, in particular (all mass fractions): 23.3 % carbon, 31.0 % oxygen, 40.8 % nitrogen and 4.9 % hydrogen. Draw its molecular structure.

It may be useful to know that there is a reaction named after this compound, which is used to detect the presence of protein; the compound undergoes this reaction because of its structural resemblance to a part of a protein.

Solution:

From the given mass fractions we can determine that the molecular formula of the unknown compound is $C_2O_2N_3H_5$. We also know that the compound should be structurally similar to parts of protein, judging by the atomic composition it is probably a peptide bond. The compound has a following structure:



It is a derivative of urea called biuret. The discussed test is called the biuret test.

Question m.6 (Terezie Císařová)

The cooks at a summer camp would prepare a simple cucumber salad for lunch every day. It was composed of 10 litres of water, some cucumbers, and 2 ml 8 % vinegar to improve the flavour. Unfortunately, the cooks ran out of vinegar before the final lunch, but as practical people they decided to take advantage of the situation and solve two problems at once. In place of vinegar, they flavoured the salad with ants, which had forever been bothering them in the kitchen. How many ants would they need to add to the water to achieve the same pH as with the usual vinegar?

Assume the average ant weighs 0.003 g and each contains 3 % formic acid by mass. The dissociation constant of formic acid is 2.1×10^{-4} and its molar mass is $46.03\,\mathrm{g\,mol^{-1}}$. The $\mathrm{p}K_\mathrm{A}$ of acetic acid is 4.75 and its molar mass is $60.052\,\mathrm{g\,mol^{-1}}$. The concentration of 8 % vinegar is 1.33 M. Ignore the dissociation of the water and round the number of ants up to an integer.

Solution:

399 ants

Such problems are typically approached by writing down a set of equations comprising the definition of dissociation constant

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

water dissociation equation ($10^{-14} = [\mathrm{OH}^-]\cdot[\mathrm{H}^+]\,,$), electroneutrality equation ($[\mathrm{A}^-]+[\mathrm{OH}^-] = [\mathrm{H}^+]$) and an equation for total concentration of acid ($c_{\mathrm{HA}} = [\mathrm{A}^-] + [\mathrm{HA}]$).

When we neglect the dissociation of water, all protons in the solution must come from acid dissocaition. The electroneutrality equation is then simplified to $[\mathrm{H}^+] = [\mathrm{A}^-]$. The pH of the acid is defined by the activity of H^+ ions, which is here expressed by the actual concentration of H^+ ions. So when the the two acids concerned have equal pH, we can say that

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

(for easier notation and reading we use HOOCH= HFORM and HOOC$-$CH$_3$= HACET).

Then we compose the remaining two equations for both acids:

$$K_{\mathrm{ACET}} = \frac{[\mathrm{ACET}^-][\mathrm{H}^+]}{[\mathrm{HACET}]}$$

$$K_{\mathrm{FORM}} = \frac{[\mathrm{FORM}^-][\mathrm{H}^+]}{[\mathrm{HFORM}]}$$

$$c_{\mathrm{HACET}} = [\mathrm{ACET}^-] + [\mathrm{HACET}]$$

$$c_{\mathrm{HFORM}} = [\mathrm{FORM}^-] + [\mathrm{HFORM}],$$

where for acetic acid we substitute [HACET] from the equation for the total concentration of acid and we know that $[\mathrm{H}^+] = [\mathrm{ACET}^-]$. Then we obtain

$$K_{\mathrm{ACET}} = \frac{[\mathrm{H}^+]^2}{c_{\mathrm{HACET}} - [\mathrm{H}^+]},$$

which is a quadratic equation for $[H^+]$. We take the positive root, since a negative concentration would be unphysical:

$$[\mathrm{H}^+] = \frac{-K_{\mathrm{ACET}} + \sqrt{K_{\mathrm{ACET}}^2 - 4\cdot(-c_{\mathrm{HACET}}\cdot K_{\mathrm{ACET}})}}{2}.$$

This evaluates to $[\mathrm{H}^+] = 6.048 \times 10^{-5}\,\mathrm{mol dm}^{-3}$.

K_A of the acetic acid was obtained from the relation $\mathrm{p}K_\mathrm{A} = -\log K_\mathrm{A}$, and c_HACET was calculated as $\frac{c_\mathrm{drop}V_\mathrm{drop}}{V_\mathrm{pot}+V_\mathrm{drop}}$.

The equation for K_FORM is analogous:

$$K_\mathrm{FORM} = \frac{[\mathrm{H}^+]^2}{c_\mathrm{HFORM} - [\mathrm{H}^+]},$$

from which we get

$$c_\mathrm{HFORM} = \frac{[\mathrm{H}^+]^2 + K_\mathrm{FORM} \times [\mathrm{H}^+]}{K_\mathrm{FORM}} = 7.79 \times 10^{-5}\,\mathrm{mol\,dm}^{-3}.$$

From the concentration of formic acid in the pot we can get the total mass of the acetic acid needed,

$$m_\mathrm{HFORM} = c_\mathrm{HFORM} \times M_\mathrm{HFORM} \times (V_\mathrm{pot} + V_\mathrm{drop}) = 7.79 \times 10^{-5} \times 46.03 \times 10.002 = 0.0359\,\mathrm{g}.$$

Finally, the total number of ants is $N = \frac{m_\mathrm{HFORM}}{m_\mathrm{ant} \times w_\mathrm{HFORM/ant}} = \frac{0.0395}{0.03 \times 0.003} = 398.8... \simeq$ 399 ants.

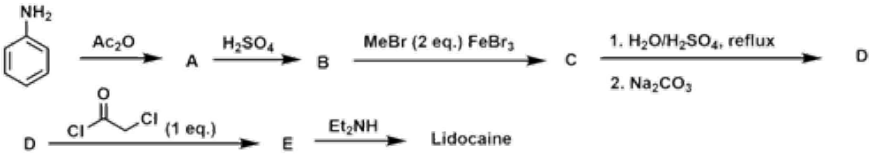
Question n.1 (Ondřej Daněk)

Lidocaine is a local anesthetic, which is used, for example, by dentists to desensitise dental nerves. It works by reversibly blocking ion channels for sodium ions, which prevents the neurons from transmitting signals. When Jardík, an amateur chemist, wanted to obtain some lidocaine (perhaps to synthesise denatonium benzoate A.K.A. *Bitrex*, one of the most bitter substances), the simplest way would probably have been to extract it from some over-the-counter product. Unfortunately for bashful Jardík, the best over-the-counter product that contains a large amount of lidocaine is a desensitising anal lubricant, so Jardík decided instead to synthesise lidocaine from scratch. After searching in his chemical cabinet for a while, he found everything he needed, and got to work.

First he reacted aniline with acetic anhydride to get compound A. Treating this compound with concentrated sulfuric acid afforded compound B, mostly the *para* isomer. The third step was the reaction of B with two equivalents of methyl bromide in presence of ferric bromide, yielding product C. This was refluxed in water acidified with sulfuric acid, after which the reaction mixture was treated with sodium

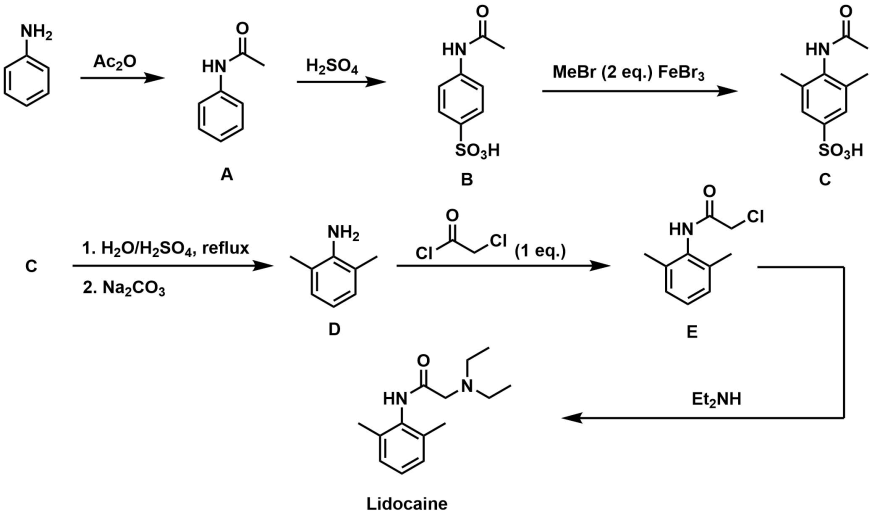
carbonate, resulting in product D. Product D was reacted with 2-chloroacetyl chloride, and lastly the product of this reaction (E) was heated with diethylamine to give the final product, lidocaine. Content with having avoided any embarrassment with this six-step synthesis, he carried out the last few steps to get denatonium benzoate, and could finally enjoy a glass of really bitter beer.

Draw the structures of A, B, C, D, E and lidocaine. Use skeletal formulae.



Solution:

Relative reactivity of acyl chloride and alkyl chloride has to be taken into account in the step from D to E. Acyl chloride is more reactive and thus mainly product E is formed.



Question n.2 (Petr Linhart)

Electrochemical methods are useful for measurements of various thermodynamic data. They take advantage of the principle of redox reactions i.e., exchange of electrons, and the fact that that when conveniently arranged, these reactions can become a source of voltage. The 'willingness' of a compound to be reduced can then be quantified by its standard reduction potential, $E^{\ominus}$, as a proxy for the change in Gibbs energy $\Delta G^{\ominus}$:

$$\Delta G^{\ominus} = -zFE^{\ominus},$$

where z is the number of electrons exchanged and F is the Faraday constant. The standard reduction potential is given as a voltage relative to the reduction potential of a standard hydrogen electrode (SHE), which has $E^{\ominus}_{\mathrm{SHE}} = 0\,\mathrm{V}$ by definition (remember that we can only measure potential *differences* i.e., voltages, hence the need to define a reference).

Given the following system of reactions, determine the standard reduction potential of the second reaction.

$$\mathrm{NO_3^-(aq)} + 3\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{HNO_2} + \mathrm{H_2O(l)};\, E^{\ominus}_1 = 0.96\,\mathrm{V}(1)$$

$$\mathrm{HNO_2(aq)} + \mathrm{H^+} + 1\,\mathrm{e^-} \longrightarrow \mathrm{NO} + \mathrm{H_2O(l)};\, E^{\ominus}_2 = ?(2)$$

$$\mathrm{NO_3^-(aq)} + 4\,\mathrm{H^+} + 3\,\mathrm{e^-} \longrightarrow \mathrm{NO} + 2\,\mathrm{H_2O(l)};\, E^{\ominus}_3 = 0.97\,\mathrm{V}(3)$$

Solution:

$E_2 = 0.99\,\mathrm{V}$.

It would be a mistake to think that since the reaction (3) is just a sum of the first two reactions, (3) = (1) + (2), then the standard potential $E^{\ominus}_3$ would be just a sum of the first two, which would lead to $E^{\ominus}_2 = 0.01\,\mathrm{V}$. Gibbs energy is, as well as other thermodynamic potentials (e.g. internal energy U, enthalpy H…), independent of path, which is sometimes (in case of enthalpy) called the Lavoisier–Laplace and the Hess' law. This means that

$$\Delta G^{\ominus}_3 = \Delta G^{\ominus}_1 + \Delta G^{\ominus}_2.$$

Let's, for simplicity, express the energy in multiples of Faraday constant, since its value is not important for the calculation. Then

$$3E^{\ominus}_3 = 2E^{\ominus}_1 + E^{\ominus}_2$$

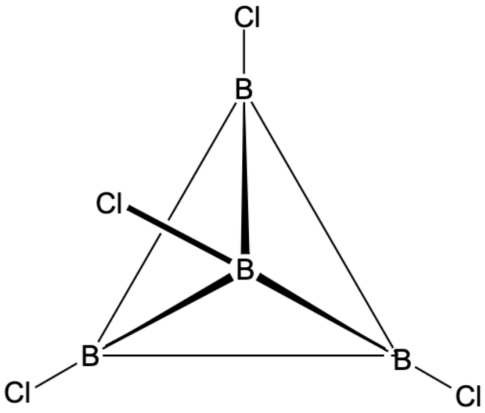
therefore the reduction potential of reaction 2 is $E^{\ominus}_2 = 0.99\,\mathrm{V}$.

Question n.3 (Kaijia Liu)

X and Y are two non-metallic elements. The sum of their atomic numbers is 22, and the sum of their valence electron numbers is 10. The compounds of X and Y include XY, XY_3 (a good acceptor of electron pairs), X_2Y_4 and X_4Y_4. X_4Y_4 has four three-fold rotational axes (meaning the structure overlaps with itself when rotated 120° around one of these axes) and there are four atoms around each X atom. Deduce the identities of X and Y and, using the correct chemical symbols, suggest a sensible structure for X_4Y_4.

Solution:

X is boron, Y is chlorine. We start by listing what X and Y could be. Since the sum of their atomic numbers is only 22, X and Y both have to be non-metallic elements—one from Period 2 and one from Period 3. The possible pairs are: B and Cl, C and S, N and P, and O and Si. However, these pairs are not all chemically sensible; only B and Cl could form all four compounds, with the valence shell of chlorine always able to reach an octet. The drawing for X_4Y_4 needs some imagination, but the shape that best fulfills the given symmetry criteria is a tetrahedron. (We could guess this by reasoning that it is probable that all four boron atoms are in the same chemical environment.) If we arrange the borons so that they form a tetrahedron and attach a chlorine to each one of them, we obtain the answer. This may require some trial and error to achieve, though.



Question n.4 (Petr Linhart)

From a previous task, we already know that electrochemical methods can tell us a lot about the redox behaviour of reactions. We measure the so-called standard reduction potential, $E^{\ominus}$, which is related to the change in Gibbs energy by

$$\Delta G^{\ominus} = -zFE^{\ominus},$$

where z is the number of electrons exchanged and F is the Faraday constant. The change in Gibbs energy describes spontaneity of a reaction and its standard value, $\Delta G^{\ominus}$, is related to the equilibrium constant by

$$\Delta G^{\ominus} = -RT \ln K.$$

Here R is the molar gas constant and T is the thermodynamic temperature.

Your task is now to calculate the solubility product of zinc(II) sulfide at temperature 25 °C and pressure 101 325 Pa (standard conditions). You are provided with the following electrochemical data:

$$\mathrm{ZnS(s)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Zn(s)} + \mathrm{S^{2-}};\, E^{\ominus} = -1.45\,\mathrm{V},$$

$$\mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Zn(s)};\, E^{\ominus} = -0.76\,\mathrm{V}.$$

Hint: The solubility product of a compound is the equilibrium constant of its dissociation.

Solution:

$K_s = 4.7 \times 10^{-24}$.

From a previous task we already know that Gibbs energy is independent of path. We want to determine the equilibrium constant of a reaction

$$\mathrm{ZnS(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{S^{2-}(aq)},$$

which can be obtained as a difference of the given two reactions, (1) - (2). Gibbs energy of the dissociation reaction is therefore $\Delta G^{\ominus} = \Delta G_1^{\ominus} - \Delta G_2^{\ominus}$. So, we first determine the Gibbs energies from the given reduction potentials:

$$\Delta G_1^{\ominus} = -2F(-1.45) \doteq 279.807\,\mathrm{kJ\,mol^{-1}}.$$

$$\Delta G_2^{\ominus} = -2F(-0.76) \doteq 146.658\,\mathrm{kJ\,mol^{-1}}.$$

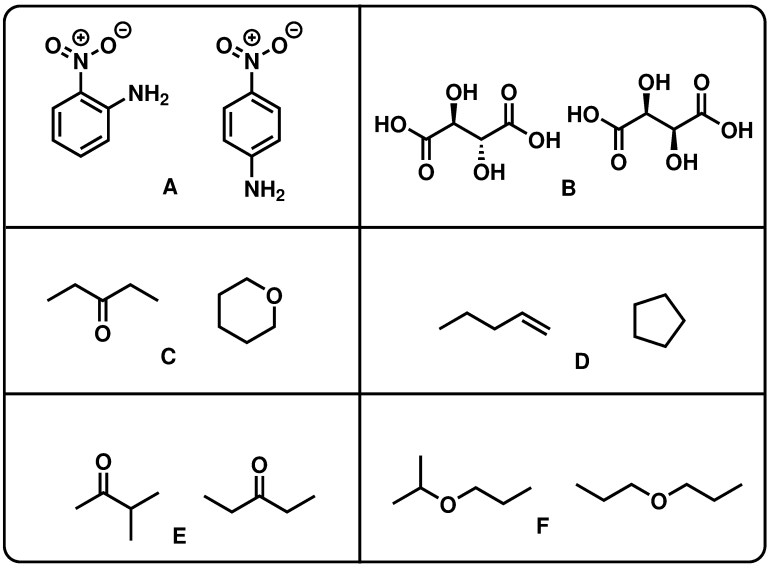
Therefore $\Delta G^{\ominus} = 133.149\,\mathrm{kJ\,mol^{-1}}$. From the task text we also know the relationship between Gibbs energy and the equilibrium constant, if we express it, we obtain

$$K = \exp\Big(-\frac{\Delta G^{\ominus}}{RT}\Big) = \exp\Big(\frac{-133149}{8.314 \cdot 298.15}\Big) \doteq 4.70 \times 10^{-24}.$$

The equilibrium constant has a small value, which corresponds to the fact that zinc(II) sulfide is (as the majority of sulfides) almost insoluble in water.

Question n.5 (Ondřej Daněk)

Summary (molecular) formulae quite often gives sufficient information about inorganic compounds. Organic compounds, on the other hand, cannot be easily described just by a summary formula; hundreds of isomers can exist for a given summary formula, so knowing the structure of the molecule is important. Fortunately, organic chemists of today have a large number of analytical methods in their arsenal by which they can determine the structure of compounds. Most of the time, NMR spectroscopy can be used, but it is useful to be familiar with other techniques too—both instrumental and classic chemical analyses.



Match pairs of isomers (A–F) to the most fitting analytical method (1–6) from the list below. Choose the methods such that you would not have to search for exact data (such as NMR shifts, melting points or optical rotations). You can choose each method only once.

1. ^{1}H NMR spectroscopy
2. Reaction with iodine in alkaline solution
3. Polarimetry (measurement of optical rotation)
4. Melting point measurement
5. Infrared spectroscopy
6. Reaction with bromine water

Solution:

A – 4, B – 3, C – 5, D – 6, E – 2, F – 1

A – Nitro group and amino group can form intramolecular hydrogen bond when in the ortho position. The melting point is thus lower (71 °C) because the molecules don't interact that strongly together. In the case of the para isomer, the nitro and amino groups of neighbouring molecules can form intermolecular hydrogen bonds resulting in long chains of molecules, and the melting point is significantly increased (146–149 °C)

B – The two pictured isomers of tartaric acid differ in their optical activity, because the D-tartaric acid is chiral and rotates the plane of polarization to the left and the meso tartaric acid has a plane of symmetry in the molecule so it doesn't rotate the plane of polarization at all.

C – The carbonyl group of pent-3-one can be clearly detected as a strong absorption band between 1600 and 1900 cm^{-1} in the infrared spectrum.

D – The presence of the double bond can be confirmed by adding bromine water, and observing the loss of color due to the reaction of bromine with the alkene (electrophilic addition to the double bond)

E – Methyl ketones can be oxidized to the corresponding carboxylic acid and trihalomethane in whats known as the haloform reaction. When the reaction is done with iodine, yellow crystals of triiodomethane form, indicating the presence of the methyl ketone. On substituted alpha carbons the alpha halogenation stops after substituting all alpha hydrogens for halogen atoms, but cannot proceed further so the formation of iodoform is not observed.

F – These two isomers differing only in the positioning of one methyl group cannot be easily distinguished without knowing exact data, such as retention times in gas chromatography, but will have clear diferences in ^{1}H NMR spectra in the multiplicities of the signals. The isopropyl propyl ether will have a septet peak typical for the isopropyl group.

Question n.6 (Ondřej Daněk)

Ben decided to find out how efficient his digestive tract is in absorbing nutrients from food. He had an idea that since the energetic values of food written on the packaging are determined by bomb calorimetry, he could use the same method to measure the leftover energy in already digested food.

To make his measurements more consistent, he ate only a dietary supplement called Soylent for a week. Soylent contains 6 grams of fibre in one portion (60 g) and since fibre is indigestible, the efficiency of the digestive tract should be calculated only from the rest of the supplement's composition. The enthalpy of combustion of fibre (cellulose) is $16.2\,\mathrm{MJ\,kg^{-1}}$.

To calibrate his bomb calorimeter (closed steel bomb containing the sample, equipped with electric ignition pressurized to 30 atm with oxygen, submerged in a vessel isolated with styrofoam containing water equipped with a stirrer and accurate thermometer) Ben chose benzoic acid, which is used as a standard for this method. The enthalpy of combustion of benzoic acid is $-3228\,\mathrm{kJ\,mol^{-1}}$. After burning 0.5681 g of benzoic acid, the temperature in the calorimeter had risen by 0.9024 °C.

To determine the efficiency of his digestive tract Ben burned 0.5445 g of the dry white powder (Soylent) and the temperature in the calorimeter rose by 0.6660 °C.

At the end, Ben had to measure the enthalpy of combustion of the digested soylent. First he lyophilized the brown gooey material, and then he weighed and burned a sample of the dry brown powder. After burning 0.5306 g of the sample, the temperature in the calorimeter had risen by 0.5089 °C.

Calculate the efficiency of Ben's digestive tract in absorbing the nutrients (relative to burning the food). The heat capacity of water can be assumed to remain constant during such small temperature changes ($c_p = 4183\,\mathrm{J\,kg^{-1}\,K^{-1}}$). Assume that for calculating the relative efficiency, the enthalpy of combustion can be used in place of inner energy change, even though the process of burning the sample in the bomb is isochoric. Assume that the mass fraction of cellulose in the lyophilized fecal matter is the same as in the starting Soylent.

Solution:

First we have to calculate the heat capacity of the calorimetric setup from the calibration with benzoic acid.

$$c = \frac{Q}{\Delta T} = \frac{m}{M} \times \frac{-\Delta H_{\text{spal}}}{\Delta T} = \frac{0.5681 \times 3228000}{122.123 \times 0.9024} = 16\,640.32\,\text{J}\,\text{K}^{-1}$$

Next, we calculate the heats of combustion of soylent and of the excrement sample:

$$Q_{\text{combustion}}(\text{soylent}) = \Delta T(\text{soylent}) \times c = 0.666 \times 16\,640.32 = 11\,082.45\,\text{J}$$
$$Q_{\text{combustion}}(\text{excrement}) = \Delta T(\text{excrement}) \times c = 0.5089 \times 16\,640.32 = 8468.26\,\text{J}$$

From the total heat of combustion of the sample, $0.1 \times m(\text{sample}) \times \Delta H_{\text{combustion}}(\text{cellulose})$ must be subtracted, and the result must be divided by the total mass of the sample to get the 'digestible' heat of combustion of one gram of soylent or excrement. Resulting 'digestible' heats of combustion must then be subtracted and the result divided by the 'digestible' heat of combustion of Soylent.

The resulting ratio is the fraction of energy absorbed during digestion. This calculation can be used, because the cellulose content is assumed to remain the same after digestion, but this assumption is quite inaccurate.

$$q_{\text{combustion}}(\text{soylent} - \text{digestible}) =$$
$$= \frac{Q_{\text{combustion}}(\text{soylent}) - 0.1 \times m(\text{soylent}) \times \Delta H_{\text{combustion}}(\text{cellulose})}{m(\text{soylent})} =$$
$$= \frac{11\,082.45 - 0.1 \times 0.0005455 \times 16.2 \times 10^6}{0.5445\,\text{g}} = 18\,696.13\,\text{J}\,\text{g}^{-1}$$

$$q_{\text{combustion}}(\text{excrement} - \text{digestible}) =$$
$$= \frac{Q_{\text{combustion}}(\text{excrement}) - 0.1 \times m(\text{excrement}) \times \Delta H_{\text{combustion}}(\text{cellulose})}{m(\text{excrement})} =$$
$$= \frac{8468.26 - 0.1 \times 0.0005306 \times 16.2 \times 10^6}{0.5306} = 14\,339.78\,\text{J}\,\text{g}^{-1}$$

$$\eta = \frac{q_{\text{combustion}}(\text{soylent} - \text{digestible}) - q_{\text{combustion}}(\text{excrement} - \text{digestible})}{q_{\text{combustion}}(\text{soylent} - \text{digestible})} =$$
$$= \frac{18\,696.13 - 14\,339.78}{18\,696.13} = 0.233 = 23.3\%$$

Question o.1 (Jaroslav Cerman)

Consider a reaction mechanism given by the following schema:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}, \qquad \mathrm{A} \xrightarrow{k_3} \mathrm{C}, \qquad \mathrm{B} + \mathrm{C} \xrightarrow{k_2} \mathrm{D} + \mathrm{C} \text{ (catalysis by C)}$$

Suppose our goal is to maximise the concentration of B in the reaction mixture. After how many seconds should the reaction be terminated, such that the maximum concentration of B is obtained in a batch reactor? The volume of reaction mixture is constant.

Listed below are the rate equations for species A–D and the solutions to these equations i.e., concentrations as explicit functions of time.

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -(k_1 + k_3) \qquad [\mathrm{A}] = [\mathrm{A}]_0 - (k_1 + k_3) \cdot t$$

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = k_1 - k_2 \cdot [\mathrm{C}] \qquad [\mathrm{B}] = [\mathrm{B}]_0 + k_1 \cdot t - k_2 \cdot ([\mathrm{C}]_0 \cdot t + k_3 \cdot \frac{t^2}{2})$$

$$\frac{\mathrm{d[C]}}{\mathrm{d}t} = k_3 \qquad [\mathrm{C}] = [\mathrm{C}]_0 + k_3 \cdot t$$

$$\frac{\mathrm{d[D]}}{\mathrm{d}t} = k_2 \cdot [\mathrm{C}] \qquad [\mathrm{D}] = [\mathrm{D}]_0 + k_2 \cdot ([\mathrm{C}]_0 \cdot t + k_3 \cdot \frac{t^2}{2})$$

$[\mathrm{A}]_0 = 5\,\mathrm{mol\,dm^{-3}}$; $[\mathrm{B}]_0$, $[\mathrm{C}]_0$, $[\mathrm{D}]_0 = 0\,\mathrm{mol\,dm^{-3}}$
$k_1 = 1 \times 10^{-3}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$; $k_2 = 1 \times 10^{-3}\,\mathrm{s^{-1}}$; $k_3 = 6.31 \times 10^{-4}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$

Solution:

The reaction should be terminated after 1584.8 s.

The concentration of B is given as an explicit function of time. This function represents a parabola when $[\mathrm{B}]_0 = [\mathrm{C}]_0 = 0$:

$$[\mathrm{B}] = k_1 \times t - k_2 k_3 \times \frac{t^2}{2}$$

(when C_0 is zero). The location of the vertex of the parabola is given by the well-known formula

$$t(B = \max(B)) = \frac{-b}{2a},$$

where b is a coefficient of the first degree and a is a coefficient of the second degree of the polynomial.

$$k_1 \times t - k_2 k_3 \times \frac{t^2}{2} = b \times t + a \times t^2$$

Since coefficient a is negative, the parabola has a maximum at its vertex.

$$t(B = \max(B)) = \frac{-k_1}{\frac{-2 \times k_2 k_3}{2}} = \frac{k_1}{k_2 k_3} = \frac{1 \times 10^{-3}}{6.31 \times 10^{-4} \times 1 \times 10^{-3}} = 1584.8\,\text{s}.$$

For participants more mathematically minded, it may be simpler to use the fact that the first derivative of a function at its maximum is zero. The time derivative of B's concentration is also given, so to obtain the solution, one has to solve the equation

$$\frac{\mathrm{d}B}{\mathrm{d}t} = k_1 - k_2 \times C = k_1 - k_2 k_3 \times t = 0$$

$$t(B = \max(B)) = \frac{k_1}{k_2 k_3} = \frac{1 \times 10^{-3}}{6.31 \times 10^{-4} \times 1 \times 10^{-3}} = 1584.8\,\text{s}.$$

Question o.2 (Tatiana Nemirovich)

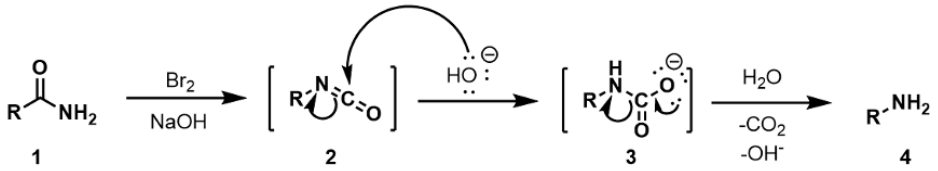
Several months ago, the planetary rover *Curiosity* detected, for the first time, an organic molecule on the surface of Mars. Identify the molecule given that its ^{1}H NMR spectrum contains 4 signals, its ^{13}C NMR spectrum contains 5 signals and its mass spectrum has the molecular peak at $m/z = 122$ in addition to a characteristic peak at $m/z = 77$.

Solution:

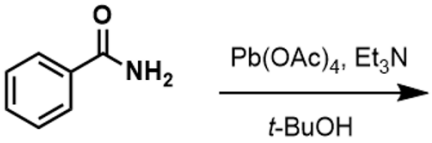
Benzoic acid C_6H_5COOH. However, there are other, less likely compounds that could also fit the data: thiobenzaldehyde (C_6H_5CHS), phenyl formate ($HCOOC_6H_5$).

Question o.3 (Jiří Ledvinka)

The Hoffmann rearrangement is a reaction in which a primary amide (**1**) is converted into an amine (**4**) which has one fewer carbon than the starting amide. In the original procedure, the amide reacts with bromine in an aqueous solution of sodium hydroxide, forming an isocyanate (**2**). The isocyanate is then attacked by a hydroxide anion, forming an anion of carbamic acid (**3**) which immediately decomposes into carbon dioxide and an amine (**4**).

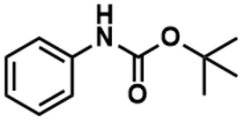


Since its discovery, the reagents used to induce the Hoffmann rearrangement have been substituted for more modern alternatives, so that it can be used for a wide range of transformations. The esters of carbamate (**3**) are significantly more stable because they cannot decompose by losing carbon dioxide. What product will be formed under the following conditions?



Solution:

Amide is converted into an amine protected by Boc (*t*-butyloxycarbonyl).



Question o.4 (Anh Phung)

Lactobacillus bulgaricus is well-known for its lactic acid fermentation and is primarily responsible for worldwide yogurt production. In general, under anaerobic conditions, *L. bulgaricus* metabolize glucose via a multi-steps glycolytic pathway (shown in the scheme in the appendix), releasing lactate as the final by-product.

A "pulse-chase" experiment using ^{14}C-labeled carbon sources is performed on *L. bulgaricus* maintained under strictly anaerobic conditions. The protocol consists of incubating a small amount of ^{14}C-labeled substrate, called a "pulse", with the bacterial culture long enough for each intermediate in the metabolic pathway to become labeled. The labels are then "chased" through the pathway by addition of excess unlabeled glucose. This prevents any further entry of labeled glucose into the pathway.

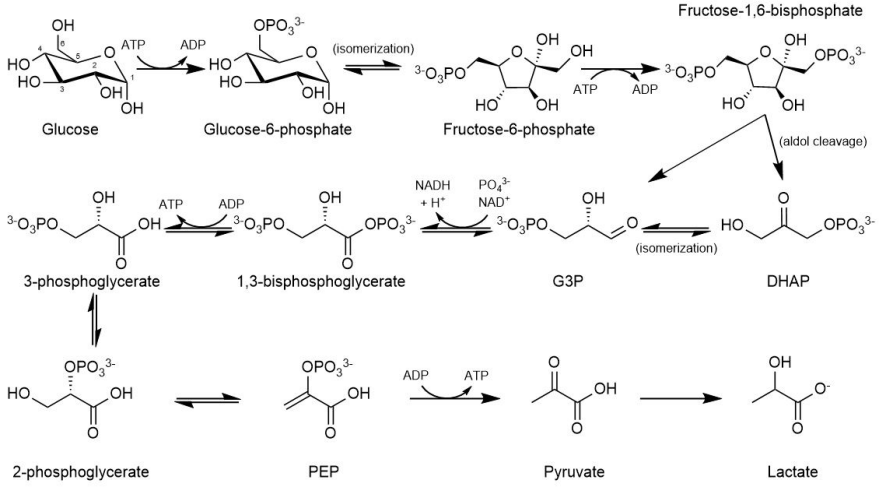
Indicate the location(s) of the radioactive label on the product lactate for each of the following cases where different substrates are used as a "chase":

1. [1-^{14}C] glucose
2. [2-^{14}C] glucose
3. [3-^{14}C] glucose
4. [4-^{14}C] glucose
5. [5-^{14}C] glucose
6. [6-^{14}C] glucose,

where [1-^{14}C] glucose is glucose with ^{14}C labeled at C1, etc.

[*Hint: it might be useful to draw out the linear structure of glucose and fructose.*]

Glycolysis scheme:



Solution:

1. C3, 2. C2, 3. C1, 4. C1, 5. C2, 6. C3

This question is difficult, however it does not require any advanced calculations or organic concepts, all have been given in the glycolysis diagram.

If C1 is labeled with ^{14}C, then following the pathway until step 4, the fructose-1,6BP is cleaved into 2 isomers, where the dihydroxyacetone contains original C1,2,3 and glyceraldehyde contains original C4,5,6. DHAP is isomerized into Glyceraldehyde by inversion, so C1 becomes indistinguishable with C6, C2 with C5 and C3 with C4. The rest of the pathway until lactate has no significant change.

The hardest step is step 2, isomerization of glucose-6-P to fructose-6-P, because the cyclical structure changed. it seems tempting to think that when the carbonyl (aldehyde) on C1 in glucose is swapped into C2 carbonyl (ketone) in fructose, the label goes from C1 to C2. However, this is not the case because carbon atoms does not move, only the functional group attached to it! so the label on C1 is still on C1 until step 4.

Question o.5 (Sam Holmes)

One of the jobs of a pharmacologist is to determine how a new drug should be administered. One possible method is injection, which is chemically simple but practically inconvenient. As such, pharmacologists aim to reduce the number of injections a person needs while still maintaining a sufficient concentration of the drug in the patient's body.

When designing the appropriate dosing regime for a new drug, it is therefore important to consider how the concentration of the drug changes in the body over time. The concentration of a drug in the bloodstream typically increases very quickly following an injection, and then decays away as it is metabolised by the body and eliminated.

A new drug is designed which is found to exhibit first order decay in the bloodstream with a biological half-life of 5 hours. A patient is given the new drug to determine its effectiveness. The first dose of 100 mg is administered at 09:00, then subsequent doses of 75 mg each are administered every 10 hours for one week. How much of the drug is present in the body one week later at 09:00?

Solution:

32.99 mg

Conveniently, this dosing regime means the drug concentration in the bloodstream will always remain on the same first order decay curve, being reset to 100 mg every 10 hours. We can therefore ignore all of the cycles before the last one…

$$24 \times 7 = 168 \text{ hours}$$

After 160 hours, there is 100 mg (as every 10 hours we reset to 100mg).

Formulating an expression for the mass at time t given half-life $t_{1/2}$ should be doable without any prior knowledge as students can draw parallels to geometric sequences with general term $a \times r^{n-1}$.

$$\text{Mass} = m_0 \times 0.5^{t/t_{1/2}}$$

32.99 mg for m_0 = 100 mg, t = 8 hours, $t_{1/2}$ = 5 hours

Question o.6 (Kaijia Liu)

You may have encountered the equilibrium mixture between gaseous NO_2 and gaseous N_2O_4 as an illustrative example of chemical equilibrium. Suppose we start with one mole of pure N_2O_4 in a transparent, cubic vessel with a frictionless piston on one side. We wait until equilibrium is established, while keeping the temperature of the mixture at 25 °C, and without fixing the position of the piston. We then use the piston to compress the mixture to half its original volume, and fix the piston in its new position. The new temperature of the mixture is found to be 38 °C. The pressure of the surroundings is atmospheric.

The equilibrium constant K_p of a reaction

$$a\,\mathrm{A}\,(\mathrm{g}) + b\,\mathrm{B}\,(\mathrm{g}) \longrightarrow c\,\mathrm{C}\,(\mathrm{g}) + d\,\mathrm{D}\,(\mathrm{g}) \quad \text{is defined as } K_p = \frac{\left(\frac{p_\mathrm{C}}{p^\ominus}\right)^c \left(\frac{p_\mathrm{D}}{p^\ominus}\right)^d}{\left(\frac{p_\mathrm{A}}{p^\ominus}\right)^a \left(\frac{p_\mathrm{B}}{p^\ominus}\right)^b}$$

where p_X is the partial pressure of gas X and $p^\ominus = 1\,\text{atm} = 101.325\,\text{kPa}$ is the standard pressure.

The equilibrium constant K_p for the reaction

$$\mathrm{N_2O_4(g)} \rightleftharpoons 2\,\mathrm{NO_2(g)}$$

is known to be 0.141 at 25 °C and 0.363 at 38 °C. Find the ratio of the concentration of N_2O_4 after the compression to the concentration of N_2O_4 before the compression.

Solution:

We start by considering a hypothetical situation where all gas (1 mole) is present in the form of N_2O_4. We then define the extent of reaction ξ which quantifies how much the reaction has proceeded: it is a decrease in the molar quantity of a reactant or an increase in the molar quantity of a product, Δn_i, divided by its stoichiometric coefficient, ν_i (its unit is also [mol]):

$$\xi = \frac{\Delta n_i}{\nu_i}.$$

Because it is related to a stoichiometric coefficient, the extent of reaction does not depend on the substance that is used for its calculation.

We can then deduce that the total molar quantity of gas is $n_{\mathrm{tot}} = (1 + \xi)$ (since there was 1 mole originally and ξ mol N_2O_4 reacts to form 2ξ mol NO_2), the molar quantity of NO_2 is $n_{\mathrm{NO_2}} = 2\xi$ and the molar quantity of N_2O_4 is $n_{\mathrm{N_2O_4}} = (1 - \xi)$.

We then assume that all of the gasses are ideal, therefore the pressure is directly proportional to the amount of substance:

the partial pressure $p_{\mathrm{NO_2}} = \frac{n_{\mathrm{NO_2}}}{n_{\mathrm{tot}}} p_{\mathrm{tot}} = \frac{2\xi}{1+\xi} p_{\mathrm{tot}}$

and

the partial pressure $p_{\mathrm{N_2O_4}} = \frac{n_{\mathrm{N_2O_4}}}{n_{\mathrm{tot}}} p_{\mathrm{tot}} = \frac{1-\xi}{1+\xi} p_{\mathrm{tot}}$.

Let the total pressure of the mixture be $p_{\mathrm{tot},1}$ at the first stage at 298 K and $p_{\mathrm{tot},2}$ at the second stage at 311 K.

At the first stage, the equilibrium constant K_p then equals

$$K_{p,1} = \frac{\left(\frac{p_{\mathrm{NO_2},1}}{p^{\ominus}}\right)^2}{\frac{p_{\mathrm{N_2O_4},1}}{p^{\ominus}}} = \frac{\left(\frac{2\xi_1}{1+\xi_1}\right)^2}{\frac{1-\xi_1}{1+\xi_1}} \times \frac{p_{\mathrm{tot},1}}{p^{\ominus}} = 0.141$$

Since the piston was free to move in the first phase, the pressure inside the cube was the same as the atmospheric pressure outside. By substituting in $p_{\mathrm{tot},1} = p^{\ominus} = 1\,\mathrm{atm}$, we can find that $\xi_1 \doteq 0.185$.

A similar equation holds at the second stage after compression:

$$K_{p,2} = \frac{\left(\frac{p_{\mathrm{NO_2},2}}{p^\ominus}\right)^2}{\frac{p_{\mathrm{N_2O_4},2}}{p^\ominus}} = \frac{\left(\frac{2\xi_2}{1+\xi_2}\right)^2}{\frac{1-\xi_2}{1+\xi_2}} \times \frac{p_{\mathrm{tot},2}}{p^\ominus} = 0.363 \tag{1}$$

We can also write the ideal gas law at both stages:

$$p_{\mathrm{tot},1}V_1 = (1+\xi_1) \times RT_1 \qquad \text{and} \qquad p_{\mathrm{tot},2}V_2 = (1+\xi_2) \times RT_2.$$

By dividing through, we can get

$$\frac{p_{\mathrm{tot},1}}{p_{\mathrm{tot},2}} = \frac{1+\xi_1}{1+\xi_2} \times \frac{T_1V_2}{T_2V_1} \tag{2}$$

and we notice that $\frac{V_2}{V_1} = 0,5$. By plugging in the values for $T_1, T_2, \frac{V_2}{V_1}, p_{\mathrm{tot},1}, p^\ominus$ and ξ_1 and solving equations (1) and (2) simultaneously, we can calculate that $\xi_2 \doteq 0,203$ and $p_{\mathrm{tot},2} \doteq 2.120\,\mathrm{atm}$.

We can now find the partial pressures of N_2O_4:

$$p_{\mathrm{N_2O_4},1} = \frac{1-\xi_1}{1+\xi_1} \times p_{\mathrm{tot},1} = 0.688\,\mathrm{atm}$$

$$p_{\mathrm{N_2O_4},2} = \frac{1-\xi_2}{1+\xi_2} \times p_{\mathrm{tot},2} = 1.405\,\mathrm{atm}.$$

The concentration ratio of N_2O_4 after and before the compression, therefore, is

$$\frac{[\mathrm{N_2O_4}]_2}{[\mathrm{N_2O_4}]_1} = \frac{\frac{n_{\mathrm{N_2O_4},2}}{V_{\mathrm{N_2O_4},2}}}{\frac{n_{\mathrm{N_2O_4},1}}{V_{\mathrm{N_2O_4},1}}} = \frac{p_{\mathrm{N_2O_4},2}}{p_{\mathrm{N_2O_4},1}} \times \frac{T_1}{T_2} = 1.96.$$

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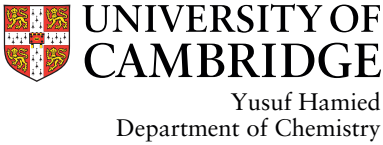
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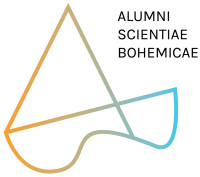
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