Chemistry Race 2020: Questions and Solutions

chemistryrace

15 February 2020

supported by

UNIVERSITY OF CAMBRIDGE
Department of Chemistry

Question A.1 (SCh)

Hydrogen, the lightest element, is the source of much interesting chemistry. Not only is it extraordinarily light, flammable and explosive, but it is also ubiquitous throughout the universe. You will meet hydrogen in a variety of forms during this year's Chemistry Race, for instance, in the cellulose on which you will write your answers, or perhaps in your own perspiration as the competition gets going.

In fact, hydrogen exists naturally as a mixture of three isotopes — protium (P), deuterium (D) and tritium (T). Deduce which isotope is described by each of statements 1 to 6 (write P, D or T in each case):

1. This isotope has one neutron in its nucleus.
2. This is the heaviest of the three isotopes.
3. This is the most abundant of the three isotopes.
4. This isotope is radioactive.
5. This is the lightest of the three isotopes.

Solution:

The nuclei of protium, deuterium and tritium are composed of a proton, a proton and a neutron, and a proton and two neutrons, respectively. This immediately gives 1D, 2T and 5P. Far and away the most common one is protium, thus 3P. Tritium is the radioactive one (4T) and its radioactivity will form the basis for a later question.

Question A.2 (OK)

What is the molecular mass (in g mol^{-1}) of the substance released during a dehydration reaction?

Solution:

The answer is straightforward, stemming from the ancient Greek word ὕδωρ [(h)ýdôr], hence water. Its molecular mass is 18.

Question A.3 (MB)

The author of this question was preparing a phosphate buffer one late December afternoon, the objective being to simulate blood. He dissolved one buffer tablet in 200 ml of water, then (using a pH meter) measured a pH of 7.76. To match blood, however, the pH had to be adjusted to 7.4. The author decided to acidify the solution using phosphoric acid (5% by volume). To do so, he poured 3.5 ml phosphoric acid (85% by volume) from a flask into a graduated cylinder. How much water did he need to add to the cylinder to obtain the desired acid concentration of 5% by volume? (Assume negligible volume contraction.)

Solution: This task assesses the candidate's ability to calculate the concentrations of mixtures. This aspect of chemistry can be taught in many different ways. The answer can be obtained by using the so-called mixing equation, where we denote the 85% acid as solution 1, and pure water as solution 2.

$$V_1\phi_1 + V_2\phi_2 = (V_1 + V_2)\phi$$
$$3.5 \times 0.85 + V_2 \times 0 = (3.5 + V_2) \times 0.05 \text{ ml}$$
$$V_2 = 56 \text{ ml}$$

Question A.4 (MB)

Oxygen is produced industrially by fractional distillation of liquid air. This process is too demanding to be used in the lab. Instead, oxygen can be easily obtained from the thermal decomposition of some inorganic compounds. Write a balanced equation describing the thermal decomposition of potassium chlorate ($KClO_3$).

Solution:

As hinted in the task, the thermal decomposition of potassium chlorate produces molecular oxygen as one of the products. Thermal decomposition often leads to very stable products. Since the oxygen from $KClO_3$ is already present in the molecular oxygen, the simplest and most stable compound that could be the second product of this reaction is potassium chloride. The balanced equation is

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

Question A.5 (AT)

Haloquadratum walsbyi is a species of archaea, discovered in the 1980s in the brine pools on the Sinai peninsula. It gets its name from the square shape of its cells and is a so-called extremophile organism: it thrives in ponds of water, saturated with sodium chloride. To determine how much salt these critters can tolerate, we took 250 ml of the pond water, allowed all of the liquid to evaporate and obtained 90.5 g of salt. The temperature of the pond was 35 °C. Determine the molar concentration of sodium chloride in the pond.

Solution:

Molar concentration is defined as the amount of substance divided by the volume. To determine the amount of sodium chloride, we divide its mass by its molar mass $M_{\mathrm{NaCl}} = A_{\mathrm{Na}} + A_{\mathrm{Cl}} = 58.44\ \mathrm{g\ mol^{-1}}$. We get $n = m/M_{\mathrm{NaCl}} = 90.5/58.44 = 1.55\ \mathrm{mol}$. The molar concentration is then $c = n/V = 1.549/0.250 = 6.19\ \mathrm{mol\ dm^{-3}}$. We do not need the temperature of the solution for this calculation.

Question A.6 (SCh)

The author of this task recalls a chemistry lesson in secondary school, where he was sent to the front row for being disruptive. Shortly after, he was reprimanded again for being distracted by the poem scribbled on his desk (loosely translated from Czech):

> *"If your mouse cannot ever stand still*
> *Crush and dissolve a cyanide pill*
> *A single drop may calm it down*
> *In fevered dreams its mind will drown*
> *As the second drop, it will surely keep*
> *The revered mouse in eternal sleep"*

Years later, the author stumbled upon this poem in the depths of the Internet, and was inspired to set an unusual task for the Chemistry Race. From the following compounds, select which ones would cause severe damage to a person upon ingesting just one gram:

Sucrose, sodium chloride, potassium cyanide, ethanol, distilled water, nicotine.

Solution:

There are only two clearly dangerous chemicals — nicotine and potassium cyanide. The rest are more or less part of a normal diet.

Question B.1 (SCh)

Hydrocarbons (in Czech *uhlovodíky*) are often considered to be "lazy" molecules with little reactivity. Their "laziness", however, can make them very useful in a variety of situations. Deduce which of the descriptions (A to D) matches which hydrocarbon (1 to 4).

1. Toluene (methylbenzene)
2. Methane
3. Octane
4. Ethylene (ethene)

A. A major component of natural gas
B. The simplest organic plant hormone released during ripening
C. A major component of solvents and thinners
D. An important component of gasoline

Solution:

The correct matches are 1C, 2A, 3D, 4B.

Question B.2 (MB,WJ)

Homeopathy is a "pseudoscientific" medical treatment, involving the dilution of an active ingredient to such a small concentration that it is no longer present in the formulation. Jardík, a biochemist, wanted to prepare homeopathic hydrochloric acid. He prepared 0.01 mol l^{-1} solution of the HCl and measured a pH of 2.0. He then diluted the solution 100 times and measured a pH of 4.0. Again, he diluted 100 times and measured a pH 6.0. What will be the pH of the solution after one more 100-fold dilution?

Solution:

Straightforward reasoning or a simple (and incorrect) calculation will lead to the incorrect answer of pH = 8.0. This is not in agreement with the principle that the pH of acids must be lower than 7. Thus, the solution is so diluted that the commonly used equation

$$\mathrm{pH} = -\log_{10}[\mathrm{H}^+] \approx -\log_{10}\big(c(\mathrm{HCl})\big)$$

is no longer valid.

We can therefore assume that the solution is essentially pure water with pH = 7.0.

Note: For very dilute solutions, the ionic product of water cannot be neglected. A strong acid dissociates completely and the solution must maintain electroneutrality.

We may write these equations:

$$c(\mathrm{HCl}) = [\mathrm{Cl^-}] \tag{1}$$

$$[\mathrm{H^+}][\mathrm{OH^-}] = 10^{-14} \tag{2}$$

$$[\mathrm{H^+}] = [\mathrm{OH^-}] + [\mathrm{Cl^-}] \tag{3}$$

Expressing $[\mathrm{Cl^-}]$ and $[\mathrm{OH^-}]$ in terms of $[\mathrm{H^+}]$ and subbing into (3) gives

$$[\mathrm{H^+}]^2 - c(\mathrm{HCl})[\mathrm{H^+}] - 10^{-14} = 0$$

After choosing the positive root and finding its base 10 logarithm we get pH = 6.98. For the purpose of the competition values between 6.9 and 7.0 were accepted.

Question B.3 (AP)

Nowadays, analytical chemistry depends mostly on data measured by instruments. However, historically, chemists relied only on their senses. Tasting is now forbidden and even smelling is discouraged. Fortunately, we can still look at chemicals, and there are some compounds that we can recognise at first sight. Suppose that, on the shelf of a school chemistry lab, you found four bottles containing solid chemicals of the following colours:

yellow/gold, violet, orange, blue

The labels on the bottles are long gone, but according to the inventory, the shelf should contain the following chemicals:

- calcium sulfate dihydrate ($CaSO_4 \cdot 2\,H_2O$),
- copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5\,H_2O$),
- potassium permanganate ($KMnO_4$),
- sodium nitrate ($NaNO_3$),
- potassium dichromate ($K_2Cr_2O_7$),
- lead(II) iodide (PbI_2),
- iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7\,H_2O$),
- calcium carbonate ($CaCO_3$)

Determine which chemical is contained in each bottle.

Solution:

The correct assignment is:

yellow/gold — lead(II) iodide,
violet — potassium permanganate,
orange — potassium dichromate,
blue — copper(II) sulfate pentahydrate.

Question B.4 (MB)

Remember the question about the isotopes of hydrogen? Perhaps it is still on your desk somewhere! The heaviest isotope of hydrogen decays into radioactive helium with a half-life of 12.3 years according to the equation:

$$^{3}_{1}\mathrm{H} \longrightarrow {}^{3}_{2}\mathrm{He} + \mathrm{X}$$

Determine the particle X.

Solution:

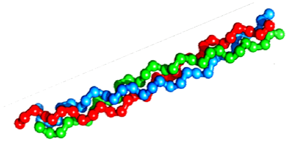
To conserve the number of nucleons and satisfy charge balance, the particle X has to be written as $^{0}_{-1}\mathrm{X}$. Thus, X is not a nucleon (neither a proton, nor a neutron) and has a charge of −1. The correct answer is therefore an electron. This kind of radioactive decay is known as beta minus decay and also produces an electron antineutrino. This was neglected so as not to complicate the task.

Question B.5 (JP)

Collagen is an important biomolecule that is commonly found in bones, ligaments, and cartilage. This question takes a closer look at this compound. Make sure to complete both parts of the question.

A. Choose the correct statement: Collagen is a
   1. protein, 2. saccharide, 3. lipid, 4. nucleic acid.

B. The 3D structure of collagen is shown below. It consists of three chains woven together. Each of the chains is left-handed, but the structure as a whole is right-handed. In order to pack all three chains tightly, every third amino acid in the chain has to be the simplest standard amino acid. What is the name of this amino acid?



Solution:

A. Collagen is a protein, as can be deduced from part B of the question.
B. The simplest standard amino acid is glycine.

Question B.6 (MG)

Would you like a cup of coffee?

There are two main types of coffee bean — Robusta and Arabica. Each of them contains different compounds, so their taste, smell, and flavour differ. However, most importantly, the amount of caffeine is higher in Robusta (2.5% by mass) than in Arabica (1.5% by mass). Assume an average university student consumes two cups of coffee per day, unless it's the exam period, when they need two extra. A cup of coffee made from a 70:30 mixture of Arabica and Robusta contains on average 100 mg of caffeine. How many students can be supplied with their daily dose of coffee on an exam day from a 1 kg pack of beans?

Solution:

There are 700 g of Arabica and 300 g of Robusta in 1 kg of a mixture consisting of 70% Arabica and 30% Robusta. To calculate the amount of caffeine in the pack, you need to multiply the mass of each kind of coffee with the corresponding mass fraction of caffeine and add these numbers together:

$$700 \times 0.015 + 300 \times 0.025 = 18$$

A 1 kg pack of coffee beans contains 18 g or 18 000 mg of caffeine. An average student usually needs 2 cups of coffee, but during an exam period they drink 2 more, for a total of 4 cups of coffee during exams. Each cup contains 100 mg of caffeine, so an average student drinks 400 mg of caffeine per exam day. Thus one bag of coffee can supply 18000/400 = 45 students during one exam day.

Question C.1 (AJ)

Identify four chemical elements using the following hints. Use their symbols to create a word one might use to describe L. da Vinci, W. A. Mozart or A. Einstein. Maybe it could even be used to describe you!

1. A metalloid used in electronics as a compound with arsenic
2. A metal, also one of the main components of the Earth's core
3. A heavy metal, one isotope of which is used as a nuclear fuel
4. A non-metal, the acid of which is one of the most important substances in the chemical industry

---

Solution:

GeNiUS

Question C.2 (SCh)

The chemical world is littered with cryptic symbols and abbreviations…
…and for students they give rise to many trials and tribulations!

In fact, mistaking one chemical for another can have serious consequences. To help eliminate such risks during this competition, arrange the following into pairs (one has been completed for you):

acetylene, methanal, propanone, hydrogen sulfide, ammonia, acetone, formaldehyde, azane, ethyne, sulfane.

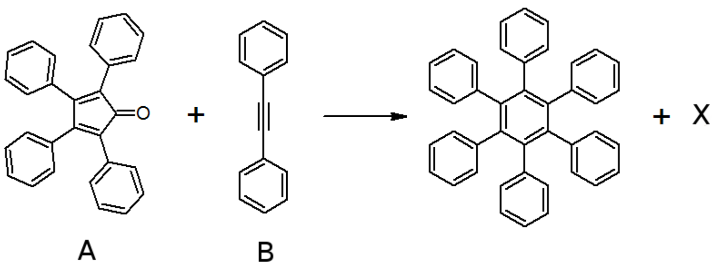
PAIR 1 — methanal, formaldehyde
PAIR 2 —
…

Solution:

The correct pairings are acetylene–ethyne, propanone–acetone, acetic acid–ethanoic acid and ammonia–azane.

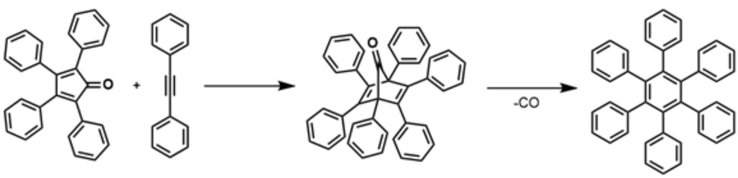
Question C.3 (JL)

One can synthesise hexaphenylbenzene (**C**) conveniently by reacting tetraphenylcyclopentadienone (**A**) with diphenylacetylene (**B**). This reaction proceeds via a bicyclic intermediate. Determine the identity of the by-product, compound X.



Solution:

First, a Diels–Alder reaction takes place to yield the bicyclic intermediate. Hexaphenylbenzene is formed by elimination of **carbon monoxide (CO)**. An easier route to the correct answer is comparison of the molecular formulae of the reactants and products.



Question C.4 (PM, AP)

Fructose, which is an isomer of glucose, is one of the most common dietary sugars. As the name suggests, it is found in high concentrations in fruit. One of the highest concentrations is in pears, 0.35 mol l^{-1}. Assuming that a pear has a volume of 250 ml and a person eats 12 pears a month, calculate the mass of fructose ingested over that period of time.

Solution:

The concentration of fructose is 0.35 mol l^{-1}. The volume of one pear is 250 ml = 0.25 l. The amount of fructose in one pear can be calculated as

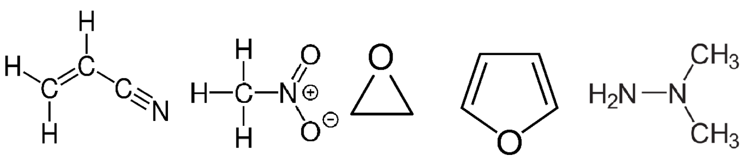
$$c(\text{fructose}) \times V = 0.0875 \text{ mol}.$$

The total amount in 12 pears is $0.0875 \times 12 = 1.05$ mol of fructose. The molecular formula of fructose is $C_6H_{12}O_6$ (same as glucose), so the molar mass $M(\text{fructose}) =$ 180 g mol^{-1}. The total amount of fructose is $n(\text{fructose}) \times M(\text{fructose}) = 189$ g of fructose.

Question C.5 (PM)

Cigarette smoke contains approximately 4 000 different chemical compounds, of which at least 50 are proven human carcinogens. Some of these are listed below. Assign the names from the list to the corresponding chemical structures.

Furan, nitromethane, oxirane, acrylonitrile, dimethylhydrazine.



Solution:

From left to right, these are structures of acrylonitrile, nitromethane, oxirane, furan and dimethylhydrazine.

Question C.6 (AT)

The sale of liquor containing more than 60% ethanol by volume is prohibited by law in many countries. In other countries, one can find mixtures with a composition close to the ethanol-water azeotrope, which is 96% ethanol by mass. Such spirits are labelled “Spirytus rektyfikowany 95%” in Poland, where they are made from potatoes, or “190-proof” in the USA, where they are produced from grain and corn. These concentrated solutions are mostly used for making herbal remedies and flavoured liquors, or as industrial solvents. Calculate the molar concentration of absolute (100%) ethanol, which has a density of 789 kg m^{-3}.

Solution:

Molar concentration is the amount of substance divided by volume

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

The amount of substance is equal to the mass divided by the molar mass

$$n = \frac{m}{M}.$$

Density is equal to the mass divided by the volume

$$\rho = \frac{m}{V}.$$

Rearranging:

$$V = \frac{m}{\rho}$$

$$c = \frac{\rho}{M}$$

For the units to agree, the molar mass of ethanol ($M = 46\,\mathrm{g\ mol^{-1}}$) has to be converted to kg mol^{-1}.

$$c = \frac{789}{0.046} = 17152 \text{ mol m}^{-3} = 17.2 \text{ mol dm}^{-3}$$

Note: instead of working out the answer symbolically and substituting numbers at the very end, we may consider a specific volume of ethanol, say 1 litre, which has a mass of 789 g given its density. Dividing this by the molar mass of 46 g mol^{-1} gives the same result.

Question D.1 (SCh)

The global production of arsenic relies mostly on three minerals — arsenopyrite, orpiment and realgar. Realgar, stoichiometrically denoted as AsS, forms beautiful crimson crystals, hence it is sometimes called "ruby sulfur". Its colour, however, fades after exposure to sunlight and oxygen, as the mineral turns into white arsenic (diarsenic trioxide) and yellow orpiment (diarsenic trisulfide). Write the balanced chemical equation describing this transformation.

Solution:

$$12\,\mathrm{AsS} + 3\,\mathrm{O_2} \longrightarrow 4\,\mathrm{As_2S_3} + 2\,\mathrm{As_2O_3}$$

also viable

$$3\,\mathrm{As_4S_4} + 3\,\mathrm{O_2} \longrightarrow 4\,\mathrm{As_2S_3} + 2\,\mathrm{As_2O_3}$$

Question D.2 (MB)

In a company that uses powdered PVC, samples of the compound are not labelled with their average molar mass (the usual practice for polymers), but rather with a so-called "K value". The K value of PVC can be obtained by the following procedure:

1. Measure the viscosity, η_0, of pure cyclohexanone.
2. Measure the viscosity, η, of PVC dissolved in cyclohexanone.
3. Calculate K by solving the equation

$$\log_{10}\left(\frac{\eta}{\eta_0}\right) = \frac{75K^2}{1+1.5K} + K.$$

Calculate the viscosity, η, of PVC with $1000K = 65$, given the viscosity of pure cyclohexanone $\eta_0 = 2.5\,\mathrm{mPa\ s}$.

Solution:

This task was adapted from an industrial instruction manual belonging to an unspecified company. First we deduce that if $1000K = 65$, then $K = 0.065$. Thus, the K value can be inserted into the given equation.

$$\log_{10}\left(\frac{\eta}{2.5}\right) = \frac{75 \times 0.065^2}{1 + 1.5 \times 0.065} + 0.065 = 0.354$$

$$\frac{\eta}{2.5} = 10^{0.354} = 2.258, \qquad \eta = 5.65\ \mathrm{mPa\ s}$$

Question D.3 (AT)

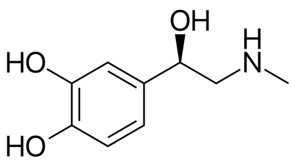
Biochemist Jardík got his hands on a cell biology textbook and decided to try out some of the experiments immediately. After being shown how to operate a flow cytometer, he took a vial of deep frozen mammalian cells from storage. He thawed the cells in a water bath, then added them to a flask containing a warm medium. Once the culture was ready, he set up the cytometer and found that each millilitre (cubic centimetre) of the suspension contained, on average, 1.6 million cells with a mean diameter of 12 micrometres. What is the volume fraction of cytoplasm in the suspension? Consider the cells as uniformly sized spheres containing no organelles, with a membrane of negligible thickness.

Solution:

A diameter of 12 micrometres means that each cell has a volume of about 900 cubic micrometres = 900 femtolitres = 9×10^{-10} ml. A total of 1.6 million cells occupies a volume of 1.44 microlitres. This accounts for 1.45‰ (or 0.145%) of the sample by volume. (Any answer between 1.4‰ and 1.5‰ was considered correct.)

Question D.4 (PM)

Lacuna Coil, an Italian heavy-metal band, released their album “Dark Adrenaline” in 2012. It is impossible for a molecule to be “dark”, so let’s make it “heavy” instead. Calculate the percentage increase in the molecular weight of adrenaline if all of its hydrogen atoms are swapped for deuterium.



Solution:

To calculate the increase in the molecular mass we have to determine the molecular mass of normal and fully deuterated adrenaline. From the structure, the molecular formula is $C_9H_{13}NO_3$, which gives $9 \times 12 + 13 \times 1 + 1 \times 14 + 3 \times 16 = 183$ g mol^{-1} for the light adrenaline and $9 \times 12 + 13 \times 2 + 1 \times 14 + 3 \times 16 = 196$ g mol^{-1} for the heavy adrenaline. The ratio of the masses is then $x = (196/183) \times 100\% = 107.1\%$, giving an increase of 7.1%.

Question D.5 (VN)

Peptides are vital to life; without them we literally would not exist. They are used as building blocks in structural proteins, and as catalysts (enzymes) that control the chemical processes in our bodies. All peptides are made from 20 basic biogenic amino acids. The number of ways in which they can combine is enormous, as we will see from the following question. Write down **all the unique** tripeptides consisting of the three lightest proteinogenic amino acids, without repetition of amino acids, using three-letter abbreviations (in the direction from N-terminus to C-terminus).

Solution:

The lightest amino acids are Alanine, Glycine and Serine. The possible combinations are:

Gly–Ala–Ser	Gly–Ser–Ala	Ala–Gly–Ser
Ala–Ser–Gly	Ser–Ala–Gly	Ser–Gly–Ala

In the case of peptides, we differentiate the N-terminus and the C-terminus. Therefore, the order of the amino acids is important.

Question D.6 (VN)

Carbon monoxide plays an important role in the crude oil industry. It is a by-product of natural gas steam reforming and coke gasification. Once formed, it is used in the synthesis of another substance with a wide range of applications in the chemical industry. Write down the balanced equation that describes the reforming of carbon monoxide by water steam. Include the states of all the substances. Highlight the commercially valuable product formed in this reaction. Hint: this product is lighter than air.

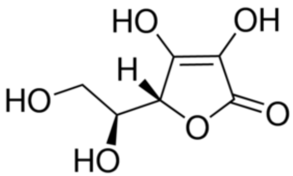
Solution:

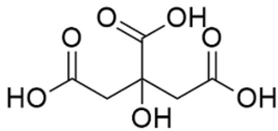
$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

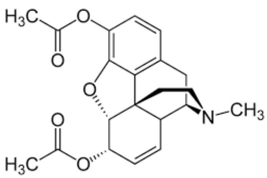
This reaction is conducted in industrial chemical reactors at high temperatures. The target product is hydrogen. Carbon dioxide is a by-product that does not have any major industrial uses.

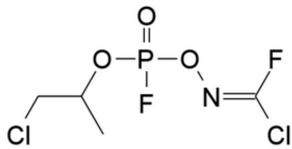
Question E.1 (AK)

Some molecules, especially organic ones, are chiral, which means that they are distinct from their mirror images. Typically this is because they contain at least one carbon atom that has four different substituents. Such carbons are referred to as "chiral". Write down the number of chiral carbons in each of the molecules shown below. These are vitamin C, citric acid, heroin and one of the compounds of the Novichok family (neurotoxic chemical agent).







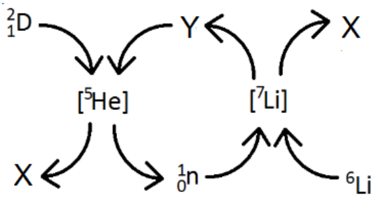


Solution:

There are two (vitamin C), zero (citric acid), five and one chiral atom/s in the respective molecules.

Question E.2 (PMer)

The biggest test of a hydrogen bomb by the USA to date was conducted in 1954, at Bikini Atoll in the Marshall Islands. The bomb was based on the Jetter cycle:



Lithium deuteride was used as fuel, in which 35% of the lithium was ^{6}Li (the rest being ^{7}Li). The resulting explosion was approximately three times more powerful than expected, to the great surprise and inconvenience of the scientists involved. The increased power was caused by ^{7}Li entering the following reaction:

$$^7\text{Li} + {}^1_0\text{n} \longrightarrow \text{X} + \text{Y} + {}^1_0\text{n}$$

Determine the identities of X and Y in the two schemes shown above.

Solution:

$$\text{X} = {}^4\text{He} \quad \text{Y} = \text{T} = {}^3\text{H}$$

Question E.3 (SCh)

If we are ever to successfully colonise the more distant planets in the Solar System or even other solar systems, a number of complex but interesting new issues would certainly arise. One such possible issue concerns the transfer of information between Earth and a distant colony. The speed of transmission would be limited by the speed of light, regardless of the method. However, transmitting large volumes of data wirelessly presents a significant challenge, which is why on Earth most data still flows through cables.

Suppose that a cable is constructed to transmit data from the Sun to our closest star, Alpha Centauri A, situated 4.37 light years away. (A light year is the distance that light travels in a vacuum in one year.) Give a rough estimate of the mass of the cable, assuming that it is woven from three polyacetylene (polyethyne) chains.

[If you do not feel brave enough to estimate, help yourself out with a calculation. Consider all C–C bonds in polyacetylene to be 125 pm long.]

Solution:

We shall take the less adventurous route to the answer. First, we express 4.37 light years in SI units:

$$4.37\ \text{ly} = 4.37 \times 60 \times 60 \times 24 \times 365.25 \times 299792458 = 4.134 \times 10^{16}\ \text{m}$$

How many carbon atoms are there in one metre of the chain?

$$\rho = \frac{1}{125 \times 10^{-12}} = 8 \times 10^{9}\ \text{m}^{-1}$$

In three chains, each one metre long, there are 24×10^9 atoms. The whole cable has a mass of

$$m = l \times \rho \times m_{\text{C}} = 19.78\ \text{kg}$$

Estimates were allowed to fall between 10 and 100 kilograms (i.e. estimating the order of magnitude properly).

Question E.4 (JM)

The age of a water sample can be determined from its content of tritium, which is formed naturally in the atmosphere through interaction with cosmic rays. Consider a water sample that has been completely shielded from cosmic radiation, such that its current tritium content is ten times smaller than that of atmospheric water. Calculate the age of the water sample (how long it has been shielded from radiation), given that tritium has a decay half-life of 12.32 years.

Solution:

Radioactive decay is a first-order process with an integrated rate law

$$N = N_0 \mathrm{e}^{-\lambda t} \tag{1}$$

Activity is proportional to the number of nuclei,

$$A = \text{constant} \times N \tag{2}$$

so that

$$A = A_0 \mathrm{e}^{-\lambda t} \tag{3}$$

We are told that

$$A = 0.1 \times A_0 = A_0 \mathrm{e}^{-\lambda t} \tag{4}$$

Rearranging for time we get

$$t = -\ln(0.1)/\lambda \tag{5}$$

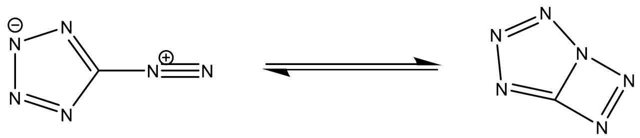
The relation between the decay constant λ and the half-life $t_{1/2}$ is

$$\lambda = \ln(2)/t_{1/2}, \tag{6}$$

which can be derived by substituting $A = 0.5A_0$ into (3). Plugging in the numbers gives the result of $t = 40.9$ years.

Question E.5 (JL)

Diazotetrazole is a very unstable molecule. This was confirmed by Thiele, who was the first person to synthesize this compound by diazotization of 5-aminotetrazole. However, he was not able to isolate it, as it instantly exploded in solution at 0 °C.



Write a balanced chemical equation to describe what Thiele observed. Assume that the products of the explosion do not react with their surroundings.

Solution:

Diazotetrazole is composed of six nitrogen atoms and one carbon atom. Carbon does not form any simple, stable binary compounds with nitrogen, thus diazotetrazole decomposes into its constituent elements. The balanced chemical equation is:

$$CN_6 \longrightarrow C + 3\,N_2$$

Question E.6 (VN)

Triathlon is one of the most demanding sports that have ever been invented. Its most extreme example is the Ironman race that takes place in Hawaii. In the first phase, the athletes must swim 3.8 km in choppy waters, followed by 180 km on a bike, and then a marathon (a race of 42.2 km). This race is demanding both physically and mentally, requiring a great deal of energy.

Enzymes facilitating muscular activity get their energy from the hydrolysis of ATP, the universal energy currency of the human body. One of last year's participants of the Ironman world championship was a Czech professor of chemical engineering František Štěpánek. How many kilograms of ATP was hydrolysed by the body of Prof Štěpánek to supply the energy for the Ironman race in Hawaii? His smartwatch showed a caloric output of 12500 kcal after the race. The molar mass of ATP is 507.18 g mol^{-1}. (1 cal = 4.18 J) Assume that the energy released by the hydrolysis of ATP is given by the equation below, and that the body uses it with 100% efficiency.

$$\mathrm{ATP} + \mathrm{H_2O} \longrightarrow \mathrm{ADP} + \mathrm{P_i} \qquad \Delta G^\circ = -57\ \mathrm{kJ\ mol^{-1}}$$

Solution:

The amount of ATP needed is calculated as the energy in kJ, divided by the free energy of the reaction.

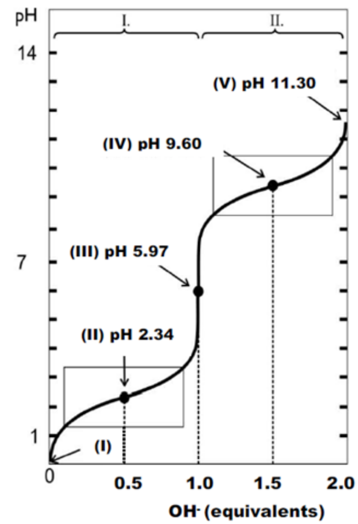
$$n = 12500 \times 4.18/57 = 916.7\ \mathrm{mol}$$

The mass of ATP is equal to the product of the amount of substance and its molar mass.

$$m = 916.7 \times 507.18 = 464\ 932\ \mathrm{g} = 464.9\ \mathrm{kg}$$

This amount is many times the full weight of the athlete, which may seem impossible at first sight. However, one must realise that the products of ATP hydrolysis are regenerated back to ATP and enter the cycle again. Another reason for such a large amount is that the molar mass of ATP itself is quite large.

Question F.1 (SO)



100 ml of a glycine solution (0.1 M), of initial pH 1.72, was titrated with a solution of sodium hydroxide (2 M). The resulting titration curve is shown below, with several key points marked I to V. Assign each point to one of the following statements:

a) Glycine is present predominantly in cationic form.
b) The pH of the solution is equal to the p$K_a$of the carboxylic group.
c) The pH of the solution is equal to the p$K_a$of the electrically neutral molecule.
d) Glycine is present mostly in the form $H_2N{-}CH_2{-}COO^-$.
e) The pH of the solution is equal to the isoelectric point (pI) of glycine.

Solution:

(I)–a, (II)–b, (III)–e, (IV)–c, (V)–d.

Question F.2 (JL)

The raw food diet involves eating only uncooked, unprocessed foods. Its proponents argue that these conditions prevent the thermal degradation of nutrients and enzymes. In order for food to qualify for this diet, it must not exceed the threshold temperature of 42 °C during preparation. What is the highest pressure under which one can boil the water to make a "raw" soup?

You may use the Clausius-Clapeyron relation in its integrated form, given by

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_\text{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Here, p_i is the vapour pressure of the substance at a temperature T_i, ΔH_vap is the enthalpy of vaporisation of that same substance, and R is the ideal gas constant. You may assume $\Delta H_\text{vap}(H_2O) = 40\ 660\ \text{J mol}^{-1}$, independent of temperature.

Solution:

The Clausius-Clapeyron equation describes the equilibrium dependence of the pressure of saturated vapours above a boiling liquid, and its temperature. In our case, we know the standard boiling point $T_2 = 373.15$ K at the standard (atmospheric) pressure $p_2 = 101325$ Pa. We want to calculate the pressure p_1 and we already know the corresponding temperature $T_1 = 315.15$ K. R is the ideal gas constant, and its value is 8.3145 J mol^{-1} K^{-1}. The calculation proceeds as follows:

$$\ln p_2 - \ln p_1 = -\frac{\Delta H_{\mathrm{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$p_1 = \exp\left(\frac{\Delta H_{\mathrm{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \ln p_2\right)$$

$$p_1 = 9082 \text{ Pa}$$

Question F.3 (AT)

Calculate the saturated vapour pressure of toluene that is boiling in an open flask at atmospheric pressure.

Boiling point of toluene $\theta = 110.6$ °C

The Antoine equation:

$$p = \exp\left(13.9987 - \frac{3096.52}{T - 53.67}\right)$$

where p is the vapour pressure in kPa, and T is the temperature in K.

Solution:

Since toluene is boiling, its saturated vapour pressure must be equal to the atmospheric pressure (as can be seen by reading the first sentence carefully). Thus $p = p_{\mathrm{atm}} = 101\ 325$ Pa.

Question F.4 (AT)

Hypochlorites (ClO^-) are important oxidising agents that are widely used for treating drinking water and disinfecting swimming pools, where they have almost entirely replaced elemental chlorine. There are, however, records of incidents when clouds of chlorine gas were formed because of inadvertent mixing of a hypochlorite salt with an acid. Two such cases were reported about a year apart: on April 8, 1983, workers at a sewage treatment plant in Knoxville, Tennessee added 600 gallons of aqueous ferric chloride ($FeCl_3$) into a hypochlorite tank by mistake. No serious injuries resulted. In November the following year, a tanker full of ferric chloride solution, wrongly marked as carrying hypochlorite, was dispatched from Greater Manchester to Yorkshire. As the driver had received no written information about the cargo, he unloaded the tanker into a chlorine bleach storage tank. A total of 29 people had to receive hospital treatment.

Write the balanced equation for the reaction that took place in the tanks. Iron does not change its oxidation state during the reaction. Assume that the hypochlorite is present in the form of an acid.

Solution:

$$\mathrm{FeCl_3(aq) + 3\,HClO(aq) \longrightarrow 3\,Cl_2(g) + Fe(OH)_3(s)}$$

Information about phases was not required.

Question F.5 (LP)

In school, pH is often defined as the negative common (decadic) logarithm of the molar concentration of H^+. This simplified definition does not take into account the chemical activity of the ions and can thus lead to inaccurate results, especially when used for concentrated acids. Using this simplified definition, calculate the pH of the most concentrated acid there is — a single proton. The radius of a proton is 8.414×10^{-16} m. Assume that the proton is a sphere.

Solution:

pH is defined as

$$\mathrm{pH} = -\log_{10}[\mathrm{H^+}]$$

In order to calculate the pH, we need the concentration of a proton in a proton. Concentration is defined as the amount of a substance over the volume it occupies, $c = n/V$. The volume of the proton is calculated as

$$V = \frac{4}{3}\pi r^3 = 2.495 \times 10^{-45}\ \mathrm{m}^3$$

The amount of a substance is defined as the number of particles divided by Avogadro's number, $n = N/N_\mathrm{A}$. Substituting this into the definition of molar concentration,

$$c = (N/N_\mathrm{A})/V = 6.6552 \times 10^{17}\ \mathrm{mol\ dm}^{-3}$$

Hence

$$\mathrm{pH} = -\log_{10}[\mathrm{H}^+] = -17.82,$$

a truly formidable value. It is clear that the result is not of any physical significance! The Hammett acidity function is a much better tool for the comparison of the acidity of very concentrated acids,[1] but even this acidity function is not suitable for the quantification of the acidity of a single proton. The best approach would be to use the Unified pH scale for all phases that was proposed in 2010.[2]

1. Hammett, L. P.; Deyrup, A. J., A series of simple basic indicators. I. The acidity functions of mixtures of sulfuric and perchloric acids with water. *Journal of the American Chemical Society* 1932, 54 (7), 2721-2739.
2. Himmel, D.; Goll, S. K.; Leito, I.; Krossing, I., A unified pH scale for all phases. *Angewandte Chemie International Edition* 2010, 49 (38), 6885-6888. dx.doi.org/10.1002/anie.201000252

Question F.6 (VN)

One day, Stanislav decided to grow long hair. This was not enough, and he wanted to go a step further to become a true metalhead. He decided to galvanically electroplate himself. To make sure his body was conductive, he was covered in a thin layer of graphite, after which he submerged himself in a solution of Zn^{2+} ions. He connected himself into an electric circuit as the cathode. A sufficiently large piece of zinc was used as the anode. How many days did it take for Stanislav to become fully electroplated, assuming that the surface area of his body is 1.8 m^2, and the zinc was deposited in a layer 2 mm thick, while a constant current of 5 A was used throughout?

Density of zinc $\rho = 7140$ kg m^{-3}
Faraday constant $F = 96485$ C mol^{-1}
Molar mass of zinc $M = 65.4$ g mol^{-1}

Solution:

The mass of zinc needed to cover Stanislav with a 2 mm layer is

$$m = V \times \rho = S \times h \times \rho = 1.8 \times 0.002 \times 7140 = 25.704 \text{ kg}$$

The mass of the metal generated at the cathode is given by Faraday's law,

$$m = A \times I \times t$$

where I is the current in amps, t is the time in s, and A is the electrochemical equivalent. This is defined as the molar mass of the metal, divided by Faraday's constant and the number of electrons needed to reduce a single ion of the metal,

$$A = M/(F \times z) = 3.39 \times 10^{-7} \text{ kg C}^{-1}$$

This tells us the mass of metal deposited per unit of charge. From Faraday's law, the time needed to complete the electroplating is

$$t = m/(A \times I) = 25.704/(3.39 \times 10^{-7} \times 5) = 176.37 \text{ days.}$$

Question G.1 (VL)

If present in alkaline solutions, molecular chlorine undergoes a disproportionation reaction to produce hypochlorite anions (ClO^-) and chloride anions. Cyanogen, with the formula $(CN)_2$, shows similar behaviour and is commonly referred to as a pseudohalogen. Write a balanced equation for the reaction of cyanogen in an alkaline solution.

Solution: By analogy with chlorine's disproportionation to chloride and hypochlorite, we get the disproportionation cyanogen to cyanide and cyanate.

$$(CN)_2 + 2\,OH^- \longrightarrow CN^- + OCN^- + H_2O$$

Question G.2 (RV)

So-called "fishimetry" is a hypothetical method of qualitative analysis that could be used to identify the unknown cation, A^+, in a pure sample of the cyanide ACN.

The method would work as follows: in a volumetric flask, 1.000 g of pure sodium cyanide (NaCN) is dissolved in distilled water to make exactly 1000 ml of solution. The same process is repeated in a second volumetric flask, but replacing sodium cyanide with the unknown cyanide ACN. The next step requires two very large, identical tanks full of fish: the sodium cyanide solution is poured slowly into one of the tanks, while stirring vigorously. Once the fish start floating belly-up, the volume V_{standard} of solution that has been added is recorded. The same process is repeated with the solution of the unknown cyanide to determine the second volume, V_{unknown}. Determine the identity of the cation, A^+, if $V_{\text{standard}} = 365$ ml and $V_{\text{unknown}} = 827$ ml.

You may assume that neither cation is poisonous to the fish, and that both cyanides dissociate perfectly in solution.

Solution:

According to our assumptions, in both cases the fish start dying when the cyanide concentration reaches the same level. The concentration of cyanide in the aquarium will be proportional to the volume of the solution that was added, and inversely proportional to the molecular mass of the cyanide salt. As the solutions were prepared from samples of cyanides of the same mass and have the same volume, the following relation holds:

$$V_{\text{ACN}}/V_{\text{NaCN}} = M_{\text{ACN}}/M_{\text{NaCN}}$$

and hence

$$M_{\text{ACN}} = (V_{\text{ACN}}/V_{\text{NaCN}}) \times M_{\text{NaCN}} = (827/365) \times 49 = 111$$

from which we deduce the atomic mass of the unknown cation (assuming it is monovalent) $M_{\text{A}} = M_{\text{ACN}} - M_{\text{CN}} = 111 - 26 = 85$, which corresponds to rubidium.

Question G.3 (WJ)

A hydride of an unknown element X contains more than 10 wt. % (i.e. by mass) hydrogen. Reacting the hydride with CO_2 at a high temperature produces a salt containing 61.59 wt. % oxygen. Given that the hydrolysis of this salt yields an organic product, determine the identity of the unknown element X.

Solution:

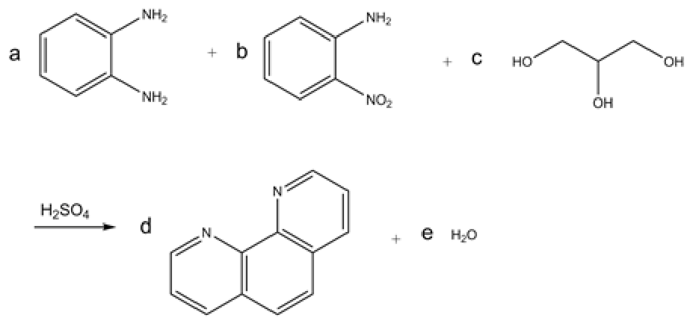
The ten-percent mass ratio of hydrogen limits the molar mass of the possible counter-atom in the hydride to 9 for the XH stoichiometry, 18 for XH_2, 27 for XH_3 and 36 for XH_4. This gives us the options of LiH, BeH_2, BH_3, AlH_3, NH_3, CH_4, SiH_4 and H_2O. If its reaction at high temperature produces a salt, the cation must either be significantly electropositive (LiH or AlH_3) or form a different cation (ammonium cation). The last option is unlikely, since there is no good hydrogen source in the reaction.

The salt's hydrolysis gives an organic product. This means that a carbonate is not formed. Since there is only a single-carbon fragment present, there is only one sound option for the anion, namely formate. A quick calculation of the weight percentage shows that the only possible salt is lithium formate, thus element X is lithium (Li).

Question G.4 (AT)

If you ask a Czech student whether they have ever heard of a person named Škroup, chances are they would recall being taught about František Škroup, a 19th century composer, whose song *Kde domov můj* (*Where my home is*) would later become the Czechoslovak and subsequently the Czech national anthem. This often overshadows the achievements of František's nephew Zdenko Hans, a chemistry professor in Vienna and Graz where he also served as the rector in 1903/04. He helped raise several generations of successful scientists and contributed to the field of natural product chemistry. His synthesis of quinoline from aniline, glycerol and a suitable oxidising agent (e.g. nitrobenzene) in the presence of sulfuric acid has become one of the classic named reactions (*the Skraup synthesis*).

Your task is to balance the equation of a similar reaction, making 1,10-phenanthroline from o-phenylenediamine, 2-nitroaniline and glycerol. Give the five coefficients in the order a,b,c,d,e.



Solution:

To balance the equation, we do not need the reaction's mechanism. It is sufficient to write the molecular formulae and balance the equation in the same way as an inorganic one:

$$a\ C_6H_8N_2 + b\ C_6H_6N_2O_2 + c\ C_3H_8O_3 \longrightarrow d\ C_{12}H_8N_2 + e\ H_2O$$

The conservation laws for each of the atoms are as follows:

$$\begin{aligned}
&N : a + b = d \\
&O : 2b + 3c = e \\
&C : 6a + 6b + 3c = 12d \\
&H : 8a + 6b + 8c = 8d + 2e
\end{aligned}$$

There are four equations in five unknowns, which we can solve by treating one variable as a parameter. Solving the system of equations, we get

$$b = 2a, c = 6a, d = 3a, e = 22a,$$

which means that the equation is balanced for the set of coefficients 1:2:6:3:22 and its multiples.

Let's just mention that glycerol serves as a source of carbon chains of three atoms each, that are built into the side aromatic rings of phenanthroline. The mechanism is quite complex: it begins with a double dehydration of glycerol to give acrolein, which then condenses with the amino group. This is followed by cyclization.

Skraup, Z.H., Eine Synthese des Chinolins. *Monatshefte für Chemie* (1880) 1:316.
https://doi.org/10.1007/BF01517073

Question G.5 (JC)

Jardík the biochemist was forced to take Practical Organic Chemistry in order to get the 30 credits he needed to complete the semester. Organic chemistry wasn't really his cup of tea, and neither was lab work. At the end of the practical, the bottom of one of his flasks became clogged, and the grime couldn't be scraped off. Jardík decided to get rid of the grime using chemistry. He tried all the polar and nonpolar solvents he could find in the lab. He even tried to clean the flask with chromosulfuric and peroxymonosulfuric acid, but it wasn't any use.

In the end, out of sheer desperation and ignoring all safety rules, he started trying random solvents mixed with sulfuric acid. When he poured sulphuric acid mixed with toluene (methylbenzene) into the flask and heated the solution with a heat gun, it slowly turned yellow. Jardík was happy with that, so he continued to flush the flask with this solution, but the grime remained stuck to the bottom. Write down the chemical reaction, describing what took place during the "cleaning".

Solution:

Since we know nothing about the grime's origin or composition, we can only propose a reaction involving the known contents of the flask. The flask is filled with toluene and sulphuric acid, which are being heated. This makes sulfonation of toluene by far the likeliest option,

$$\text{toluene} + H_2SO_4 \longrightarrow p\text{-TsOH}.$$

Both ortho- and para isomers of toluenesulfonic acid were accepted.

Question G.6 (VN)

Separating solid particles from liquid is fundamental for a wide variety of chemical industries. Filtration is encountered not only in laboratories, but also at home when making coffee, or in water circulation systems in swimming pools. The kind of filter used industrially for processing large volumes of suspension is known as a "filter press". It operates by having a suspension pumped into a filtration chamber, which is enclosed in a membrane that is only permeable to water. The solid particles remain inside the apparatus, and are known as "filter press sludge". There are several filtration chambers joined together. Due to the large filtration surface area, it is possible to process large volumes of suspension.

Calculate how many tonnes of wet kaolin with a 28% water content (by mass) can be obtained from one filtration cycle. The density of the suspension is 1.187 g cm^{-3}, and the mass concentration of dry kaolin in the suspension is 300 g dm^{-3}. The volumetric flow of the suspension is 3.2 dm^3 s^{-1}, and one filtration cycle takes 50 minutes.

Solution:

The volume of suspension processed in a 50 min cycle is equal to the product of the volumetric flow and the length of the cycle in seconds

$$V = t \times \dot{V}_{\text{flow}} = (50 \times 60) \times 3.2 = 9600\ \text{dm}^3$$

The amount of dry kaolin in suspension is given by the product of its mass concentration and the total volume of the suspension

$$m = c \times V = 300 \times 9600 = 2.88 \times 10^6\ \text{g} = 2.88\ \text{t}$$

We can calculate the mass of wet kaolin by dividing the mass of the dry kaolin by its mass fraction in the product

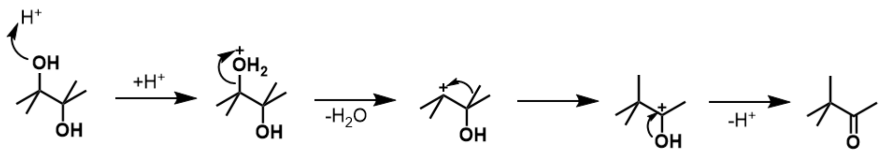
$$w_{\text{dry kaolin}} = 1 - w_{\text{water}}$$

$$m_{\text{final}} = m_{\text{dry kaolin}}/(1 - w_{\text{water}}) = 2.88/0.72 = 4\ \text{t}$$

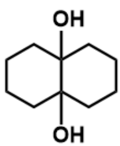
The yield of wet kaolin will be 4 tonnes per filtration cycle.

Question H.1 (JL)

The pinacol rearrangement is a reaction undergone by 1,2-diols (such as pinacol itself) under acidic conditions, which results in the formation of ketones. In the first step, one of the OH groups is protonated by the acid, enabling it to separate from the molecule in the form of water. The resulting carbocation then rearranges to form a ketone. The full mechanism for the case of pinacol → pinacolone is drawn below.

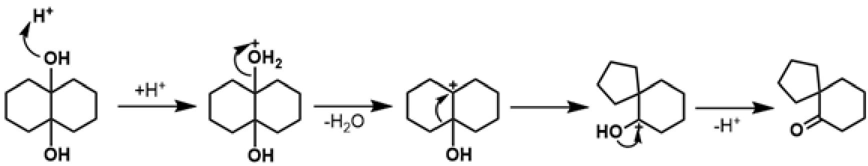


Draw the structure of the rearrangement product of the following compound:



Solution:

At first sight, the structures of the pinacol and the specified diol might seem different and the product might not be obvious. However, if we follow the drawn mechanism, we end up at the product, a spirocyclic ketone. The mechanism is shown below. The rearrangement itself proceeds via the most stable carbocation, adjacent to the OH group.



Question H.2 (RV)

Colligative properties of solutions are properties that do not depend on the nature of the solute, but solely on its molar concentration. One such property is the depression of the freezing point: dissolving any substance (e.g. salt) in a solvent (e.g. water) will lower the freezing point of the solvent. This behaviour is exploited during the winter, when salt is used to melt ice on roads and pavements. The difference in freezing point is

$$\Delta T = \frac{RcT^2}{\Delta H}$$

where c is the sum of the concentrations of all dissolved particles, R is the ideal gas constant, T is the freezing point of the pure solvent, and ΔH is the molar enthalpy of fusion of the solvent.

Suppose that you wish to lower the freezing point of water by 1 °C in a pool of dimensions $2 \times 5 \times 20$ m^3. You may achieve this by dissolving a sufficient amount of any one of the substances listed in the table below. For which of these substances would you pay the least? Assume that all the substances dissociate perfectly in solution (i.e. 1 mole of sodium sulfate Na_2SO_4 would dissociate into 3 moles of ions).

$T = 273$ K	$\Delta H = 79.72$ cal g^{-1}
$R = 62.64$ dm^3 Torr K^{-1} mol^{-1}	$\rho_{\text{water}} = 996$ kg m^{-3}

Compound	**Molar mass** (g mol^{-1})	**Price** (CZK kg^{-1})
Gold(III) bromide	436.7	3 150 000.00
Potassium chloride	74.6	3.80
Potassium acetate	98.2	200.00
Sodium chloride	58.4	3.96
Sodium cyanide	49.0	49.0
Ammonium sulfate	132.1	225.00
Gold(III) chloride	303.0	3 468 000.00
Calcium chloride	111.0	3.40
Urea	60.6	21.00

Solution:

In the given formula, the molar gas constant R, the freezing point of the pure solvent T, and the molar enthalpy of fusion of the solvent ΔH are constant. Hence it is clear that the only variable that we must take into account is the concentration of all dissolved species. The greater the amount of dissolved species species, the greater the depression of the freezing point.

Let's call the number of particles into which one molecule will dissociate i. The greater the molar mass of a substance, the greater mass is needed to from 1 mole. Therefore, the compound for which you would have to pay the least will have the greatest value of the ratio

$$r = \frac{i}{\text{price} \times M}.$$

If we take a look at the table, then it is obvious that we do not have to consider anything that costs more than 5 CZK/kg. The remaining compounds are $CaCl_2$, NaCl, and KCl with

$$\begin{aligned} r(\mathrm{NaCl}) &= 8.65 \times 10^{-3}\ \mathrm{kg^2\ mol^{-1}\ CZK^{-1}} \\ r(\mathrm{KCl}) &= 7.06 \times 10^{-3}\ \mathrm{kg^2\ mol^{-1}\ CZK^{-1}} \\ r(\mathrm{CaCl_2}) &= 7.95 \times 10^{-3}\ \mathrm{kg^2\ mol^{-1}\ CZK^{-1}} \end{aligned}$$

Hence the cheapest option is sodium chloride.

Question H.3 (JL)

A popular drink among the organisers of the Czech Chemistry Race is called *drátěnka* (literally meaning “scourer” or “wire sponge”) is prepared by mixing one shot (40 ml) of vinegar (8% acetic acid by mass, density 1.01 g ml^{-1}) and one shot of rum (40% ethanol by volume, density 0.947 g ml^{-1}). Calculate the volume percentage of ethanol in this drink after equilibration.

Molar weights:

$$M_{\text{water}} = 18.02 \text{ g mol}^{-1} \quad M_{\text{EtOH}} = 46.07 \text{ g mol}^{-1} \quad M_{\text{AcOH}} = 60.05 \text{ g mol}^{-1}$$

Density of absolute ethanol $\rho_{\text{EtOH}} = 0.7951$ g ml^{-1}.

Equilibrium constant of esterification $K = 5.3$,
where all species including water are expressed as concentrations.

Assume that volumes of mixtures are sums of the volumes of individual components, and that the volume of the drink does not change during the reaction.

Solution:

The final volume of the drink is:

$$V_{\text{final}} = V_{\text{vinegar}} + V_{\text{rum}} = 80 \text{ ml}$$

For the following calculation, we have to calculate the number of moles of individual compounds in the drink. For ethanol, this can be calculated as follows

$$n_{\text{EtOH}} = V_{\text{rum}} \times \Phi_{\text{EtOH}}(\text{volume}) \times \rho_{\text{EtOH}}/M_{\text{EtOH}} = 0.2761 \text{ mol}$$

An analogous expression holds for acetic acid

$$n_{\text{AcOH}} = V_{\text{vinegar}} \times \rho_{\text{vinegar}} \times \Phi_{\text{AcOH}}(\text{mass})/M_{\text{AcOH}} = 0.0533 \text{ mol}$$

The number of moles of water can be calculated from its weight. The sum of the weights of water, ethanol and acetic acid is equal to the total weight:

$$n_{\text{H}_2\text{O}} = (m_{\text{final}} - m_{\text{AcOH}} - m_{\text{EtOH}})/M_{\text{H}_2\text{O}} = 3.440 \text{ mol}$$

Now we can account for equilibration. The reaction is

$$\text{EtOH} + \text{AcOH} \rightleftharpoons \text{H}_2\text{O} + \text{EtOAc}$$

The equilibrium constant of this reaction can be expressed in terms of equilibrium concentrations. The equilibrium concentrations can be derived from the numbers of moles of individual compounds. We subtract the extent of reaction x from the amount of each reactant, and add it to the products. The equilibrium constant is then

$$K = \frac{\left(\frac{n_{\text{water}}+x}{V_{\text{fin}}}\right)\left(\frac{x}{V_{\text{fin}}}\right)}{\left(\frac{n_{\text{EtOH}}-x}{V_{\text{fin}}}\right)\left(\frac{n_{\text{AcOH}}-x}{V_{\text{fin}}}\right)} = \frac{(n_{\text{water}}+x)\times x}{(n_{\text{EtOH}}-x)(n_{\text{AcOH}}-x)}$$

The final volume of the drink cancels out and we obtain an equation for the unknown x. The solution is $x = 0.01464$ mol. Now we only need to calculate the volume percentage of ethanol from the remaining number of moles of ethanol in the final drink:

$$\Phi_{\text{EtOH}}(\text{volume}) = \frac{V_{\text{EtOH}}}{V_{\text{fin}}} = \frac{(n_{\text{EtOH}}-x)\times M_{\text{EtOH}}/\rho_{\text{EtOH}}}{V_{\text{final}}} = 0.1894.$$

For comparison, without taking the reaction into account, the volume percentage of ethanol in the final drink is 20 %.

Question H.4 (TD)

In contrast to the other silver halides, silver fluoride (AgF) is soluble in water. This can be used in gravimetric analysis. A mixture of KF, KCl and KBr weighs 5 g. To precipitate all possible salts, one needs exactly 145 ml of a 0.200 mol dm^{-3} aqueous solution of $AgNO_3$. The precipitate weighs 4.5 g. Determine the composition of the mixture of potassium halides. Give the result as a mass percentage.

Solution: We start by calculating the molar amount of silver required to precipitate all insoluble halogenides

$$n_{\text{AgNO}_3} = V_{\text{AgNO}_3} \times c_{\text{AgNO}_3} = 0.029 \text{ mol}$$

We know that the molar amount of silver is equal to the amount of insoluble halogenides

$$n_{\text{AgNO}_3} = n_{\text{AgCl}} + n_{\text{AgBr}}$$

and that the total mass of the precipitate is the sum of the masses of insoluble halogenides

$$m_{\text{precipitate}} = m_{\text{AgCl}} + m_{\text{AgBr}}$$

while the original mass is the sum of te potassium halogenide masses

$$m_{\text{sample}} = m_{\text{KCl}} + m_{\text{KBr}} + m_{\text{KF}}.$$

Using the fact that $n_i = m_i/M_i$, we can solve these three equations for the three unknowns to get

$$m_{\text{KCl}} = 1.5855 \text{ g} \qquad m_{\text{KBr}} = 0.9202 \text{ g} \qquad m_{\text{KF}} = 2.4943 \text{ g}$$

Converting to mass percentages gives:

$$w_{\text{KCl}} = 31.71\% \qquad w_{\text{KBr}} = 18.4\% \qquad w_{\text{KF}} = 49.89\%$$

Question H.5 (RV)

SMILES (simplified molecular-input line-entry system) is a handy way of representing molecules using plain text that can be directly translated into a structure. (Should you want to draw a complicated molecule using a chemistry editor, you can look up the corresponding SMILES representation on Wikipedia and paste it into the editor, which should convert it into the actual structure). Let's take a look at the rules for constructing this representation.

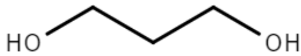
1) Atoms are represented by their symbol [C for carbon, O for oxygen]
2) Single bonds and hydrogens are omitted [CCCCCC is hexane, CCO is ethanol]
3) Branching is indicated with brackets [CCC(CC)CC(C)CC is 3-ethyl-5-methylheptane, CC(O)C is propan-2-ol]
4) Double and triple bonds are denoted by = and #, respectively [C#C is ethyne, CC(=O)C is acetone (propan-2-one), CC=CC is but-2-ene] There are more rules but these will be sufficient for our purposes.

Draw the structures of molecules A–C.

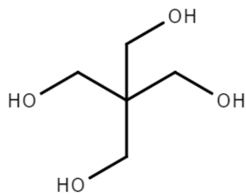
A) OCC(CO)(CO)CO
B) N#CC(=O)C(=O)C#N
C) OOS(=O)(=O)O

Solution:

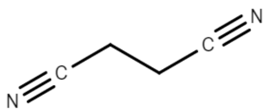
It is best to start with the unbranched part in each case. For molecule A, the part in bold is unbranched, **OCC**(CO)(CO)**CO**, which corresponds to



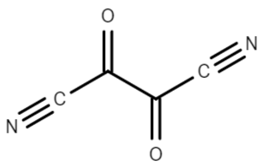
Then we have to take branching into account. The group in the brackets is connected to the atom right before the first bracket. In our case, both branching groups are the same, and are connected to the same atom. The resulting molecule looks like this:



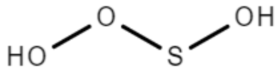
In the other molecules, double (=) and triple (#) bonds also play a role. The unbranched part of molecule B is (**N#CC**(=O)**C**(=O)**C#N**):



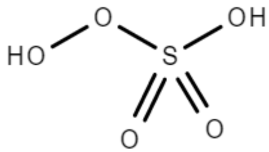
After adding the oxygen atoms we get:



The unbranched part in molecule C (**OOS**(=O)(=O)**O**) looks like this:



and after adding the branched part we get:



The last molecule is widely known to the Czech general public thanks to the work of arguably the greatest Czech genius, Jára Cimrman (a character similar to Forrest Gump).

Question H.6 (JL)

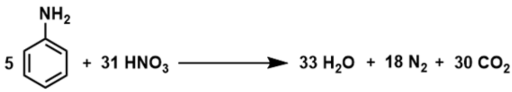
In the 1940s and early 1950s, aniline was used as rocket fuel, in combination with fuming nitric acid HNO_3 (assume this to be 100% pure) as an oxidising agent. A mixture of these two components is hypergolic, which means that it self ignites. How many ml of nitric acid are required for the complete combustion of one litre of aniline (aminobenzene), assuming the only reaction products are nitrogen, water and carbon dioxide?

Molar masses: aniline 93.13 g mol^{-1}, HNO_3 63.01 g ml^{-1}
Densities: aniline 1.03 g ml^{-1}, HNO_3 1.51 g ml^{-1}

Solution:

First, we balance the chemical equation for the combustion. Carbon atoms in the C—H bonds in aniline have the oxidation number of −I, whilst that of the carbon atom next to the amino group is +I. The oxidation number of the nitrogen in the amino group is −III and the oxidation numbers of all the hydrogen atoms are +I. To oxidise one aniline molecule, we need 25 electrons for the carbons in the C−H bonds, 3 electrons for the carbon next to the amino group and 3 electrons for the nitrogen in the amino group.

Altogether, to oxidise one aniline molecule, 31 electrons are required, and nitric acid is reduced by 5 electrons. To conserve the number of electrons, the balanced equation has to be



For the ratio of the individual reactants we get

$$\frac{n_{\mathrm{HNO_3}}}{n_{\mathrm{aniline}}} = \frac{31}{5}$$

The number of moles is related to the volume via

$$n = m/M = \rho \times V/M$$

Hence

$$\rho_{\mathrm{HNO_3}} \times V_{\mathrm{HNO_3}}/M_{\mathrm{HNO_3}} = (31/5) \times \rho_{\mathrm{aniline}} \times V_{\mathrm{aniline}}/M_{\mathrm{aniline}}$$

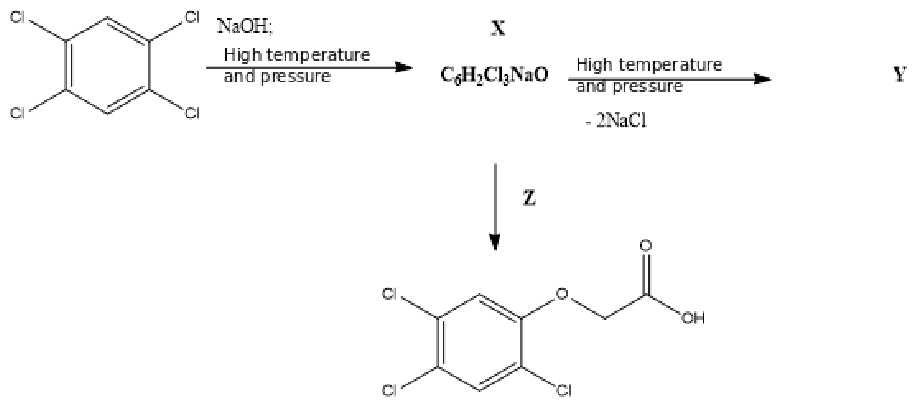
Rearranging for the volume of nitric acid we get

$$V_{\mathrm{HNO_3}} = \frac{31}{5} \times \frac{\rho_{\mathrm{aniline}} \times M_{\mathrm{HNO_3}}}{\rho_{\mathrm{HNO_3}} \times M_{\mathrm{aniline}}} \times V_{\mathrm{aniline}} = 2861 \text{ ml}$$

Question K.1 (PMer)

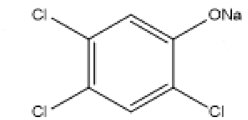
2,4,5-trichlorphenoxyacetic acid was once used as a non-selective herbicide. It gained wide recognition as a component of “Agent Orange”, a defoliant used by the US Armed Forces in Vietnam. It was also produced in Czechoslovakia (by the company Spolana Neratovice). By itself, 2,4,5-trichlorphenoxyacetic acid is not particularly toxic. However, its synthesis produces the byproduct Y, a highly toxic dioxine that is a known carcinogen and teratogen.

Draw the structures of X, Y, and Z from the reaction scheme below, given that Z contains exactly two carbon atoms.

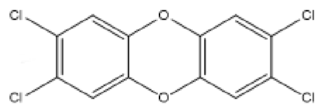


Solution:

Compound X:



Compound Y:



Compound Z:
Cl−CH$_2$−COOH
or Br−CH$_2$−COOH
or I−CH$_2$−COOH

Question K.2 (RV)

Sodium bicarbonate ($NaHCO_3$) is often added to dough as a raising agent. Its action can be explained relatively easily by assuming that the sodium bicarbonate decomposes to form sodium carbonate (Na_2CO_3), water, and carbon dioxide. The gaseous products bubble through the dough to make it "fluffy". While sodium bicarbonate is usually sufficient for this purpose, in some cases ammonium carbonate ($(NH_4)_2CO_3$) is required instead. It decomposes to form ammonia, water and carbon dioxide. Since more gas is released per mole of reactant, the dough can be made even fluffier. Calculate the ratio of the volume of gas released by the decomposition of 42 g of ammonium carbonate to that released by 42 g of sodium bicarbonate. Assume that all gasses behave ideally and that the water is in its gaseous form (as we baked the dough at 175 °C).

Solution:

The ideal gas law gives an equation for the volume of an ideal gas: $V = nRT/p$, where n is the amount of the substance, R is the molar gas constant, p is pressure, and T is the thermodynamic temperature. Hence we can see that the ratio of volumes of gases is given by the ratio of their amounts n. The equations of the reactions are:

$$2\,NaHCO_3(s) \longrightarrow H_2O(g) + CO_2(g) + Na_2CO_3(s)$$

$$(NH_4)_2CO_3(s) \longrightarrow H_2O(g) + CO_2(g) + 2\,NH_3(g)$$

According to these equations, one molecule of sodium bicarbonate gives one molecule of a gaseous product, whilst one molecule of ammonium carbonate gives four. The number of gaseous molecules produced from x grams of a substance is inversely proportional to the molecular mass of that substance. Hence the final ratio r is given by the following relation:

$$r = \frac{4/M_{(NH_4)_2CO_3}}{1/M_{NaHCO_3}} = \frac{4/96}{1/84} = 3.5.$$

Question K.3 (RV)

Chemical kinetics is the branch of physical chemistry concerned with understanding the rates of chemical reactions. Consider a hypothetical reaction

$$X + Y + Z \longrightarrow \text{products},$$

where X, Y, and Z are arbitrary molecules. Its rate equation is generally given by

$$r = k_r[X]^x[Y]^y[Z]^z$$

where k_r is the rate constant and [A] denotes the concentration of substance A. The exponents x, y and z are the partial orders of reaction. Your task is to determine the overall order of reaction, $N = x + y + z$, given $k_r = 43\ 285\ s^{-1}\ mol^{-4}\ dm^{12}$ and the following data obtained from an experiment:

r / mol dm^{-3} s^{-1}	[X] / mol dm^{-3}	[Y] / mol dm^{-3}	[Z] / mol dm^{-3}
106.05	0.1	0.5	0.7
530.24	0.7	0.1	0.5
75.759	0.5	0.7	0.1

Solution:

The simplest path to the result is dimensional analysis. From the rate equation we get the following relation:

$$\begin{aligned}\text{mol dm}^{-3}\ \text{s}^{-1} &= \text{s}^{-1}\ \text{mol}^{-4}\ \text{dm}^{12}\ (\text{mol dm}^{-3})^{x+y+z}\\ &= \text{s}^{-1}\ (\text{mol dm}^{-3})^{-4}\ (\text{mol dm}^{-3})^{N}\\ &= \text{s}^{-1}\ (\text{mol dm}^{-3})^{1}\end{aligned}$$

This gives a rather simple equation for N: $N - 4 = 1$, hence $N = 5$.

An alternative method uses the data to get a system of three equations in three variables:

$$r_i = k_\text{r}[\text{X}]_i^x[\text{Y}]_i^y[\text{Z}]_i^z,$$

with i ranging from meausrement 1 to measurement 3.

Its solution is $x = 2$, $y = 1$, $z = 2$, which also gives us the result of N = 5.

Question K.4 (SCh)

You may have encountered the names of Friedel and Crafts in your chemistry lessons in the context of aromatic alkylation and acylation reactions. In these, benzene reacts with an alkyl (or acyl) chloride in the presence of an aluminium(III) chloride catalyst. A thorough knowledge of the mechanism of this reaction opens the door to some really interesting syntheses. Give the dominant aromatic product of the reaction of benzene with phosgene in the presence of aluminum(III) chloride.

Solution:

The first step is a Friedel-Crafts acylation, giving benzoyl chloride as product. This intermediate product is itself very reactive and immediately takes part in another Friedel-Crafts acylation of a benzene molecule, to give benzophenone. This product is unlikely to take part in any further reactions. This is because the electron-withdrawing ketone group decreases the reactivity of benzophenone, and the more reactive benzene starting material is present in large excess. This gives us **benzophenone** as the dominant product.

Question K.5 (VK)

“Gone, reduced to atoms,” said Thanos when asked about what happened to the infinity stones. From this we can deduce that the half of humanity which was killed met the same fate. An average human weighs 68 kg and is largely composed of 66% oxygen, 19.5% carbon, 9.7% hydrogen, 3.3% nitrogen, and 1.5% calcium by weight. Since the number of the bond types that can form between these elements greatly exceeds the scope of this problem, let us use an average of 4 eV/bond, and assume the most common bond order for each element. At the time of writing this problem, the world population was 7 737 612 322 humans. Calculate how much energy Thanos would require to literally “snap humanity in half”, completely atomising half of Earth’s population. The result should be in exajoules. One exajoule is equal to 10^{18} J.

Solution:

The calculation is based on determining the amount of moles of all the aforementioned elements in a human body. Next, the number of all the bonds is determined from the elements’ valences and divided by two (since each bond consists of two atoms), multiplied by 4 eV and scaled by one half of Earth’s population. One human’s worth of a snap is about 3.291 GJ, which gives 12.73 EJ as the final result.

Question K.6 (PMer)

Isomerism is ubiquitous in organic chemistry. However, it was first described for two inorganic silver salts. Compound A can be prepared by the reaction of silver nitrate ($AgNO_3$) with urea. As a byproduct, ammonium nitrate (NH_4NO_3) is formed. Compound B is prepared by the reaction of metallic silver with ethanol. This reaction is very complex, giving many byproducts. Compound A is a stable grey powder with few interesting properties. Compound B is a very sensitive explosive used, for example, in firecrackers. Analysis shows that both A and B contain only silver, nitrogen, oxygen and carbon. Draw the structures of A and B, including all charges and depicting any lone pairs as •• (i.e. the Lewis structures).

Solution:

A B

Question L.1 (NV)

Even living systems are bound by the laws of thermodynamics. This implies that every process taking place in our bodies must be heading towards some equilibrium state. One such process is the transport of molecules through a membrane; treated as a chemical reaction, the reactants and products are the same species on different sides of the membrane. Hence the overall change in molar Gibbs free energy can be calculated from

$$\Delta G = nF\Delta\phi + RT\ln\frac{[\text{products}]}{[\text{reactants}]},$$

where n is the charge on the transported ion (see below), F is the Faraday constant, $\Delta\phi$ is the potential difference across the cell membrane, R is the ideal gas constant and T is the absolute (thermodynamic) temperature.

Consider an enterocyte cell, which absorbs glucose in the intestine by the process of *symport*. The cell exploits the influx of sodium ions (which is spontaneous) to drain the digested food of glucose. Calculate the maximum possible ratio of glucose concentrations across the membrane of an enterocyte cell,

$$X = \frac{[\text{Glc}]_{\text{in}}}{[\text{Glc}]_{\text{ex}}},$$

given that one sodium ion enables the transport of one molecule of glucose.
$[\text{Na}^+]_{\text{ex}} = 143$ mM, $[\text{Na}^+]_{\text{in}} = 14$ mM, $\Delta\phi = -50$ mV

Solution:

A reaction occurs spontaneously if the change of Gibbs energy is negative. In order to avoid all calculations with limits we set the extreme point of this reaction's desired direction at $\Delta G = 0$. The reaction corresponding to the process described in the text is

$$\text{Na}^+_{\text{ex}} + \text{Glc}_{\text{ex}} \longrightarrow \text{Na}^+_{\text{in}} + \text{Glc}_{\text{in}}$$

Setting $X = \frac{[\text{Glc}]_{\text{in}}}{[\text{Glc}]_{\text{ex}}}$, we get the following equation:

$$0 = nF\Delta\phi + RT\ln\left(X\frac{[\text{Na}^+]_{\text{in}}}{[\text{Na}^+]_{\text{ex}}}\right)$$

and for the human body temperature $T = 310$ K we get

$$X = \frac{[\text{Na}^+]_{\text{ex}}}{[\text{Na}^+]_{\text{in}}}\exp\left(\frac{-nF\Delta\phi}{RT}\right) = 66.4.$$

Question L.2 (JL)

Dicyanoacetylene (systematic name but-2-ynedinitrile) is a colourless liquid under standard conditions. The compound is of interest to chemists for two main reasons, one being that it is able to react with durene (1,2,4,5-tetramethylbenzene) in a Diels-Alder reaction. The second reason, which is the topic of this question, is that it burns with an extremely hot flame in a stream of oxygen - the hottest of any known chemical.

Calculate the *adiabatic flame temperature* (in °C) obtained during the combustion of liquid dicyanoacetylene in a stoichiometric amount of oxygen, both supplied at 25 °C. (The adiabatic flame model assumes that the entire reaction enthalpy contributes to heating the gaseous products of combustion. Note that liquids burn after evaporation.) You may use the following data:

Standard enthalpy of fusion $\Delta H_f^\circ(CO_2(g))$:	-393.5 kJ mol^{-1}
Standard enthalpy of fusion ΔH_f°(dicyanoacetylene(l)):	$+500.4$ kJ mol^{-1}
Enthalpy of vaporisation ΔH_{vap}(dicyanoacetylene):	$+28.9$ kJ mol^{-1}
Mean heat capacity of CO_2(g) at constant pressure:	92.09 J K^{-1} mol^{-1}
Mean heat capacity of N_2(g) at constant pressure:	55.26 J K^{-1} mol^{-1}

Assume all the above quantities to be temperature independent.

Solution:

Given the definition of adiabatic flame temperature, we first calculate the standard reaction enthalpy. The balanced chemical equation of combustion is

$$C_4N_2(g) + 4\,O_2(g) \longrightarrow 4\,CO_2(g) + N_2(g).$$

We now calculate the standard reaction enthalpy as the difference between the standard enthalpy of formation of the products and the reactants. Standard enthalpies of formation of pure elements in their reference states are zero by definition. The standard enthalpy of formation of dicyanoacetylene in the gas phase is equal to the sum of its enthalpy in the liquid phase and its vaporisation enthalpy:

$$\Delta H_r = 4\Delta H_f(CO_2) - \Delta H_f(C_4N_2) - \Delta H_{vap}(C_4N_2) = -2045.5 \text{ kJ mol}^{-1}$$

The whole reaction enthalpy is used to heat up the gaseous products of the combustion. The flame is therefore warmed up by

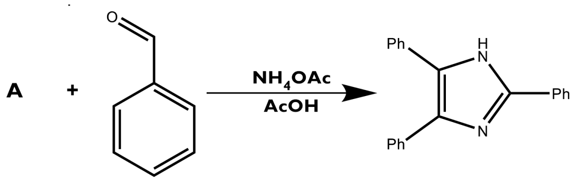
$$\Delta T = -\Delta H_r/(4c_p(CO_2) + c_p(N_2)) = 4829 \text{ K}$$

Since we were warming up the combustion products from 25 °C, the final adiabatic flame temperature is 4854 °C.

Question L.3 (JH)

Substituted imidazole rings can be synthesised from carbonyl compounds. For instance, the product of the reaction between benzaldehyde (C_6H_5CHO), ammonium acetate (NH_4OOCCH_3), compound A and acetic acid is 2,4,5-triphenylimidazole.

Draw the structure of compound A.



Solution:

Compound A is benzil (systematically known as 1,2-diphenylethane-1,2-dione), an organic compound with the formula $(C_6H_5CO)_2$, generally abbreviated $(PhCO)_2$.

Question L.4 (SCh)

The chemical world is still littered with cryptic symbols and abbreviations ...

We hope this sentence is now firmly embedded into all the racers' memories, since it is of historical significance to the Czech branch of the Chemistry race. One of the many abbreviations known even to the general public is LPG (liquefied petroleum gas), a mixture of propane and butane used as a fuel for cars.

Let us burn a small amount of this mixture in an exactly stoichiometric amount of oxygen. The combustion products are then passed through a freezer, and any remaining gas heated back up to its original temperature. The freezing and subsequent heating results in a 57% decrease in pressure.

Calculate the molar fraction of butane in the LPG sample if we consider it to be completely pure (containing only propane and butane), and the ignition and combustion to be perfect.

Solution:

The key challenge is figuring out what exactly happens during and after the combustion. First, the mixture is burned according to

$$C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$$
$$C_4H_{10} + 6.5\,O_2 \longrightarrow 4\,CO_2 + 5\,H_2O$$

Perfect combustion in a stoichiometric amount of oxygen gives us only carbon dioxide and water as products. The water freezes when the mixture is passed through the freezer. Considering Dalton's and Avogadro's laws and the equations above, we deduce that burning pure propane would give a decrease in pressure by four sevenths, whilst burning pure butane would give a decrease in pressure by five ninths. We can simply interpolate between the two values:

$$\frac{5}{9}x + \frac{4}{7}(1-x) = \frac{57}{100},$$

which gives the molar fraction of butane as $x = 0.09$.

Question L.5 (LP)

Determining the water content of a sample is one of the main tasks of a modern analytical chemist, important in a variety of industries from food processing and cosmetics to organic synthesis. The coulometric modification of the Karl Fisher titration is used for this nowadays. The analytical cell contains an anode that is separated from the cathode by an ion-permeable membrane. The solution in contact with the anode contains iodide, methanol, imidazole (im), sulfur dioxide and the sample. Iodine is generated from iodide at the anode.

The key reactions that take place during titration are

$$\mathrm{MeOH + SO_2 + im \longrightarrow [imH][SO_3Me]} \tag{1}$$

$$\mathrm{H_2O + I_2 + [imH][SO_3Me] + 2\,im \longrightarrow [imH][SO_4Me] + 2\,[imH]I} \tag{2}$$

Imagine that you are an organic chemist whose task it is to synthesise a complex natural product, *beat-a-grad-student-down-o-toxin*. You have reached the final step of your synthesis, which involves making a Grignard reagent from an alkyl bromide and magnesium, and reacting it with a carbonyl compound (a Grignard reagent has the general structure RMgBr, where R is an alkyl group).

Unfortunately, you only have 0.5 mg of your precious (45 reaction steps and 5 years of work) alkyl bromide left (M = 5000 g/mol). The reaction needs to be run in dry tetrahydrofuran (THF, 300 µl). There are several methods you can use to dry the THF.

The table below gives the charges necessary to titrate 5 ml samples of THF according to Karl Fisher, each of which has been dried using a different method. Which method will you choose to achieve the highest possible yield of Grignard reagent? Calculate the yield assuming that the only loss is caused by the quantitative reaction of the Grignard reagent with water.

$M(\text{THF}) = 72.107\ \text{g mol}^{-1}$, $\rho = 0.8892\ \text{g ml}^{-1}$, $M(\text{H}_2\text{O}) = 18.015\ \text{g mol}^{-1}$,
$F = 96\,485.3329\ \text{C mol}^{-1}$

Method of drying	**Charge (5 ml THF) / C**
Na/benzophenone	2.0455
3 Å MS (molecular sieve)	0.1907
Alumina	0.2856

Solution:

The oxidation of iodide to iodine is a two-electron process:

$$2\,\text{I}^- \longrightarrow \text{I}_2 + 2\,\text{e}^-$$

The iodine then reacts with water according to equation (2), thus the stoichiometric ratio is 1:1. The amount of water in the sample is hence equal to the amount of generated iodine. According to Faraday's law of electrolysis, the amount of iodine is directly proportional to the charge. The Grignard reagent reacts with water according to

$$\text{RMgBr} + \text{H}_2\text{O} \longrightarrow \text{RH} + \text{MgBrOH}$$

A greater amount of water will lead to a smaller reaction yield. Thus the highest yield will be obtained by using the solvent which required the smallest amount of charge to titrate, i.e. THF dried by the 3 Å molecular sieves (3 Å MS).

Using Faraday's law of electrolysis, we can calculate the amount of iodine generated from titrating 5 ml of the MS-dried THF:

$$n(\text{I}_2) = Q/(z \times F) = 0.1907/(2 \times 96485) = 9.8823 \times 10^{-7}\ \text{mol}.$$

The amount of water in the THF sample (5 ml) is the same as the amount of iodine which is formed. Therefore for 300 µl THF:

$$n(\text{H}_2\text{O}) = \frac{0.3}{5} \times 988.23 = 59.29\ \text{nmol}$$

The amount of our alkyl bromide is

$$n(\mathrm{RBr}) = m/M = 0.0005/5000 = 10^{-7}\ \mathrm{mol} = 100\ \mathrm{nmol}$$

Since the stoichiometry of hydrolysis of the Grignard reagent is 1:1, the yield can be calculated easily as:

$$\eta = (n_{\mathrm{RBr}} - n_{\mathrm{H_2O}})/n_{\mathrm{RBr}} \times 100\% = 40.71\%$$

Clearly, your experiment is poorly designed.Possible solutions would be to

a) reduce the amount of solvent (and thus water)

or

b) (subject to the availability of the carbonyl compound) generate the Grignard reagent by transmetalation from an excess of another, commercially available, Grignard reagent, that would consume the water. The resulting mixture could then be reacted with an excess of the carbonyl compound.

Question L.6 (SCh)

Despite beginning with the same three letters, there is little overlap between the worlds of chess and chemistry. We can glimpse some of it in the theory of chess openings. For instance, there are references to attacks by sodium (1. Na3), barium (1. b3 followed by 2. Ba3) and borane (1. g3 followed by 2. Bh3).

Two years ago (in 2018) the World Championship match between Magnus Carlsen and Fabiano Caruana ended in a series of twelve draws in classical games. Each time when the American grandmaster played with the white pieces, both players would keep exploring a particular line from the Sicilian opening. As black, he tried to avoid any complications by choosing simple openings. This led to fairly dull classical games.

Let us now imagine Fabiano Caruana had ditched the opening move 1. e4 for a one-time "sodium attack" — dropping a secretly brought knight made of sodium into a glass of water brought to the board by his Norwegian opponent. Calculate the temperature of the hydroxide solution formed in the glass.

Necessary data:

Magnus Carlsen brought 0.5 litre of water, its temperature was 20 °C and its density 0.9982 g cm^{-3}. In the concentration range of interest, the heat capacity of a solution of sodium hydroxide follows the equation

$$c_p/\left(\mathrm{J\ g^{-1}\ K^{-1}}\right) = 4.152 - 0.182b + 0.023b^2$$

where b is the molality of the hydroxide (as in mol NaOH / kg H_2O).

The enthalpies of formation of the reaction components are:
Na^+: −240.1 kJ mol^{-1}, OH^-: −230 kJ mol^{-1}, H_2O: −285.8 kJ mol^{-1}.

The mass of the knight is m = 10 g.

Neglect the heat capacity of the glass and any dissipation of heat to the surrounding air. Consider this reaction to happen non-explosively.

Solution:

The calculation can be split into two parts: calculating the heat released first, and the temperature right after. The reaction that takes place in the glass is the renowned

$$\mathrm{Na} + \mathrm{H_2O} \longrightarrow \mathrm{Na^+} + \mathrm{OH^-} + \tfrac{1}{2}\mathrm{H_2}$$

Since the enthalpy of formation of hydrogen is zero we get

$$\begin{aligned}\Delta H_{\mathrm{rxn,m}} &= \Delta H_{\mathrm{f}}(\mathrm{Na^+}) + \Delta H_{\mathrm{f}}(\mathrm{OH^-}) - \Delta H_{\mathrm{f}}(\mathrm{H_2O}) \\ &= -240.1 - 230 - (-285.8) = -184.3\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\Delta H_{\mathrm{rxn}} = n(\mathrm{Na}) \times \Delta H_{\mathrm{rxn,m}} = 0.435 \times (-184.3) = -80.1661\ \mathrm{kJ}$$

For the heating of the solution, we first calculate its molality. The amount of NaOH is equal to the amount of Na,

$$n_{\mathrm{NaOH}} = n_{\mathrm{Na}} = 0.435\ \mathrm{mol}$$

The initial amount of water is:

$$n_{\mathrm{H_2O}} = \rho \times V/M = \frac{0.9982 \times 0.5}{0.018} = 27.728\ \mathrm{mol}$$

After the reaction there are $(27.728 - 0.435) = 27.293$ moles of water. The molality is

$$b = \frac{n_{\mathrm{NaOH}}}{n_{\mathrm{H_2O}} \times M_{\mathrm{H_2O}}} = \frac{0.435}{27.293 \times 0.018} = 0.885\ \mathrm{mol\ kg^{-1}},$$

which gives a heat capacity of $c_p = 4.0089\ \mathrm{J\ K^{-1}\ g^{-1}}$.

The last step is to calculate the final temperature. To conduct our sodium attack as precisely as possible we must remember that there are now 10 grams of sodium in the glass and some hydrogen has escaped, so the total mass of the solution is

$$\begin{aligned} m_{\mathrm{sol}} &= m_{\mathrm{H_2O}} + m_{\mathrm{Na}} - m_{\mathrm{H_2}} \\ &= 0.9982 \times 500 + 10 - \frac{n_{\mathrm{Na}}}{2} \times M_{\mathrm{H_2}} \\ &= 0.9982 \times 500 + 10 - 0.438 \\ &= 508.665\ \mathrm{g} \end{aligned}$$

Now for the checkmate: the temperature of the hydroxide solution.

$$\begin{aligned} T &= T_0 + \frac{|\Delta H_{\mathrm{rxn}}|}{m \times c_p} \\ &= 20 + \frac{80169}{508.665 \times 4.0089} \\ &= 59.31\ ^{\circ}\mathrm{C}. \end{aligned}$$

Questions were created, edited and reviewed by:

Adam Jaroš (AJ)
Anna Kovárnová (AK)
Adam Přáda (AP)
Adam Tywoniak (AT)
Jaroslav Cerman (JC)
Jan Hrubeš (JH)
Jiří Ledvinka (JL)
Juraj Malinčík (JM)
Jakub Petrús (JP)
Ladislav Prener (LP)
Martin Balouch (MB)
Marie Grunová (MG)
Nikola Vršková (NV)
Ondrej Kopilec (OK)
Pavlína Muchová (PM)
Pavel Měrka (PMer)
Richard Veselý (RV)
Stanislav Chvíla (SCh)
Soňa Ondrušová (SO)
Tereza Dobrovolná (TD)
Vadim Kablukov (VK)
Vojtěch Laitl (VL)
Vladimír Němec (VN)
Wojciech Jankowski (WJ)
Jan Bartáček
Raz L. Benson
Matúš Drexler
Vladimír Finger
Anna Freislebenová
Tereza Gistrová
Jan Hrabovský
Lukáš Marek
Jan Němec
Clare Rees-Zimmerman
George Trenins
Alexandr Zaykov

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

Acknowledgements

The Cambridge Chemistry Race 2020 was organised with the support of the Department of Chemistry, University of Cambridge.

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.

UNIVERSITY OF CAMBRIDGE
Department of Chemistry

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

The Cambridge Chemistry Race was developed in close collaboration with the Pardubice Chemistry Race (Chemiklání), which is organised by the Faculty of Chemical Technology, University of Pardubice and the voluntary association Alumni scientie bohemicae.

chemiklání

http://chemiklani.cz/

University of Pardubice Faculty of Chemical Technology

ALUMNI SCIENTIAE BOHEMICAE

https://fcht.upce.cz/en http://www.czechscience.cz/

Questions corrected since the printed version:

F.2 What is the highest pressure under which one can boil the water to make a "raw" soup?

F.5 The value given is the radius of a proton, not a diameter.

L.1 The definition of X + error in the final equation.

Please report any errors to `chemistryrace@srcf.net`.

More information about the competition can be found at:
`http://chemistryrace.soc.srcf.net/`