

# Chemistry Race 2021: Questions and Solutions



# chemistryrace

6th February 2021

supported by



UNIVERSITY OF  
CAMBRIDGE

Yusuf Hamied  
Department of Chemistry



### Question A.1 (Richard Veselý)

Imagine that somebody loses 10 kg of fat over three months. 10 kg is quite a significant amount of matter; however, we don't see pieces of meat falling off of people who lose weight. How does the "fat" leave the body? Write down the formulae of the **two main substances** into which fat is broken down.

---

#### Solution:

Carbon dioxide and water. One could figure this out using common sense, by realising that we exhale carbon dioxide all the time and that camels "store" water into fat.

### Question A.2 (Pavína Muchová)

We want to provide a patient with an intravenous treatment of a calming medication. We prepare 50 ml of an infusion with the contents of 10 two-millilitre ampoules, where each ampoule contains 100 mg of the medicine. The remaining volume is made up with physiological solution. We want to administer the infusion at the rate of  $2 \text{ ml h}^{-1}$ . A nurse realises that they have forgotten to dilute the infusion with the physiological solution. What should the flow rate be to achieve the same rate of medicine administration as for the properly diluted solution?

---

#### Solution:

Since one ampoule contains 2 ml of a solution of 100 mg of the given drug, ten ampoules contain 1000 mg of the drug in total. The concentrations of the diluted and undiluted solution are then, respectively:

$$\rho_{\text{dil}} = \frac{m}{V_{\text{dil}}} = \frac{1000}{50} = 20 \text{ mg ml}^{-1}$$
$$\rho_{\text{undil}} = \frac{m}{V_{\text{undil}}} = \frac{1000}{20} = 50 \text{ mg ml}^{-1}$$

2 ml of the correctly diluted solution would give 40 mg of the drug per hour, thus the flow rate of the undiluted solution has to be set at

$$\dot{V}_{\text{undil}} = \frac{\dot{m}_{\text{drug}}}{\rho_{\text{undil}}} = \frac{40}{50} = 0.8 \text{ ml h}^{-1}$$

**Question A.3 (Marie Grunová)**

Eddie has been tasked with cleaning up an old storage room. He found an unmarked bottle in the back of a cabinet. His curiosity led him to open it. There was a piece of metal hidden under a layer of liquid. The metal was so soft it could be easily cut with a knife. Eddie tried dropping a piece of the metal into water, which resulted in a vigorous reaction. The resulting solution turned pink after Eddie added a couple of drops of phenolphthalein. Eddie neutralised the solution with hydrochloric acid. A flame test of the resulting chloride gave a bright yellow colour. Determine the metal that was stored in the bottle.

---

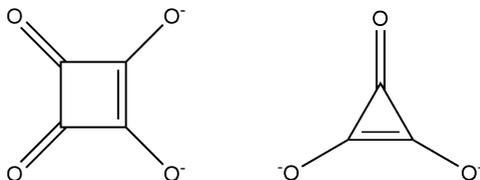
**Solution:**

Eddie clearly found metallic sodium.

**Question A.4 (Adam Tywoniak)**

Squaric and deltic acid are two organic molecules named after their geometric forms. Their respective second conjugate bases, the squarate and deltate anion ( $C_4O_4^{2-}$  and  $C_3O_3^{2-}$  respectively, shown left and right below) are two examples of oxocarbon anions, that is, anions composed solely of those two elements. Write down the formula of the simplest naturally occurring oxocarbon anion.

*Hint: It is also highly symmetric, and more commonly mentioned in books on inorganic chemistry.*



---

**Solution:**

The carbonate anion,  $CO_3^{2-}$

### Question A.5 (Vít Procházka)

Alums are double sulfate salts with the general formula  $M^I M^{III}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ . They have many applications including in the production of fire-proof materials, as mordants, and to help stop bleeding. They were previously also used as deodorants and, more recently, their use in natural cosmetics is increasing. A typical example is potassium alum  $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ . The solubility of anhydrous  $\text{KAl}(\text{SO}_4)_2$  in water at  $20^\circ\text{C}$  is  $5.90 \text{ g}/(100 \text{ g H}_2\text{O})$ . How many grams of potassium alum dodecahydrate should we weigh to prepare 200 g of saturated aqueous solution at  $20^\circ\text{C}$ ?

#### Solution:

Considering the solubility of the potassium alum ( $5.90 \text{ g}/(100 \text{ g H}_2\text{O})$ ), 5.9 g of the alum is present in 105.9 g of the saturated solution. 200 g of the solution then holds

$$m_{\text{anhydrous}} = \frac{m'_{\text{anhydrous}} \times m_{\text{solution}}}{m'_{\text{solution}}} = \frac{5.9 \times 200}{105.9} = 11.143 \text{ g}$$

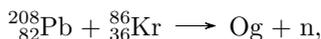
of anhydrous alum, which is then

$$m_{\text{dodecahydrate}} = \frac{m_{\text{anhydrous}} \times M_{\text{dodecahydrate}}}{M_{\text{anhydrous}}} = \frac{11.143 \times 474.39}{258.206} = 20.472 \text{ g}$$

of dodecahydrate.

### Question A.6 (Adam Tywoniak)

Oganesson (Og) is a recently discovered element with an electron configuration of  $5f^{14} 6d^{10} 7s^2 7p^6$ . Its first reported preparation was claimed to have proceeded according to the equation



but attempts of replication have failed. There were some allegations of data fabrication.

An isotope of Og heavier by one atomic mass unit was finally prepared, by exposing a target made of californium-249 to accelerated particles Q. The equation describing this process is:



Determine the identity of the particle Q, including its nucleon number (atomic mass number).

**Solution:**

$Q = {}_{20}^{48}\text{Ca}$ , a rare yet fairly long-lived isotope of calcium.

**Question B.1 (Stanislav ChvÍla)**

After the fruitful season of 2020, Harry the biochemist has decided to dabble with fermentation chemistry as well. He is storing two jugs of apple juice and a few crates of green pears. After a week, he found that the pears had attracted a large number of insects, so he planted a flytrap near the doorframe. Two days later, Harry noticed that there were twenty fruit flies and a moth stuck to the flytrap. He paused, thought for a moment and swapped the old flytrap for a new one, which he collected two days later. This time, three moths and fifteen fruit flies were stuck to it. Harry weighed both flytraps, carefully removed all insects and weighed the used flytraps again. The first frame was 31.5 mg lighter after removing the insects, while the second frame was lighter by 40.5 mg. Following Harry's experiment, determine the mass of one mole of moths in kilograms.

---

**Solution:**

Two flytraps and two insect species clearly indicate a two-equation, two-variable system. Setting  $m$  and  $f$  as the masses of a moth and of a fruit fly, we obtain

$$m + 20f = 31.5$$

$$3m + 15f = 40.5$$

which gives  $m = 7.5$  mg and  $f = 1.2$  mg. One mole of moths then weighs

$$m(m_m) = N_A \times 1 \times 10^{-6} \times m = 6.022 \times 10^{23} \times 1 \times 10^{-6} \times 7.5 = 4.52 \times 10^{18} \text{ kg}$$

**Question B.2 (Ryan Kang)**

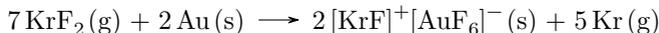
Bismuth subsalicylate ( $\text{C}_7\text{H}_5\text{BiO}_4$ ) is a medication that can be used to treat multiple conditions of the digestive system, including heartburn and diarrhoea. It can be made by the hydrolysis of bismuth salicylate. One tablet of *Pepto-Bismol* contains 262 mg of bismuth subsalicylate. How many grams of bismuth metal are in a box of 48 tablets?

---



**Question B.4 (Jiří Ledvinka)**

Krypton difluoride,  $\text{KrF}_2$ , is the strongest known oxidant and therefore has many interesting chemical properties. For example, it is capable of oxidizing metallic gold to its highest known oxidation state. The reaction is described by the following equation:



Determine the highest known oxidation state of gold.

---

**Solution:**

The reaction of krypton difluoride with gold is obviously a redox reaction. Five molecules of krypton difluoride are reduced to elemental krypton (10 electrons in total) and concurrently two gold atoms are oxidized (of course by 10 electrons in total). The oxidation state of gold in the product is therefore **+V**.

The same result can be obtained by analysis of the gold complex formula: the anion has overall charge  $-1$  and thus the charge of the fluorides is compensated by the gold in **+V** oxidation state.

**Question B.5 (Vít Procházka)**

The mass mixing ratio gives the concentration of a compound in a mixture as its mass relative to the mass of another compound in the same mixture, usually the solvent. It is often used in chemical engineering – some important relations are linear when expressed in terms of mass mixing ratios, but not mass fractions, so mass ratios are often easier to work with. Consider an aqueous ammonia solution with mass mixing ratio  $X'(\text{NH}_3) = 0.15$ . Calculate the mass fraction of ammonia in this solution.

---

**Solution:**

The question presents the definition of the mass mixing ratio (here labeled as  $X'$ ) as

$$X' = \frac{m_{\text{NH}_3}}{m_{\text{solvent}}}$$

while the mass fraction is defined as

$$w = \frac{m_{\text{NH}_3}}{m_{\text{solvent}} + m_{\text{NH}_3}}$$

Expressing  $m_{\text{NH}_3}$  from the first equation as  $X' m_{\text{solvent}}$  and subsequent insertion into the second equation gives

$$w = \frac{X' m_{\text{solvent}}}{X' m_{\text{solvent}} + m_{\text{solvent}}} = \frac{X'}{X' + 1}$$

We obtain, provided that  $X' = 0.15$ :

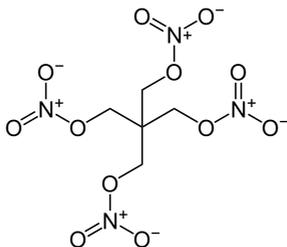
$$w = \frac{0.15}{1.15} = 0.1304$$

### Question B.6 (Jan Hrubeš)

The Czech city of Pardubice is known for its famous gingerbread and horse races, as well as for manufacturing explosives (such as *Semtex*). Explosives can be described via oxygen balance. This describes the extent to which the explosive is oxidised during the explosion, by indicating the percentage of oxygen leftover after complete oxidation to carbon dioxide, water and nitrogen has occurred. It can be calculated using the equation

$$OB = 16 \times \frac{N_{\text{O}} - 2N_{\text{C}} - \frac{1}{2}N_{\text{H}}}{M_{\text{compound}}} \times 100\%$$

where  $N_{\text{O}}$ ,  $N_{\text{C}}$ , and  $N_{\text{H}}$  are the numbers of oxygen, carbon and hydrogen atoms in the molecule. For example for methanol,  $\text{CH}_3\text{OH}$ :  $N_{\text{C}} = 1$ ,  $N_{\text{H}} = 4$ ,  $N_{\text{O}} = 1$ .  $M_{\text{compound}}$  is the molar mass of the molecule. Calculate the oxygen balance of pentrite, the structure of which is shown below.



**Solution:**

Using the structure of pentrite, we can calculate the empirical formula ( $\text{C}_5\text{H}_8\text{N}_4\text{O}_{12}$ ) and the molar mass of pentrite as  $316.137 \text{ g mol}^{-1}$ . Then the oxygen balance is obtained as

$$OB = 16 \times \frac{12 - 2 \times 5 - \frac{1}{2} \times 8}{316.137} \times 100\%$$

The result is  $-10.12\%$ . It is noteworthy that commercial explosives are designed to have an oxygen balance close to zero to limit the formation of harmful byproducts (e.g. carbon monoxide in coal mine shafts).

**Question C.1 (Adam Jaroš)**

How many atoms are there in  $1.66 \times 10^{-24}$  moles of argon?

---

**Solution:**

$$N = n \times N_A = 1.66 \times 10^{-24} \times 6.022 \times 10^{23} = 1$$

**Question C.2 (Stanislav Chvíla)**

Heavier or lighter than air? This simple question is often considered in basic chemistry courses, and the answer to it also carries valuable information on handling substances in the case of leakage, poisoning or other accidents. Any chemist should know or be able to deduce this property of various gases, and now it's your turn to do so. State whether the following gases are heavier or lighter than air:

Argon, oxygen, methane, carbon dioxide, hydrogen, neon, trichloromethane.

*Hint: Consider air as a mixture of 80 molar percent of nitrogen, the rest being oxygen.*

---

**Solution:**

Our approximation of air as a mixture of 80 molar percent of nitrogen, the rest being oxygen, gives the molar mass of approximately

$$M_{\text{air}} = M_{\text{N}_2}x_{\text{N}_2} + M_{\text{O}_2}x_{\text{O}_2} = 0.8 \times 28 + 0.2 \times 32 = 28.8 \text{ g mol}^{-1}$$

Of the presented gases, three are lighter than air: methane ( $M = 16 \text{ g mol}^{-1}$ ), hydrogen ( $M = 2 \text{ g mol}^{-1}$ ) and neon ( $M = 20.18 \text{ g mol}^{-1}$ ).

### Question C.3 (Wojciech Jankowski)

What is the highest possible mass percentage of hydrogen (H) for a neutral hydrocarbon?

Give the answer as a percentage.

---

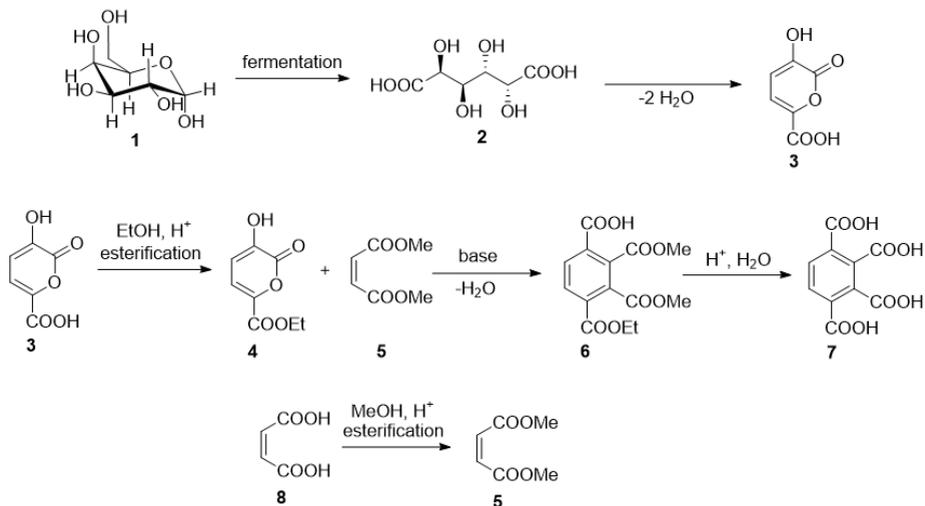
#### Solution:

Maximizing the mass percentage of hydrogen can be done in two ways: by complete saturation (thus we consider alkanes) and by minimizing the number of carbon atoms. This is done, because for alkanes (empirical formula  $C_nH_{2n+2}$ ) the addition of one carbon atom and two hydrogen atoms shifts the mass percentages in favor of carbon. We therefore seek the shortest alkane: methane. The mass percentage of hydrogen in methane is then 25.1%.

### Question C.4 (Jiří Ledvinka)

The drive to be less dependent on fossil fuel is increasingly influencing organic chemistry. For example, terephthalic acid, a PET polymer precursor, is usually produced by aerial oxidation of *p*-xylene obtained from petroleum. A synthesis of terephthalic acid from renewable sources is possible but considerably more challenging. In this task, we will prepare a terephthalic acid derivative (**7**) starting from galactose (**1**). First, the galactose is fermented to produce mucic acid (**2**), which in turn is converted to 3-hydroxy-2-pyron-6-carboxylic acid (**3**) by dehydration. The acid (**3**) is then esterified using bioethanol from rapeseed (a typical Czech bioethanol source). The resulting ester **4** undergoes a base-catalyzed reaction with dimethyl maleate (**5**) to form compound **6**, which is then hydrolyzed under acidic conditions to produce the final compound **7**. The dimethyl maleate was synthesised using methanol (produced from synthesis gas) from maleic acid (**8**) obtained from a biological source.

How many carbon atoms of the product **7** originated from renewable sources?

**Solution:**

As written in the text, the only “synthetic” carbon source is the methanol. These methyl groups then appear in the methyl esters; however, they are not present in the final compound **7**. Thus, all **10 carbon atoms** of acid **7** came from renewable sources.

**Question C.5 (Adam Jaroš)**

Once, a hotel called “The Periodic Table” provided accommodation for an unknown element (the truth is that the receptionist didn’t write his name down). Since the receptionist was too ashamed to ask again, he had to use his knowledge of the unknown element’s neighbours. The first neighbour likes to be in shampoos and rare amino acids. The second is rather half-hearted in his effort to become metal. The third was helpful in the printing industry throughout history. And finally, the fourth literally bursts with love for friction. Who is the unknown element?

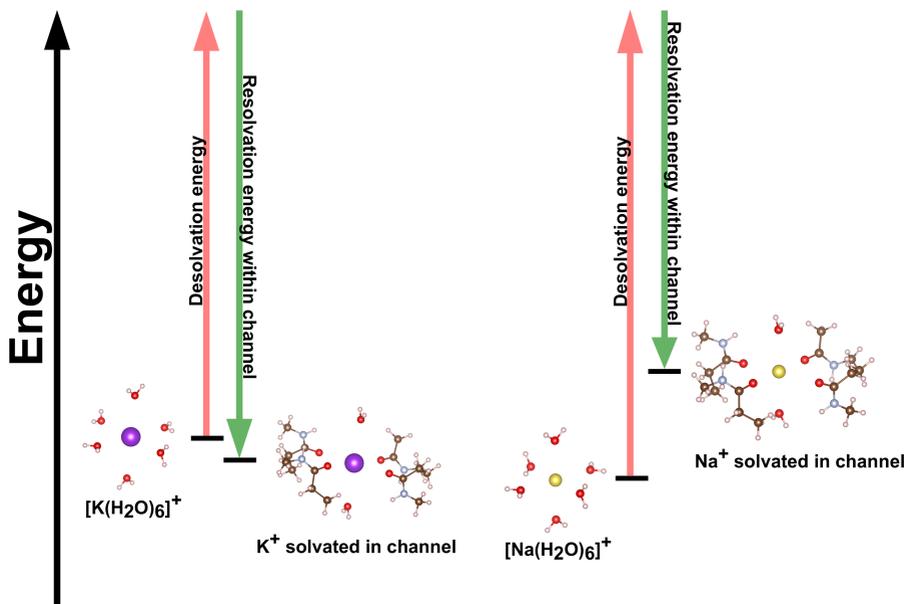
**Solution:**

The neighbours are selenium, antimony, germanium and phosphorus. The unknown element is thus arsenic.

### Question C.6 (Matúš Drexler)

The following figure shows the difference in solvation energy between sodium and potassium ions inside a cell. During active transport of these ions, the first coordination layer is occupied by carboxyl or carbonyl groups in place of water molecules. Which of the following statements are true?

- A) Both ions will permeate through the channel.
- B) The sodium ion will permeate, since it's smaller than the potassium ion.
- C) The potassium ion will permeate, since it's smaller than the sodium ion.
- D) Neither of the two ions mentioned will permeate.
- E) The potassium ion will permeate, as it's better solvated in the channel.
- F) The sodium ion will permeate, as it's better solvated in the channel.



#### Solution:

The scheme shows that the channel-solvated potassium ion (on the left) is energetically favored to the freely solvated ion, thus it will be transported through the channel. This is not the case for the sodium ion, thus the only correct answer is E.

**Question D.1 (Stanislav ChvÍla)**

Many students have certainly experienced the feeling during an oral exam in school... they have blanked completely, then the teacher asks another hard question and tries to squeeze blood from the stone as the student is trying to escape from the torture. You might even recall such teachers from your own experience. How many students would have to have their blood drained during a Thursday exam (at 4 pm) in order to sate the teacher till Monday morning (8 am)? Let us estimate that squeezing one student yields 500 ml of blood. The only relevant nutrient in blood is blood protein (7 g per 100 ml of blood), yielding 17 kJ per gram of protein. The teacher's basal metabolism is covered by 6000 kJ of energy per day.

*Side note: In Czech, the phrase "pít krev", i.e. that somebody drinks someone else's blood, signifies that somebody is strongly irritating somebody else.*

---

**Solution:**

The timespan from Thursday afternoon till Monday morning is 88 hours. This gives the necessary intake of calories as

$$E_{\text{total}} = \frac{t_{\text{total}}}{t_{\text{day}}} \times E_{\text{day}} = \frac{88 \times 6000}{24} = 22\,000 \text{ kJ.}$$

One examination then yields

$$E_{\text{exam}} = \frac{V_{\text{total}}}{V_{\text{ref}}} \times m_{\text{protein}} \times c_{\text{protein}} = \frac{0.5}{0.1} \times 7 \times 17 = 595 \text{ kJ.}$$

The number of students is then easy to determine:

$$N_{\text{students}} = \frac{E_{\text{total}}}{E_{\text{exam}}} = 36.97,$$

which is rounded up to 37 students.

### Question D.2 (Stanislav Chvřila)

Many plants and animals have gradually adapted to the harsh conditions in the Sahara desert, where the key need is to have enough water. Plants, such as cacti, store water directly in their bodies. Animals cannot do so as easily; however, camels have found a workaround - they store fat in humps on their back, preventing overheating - and furthermore, the fat is also a valuable source of metabolic water.

Calculate the mass of water (in grams) that can be obtained by the complete oxidation of one kilogram of fat — modelled by glyceryl tripalmitate (its molar mass is  $807.34 \text{ g mol}^{-1}$ ).

*Hint: Palmitate contains sixteen carbon atoms.*

---

#### Solution:

The hardest step is most likely calculating the empirical formula of glycerol tripalmitate. Since there are 51 carbon atoms in the molecule ( $3 \times 16$  plus 3 in glycerol) and three double bonds in total, one in each ester group, the formula is  $\text{C}_{51}\text{H}_{98}\text{O}_6$ . Aerobic metabolic oxidation of one mole of glycerol tripalmitate then yields 49 moles of water. Lastly, we are given one kilogram of fat:

$$m_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}} \times M_{\text{H}_2\text{O}} = 49 \times \frac{m_{\text{fat}}}{M_{\text{fat}}} \times M_{\text{H}_2\text{O}} = 49 \times \frac{1000}{807.34} \times 18 = 1092.5 \text{ g}$$

### Question D.3 (Tereza Dobrovnřá)

A molecule consists of 82.8 % carbon and 17.2 % hydrogen, its molar mass is  $58 \text{ g mol}^{-1}$ . How many constitutional isomers of such molecule exist?

---

#### Solution:

It's possible to calculate the empirical formula *via* standard protocols. It can be done faster, however: each carbon atom contributes 12 grams towards the molar mass, thus the carbon contribution is 12 or a multiple of 12. Since 60 is too much, the best guess is 48 (four carbon atoms), leaving 10 for hydrogen (ten hydrogen atoms). This leads to the formula of  $\text{C}_4\text{H}_{10}$ . Two options are viable for  $\text{C}_4\text{H}_{10}$  — butane and 2-methylpropane.

### Question D.4 (Yeha Lee)

Molecules can move in different ways: they can translate, rotate or vibrate. In addition, the electrons can be excited to an upper energy orbital. The typical energy scales associated with these excitations are in the following order:  $E(\text{translation}) \ll E(\text{rotation}) < E(\text{vibration}) < E(\text{electronic})$ .

Suppose that you are asked to cause one of these types of excitations. Three lamps are available: microwave, UV and infrared. You also have a hair dryer. You can use each tool only once. Which of these tools would you use for each excitation?

---

**Solution:**

Translation — hair dryer

Rotation — microwave

Vibration — infrared

Electronic — UV

Spectroscopy is an analytical method looking at the emission, absorption or scattering of light at different wavelengths.

Microwave spectroscopy is used to study rotational energy levels, which tells us about the geometry and bond lengths of the molecule. Infrared spectroscopy gives us information about the different functional groups present in the molecule, as well as some information about the bond strengths. UV spectroscopy investigates the electronic structure, yielding information on the nature of the bonds present in the molecule, e.g. the orbital energies.

When combined, spectroscopic methods provide an incredible amount of information about the structure of molecules!

**Question D.5 (Tereza Dobrovolná)**

A snail shell weighing 27.7 g was dissolved in hydrochloric acid. The reaction yielded 6440 ml of  $\text{CO}_2$ . Determine the mass percentage of  $\text{CaCO}_3$  in the shell, given that the experiment was carried out at 25 °C and 1 atm.

**Solution:**

The number of moles of gaseous carbon dioxide released at the given conditions (1 atm, i.e. 101 325 Pa, and 25 °C, or 298.15 K) can be evaluated as follows:

$$n(\text{CO}_2) = \frac{V}{V_m} = \frac{Vp}{RT} = \frac{0.00644 \times 101325}{8.314 \times 298.15} = 0.263 \text{ mol}$$

One mole of  $\text{CO}_2$  is produced from one mole of  $\text{CaCO}_3$ , as per the reaction



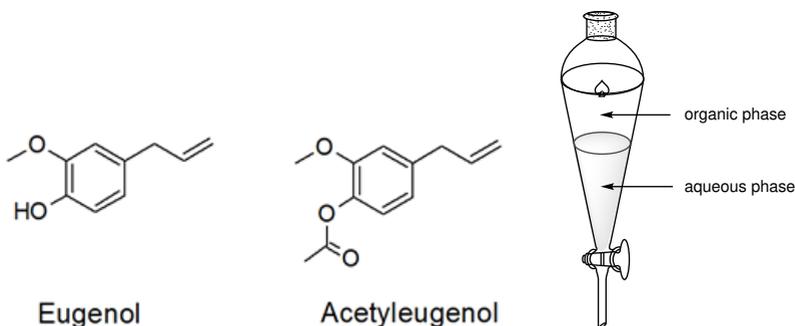
$$w_{\text{CaCO}_3} = \frac{n_{\text{CaCO}_3} \times M_{\text{CaCO}_3}}{m_{\text{ulita}}} = \frac{0.263 \times 100.09}{27.7} = 0.9512$$

i.e. 95.12 mass percent.

**Question D.6 (Jiří Ledvinka, Jan Hrubeš)**

Steam distillation of cloves (flower buds of the tree *Syzygium aromaticum*) produces a distillate containing mainly eugenol and acetyleneugenol. These two compounds can be separated by solvent extraction. The distillate is treated with ether and the ether solution is then extracted (shaking followed by separation of the layers) three times with 5% aqueous NaOH.

Considering that each extraction step transfers 95 % of one of the compounds into the aqueous layer (the sodium hydroxide solution) while 0 % of the other compound is transferred, calculate the purity of the compound obtained by evaporation of the combined etheric extract in mass percent with the precision of 0.001 %. Assume that the steam distillate contains an equimolar amount of both compounds prior to the extraction.  $M(\text{eugenol}) = 164.2 \text{ g mol}^{-1}$ ,  $M(\text{acetyleneugenol}) = 206.2 \text{ g mol}^{-1}$ .



### Solution:

Sodium hydroxide deprotonates the phenolic group present in eugenol, which in its deprotonated form migrates into the aqueous phase. The fraction of eugenol molecules remaining in the etheric phase after three extractions is  $(1 - 0.95)^3 = 1.25 \times 10^{-4}$ , and the amount of acetyleneugenol remains unchanged. The molar purity of eugenol is therefore

$$100 \% \times \frac{1}{1 + 1.25 \times 10^{-4}} = 99.9875 \%$$

The mass purity can be calculated using a similar formula, but with each molar fraction replaced with its corresponding mass. The corresponding masses are calculated by multiplying each molar fraction by the respective compound's molar mass, giving the final formula

$$100 \% \times \frac{1 \times M_{\text{acetyleneugenol}}}{1 \times M_{\text{acetyleneugenol}} + 1.25 \times 10^{-4} \times M_{\text{eugenol}}} = 99.9900 \%$$

The mass purity is higher than the molar purity because of the higher molecular mass of acetyleneugenol compared to that of eugenol.



**Question E.2 (Jiří Ledvinka)**

In a Prague aquatic centre, there is a swimming pool that measures 10 m by 50 m with a depth of 120 cm. This pool is visited by 1500 swimmers daily. The pH regulator got broken which resulted in the pH of the water increasing to 12. The concentration of chlorine is maintained at  $0.6 \text{ mg l}^{-1}$ . The probability that a given visitor urinates in a swimming pool in a single visit is 0.2. Taking the average volume of urine to be 200 mL and the concentration of urea in urine to be  $9.3 \text{ g l}^{-1}$ , how many grams of hydrazine is formed in this swimming pool during the day, assuming a 50% yield for the following reaction?



$$M_r(\text{CO}(\text{NH}_2)_2) = 60.06$$

$$M_r(\text{N}_2\text{H}_4) = 32.05$$

---

**Solution:**

The limiting reagent is obviously urea, because chlorine is constantly supplied and disproportionates in the basic environment to chloride and hypochlorite ions. The number of moles of urea introduced daily in the swimming pool is calculated as follows:

$$n_{\text{urea}} = \frac{N_{\text{swimmers}} \mathbb{P}_{\text{urination}} V_{\text{urine}} \rho_{\text{urea}}}{M_{\text{urea}}} = \frac{1500 \times 0.2 \times 0.2 \times 9.3}{60,06} = 9.29 \text{ mol.}$$

One molecule of hydrazine is formed from one molecule of urea; however, we must take into account the 50% yield of the reaction ( $\phi$ ). The mass of hydrazine formed during one day is therefore

$$m_{\text{hydrazine}} = n_{\text{urea}} \times \phi \times M_{\text{hydrazine}} = 9.29 \times 0.5 \times 32.05 = 149 \text{ g}$$

### Question E.3 (Stanislav Chvřla)

Since pH-related tasks have always tripped up students in the previous editions of the Chemistry Race, it is only appropriate to include another one this time round as well!

Which of these equilibria are valid in an aqueous potassium chloride solution prepared for electrolysis?

- A)  $[\text{Na}^+] = [\text{Cl}^-]$
- B)  $[\text{H}^+] + [\text{Na}^+] = [\text{Cl}^-] + [\text{OH}^-]$
- C)  $[\text{H}^+] + [\text{Na}^+] = [\text{Cl}^-]$
- D)  $[\text{H}^+] = [\text{Na}^+]$
- E)  $[\text{H}^+] = [\text{OH}^-]$

#### Solution:

The task is deliberately a trick question. Since the solution contains potassium chloride, the concentration of sodium ions is equal to zero, rendering all equilibria invalid, save for the last one, for potassium chloride is formed from a strong base and a strong acid.

### Question E.4 (Jiří Ledvinka)

Complex organic compounds usually require complicated syntheses with potentially a lot of reaction steps. An alternative approach to synthesize complex organic molecules from simple starting materials is multi-component reaction. The starting materials are mixed together and we directly obtain often highly sophisticated products. For example, the well-known Hantzsch synthesis of dihydropyridines can produce many products which are used in treating high blood pressure.

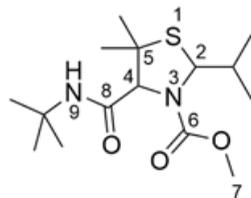
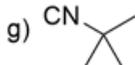
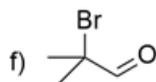


A more recent example of a multi-component reaction is the Ugi reaction, which takes advantage of an isonitrile ( $R-NC$ ) reacting with a carbonyl. The original reaction had four components; however, in 1993, Ugi published a seven-component modification, which is shown below:

a) NaSH    b) MeOH    c)  $NH_3$



e)  $CO_2$



Assign each atom in the product labelled 1–9 to the compound a)–g) from which it originated.

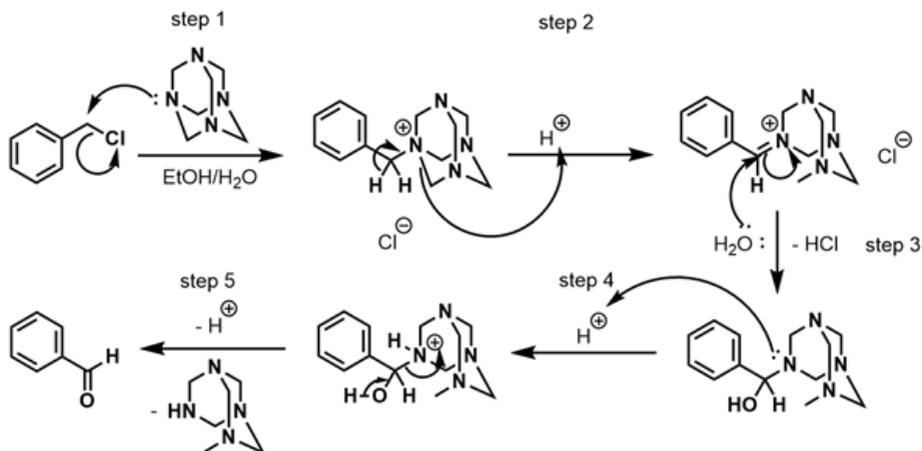
### Solution:

From the structure of the product, it is clear that sulfur 1 came from hydrosulfide a). The *tert*-butyl group of the isonitrile is present on nitrogen 9. Therefore, nitrogen 9 and carbon 8 are from the isonitrile g) molecule. As was mentioned in the text, the isonitrile reacts with the carbonyl group (in this setting, an imine is formed prior to the reaction with the isonitrile), which is present only in aldehydes d) and f). The isopropyl group of the product must originate from aldehyde d), which also contains carbon 2. The second aldehyde therefore provides carbons 4) and 5), and nitrogen 3 is from ammonia c) (which forms the mentioned imine). We are left with only methanol b), which obviously ended as carbon 7 of the methyl ester, and carbon dioxide e), which formed the carboxy group with carbon 6.

Solution: a) 1; b) 7; c) 3; d) 2; e) 6; f) 4,5; g) 8,9.

### Question E.5 (Jiří Ledvinka)

The Sommelet reaction is an exotic synthetic route to aromatic aldehydes. First, benzyl chloride reacts with urotropine (hexamethylenetetramine), resulting in the formation of a quaternary ammonium salt. This salt is then transformed into benzaldehyde under acidic conditions, forming “opened urotropine” as a byproduct. Overall, urotropine oxidizes the aromatic substrate. Determine the step in which the substrate is oxidised and the step in which urotropine is reduced.



#### Solution:

All well-behaved chemists surely know that the higher the number of bonds to electronegative elements an atom has, the higher is its oxidation number. This is also true in this case. In the second reaction step, an iminium salt with a double bond to an electronegative element is formed from the ammonium salt with only a single bond between the benzylic carbon and the electronegative element. The oxidation of our substrate thus occurred in the second step, as well as the reduction of the urotropine part, as can be seen from the transformation of the methylene group into a methyl group.

**Question E.6 (Jaroslav Cerman)**

A blue crystalline substance which is used as a desiccant turns pink in the presence of water. Analysis shows that these pink crystals consist of 24.77 % by mass of cobalt and 45.44 % by mass of water, with the rest being chlorine.

Find the formula of this hydrate.

---

**Solution:**

The solution consists of calculating three ratios:

1. It is given that the rest of the molecule is chlorine, so the mass percentage of chlorine,  $w_{\%}(\text{Cl})$ , is

$$w_{\%}(\text{Cl}) = 100 - w_{\%}(\text{H}_2\text{O}) - w_{\%}(\text{Co}) = 100 - 45.44 - 24.77 = 29.79\%.$$

We also know that the molecule contains 24.77 % of cobalt: cobalt has molecular weight  $M(\text{Co}) = 58.93 \text{ g mol}^{-1}$ , so 1 % of the molar mass of the hydrate molecule,  $M(1\%)$ , is

$$M(1\%) = \frac{M(\text{Co})}{w_{\%}(\text{Co})} = \frac{58.93}{24.77} = 2.38 \text{ g mol}^{-1}.$$

2. We can multiply this number by the mass percentage of chlorine in the unknown molecule and divide the result by its molecular weight. This leads to the ratio of the amount of chlorine to cobalt in the molecule:

$$M(1\%) \times \frac{w_{\%}(\text{Cl})}{M(\text{Cl})} = 2.38 \times \frac{29.79}{35.45} = 2.$$

3. The same algorithm needs to be applied to find out the number of molecules of coordinated water:

$$M(1\%) \times \frac{w_{\%}(\text{H}_2\text{O})}{M(\text{H}_2\text{O})} = 2.38 \times \frac{45.44}{18} = 6.$$

Therefore, the unknown formula is  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ .

**Question F.1 (Anna Kovárnová, Miroslava Novoveská)**

Despite the growing number of Covid-19 cases, the French city of Landerneau hosted the greatest gathering of Smurfs in history. However, there was little publicity about the parallel gatherings of Shreks, Elmos, Minions and Annoying Oranges in the surrounding cities, also hosted under the slogan “We must not stop living”. The colours for the gathering were to be supplied by the *Couleurs de Vie et de Mort* company. Unfortunately, the boxes for each city were labeled only with the dyes absorption spectra.

Help the suppliers match the compounds with their spectra (i.e. the absorption maxima), so that the boxes do not have to be opened.

- |  |                      |
|--|----------------------|
| a. 430 nm                                    | 1. $\beta$ -carotene |
| b. 455 nm and 485 nm                         | 2. haemoglobin       |
| c. 555 nm                                    | 3. chlorophyll       |
| d. 612 nm                                    | 4. indigo            |
| e. 660 nm (and an unimportant one at 430 nm) | 5. curcumin          |

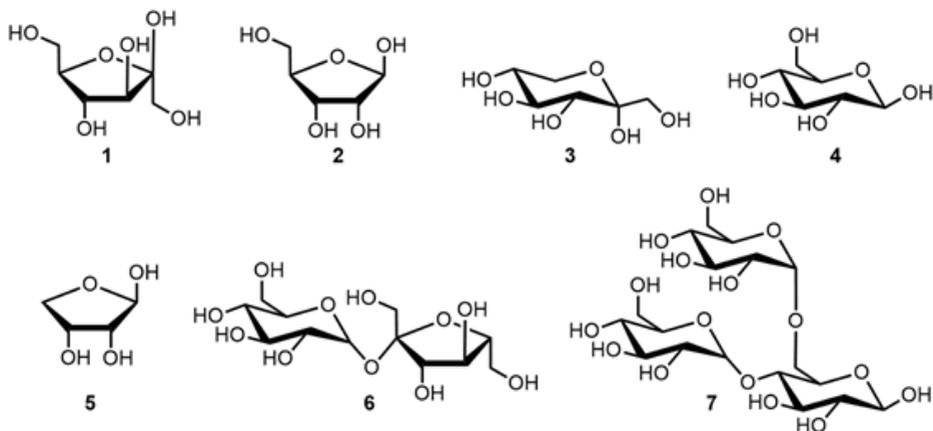
---

**Solution:**

1b; 2c; 3e; 4d; 5a

**Question F.2 (Jiří Ledvinka)**

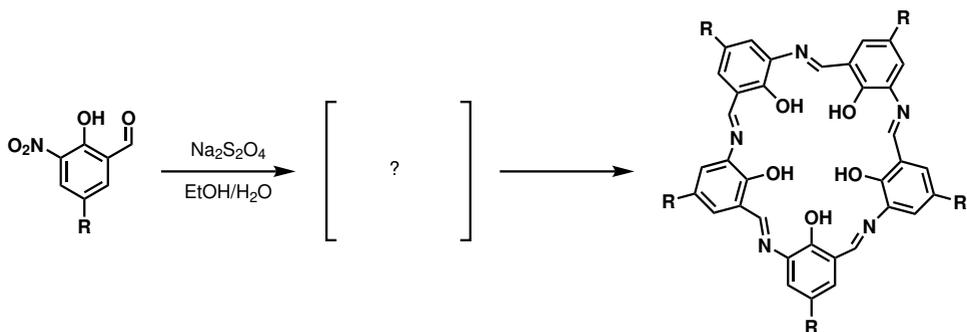
Carbohydrates are biomolecules ubiquitous in nature. Chemically, carbohydrates are polyhydroxyaldehydes (aldoses) and polyhydroxyketones (ketoses). Historically, these were distinguished by their redox properties. One common test is the Fehling test, which utilizes complexed copper(II) ions. The copper(II) ions are capable of oxidizing aldoses upon heating, resulting in precipitation of orange copper(I) oxide. In solution, carbohydrates form cyclic structures (hemiacetals and acetals) and we therefore wouldn't find any aldehydic carbonyl groups in their structures. In neutral aqueous solution, only hemiacetals which are in equilibrium with free aldehydes display reducing properties. Choose from the following carbohydrates those with reducing properties (i.e. those which contain a hemiacetal of aldehyde).

**Solution:**

In the cyclic structure of carbohydrate, the hemiacetal of aldehyde is connected to heterocyclic oxygen, free hydroxy group and hydrogen. This structure motif can be seen in molecules **2**, **4**, **5** and **7**.

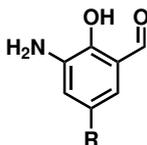
### Question F.3 (Jiří Ledvinka)

The reaction of formaldehyde with phenol famously produces bakelite. However, if the para position of the phenol ring is blocked by a *tert*-butyl group then only the ortho positions can react with formaldehyde, leading to mostly cyclic products. The number of phenol units contained in the cyclic product depends on the reaction conditions. By reacting 4-*tert*-butylphenol and formaldehyde in a basic environment, one can obtain products with 4-, 6-, and 8-fold symmetry (i.e. containing 4, 6, and 8 phenol units). However, other homologues are relatively inaccessible. A recent publication reports the synthesis of several campestarene derivatives, which are planar and have the rarely seen 5-fold symmetry. The synthesis is based on the reduction of 5-substituted 3-nitrosalicylaldehydes to form an intermediate, which spontaneously condenses to give the corresponding macrocycle. Draw a suitable structure for this intermediate.



#### Solution:

As can be seen from the structure of the product, the aldehydic group condenses with a nitrogen-containing group. The only reasonable group is an amino group which forms water upon reaction with the aldehyde forming the imine bridge. The structure of the intermediate is given below:



**Question F.4 (Stanislav Chvřla)**

It's commonly said that opposites attract. This may be true in the case of salts and ionic compounds; however, it does not translate well into the realm of liquids. For example, hexane and water are almost completely immiscible - the solubility of hexane in water is 0.00124 mass percent and the solubility of water in hexane is 0.009 mass percent. Suppose that we poured 5 ml of water ( $\rho = 0.9982 \text{ g cm}^{-3}$ ) into 45 ml of hexane ( $\rho = 0.655 \text{ g cm}^{-3}$ ), shook violently and let the phases separate for 30 minutes. Calculate the percentage of water molecules present in the cylinder that are now dissolved in the organic layer.

---

**Solution:**

Having read the question carefully, we may conclude a priori that the loss of hexane dissolved into the aqueous phase will be rather low. We may therefore neglect it and calculate the amount of water dissolved in hexane at equilibrium directly.

$$m_{\text{hex}} = \rho_{\text{hex}} \times V_{\text{hex}} = 0.655 \times 45 = 29.475 \text{ g}$$
$$m_{\text{aq}} = m_{\text{hex}} \times \text{ppm}_{\text{aq-hex}} = 29.475 \times 90 \times 10^{-6} = 0.00265 \text{ g}$$

The total mass of the added water is then equal to

$$m_{\text{aq-all}} = V_{\text{aq}} \times \rho_{\text{aq}} = 5 \times 0.9982 = 4.991 \text{ g}$$

which then gives the result of

$$p = m_{\text{aq}}/m_{\text{aq-all}} = 0.00265/4.991 = 0.00053,$$

i.e. 0.053 %.

**Question F.5 (Vojtěch Laitl)**

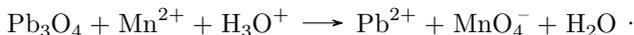
The “inert pair effect” is a phenomenon involving certain metal cations, in which there is a lone electron pair in the electron structure. Such a structure acts as a stabiliser of a positive charge, thereby making the corresponding oxidation state energetically favourable. A typical example is a  $\text{Pb}^{2+}$ :  $[\text{Xe}] 4f^{14} 6d^{10} 6s^2 6p^0$ . If lead occurs in higher oxidation states, typically  $\text{Pb(IV)}$ , it therefore acts as a powerful oxidizing agent, reducing itself into stable  $\text{Pb(II)}$  compounds. If, for instance, red lead tetroxide is mixed with an acidified solution of a colourless manganese(II) salt, a chemical reaction starts and the solution turns purple. Write a balanced chemical equation for this process using only integers.

*Note:* The acidic medium in which the reaction occurs is to be represented by  $\text{H}_3\text{O}^+$  ions.

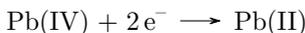
---

**Solution:**

Pb(IV) appears in the structure of lead tetroxide,  $2\text{PbO} \cdot \text{PbO}_2$ . The described behaviour of Pb(IV) hints at its strong oxidizing properties; the reaction will therefore proceed as an oxidation of the present manganese (II) ions. From the acidified reaction mixture turning purple, one can deduce that a highly oxidized state of manganese, permanganate ions, are produced. Lead (IV) is reduced into the stabilized  $\text{Pb}_2^+$ -ion as shown by a schematic equation



Let us give the redox half-reactions for the process:



For the number of exchanged electrons to be balanced, the lead tetroxide and  $\text{Mn}^{2+}$ -ions must react in the ratio 5:2. The stoichiometric coefficients of all metal-containing products can thereby be evaluated. Using the stoichiometric coefficients of  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$ , we can complete the charge balance and balance of H- and O-atoms. Such a stepwise solution leads us to the equation

**Question F.6 (Stanislav ChvÍla)**

Drawing Lewis structures is a commonly tested skill in inorganic chemistry tests. There was also one in last year's Cambridge Chemistry Race. Not in this year's competition, however...

The reaction of copper with dilute nitric acid is a typical example used to practise balancing redox equations. If we were to swap copper for zinc, however, then the spectrum of possible products becomes much wider. As well as the known oxides, such as the colourless oxide **A** and the ginger-reddish oxide **B** prone to dimerisation, one can obtain:

- a salt of a notoriously pungent binary compound **C** that contains more than 80 weight percent of nitrogen,
- a lazy element **X**, or
- an oxide **D** which is almost as symmetrical as **X** and has narcotic effects.

Let's add that **A** when exposed to air slowly oxidises to yield **B**.

Sort the compounds **A**, **B**, **C**, and **D** and the element **X** in order of their average oxidation state of nitrogen, from the most reduced to the most oxidized.

---

**Solution:**

We may safely assign compound **B** to be nitrogen dioxide. Similarly, **X** is certainly nitrogen and **C** is ammonia. Nitrous oxide is the one with narcotic effects (thus assigned as **D**). This leaves **A** as nitric oxide. The ultimate sorting by oxidation state is very simple: **1C 2X 3D 4A 5B**, or  $\text{NH}_3 < \text{N}_2 < \text{N}_2\text{O} < \text{NO} < \text{NO}_2$ .

**Question G.1 (Jaroslav Cerman)**

In the last couple of years, Europe has been trying to reduce its  $\text{CO}_2$  emissions. Whilst this oxide has an indisputable environmental impact, it is nonetheless still useful in many branches of science and technology. This gas was discovered by Jean-Baptiste van Helmont around 1640 as the first gas other than air. This way he explained why organic materials lose weight during combustion.

$\text{CO}_2$  has a molecular weight of  $44 \text{ g mol}^{-1}$ , a linear molecular shape and has acidic properties. Its critical temperature is 304.17 K and its critical pressure is 7.39 MPa. The molar concentration of liquid  $\text{CO}_2$  at  $10^\circ\text{C}$  and at a pressure of 4.5 MPa is  $19.6 \text{ mol l}^{-1}$ .

$\text{CO}_2$  is used in the solid state as the so-called dry ice for cooling down reaction mixtures in laboratories all around the world. It can also be found in "snow" fire extinguishers in its liquid form.  $\text{CO}_2$  was liquefied for the first time in 1823 by Michael Faraday. He cooled the gas to a temperature lower than  $0^\circ\text{C}$  to avoid using excessive pressure. This is because, for example, at a temperature of  $10^\circ\text{C}$ ,  $\text{CO}_2$  starts to condense only at the pressure of 4.5 MPa.

We have one mole of  $\text{CO}_2$  at 283.15 K enclosed in a 600 ml vessel with a piston. This gas is isothermally compressed down to a volume of 400 ml. Calculate the final pressure in the vessel.

---

**Solution:**

We can calculate the hypothetical pressure of an ideal gas after the compression:

$$pV = nRT$$

$$p = \frac{nRT}{V} = \frac{8.314 \times 283.15}{400 \times 10^{-6}} = 5.9 \times 10^6 \text{ Pa.}$$

From the given information, we can see that  $\text{CO}_2$  at 283 K condenses at 4.5 MPa. Ideal behaviour at such high pressure is far from reality and the pressure in the vessel stays at 4.5 MPa, until all the gas has condensed. We can now check that not all the  $\text{CO}_2$  in the vessel is in liquid form. We know, that the molarity of  $\text{CO}_2$  at  $10^\circ\text{C}$  is  $19.6 \text{ mol l}^{-1}$ :

$$c = \frac{n}{V}$$

$$V = \frac{n}{c} = \frac{1}{19.6} = 0.051 = 50 \text{ ml.}$$

All of the gas would have condensed if the fluid had been isothermally compressed to a volume of 50 ml. To correct for real gas behaviour we would have, of course, incorporated equations of state. Probably the most famous one is the Van der Waals equation of state. Its disadvantages lie in adding two more parameters and in being a cubic equation in volume. The additional parameters are usually acquired from the critical values of a given substance. These must be measured experimentally. We can now compare the ideal result with more precise equation of state:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2},$$

where  $V_m$  is the volume of one mole of a gas and  $a$ ,  $b$  are constants for a given gas:

$$a = \frac{27R^2T_c^2}{64p_c} = \frac{27 \times 8.314^2 \times 304,17^2}{647.386 \times 10^6} = 0.37 \text{ Pa m}^6 \text{ mol}^{-2}$$

$$b = \frac{RT_c}{8p_c} = \frac{8,314 \times 304,17}{8 \times 7.386} = 4.3 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$p = \frac{8.314 \times 283.15}{400 \times 10^{-6} - 4.3 \times 10^{-5}} - \frac{0,37}{(400 \times 10^{-6})^2} = 4.3 \times 10^6 \text{ Pa,}$$

which is a result lower than reality, but more precise than the one obtained using the ideal gas approximation.

**Question G.2 (Jiří Ledvinka)**

Chemical accidents are not limited to the chemical industry. In one American school, students were trying to iodinate 4-hydroxybenzotrile. They accidentally introduced the reactants in the flask in the wrong order: into a concentrated aqueous ammonia solution, they gradually added potassium iodide, iodine and then 4-hydroxybenzotrile. After the reaction was over, the students accidentally spilled a small part of the product. The supervising assistant was worried after hearing a crackling noise from the floor and tried to figure out what happened. Meanwhile, a part of the product exploded, resulting in a purple cloud and evacuation of the laboratory. The reaction mixture was worked up by a pyrotechnician instead of a chemist. Write a balanced chemical equation of the reaction actually performed by the students. The incidentally prepared primary explosive product is a binary compound.

---

**Solution:**

Since the accidentally prepared product was a binary compound, containing iodine due to the purple cloud, it had to be nitrogen triiodide (there are barely any oxygen binary compounds that exist in aqueous solution). The equation of the performed reaction is

**Question G.3 (Ondřej Daněk)**

The ultimate way of scaring off your enemies is to make a sword from the blood of their comrades-in-arms. But how many of these comrades would you have to defeat with a normal sword first?

An average warrior has 6 litres of blood, and contains  $6 \times 10^6$  red blood cells per cubic millimetre. Each red blood cell contains 250 million molecules of haemoglobin on average, and each molecule of haemoglobin is made of four subunits, every one of which contains one haem group (thus can complex one ferrous ion). The molar mass of iron is  $55.845 \text{ g mol}^{-1}$ .

How many prisoners of war would you have to execute, and drain the blood of, to be able to forge one Scottish two handed sword — a “claymore”? The total mass of the iron parts of the sword is 4.8612 lb (i.e. pounds), and the overall losses of the blood draining, iron extraction and forging is 35%.

---

**Solution:**

First, we have to convert the mass of the sword to more civilised units:

$$4.8612 \text{ lb} = 2.205 \text{ kg}$$

Taking losses into account, we need  $2.205/0.65 = 3.3923$  kg of iron.

Calculating the molar amount of iron:

$$n(\text{Fe}) = m/M = 3392.3/55.845 = 60.7451 \text{ mol}$$

$$n(\text{hemoglobin}) = n(\text{Fe})/4 = 15.1863 \text{ mol}$$

$$n(\text{rbc}) = \frac{n(\text{hemoglobin})}{250 \times 10^6} = 6.074 \times 10^{-8} \text{ mol} \longrightarrow N(\text{rbc}) = n \times N_{\text{A}} = 3.6582 \times 10^{16}$$

$$V(\text{blood}) = \frac{N(\text{rbc})}{N(\text{rbc per } \mu\text{l}) \times 1 \times 10^6} = 6096.922 \text{ dm}^3$$

$$N(\text{prisoners}) = V(\text{blood})/V(\text{blood per prisoner}) = 1016.154$$

It would be necessary to execute 1017 prisoners of war.

**Question G.4 (Ondřej Daněk)**

An employee of one Czech chemical plant was supposed to operate the caustification unit on the night shift. According to his colleagues, it was supposed to be an easy job, so he only checked that the reactor lid was open and supported with a piece of wood, so the pressure in the reactor wouldn't build up, and, after turning on the heating, he took a nap.

In the caustification unit, sodium carbonate reacts with slaked lime producing calcium carbonate and sodium hydroxide.  $18 \text{ m}^3$  of soda ash mixture coming as a waste product from a different part of the plant (called *the stinker* in the company lingo) was pumped into the reactor.

This has a density of  $1460 \text{ kg m}^{-3}$  and contains 42 % of sodium carbonate monohydrate by weight.  $6 \text{ m}^3$  of water is then added to the reactor, and  $3 \text{ m}^3$  of slaked lime was added portionwise.

As the employee was sleeping, the mixture in the reactor started boiling violently and  $12 \text{ m}^3$  of the mixture escaped through the open lid out of the reactor into a nearby river. For this, the employee was fined 2500 CZK (Czech crowns, approx. 85 GBP) by the company.

Assuming full conversion, that other products of the reaction are of no value to the company, and that the fine was supposed to exactly cover the cost of the lost hydroxide, calculate the price of sodium hydroxide produced by the company in CZK kg<sup>-1</sup>. (The company does not fear paying fines for causing an environmental disaster, since it has its people in the right places.) Assume all volume contractions are negligible.

---

**Solution:**

First, we have to calculate the molar amount of escaped sodium hydroxide. That makes up 12/27 of the total amount of NaOH, which from reaction stoichiometry is double the molar amount of sodium carbonate, which is the limiting reagent in this case, because the calcium hydroxide is used in excess.

$$\begin{aligned}n(\text{NaOH}) &= \frac{12}{27} \times n(\text{Na}_2\text{CO}_3) \times 2 = \frac{12}{27} \times \frac{m(\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O})}{M(\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O})} \times 2 \\&= \frac{12}{27} \times \frac{V\rho w}{M(\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O})} \times 2 = \frac{12}{27} \times \frac{18 \times 1460 \times 1000 \times 0.42}{124.004} \times 2 \\&= 79\,120.03 \text{ mol}\end{aligned}$$

The mass of escaped NaOH is thus

$$m = n \times M = \frac{79\,120.03 \times 39.997}{1000} = 3164.56 \text{ kg}$$

The price of sodium hydroxide is then

$$\frac{2500}{3164.56} = 0.7900 \text{ CZK/kg.}$$

### Question G.5 (Jiří Ledvinka)

“Fluffy cup\* gingerbread” requires a baking temperature of 170 °C for 20 minutes. Unfortunately, we have accidentally preheated the oven to 250 °C. Instead of waiting for the oven to cool down, we will use our knowledge of physical chemistry. We will assume that gingerbread baking obeys the Arrhenius law. How long will it take for the gingerbread to become baked? (The activation energy can be approximated simply by the vaporization enthalpy of water at its standard boiling point.)

The Arrhenius law is given by the equation

$$k = A \exp\left(\frac{-E_a}{RT}\right),$$

where  $k$  is the reaction rate constant,  $A$  is a constant coefficient for the particular reaction,  $E_a$  is the activation energy,  $R$  is the universal gas constant and  $T$  is the thermodynamic temperature. Water vaporization enthalpy at standard pressure is 40 660 J mol<sup>-1</sup>.

---

#### Solution:

Let's use  $t(T_1)$  to denote the time of baking at temperature

$$T_1 = 170 \text{ K} + 273.15 \text{ K} = 443.15 \text{ K},$$

and  $t(T_2)$  for the time at temperature

$$T_2 = 250 \text{ K} + 273.15 \text{ K} = 523.15 \text{ K}.$$

The shorter the baking period is, the quicker the “baking reaction” is, and thus the higher the value of the corresponding reaction rate constant is. Therefore, we can write:  $\frac{t(T_2)}{t(T_1)} = \frac{k_1}{k_2}$ , where  $k_1$  and  $k_2$  are reaction rate constants at temperatures  $T_1$  and  $T_2$ , respectively. Using the Arrhenius law, we can obtain:

$$\frac{t(T_2)}{t(T_1)} = \frac{A \exp\left(\frac{-E_a}{RT_1}\right)}{A \exp\left(\frac{-E_a}{RT_2}\right)} = \exp\left[-\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$t(T_2) = 3.7$  min. It should be mentioned that estimating the activation energy is often more challenging than this, and the enthalpy of vaporization does not usually have much influence.

---

\*As in that the ingredients are always measured in amounts of cups.

**Question G.6 (Ondřej Daněk)**

Chemist Zdenko was drying diethylether with sodium metal. After a sufficiently long time, when the diethylether was dry, he wanted to use it as a solvent to prepare a Grignard reagent. When Zdenko opened the bottle, the inner plastic plug flew up in the air. From the height that the plug had reached, Zdenko calculated that the overpressure relative to the atmospheric pressure (1 atm) was 5 atm.

The 1 litre bottle was filled with 900 ml of diethylether (neglecting the volume of the sodium metal) and the remaining 100 ml was pressurized gas. Calculate how much water the diethylether contained before drying (in g/100 ml), assuming that all the gasses behave ideally. Also assume that the bottle was closed during a hot summer afternoon, so the volume above the liquid diethylether was filled only with diethylether vapour at the time of closing the bottle. Also neglect dissolution of any gases in diethylether. The last assumption you should make is that the only non gaseous product formed from sodium is sodium hydroxide. The saturated vapour pressure of diethylether at 20 °C (the ambient temperature in the lab) is 379.6 Torr.

---

**Solution:**

The pressure in the bottle is the sum of the ambient pressure and the overpressure, 6 atm = 607 950 Pa. This total pressure is also the sum of the saturated vapour pressure of diethylether (379.6 Torr = 50 609.1711 Pa), and the pressure of hydrogen gas formed by the reaction of water with sodium. The pressure of hydrogen is thus:

$$p_{\text{H}_2} = p - p_{\text{Et}_2\text{O}} = 607950 - 50\,609.1711 = 557\,340.8289 \text{ Pa}$$

The molar amount of hydrogen can be calculated from the ideal gas law:

$$n = \frac{p \times V}{R \times T} = \frac{557\,340.8289 \times 0.0001}{8.314 \times 293.15} = 0.02287 \text{ mol}$$

The molar amount of water is, according the reaction stoichiometry, double that of hydrogen, giving

$n_{\text{H}_2\text{O}} = 0.04574 \text{ mol}$ , and the total mass of water in the bottle before drying is thus

$$m = n \times M = 0.04574 \times 18.01528 = 0.82402 \text{ g}$$

After dividing by 9 we arrive at the correct answer 0.09156 g/100 ml.

### Question H.1 (Jiří Ledvinka)

A Grignard reagent R-MgBr is a source of nucleophilic carbon, which reacts, for example, with carbonyl compounds. Reacting a Grignard reagent with carbon dioxide produces the corresponding carboxylic acid salt:



This reaction can be conveniently conducted by pouring an etheric solution of a Grignard reagent onto dry ice. Chemist Victor carried out a similar reaction, where phenylmagnesium bromide reacts with oxygen, resulting in the formation of the corresponding phenolate:



Since he was too lazy to bubble oxygen through the etheric solution, he instead used the setting as in the reaction with dry ice: he poured the dilute Grignard reagent solution directly in liquid oxygen. It is worth mentioning that the reaction was considerably more exothermic than he expected. Write down the two main products prepared by Victor.

---

#### Solution:

Victor experienced that oxygen readily oxidizes organic compounds. Since he poured a dilute etheric solution, which mostly contained ether, into the oxygen, he prepared primarily **water** and **carbon dioxide**.

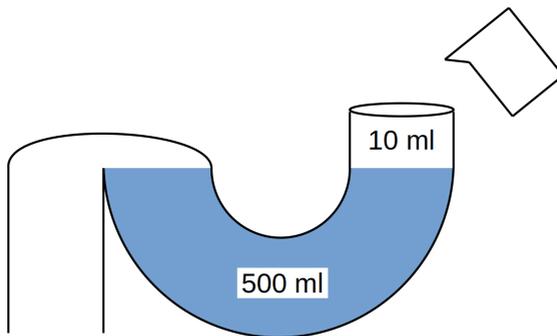
## Question H.2 (Adam Přáda)

Adam, a theoretical chemist, was recently presented with a practical problem. The drain in the shower was clogged with hair. He went to a shop and bought a drain cleaner, which to first approximations is a sodium hydroxide solution at pH 11. To achieve efficient hydrolysis of keratin, the structural protein in hair, the pH must be at least 10.

Adam can only pour in 10 ml at a time (i.e. enough to fill the clogged drain to the rim). Then he has to wait for the liquid to slowly go down the drain before he can pour in the next batch. The volume of the liquid in the trap (U-bend) after the water level has reached its equilibrium level is 500 ml.

How many times does Adam have to pour in the hydroxide in this way to achieve efficient unclogging?

Assume that every time he pours in a batch, the solution mixes perfectly, before it starts slowly going down the drain. At the beginning, the mixture has a pH of 7, and, for the purpose of this question, it behaves like pure water (even though it is disgustingly far from it!).



**Solution:**

Let us call the hydroxide concentration of the batch and its volume,  $c_b$  and  $V_b$ , respectively. The volume of the trap is  $V_t$ . The concentration of the hydroxide in the trap after  $n$  batches is  $c_n$ .

Using the definition of concentration (molar amount per volume), we calculate the concentration after  $(n + 1)$ st batch like

$$c_{n+1} = \frac{c_b V_b + c_n V_t}{V_b + V_t}$$

We can keep repeating this calculation to find that 6 batches are necessary to reach a pH higher than 10. Alternatively, we can recognise that it is a geometric series:

$$c_N = \sum_{n=0}^{N+1} ab^n,$$

where

$$a = \frac{c_d V_d}{V_d + V_s}$$

and

$$b = \frac{V_t}{V_b + V_t}.$$

The summation gives

$$c_N = \frac{a(1 - b^N)}{1 - b}$$

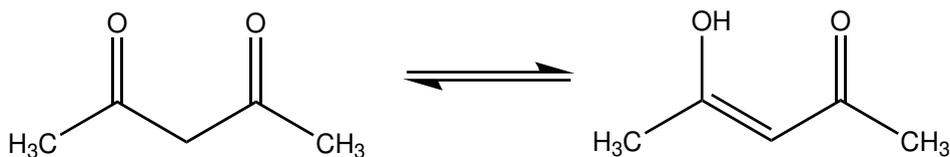
Then, expressing  $N$  as a function of  $c_N$  gives

$$N = \frac{\log\left(1 - \frac{c_N}{a}(1 - b)\right)}{\log b},$$

which, upon substituting the concentration for the final pH, gives  $N = 5.32$ , i.e. 6 batches (we need to round up, since the number of batches is an integer and 5 batches are insufficient).

### Question H.3 (Adam Tywoniak)

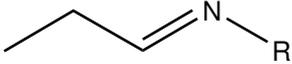
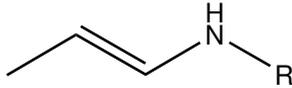
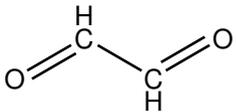
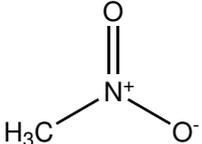
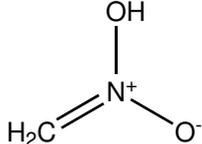
Tautomerism is a type of isomerism in which two molecules differ only in the positions of a hydrogen atom and a nearby multiple (i.e. double or triple) bond. They readily interconvert and often exist in equilibrium with one another. The textbook example of tautomerism is the equilibrium between a ketone or aldehyde and the corresponding enol (an alcohol with an adjacent double bond).



Below you are asked to consider some less well-known examples of tautomerism. Complete the table with the missing member of each pair of tautomers. Keep in mind that both members of each pair, being isomers of each other, must have the same molecular formula.

keto-like tautomer	enol-like tautomer
	$\text{HC}\equiv\text{C}-\text{OH}$
Note: In this example, the procedure must be applied twice to derive the correct tautomer.	$\text{HO}-\text{C}\equiv\text{C}-\text{OH}$

Solution:

keto-like tautomer	enol-like tautomer
	
$\text{H}_2\text{C}=\text{C}=\text{O}$	$\text{HC}\equiv\text{C}-\text{OH}$
	$\text{HO}-\text{C}\equiv\text{C}-\text{OH}$
	

Ethyne-1,2-diol converts to glyoxal (ethanedial) via 2-hydroxyethen-1-one.

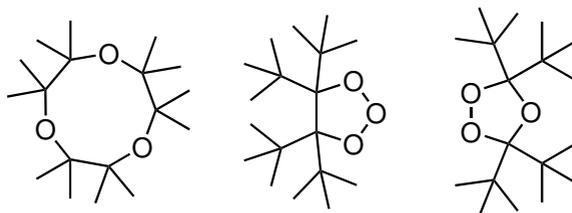


#### Question H.4 (Richard Veselý)

You wish to determine the structure of an unknown molecule that has the formula  $\text{C}_{18}\text{O}_3\text{H}_{36}$  (as determined by mass spectrometry). There are a huge number of possible molecules with this formula; fortunately, we have the  $^1\text{H}$  NMR spectrum of this molecule which contains just one peak. Draw the structure of this molecule.

**Solution:**

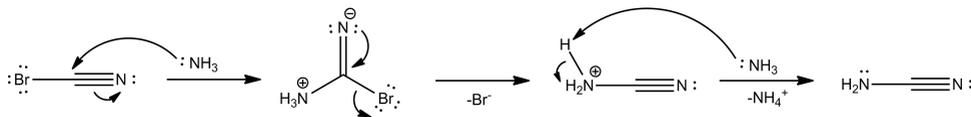
One peak implies that all the hydrogens are equivalent. This is satisfied by the following three molecules:

**Question H.5 (Vojtěch Laitl)**

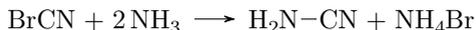
Carboxylic acid derivatives and the reactions that convert between them play an important role in organic synthesis. However, neither functional nor substitutional derivatives of acids are limited to the domain of organic chemistry; interesting reactions can also be observed involving inorganic molecules. For instance, the reaction of cyanogen bromide ( $\text{Br}-\text{C}\equiv\text{N}:$ ) with aqueous ammonia is found to proceed via a mechanism similar to nucleophilic acyl substitution. The main product is a compound containing a carbon atom bonded to two nitrogen atoms. Propose a complete chemical equation to describe this process (the mechanism is not required). Mind the acid-base properties of reactants and possible (by)products!

**Solution:**

Taking advantage of the description given, it can be deduced that aqueous ammonia substitutes Br atom in cyanogen bromide, forming thereby cyanamide,  $\text{H}_2\text{N}-\text{C}\equiv\text{N}:$ . Let us sketch the total mechanism, the key step of which is a temporary enhancement of hybridization ascribed to the substrate central atom (C-atom of  $\text{BrCN}$ ) from  $\text{sp}$  to  $\text{sp}^2$ -hybridization:



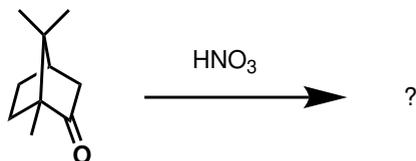
The transformation produces cyanamide, bromide anion and ammonium cation, the summary equation therefore reads



It was not necessary to declare the total mechanism in order to solve the problem successfully, to understand the reaction as a formal substitution should be instructive enough. In such a case, we must note that in basic environment, a strongly acidic HBr molecule cannot be forced out of the substrate (as a trivial stoichiometry 1:1 may indicate) and that the correct by-product is an ammonium salt.

### Question H.6 (Jiří Ledvinka)

Camphor is a naturally occurring ketone with a pleasant aroma. Camphoric acid is used in manufacture of pharmaceuticals and is obtained from the oxidation of camphor using nitric acid, in which one of the C–C bonds to the carbonyl group is oxidatively cleaved. Which one of the acids drawn below can result from oxidation of the following camphor stereoisomer?



- a) b) c)
- d) e) f)

#### Solution:

We should first rotate the camphor molecule so we can see the cyclopentane ring of the product (i.e. the left ethylene bridge pointing back and the right bridge with ketone towards us). Then it is obvious that cleavage of the ketone activated bond results in acid **b**), which has both carboxylic groups pointing toward us.

**Question K.1 (Stanislav ChvÍla)**

In the Czech Republic, four of the last five years were significantly drier than the long-term average. In contrast, last year was very rainy. On one Thursday in July there was heavy rainfall in the central region of the country, whereas the next day was calm and sunny, reaching a temperature of 28.5 °C at 2 PM with relative humidity of 57 %. That night, the temperature dropped to 16 °C.

Calculate the fraction of air moisture (as a percentage) one should expect to have condensed to form dew. You may assume that the saturated vapour pressure (in mm Hg) of water follows the Antoine equation,

$$\log_{10} p^s = 8.07131 - \frac{1730.63}{233.426 + t},$$

where  $t$  is the temperature in °C.

---

**Solution:**

Since we are asked to calculate the percentage only, we need not be bothered with the pressure expressed in mm Hg. Using the Antoine equation, we calculate the saturated water vapour pressure during daytime and at night:

$$\begin{aligned}\log_{10} p_{\text{day,sat.}}^s &= 8.07131 - \frac{1730.63}{233.426 + 28.5} \\ p_{\text{day,sat.}}^s &= 29.106 \text{ mm Hg} \\ \log_{10} p_{\text{night}}^s &= 8.07131 - \frac{1730.63}{233.426 + 16} \\ p_{\text{night}}^s &= 13.579 \text{ mm Hg} \\ p_{\text{day}}^s &= \phi \times p_{\text{day,sat.}}^s = 0.57 \times 29.106 = 16.591 \text{ mm Hg}\end{aligned}$$

The humidity of 57 % during daytime means the actual water vapour pressure was equal only to 57 % of the saturated vapour pressure, thus

$$p_{\text{day}}^s = \phi \times p_{\text{day,sat.}}^s = 0.57 \times 29.106 = 16.591 \text{ mm Hg}$$

The amount of liquefied water is in turn expressed as the ratio

$$q = \frac{p_{\text{day}}^s - p_{\text{night}}^s}{p_{\text{day}}^s} = \frac{16.591 - 13.579}{16.591} = 0.1815,$$

or, as requested, 18.15 %.

## Question K.2 (Vojtěch Laitl)

Ions of d-block and p-block metals are characterised by their Lewis acidity, due to which they tend to hydrolyse in aqueous solutions. Typically, s-block metals show no such behaviour; an exception is beryllium – the Be(II) ion of which is found to react with water to produce insoluble beryllium(II) hydroxide:

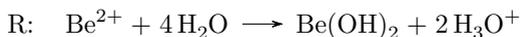


Calculate the equilibrium constant of hydrolysis of the  $\text{Be}^{2+}$  cation (the above reaction), given that the solubility product of the solid hydroxide is  $K_{\text{sp}}(\text{Be}(\text{OH})_2) = 6.92 \times 10^{-22}$ . Assume also that  $K_{\text{w}} = 1 \times 10^{-14}$ .

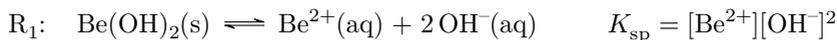
---

### Solution:

The equilibrium constant of hydrolysis of the  $\text{Be}^{2+}$  ion is the equilibrium constant of the reaction



Let us declare the reactions for which the constants  $K_{\text{sp}}$  and  $K_{\text{w}}$  are defined:



The reaction R may be formally understood as a combination of  $\text{R}_1$  and  $\text{R}_2$  in the form  $\text{R} = -\text{R}_1 + 2\text{R}_2$ . The same algebraic relation holds for standard reaction Gibbs energies, from which the equilibrium constant sought for can be expressed. Below, we further exploit the general expression  $\Delta_r G^\ominus = -RT \ln(K)$ :

$$\begin{aligned} \Delta_r G^\ominus &= -\Delta_r G^\ominus(\text{R}_1) + 2\Delta_r G^\ominus(\text{R}_2) \\ -RT \ln(K) &= +RT \ln(K_{\text{sp}}) - 2RT \ln(K_{\text{w}}) \\ K &= \frac{K_{\text{w}}^2}{K_{\text{sp}}} \doteq 1.45 \times 10^{-7} \end{aligned}$$

The same result is obtained if the  $[\text{H}_3\text{O}^+]$  equilibrium concentration is substituted in the explicit definition of  $K$ . We mark that by definition

$$K = \frac{[\text{H}_3\text{O}^+]^2}{[\text{Be}^{2+}]}$$

and recall the definition of the ionic product  $K_w$ :

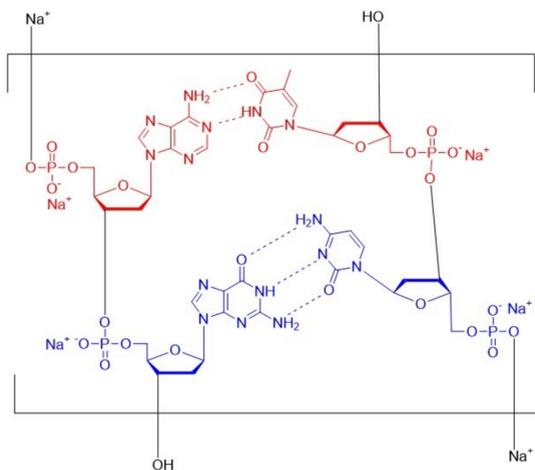
$$K = \frac{K_w}{[\text{Be}^{2+}][\text{OH}^-]^2} = \frac{K_w^2}{K_{\text{sp}}}$$

### Question K.3 (Ladislav Prener)

*Plasmodium falciparum* is a protozoan parasite which causes malaria in humans. Currently, 220 million people are infected worldwide, with almost half a million deaths per year. In 2002, the entire genome of *P. falciparum* was sequenced. It contains 7406 introns with an average length of 178.7 base pairs. Elemental analysis of a mixture of all the introns revealed a nitrogen content of  $x_{\text{N}} = 15.11\%$  by weight. Calculate the molar fraction (in percent) of G–C base pairs in the introns of *P. falciparum*.

Assume that the negative charge on phosphates is compensated by sodium cations. Round the mass fractions to 4 decimal points. The result should be given as a percentage with 1 decimal point precision.

$M_r(\text{C}) = 12.011$ ;  $M_r(\text{H}) = 1.008$ ;  $M_r(\text{O}) = 15.999$ ;  $M_r(\text{N}) = 14.007$ ;  $M_r(\text{P}) = 30.974$ ;  $M_r(\text{Na}) = 22.989$



**Solution:**

The DNA chain is formed by condensation (joining of two molecules accompanied by a loss of a water molecule) of the 3' hydroxyl of a nucleotide phosphate with the 5' phosphate group of the following nucleotide phosphate. The DNA strands form a double-stranded helix. In the helix, deoxyadenosine (A) is always paired with thymidine (T), and deoxyguanosine (G) with deoxycytidine (C). Each base pair (A–T in red, G–C in blue) is thus a subunit of the double-stranded helix (the sample hence contains the same amount of A and T).

The A–T base pair (red) has a formula of  $C_{20}H_{23}N_7Na_2O_{12}P_2$ . The G–C base pair (blue) has a formula of  $C_{19}H_{22}N_8Na_2O_{12}P_2$ . Each intron has 2 additional hydroxyls and sodium cations at the ends of the strands. If we wanted to be really precise, we would have to add a fraction of these terminal groups' molecular masses to each of the base pairs and try to iteratively solve a system of equations. However, the average intron length of 178.7 bp makes the masses of the end groups negligible, simplifying the problem significantly.

The A–T base pair has a molar mass of  $661.367 \text{ g mol}^{-1}$  and a mass fraction of nitrogen  $x_{AT} = 0.1483$ , whilst the G–C base pair has a molar mass of  $662.355 \text{ g mol}^{-1}$  and a mass fraction of nitrogen  $x_{GC} = 0.1692$ . The mass fraction of nitrogen in the sample is the sum of the nitrogen mass fractions of the base pairs multiplied by their corresponding molar fractions in the sample:

$$\begin{aligned}x_N &= y_{GC} \times x_{GC} + y_{AT} \times x_{AT} \\x_N &= y_{GC} \times x_{GC} + (1 - y_{GC}) \times x_{AT} \\0.1511 &= y_{GC} \times 0.1692 + (1 - y_{GC}) \times 0.1483 \\y_{GC} &= 0.1340\end{aligned}$$

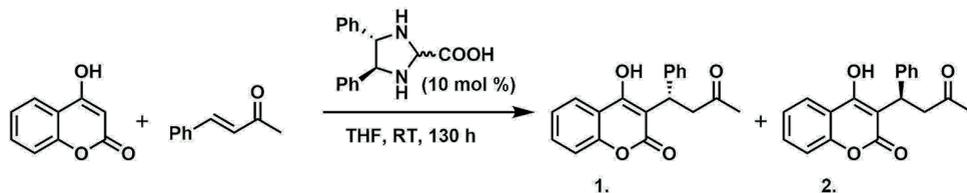
The introns of *Plasmodium falciparum* thus contain 13.4 % G–C base pairs — this makes it one of the most A–T rich organisms in the world.

### Question K.4 (Ondřej Daněk)

Fritz was experiencing problems with blood coagulation after having surgery to treat his war wounds, so he decided to synthesise warfarin, which is used as a blood thinner. He wanted his synthesis to yield the highest possible proportion of the *S*-isomer, because this is more potent than the *R*-isomer and would therefore allow him to consume the minimum amount of warfarin needed to achieve the desired effect.

Warfarin can be prepared via the Michael addition of 4-hydroxycoumarin to 4-phenylbut-3-en-2-one (as shown in the scheme below). A new chiral centre is formed during this reaction, and without any chiral catalyst, a racemic mixture of both enantiomers (*R*- and *S*-isomers) would be produced. By using a chiral catalyst, however, a significant bias towards one of the enantiomers can be achieved. *S*-warfarin has a specific rotation of  $-25.50^\circ \text{g}^{-1} \text{cm}^3 \text{dm}^{-1}$  when measured in glacial acetic acid at  $25^\circ\text{C}$  and with a polarized light source with a wavelength of 589.5924 nm (sodium D-lines). After performing the reaction and isolating the product, Fritz weighed out 2.5096 g of his warfarin and dissolved it in 20.00 ml of glacial acetic acid. He filled a polarimetry cuvette of length 1 dm with the prepared solution.

At  $25^\circ\text{C}$ , Fritz measured a rotation of  $\alpha = -2.67^\circ$  on his polarimeter with a sodium lamp as the light source. Calculate the molar percentage (rounded to a hundredth of a percent) of **product 1**, that is present in his warfarin sample.



**Solution:**

Angle of rotation is, as can be seen from the unit of specific rotation, proportional to the concentration of the optically active substance, and the length of the cuvette. Enantiomers have same and opposite specific rotations and a racemic mixture of enantiomers thus doesn't rotate the polarization plane at all, so we can express the mass concentration of (S) warfarin responsible for the measured angle of rotation as:

$$\rho = \rho^{\text{mix}} - 2\rho^{(R)}$$

We know the mass concentration of the mixture ( $\rho^{\text{mix}}$ ):

$$\rho^{\text{mix}} = \frac{m}{V} = \frac{2.5096}{20} = 0.1255 \text{ g cm}^{-3}$$

And we can calculate the concentration of (S) warfarin responsible for the measured angle of rotation from the angle of rotation as such:

$$\rho = \frac{\alpha}{[\alpha]} = \frac{-2.67}{-25.5} = 0.1047 \text{ g cm}^{-3}$$

As the angle of rotation was measured at the same temperature for which we know the specific rotation, and it was measured in a 1 dm long cuvette, we can just divide the angle of rotation by the specific rotation of *S*-warfarin.

By substituting the calculated concentrations to the first formula, we get:

$$\begin{aligned} 0.1047 &= 0.1255 - 2\rho^{(R)} \\ \rho^{(R)} &= 0.0104 \text{ g cm}^{-3} \\ w^{(R)} &= \frac{\rho^{(R)}}{\rho^{\text{mix}}} = \frac{0.0104}{0.1255} = 0.08287 \\ w^{(S)} &= 1 - w^{(R)} = 0.91713 \end{aligned}$$

Because we are dealing with a mixture of isomers the mass fraction is equal to the molar fraction, and the correct answer in molar % is 91.71% (compound 1 is the desired *S* isomer).

**Question K.5 (Stanislav ChvÍla)**

For a newly synthesised dibasic organic acid, the first  $pK_a$  value measured was 4.67. A preliminary titration curve showed two distinguishable equivalence points. The monobasic form of the acid was found to be coloured, and its visible absorption spectrum was measured under various conditions. The absorbance,  $T$ , of the solution at wavelength  $\lambda = 581$  nm was 0.227 at pH 5.02 and 0.208 at pH 7.95 (with the same concentration of acid and the same cuvette used in both cases).

Assuming that the dianionic and neutral forms of the acid do not show any absorption at  $\lambda = 581$  nm, calculate the second  $pK_a$  of the acid.

---

**Solution:**

The Henderson-Hasselbalch equation for calculating the pH of a buffered mixture is the key for calculating the second  $pK_a$  value. First, we will concern ourselves with the first  $pK_a$  value — the monobasic form now acts as a base and the neutral form is the acid. Since all measurements have been carried out at the same concentration, in the same cuvette and on the same acid, we may regard the absorbance values as concentrations when inserted into the Henderson-Hasselbalch equation. At the pH of 5.02, the conjugate base concentration is equivalent to the absorbance and the conjugated acid concentration may be expressed as the difference of the total analytic concentration (in our case, absorbance)  $T$  minus the monobasic form:

$$\begin{aligned} \text{pH}_1 &= pK_{a,1} + \log_{10} \frac{A_{\text{conj.base}}}{(T - A_{\text{conj.base}})} \\ 5.02 &= 4.67 + \log_{10} \frac{0.227}{(T - 0.227)} \end{aligned}$$

The solution of the equation is  $T = 0.3284$ . This “total possible absorbance” can be then used for the calculation of the second  $pK_a$  value. This time, the colorful monobasic form is the conjugate acid:

$$\begin{aligned} \text{pH}_2 &= pK_{a,2} + \log_{10} \frac{(T - A_{\text{conj.acid}})}{A_{\text{conj.acid}}} \\ 7.95 &= pK_{a,2} + \log_{10} \frac{(0.3284 - 0.208)}{0.208} \\ pK_{a,2} &= 8.19 \end{aligned}$$

**Question K.6 (Vojtěch Laitl)**

Purple permanganate anions undergo reduction in a strongly alkaline environment to give dark-green manganate ions. When the solution is acidified, hydrogen manganate ions are produced. These may disproportionate according to the schematic chemical equation



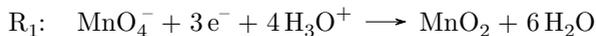
Calculate the associated molar standard Gibbs free energy change (i.e. the change with one mole of reaction equivalents, when balanced with the smallest possible integer stoichiometric coefficients). You may use the following standard redox potential data:

$$\begin{aligned} E^\ominus(\text{MnO}_4^-, \text{H}_3\text{O}^+ | \text{MnO}_2) &= +1.9 \text{ V} \\ E^\ominus(\text{MnO}_4^-, \text{H}_3\text{O}^+ | \text{HMnO}_4^-) &= +0.9 \text{ V} \end{aligned}$$

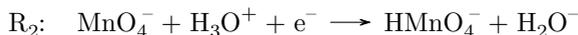
---

**Solution:**

Let us start with sketching the redox half-reactions for which the standard redox potentials given are defined. It is convenient to depict both of them in the sense of reduction, since  $E^\ominus$  is defined analogously:

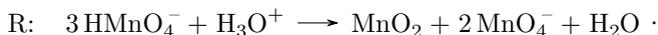


$$E^\ominus(\text{MnO}_4^-, \text{H}_3\text{O}^+ | \text{MnO}_2) = +1.9 \text{ V}$$



$$E^\ominus(\text{MnO}_4^-, \text{H}_3\text{O}^+ | \text{HMnO}_4^-) = +0.9 \text{ V}$$

The disproportionation considered is described by a balanced chemical equation as follows



The reaction R may be understood as a formal combination  $R = R_1 - 3R_2$ . Identical algebraic relation holds for the standard reaction Gibbs energies, which in case of the half-reactions may be enumerated by the relation  $\Delta_r G^\ominus = -zFE^\ominus$ , where  $z$  is the number of electrons exchanged,  $F = 96\,485 \text{ C mol}^{-1}$  is the Faraday constant.

$$\Delta_r G^\ominus = \Delta_r G^\ominus(R_1) - 3\Delta_r G^\ominus(R_2)$$

$$\Delta_r G^\ominus = -z_1 F E^\ominus(\text{MnO}_4^-, \text{H}_3\text{O}^+ | \text{MnO}_2) + 3z_2 F E^\ominus(\text{MnO}_4^-, \text{H}_3\text{O}^+ | \text{HMnO}_4^-)$$

$$\Delta_r G^\ominus \doteq -289.5 \text{ kJ mol}^{-1}$$

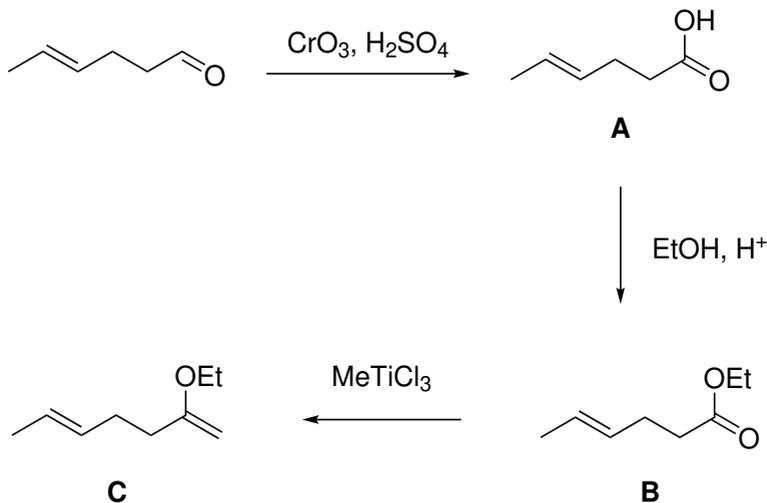
While enumerating, we used  $z_1 = 3$  for the three-electron reduction  $R_1$  and  $z_2 = 1$  for the one-electron reduction  $R_2$ . Since the resultant Gibbs energy is negative, we should expect hydrogen manganate ions to disproportionate spontaneously; Mn(VI) oxidation state is only stable in strongly alkaline solutions.

### Question L.1 (Jan Hrubeš)

The Wittig reaction is well known to be a useful synthetic route from carbonyls to alkenes. However, organometallic compounds of titanium can also be used for this transformation, since they very easily coordinate the oxygen. An advantage is that these can react even with less activated ketones and even with esters, which produces vinyl-ethers. Hex-4-enal is reacted with the Jones reagent to give compound A. The total number of hydrogens in the molecule is not changed by this reaction. Compound A then reacts with ethanol with acid catalysis to give compound B, which reacts with methyltitanium trichloride to give compound C. Molecule C contains only carbon, hydrogen and oxygen atoms. Give the structures of A, B and C.

#### Solution:

The first reaction is a simple oxidation of an aldehyde to a carboxylic acid with no change to the double bond. The second step is an acid catalysed esterification. The last reaction is a replacement of the carbonyl oxygen with the methylenid group  $\text{CH}_2=$ . The reaction scheme is shown below.



A: hex-4-enoic acid, B: ethyl hex-4-enoate, C: hepta-1,5-dien-2-yl(ethyl)ether]

**Question L.2 (Wojciech Jankowski)**

At ambient temperature, metal X reacts slowly with oxygen to form a compound Y, which contains 25.17% oxygen by mass. Y reacts with gaseous fluorine to yield a yellow product Z (13.76% F by mass) and gas W is formed as a by-product, with one molecule of W released for every two fluorine molecules that react with Y.

Give the chemical formulae of X, Y, Z and W.

*Hint: X is an element with extraordinarily high density and a very high melting point.*

---

**Solution:**

Having tested all possible formulae for oxides ranging from  $X_2O$  to  $XO_4$ , we find out that the metal in question is osmium (Os) and the relevant oxide is  $OsO_4$ . The only reasonable gas that may be released during its fluorination is oxygen. The fluorinated oxide may then be determined with the help of a few calculations, and it is  $OsO_3F_2$ .

The formulae are as follows:

X: Os

Z:  $OsO_3F_2$

Y:  $OsO_4$

W:  $O_2$

**Question L.3 (Jiří Ledvinka)**

Formaldehyde is used, in the form of aqueous solution, for tissue preservation and animal preparation. It can be found in new furniture and as an undesirable component of cigarette smoke. Even electronic cigarettes produce small amounts of formaldehyde by decomposition of propylene glycol or glycerol.

Suppose you would like to estimate the amount of formaldehyde in a single breath inhaled by someone using an electronic cigarette. Formaldehyde can be detected by several redox titrations, but to prevent any interference from the alcohols that are also present, we will use a more selective method. In a basic environment, formaldehyde reduces divalent mercury to its elemental form, being oxidised in the process to give formate. While divalent mercury forms a stable complex with EDTA, metallic mercury does not react.

The estimation procedure is as follows:

Bubble ten breaths from an e-cigarette user into 50 ml of distilled water in a volumetric flask (assume complete absorption by the water), then top up to the 100 ml mark with more distilled water. Pipette 20 ml of 0.1 M EDTA and 15 ml of 0.1 M  $\text{Hg}(\text{NO}_3)_2$  solution into a titration flask, and leave until the solution clears up. Then, add 10 ml of the earlier prepared sample solution, adjust the pH to between 9 and 10 with 2 M NaOH, and leave to react for two hours. After this time, black deposited mercury should be seen on the bottom of the flask. Adjust the pH to between 4 and 5 with 2 M  $\text{HNO}_3$  and add a teaspoon of urotropine. Finally, titrate the leftover EDTA against 0.1 M  $\text{Hg}(\text{NO}_3)_2$  in the presence of methylthymol blue, stopping when the contents of the flask turns from yellow to blue.

You follow the above procedure and get a titre of 15 ml. How many milligrams of formaldehyde are present in one breath from the e-cigarette user?

---

**Solution:**

Titration of leftover EDTA with 15 ml of 0.1 M  $\text{Hg}(\text{NO}_3)_2$  corresponds to 1.5 mmol of free EDTA. Therefore from initial 2.0 mmol of EDTA, 0.5 mmol reacted with divalent mercury during the estimation. The rest of the divalent mercury, i.e. 1.0 mmol, reacted with the formaldehyde. The reaction mentioned in the text has the following equation:



Most importantly, 1.0 mmol of divalent mercury therefore corresponds to 1.0 mmol of formaldehyde. Ten breaths were introduced into the volumetric flask and the fraction of sample taken for the determination contains only one. The mass of formaldehyde in one breath from electronic cigarette is then  $m = n \times M = 30$  mg.

**Question L.4 (Jiří Ledvinka)**

The issue of dual food and drink quality has been a central theme of the European Parliamentary election campaigns in the past. Candidates have focused on the inconsistent taste properties among food produced by international companies for different EU countries. However, voters should be equally concerned by the inconsistent physical properties. For example, Coke sold in Germany contains 10.6 g of sucrose per 100 ml, whereas Coke in Czechia contains glucose-fructose syrup with a total saccharide content of 11.2 g per 100 ml. What is the difference between the melting points of these two beverages? (Neglect the influence of the other components of the beverages.)

**Necessary data:**Coke density:  $1.042 \text{ g ml}^{-1}$ 

$$\Delta H_{\text{f}}(\text{H}_2\text{O}) = 333.55 \text{ J g}^{-1}$$

Change in melting point:

$$\Delta T_{\text{m}} = ibK_{\text{f}}, \quad (1)$$

where  $i$  is the number of particles to which the substance dissociates,  $K_{\text{f}}$  is the cryoscopic constant and  $b$  is the molality in moles per kg of solvent.

Cryoscopic constant:

$$K_{\text{f}} = \frac{RMT_{\text{m}}^2}{\Delta H_{\text{f}}}, \quad (2)$$

where  $R$  is the ideal gas constant,  $M$  is the molar mass of the solvent,  $T_{\text{m}}$  is the melting point of the pure solvent and  $\Delta H_{\text{f}}$  is the enthalpy of fusion of the solvent.

$$M(\text{water}) = 18.02 \text{ g mol}^{-1},$$

$$M(\text{glucose}) = 180.16 \text{ g mol}^{-1},$$

$$M(\text{sucrose}) = 342.30 \text{ g mol}^{-1},$$

$$M(\text{fructose}) = 180.16 \text{ g mol}^{-1}$$

---

**Solution:**

We can see that the two different Coca-Cola beverages will display different melting point than pure water. In both cases, we will calculate the melting point depression from equation (1). Because saccharides do not dissociate in solutions,  $i$  is equal to one. Now we can calculate the cryoscopic constant of water from equation (2). However, we should first perform dimensional analysis. In equation (1),  $i$  is obviously dimensionless and the molality is in units  $\text{mol kg}^{-1}$ . Therefore, cryoscopic constant is in units  $\text{K kg mol}^{-1}$ .

The dimensional analysis is as follows:

$$\text{K kg mol}^{-1} = \frac{\text{J mol}^{-1} \text{K}^{-1} \times \text{kg mol}^{-1} \times \text{K}^2}{\text{J mol}^{-1}}.$$

molar mass is thus in  $\text{kg/mol}$  and enthalpy of melting is in  $\text{J/mol}$ . Plugging in the numbers gives

$$K_f = \frac{8.314 \times 0.01802 \times 273.15^2}{333.55 \times 18.02} \text{K kg mol}^{-1} = 1.860 \text{K kg mol}^{-1}.$$

The remaining unknowns are the two molalities which we will calculate from their definition. Molality is number of moles of solute in one kilogram of solvent, so we can write:

$$b(\text{sucrose}) = \frac{10.6/342.3}{0.1042 - 0.0106} \text{mol kg}^{-1} = 0.3308 \text{mol kg}^{-1}$$

and in the same manner

$$b(\text{glu} - \text{fru}) = \frac{11.2/180.16}{0.1042 - 0.0112} \text{mol kg}^{-1} = 0.6685 \text{mol kg}^{-1}.$$

Now we can calculate melting point depression of both drinks from equation (1):

$$\Delta T_m(\text{sucrose}) = 1 \times 1.860 \times 0.3308 \text{K} = 0.6153 \text{K}$$

and

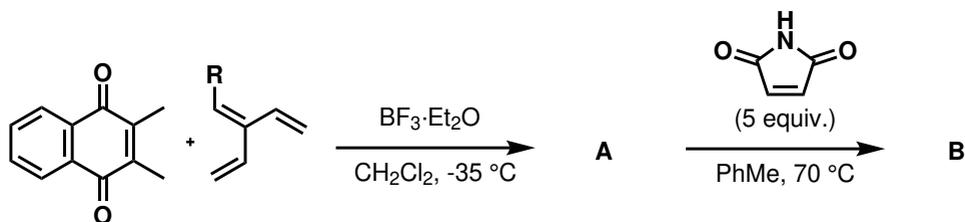
$$\Delta T_m(\text{glu} - \text{fru}) = 1 \times 1.860 \times 0.6685 \text{K} = 1.243 \text{K}.$$

The difference in melting points of the two beverages is then

$$\Delta T_m = |\Delta T_m(\text{sacharosa}) - \Delta T_m(\text{glu} - \text{fru})| = 0.628 \text{K}.$$

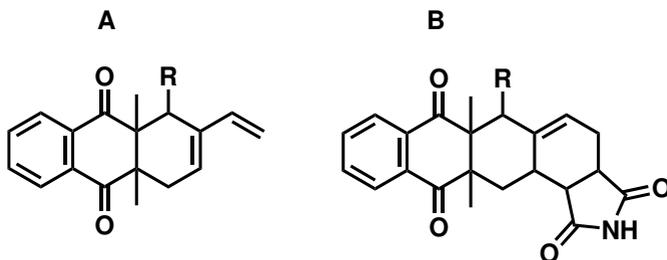
## Question L.5 (Jiří Ledvinka)

Pericyclic reactions are a class of reactions that proceed via cyclic transition states. As the name may suggest, they are often useful in organic synthesis for creating new cyclic structures, e.g. in the synthesis of tetracyclines and their analogues. Draw the structures of the intermediate A and product B. Do not include stereochemistry.



## Solution:

As mentioned in the introductory text, the reactions used to synthesize B are pericyclic reactions, namely the Diels-Alder reactions. In the first reaction, quinone acts as a dienophile affording intermediate A with cyclohexene structure motif. The structure of diene used in this reaction results in diene character of intermediate A, which can therefore react with the succinimide acting as a dienophile in the second reaction. Compound B also contains cyclohexene ring and in total two six-membered rings were formed by the two subsequent Diels-Alder reactions.

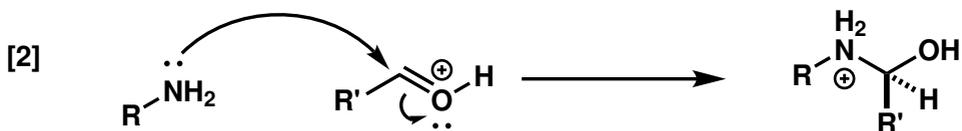
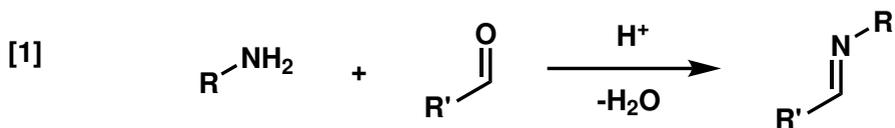


## Question L.6 (Richard Veselý)

One of the most enjoyable topics in organic chemistry is the kinetics of organic reactions. Here we consider the formation of an imine from an aldehyde and an amine under mildly acidic conditions (Figure 1). The reaction rate is limited mostly by the slowest step in the reaction mechanism, which in this case is the nucleophilic attack on the carbonyl group by the amine nitrogen (Figure 2). If the solution is too acidic, the nitrogen will be protonated and the reaction unable to proceed, whereas if the solution is too basic, the carbonyl will not be protonated and the reaction will proceed extremely slowly.

Assuming the reaction rate is limited (and therefore determined) only by that of the slowest step, find the overall rate  $r$  as a function of:

- the proton concentration  $c_{\text{H}}$
- the total (i.e. neutral and protonated) amine concentration  $c_{\text{N}}$
- the total (i.e. neutral and protonated) aldehyde concentration  $c_{\text{O}}$
- the dissociation constant  $K_{\text{N}}$  of the protonated amine
- the dissociation constant  $K_{\text{O}}$  of the protonated aldehyde
- the rate constant  $k_{\text{r}}$  for the slowest step.



**Solution:**

The reaction rate is given by

$$r = k_r[\text{N}][\text{O}^+],$$

where  $[\text{N}]$  denotes the concentration of the deprotonated form of the amine and  $[\text{O}^+]$  denotes the concentration of the protonated form of the aldehyde.

Let's use all the information we have about the system. Mass balance of amine:

$$c_{\text{N}} = [\text{N}] + [\text{N}^+],$$

where  $[\text{N}^+]$  is the concentration of the protonated form of the amine.

Mass balance of aldehyde:

$$c_{\text{O}} = [\text{O}] + [\text{O}^+],$$

where  $[\text{O}]$  is the concentration of the neutral form of the aldehyde.

Dissociation constant of the protonated amine:

$$K_{\text{N}} = \frac{c_{\text{H}}[\text{N}]}{[\text{N}^+]}$$

Dissociation constant of the protonated aldehyde:

$$K_{\text{O}} = \frac{c_{\text{H}}[\text{O}]}{[\text{O}^+]}$$

Combining all the above we get:

$$[\text{N}] = \frac{K_{\text{N}}c_{\text{N}}}{c_{\text{H}} + K_{\text{N}}}$$

and

$$[\text{O}^+] = \frac{c_{\text{H}}c_{\text{O}}}{K_{\text{O}} + c_{\text{H}}}$$

Plugging in to the equation for the reaction rate we get the solution:

$$r = k_r \frac{K_{\text{N}}c_{\text{N}}c_{\text{H}}c_{\text{O}}}{(c_{\text{H}} + K_{\text{N}})(K_{\text{O}} + c_{\text{H}})}$$

**Questions were created, edited and reviewed by:**

Martin Balouch	Vojtěch Laitl
Jan Bartáček	Jiří Ledvinka
Raz L. Benson	Yeha Lee
Jaroslav Cerman	Juraj Malinčík
Stanislav Chvíla	Lukáš Marek
Ondřej Daněk	Pavel Měrka
Tereza Dobrovolná	Pavλίna Muchová
Matúš Drexler	Vladimír Němec
Vladimír Finger	Jan Němec
Anna Freislebenová	Miroslava Novoveská
Tereza Gistrová	Soňa Ondrušová
Marie Grunová	Jakub Petrús
Jan Hrabovský	Adam Příklad
Jan Hrubeš	Ladislav Prener
Rostislav Huňa	Vít Procházka
Wojciech Jankowski	Clare Rees-Zimmerman
Adam Jaroš	Holly Smith
Vadim Kablukov	Adam Tywoniak
Ryan Kang	Richard Veselý
Ondřej Kopilec	Nikola Vršková
Anna Kovárnová	Alexandr Zaykov

*Initials in parentheses indicate authors of questions bearing that label. Academic degrees are omitted for clarity.*

Typeset in X<sub>Y</sub>L<sup>A</sup>T<sub>E</sub>X using the `natsci` package by Adam Příklad

## Acknowledgements

We would like to thank:

Dr James Keeler (Head of the Department),

Dr Peter Wothers (School and Outreach Officer),

Emma Powney (Outreach Co-ordinator),

and other members the departmental staff for their work and support.

The Cambridge Chemistry Race 2021 and Chemiklání 2021 were organised by the Yusuf Hamied Department of Chemistry, University of Cambridge, the Faculty of Chemical Technology, University of Pardubice and the voluntary association Alumni scientie bohemicæ.



**UNIVERSITY OF  
CAMBRIDGE**

Yusuf Hamied  
Department of Chemistry

<https://www.ch.cam.ac.uk/>



**UNIVERSITY  
OF PARDUBICE  
FACULTY  
OF CHEMICAL  
TECHNOLOGY**

<https://fcht.upce.cz/en>



**chemiklání**

<http://chemiklani.cz/>



ALUMNI  
SCIENTIAE  
BOHEMICAE

<http://www.czechscience.cz/>

Please report any errors to [chemistryrace@srcf.net](mailto:chemistryrace@srcf.net).

More information about the competition can be found at:  
<http://chemistryrace.com/>

This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License (CC BY-NC-SA 4.0).

<http://chemistryrace.com/>