

Chemistry Race 2020: Question Examples

December 2019



supported by



UNIVERSITY OF
CAMBRIDGE

Department of Chemistry

About this document

Here you will find example questions of varying difficulty, similar to those you will encounter in the Chemistry Race. You will be presented with questions covering various areas of chemistry, arranged into ten levels of difficulty. They are conceived and ordered in such a way that no team can solve all of them within the assigned time limit — your goal will be to solve as many as possible. After a few unsuccessful attempts of solving a question, you will be provided with hints so that no team gets stuck at a particular question forever. A final recommendation: the choice of questions presented here serves as a showcase of the skills and problem-solving strategies required to succeed, rather than of the actual topics covered by the questions. Therefore, trying to memorise as many facts about radioactivity, fluorine chemistry or peptide sequencing (as presented here) is definitely not an approach we would recommend. Instead, be ready for the unexpected and keep your mind sharp. And remember to bring your calculator and favourite textbooks.

Your Chemistry Race organisers

P.S.: Nobody is perfect, therefore, if you find any problems with the questions in the document, be it mistakes or ambiguities, we would be grateful if you let us know at chemistryrace@srcf.net.

Examples of 1st level questions (entry-level difficulty)

Question a)

To be able to handle chemicals safely, one must know their properties and related hazards. Based on the following hints, give the formula or name of a particular highly toxic and cancerogenic compound.

- It is an orange-coloured solid
- Upon addition of hydroxide, its aqueous solution changes colour to yellow
- It is a widely used oxidant in inorganic, organic as well as analytical chemistry
- The most stable isotope of the metal present in this substance's cation has a relative mass of 39

Answer:

Potassium dichromate – $\text{K}_2\text{Cr}_2\text{O}_7$

Question b)

An inorganic salt composed solely of nitrogen, hydrogen and oxygen in molar ratios of 10.8 : 1.54 : 18.5 was dissolved in water and yielded a colourless solution. Addition of concentrated lye led to formation of a pungent gas that turned an universal pH indicator paper blue. Give the formula of this gas.

Answer:

The gas is ammonia; its formula is NH_3 .

Question c)

Hydrochloric acid is often supplied as a 35 % by weight (= wt. %) aqueous solution. Jeff, a distracted chemist, was planning to prepare a 15 wt. % solution of HCl for his experiment. By mistake, he prepared a solution of only 10 wt. %. In what ratio should he mix solutions of 35 wt. % and 10 wt. % hydrochloric acid to obtain a 15 wt. % solution?

Answer:

One can equate the total masses of HCl before and after mixing:

$$(m_1 + m_2)w_{\text{tot}} = m_1w_1 + m_2w_2$$

To find the ratio of the masses, the equation is divided by the mass of the 10 % solution.

$$\left(\frac{m_1}{m_2} + 1\right)w_{\text{tot}} = \frac{m_1}{m_2}w_1 + w_2$$

$$\frac{m_1}{m_2}(w_1 - w_{\text{tot}}) = w_{\text{tot}} - w_2$$

$$\frac{m_1}{m_2} = \frac{w_{\text{tot}} - w_2}{w_1 - w_{\text{tot}}}$$

$$\frac{m_1}{m_2} = \frac{0.15 - 0.10}{0.35 - 0.15} = \frac{1}{4}$$

The solutions have to be mixed in a ratio of 1:4 (expressed as 35%:10%).

Examples of 2nd level questions

Question a)

Some years ago, there was a petition requesting the ban of a substance identified as DHMO. It listed the following reasons:

- Inhalation of larger amounts of DHMO is fatal.
- It has been found in tumour tissues.
- It supports pathogenic bacteria.
- It contributes to corrosion of many useful materials.
- It has been identified as a main component of acid rain.
- It significantly contributes to the greenhouse effect.
- It is also known as oxidane.
- Its traces cannot be effectively removed from human skin by washing.

Give the most common name of this substance.

Answer:

Water.

Question b)

Lactic acid is formed in muscles from pyruvic acid during exercise. Although it is a rather weak acid, lactic acid is found in the organism almost exclusively as an anion. Show this by finding the molar ratio of its deprotonated and its protonated forms at a physiological pH of 7.4. The Henderson-Hasselbalch equation is given by

$$\text{pH} = \text{p}K_{\text{a}} - \log \frac{c_{\text{HA}}}{c_{\text{A}^-}}$$

$$\text{p}K_{\text{a}}(\text{lactic acid}) = 3.86$$

Answer:

Substituting into the Henderson-Hasselbalch equation gives:

$$7.4 = 3.86 - \log \frac{c_{\text{HA}}}{c_{\text{A}^-}}$$

This can be reformulated as:

$$\frac{c_{\text{HA}}}{c_{\text{A}^-}} = 10^{-3.54} = 2.884 \times 10^{-4}$$

Inverting the fraction:

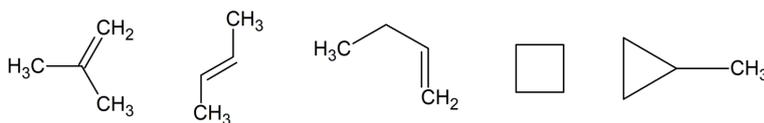
$$\frac{c_{\text{A}^-}}{c_{\text{HA}}} = \frac{1}{2.884 \times 10^{-4}} = \frac{3467}{1}$$

Thus there are 3467 molecules of the deprotonated form for each protonated molecule of lactic acid.

Question c)

Draw all five constitutional isomers of a substance that has the molecular formula C_4H_8 .

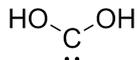
Answer:



All five isomers are depicted. The *E/Z*-isomerism of but-2-ene is not constitutional isomerism, thus both its geometric isomers count as one.

Question d)

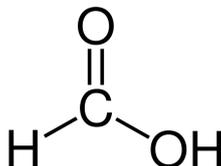
One might wonder whether besides the well known carbonic acid, carbonous acid H_2CO_2 also exists. Its structural formula should be as shown: Note the lone electron pair on its carbon atom.



As an organic compound, its name should be dihydroxymethylidene, its formula can be written as $\text{C}(\text{OH})_2$ and it has been detected only in the gas phase. Its conjugate base is the carbonite anion CO_2^{2-} , the salts of which have been found to exist at low temperatures (15 K). An example is Li_2CO_2 . Protonation of these salts, however, does not yield free carbonous acid. Its isomer is formed instead, a compound we usually consider to be an organic molecule. Give the name of this acid and a formula that shows the connectivity of atoms (a rational or a structural formula, not a molecular/summary/empirical one).

Answer:

The product is formic acid, the simplest carboxylic acid (which of course is H_2CO_2 too).



Examples of 3rd level questions

Question a)

Calculate the average molar mass of a mixture of 1.0 g of light hydrogen (protium) gas and 1.0 g of deuterium gas. Use integer relative atomic masses for the two isotopes equal to their nucleon number.

Answer:

We calculate the molar mass from the expression that defines it

$$M = \frac{m_{\text{tot}}}{n_{\text{tot}}} = \frac{m_1 + m_2}{n_1 + n_2}$$
$$M = \frac{\frac{m_1}{M_1} + \frac{m_2}{M_2}}{\frac{1}{2} + \frac{1}{4}} = 2.67 \text{ g mol}^{-1}$$

The molar mass of the gaseous mixture is 2.67 g mol^{-1} .

Examples of 4th level questions

Question a)

To compare the strength of various acids, a useful quantity termed acid dissociation constant is commonly used, denoted K_a . Alternatively, the negative $\log_{10} K_a$, denoted $\text{p}K_a$, may also be used. One can either look up $\text{p}K_a$ values for a pair of acids in literature, or judge from their structural formulas and electronic effects. Among the organic substances below, select the stronger acid in each row:

propanoic acid	2-oxopropanoic acid (pyruvic a.)
difluoroacetic acid	chloroacetic acid
acetic acid	peroxyacetic acid (peracetic a.)
benzoic acid	<i>p</i> -hydroxybenzoic acid

Hint: the dissociation is more likely when the resulting anion is stabilized.

Answer:

In each pair, the stronger acid is the one where the anion is stabilised by a redistribution of the negative charge due to electron withdrawing groups. These are the stronger acids: **2-oxopropanoic** (presence of an electron withdrawing carbonyl group, $\text{p}K_a$ of 2.5 vs 4.9), **difluoroacetic** (two F atoms have a stronger effect than one Cl atom, $\text{p}K_a$ of 1.3 vs 2.9), **acetic** (no resonance stabilization is possible in the case of peroxyacids, $\text{p}K_a$ of 4.7 vs 8.2), **benzoic** (positive mesomeric effect of an electron donating group on the aromatic ring makes the substituted acid a weaker one, $\text{p}K_a$ of 4.20 vs 4.54).

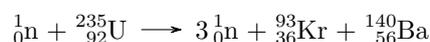
Examples of 5th level questions

Question a)

In an exploding atomic bomb, many nuclear reactions take place simultaneously. One such example is a collision of a neutron with a nucleus of ^{235}U , that leads to the formation of three neutrons, one ^{93}Kr and one more particle. Give the symbol of this particle including its nucleon number.

Answer:

One has to keep in mind that both the sums of proton numbers and of nucleon numbers are conserved in nuclear reactions. The equation is as follows:



The particle in question is a barium atom ${}^{140}_{56}\text{Ba}$.

Examples of 6th level questions

Question a)

The Cannizzaro reaction, occurring under basic conditions, is an interesting example of disproportionation in organic compounds. Only aldehydes having no acidic hydrogen atoms directly neighbouring their carbonyl group (in the α -position, i.e. on the next carbon atom) undergo this reaction; otherwise, aldol reaction occurs. A general scheme of the Cannizzaro reaction is



Based on the criteria above, decide whether the following reactants can undergo the Cannizzaro reaction (state YES or NO).

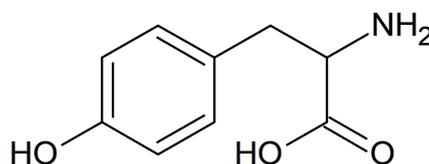
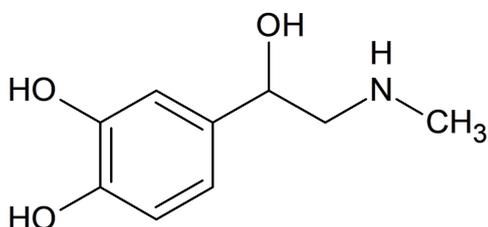
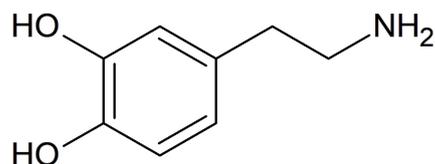
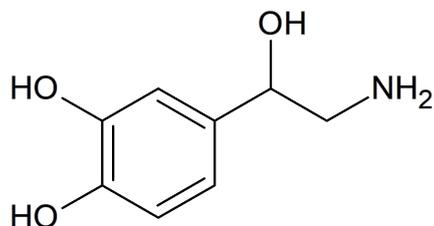
- a) hexan-1,6-dial
- b) 4-methoxybenzenecarbaldehyde
- c) 2,2-dimethylpropanal
- d) cyclopentanecarbaldehyde
- e) 3-hydroxy-2,2-bis(hydroxymethyl)propanal

Answer:

- a) NO, there are many acidic α -hydrogens next to each carbonyl group.
- b) YES, aromatic hydrogens are not acidic and also too far away.
- c) YES, since there are methyl groups in the α -position instead of hydrogen atoms.
- d) NO, there is one acidic hydrogen attached to a carbon atom of the ring.
- e) YES, for the same reason as c), further substitution on the methyl groups has no effect.

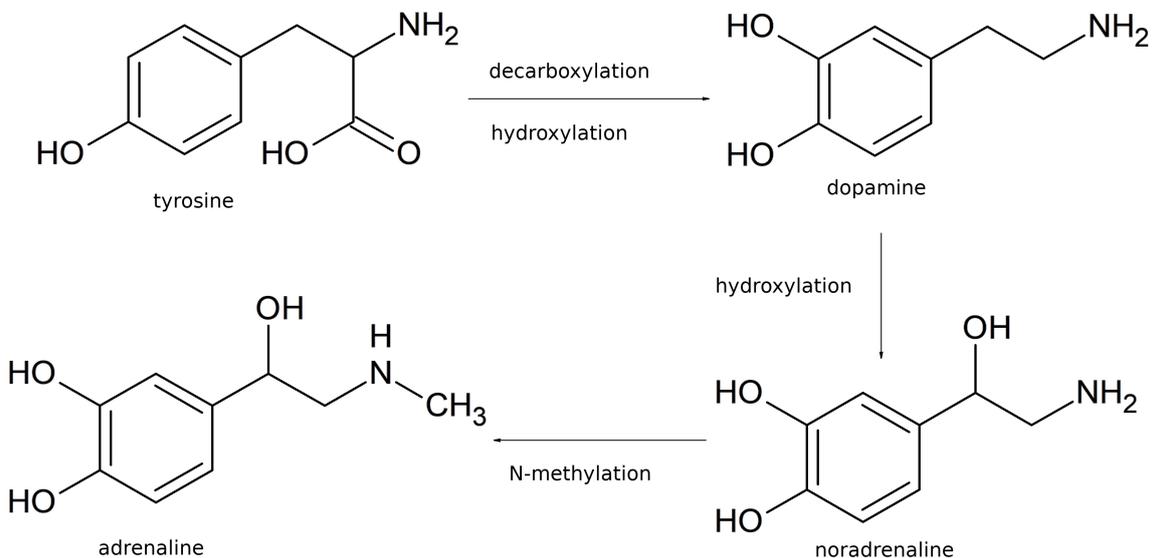
Question b)

Dopamine, adrenaline and noradrenaline are examples of neurotransmitters. They are all produced by biosynthetic pathways starting from the amino acid tyrosine. Its hydroxylation followed by decarboxylation leads to dopamine, which can be converted to noradrenaline by action of β -hydroxylase. Noradrenaline serves as a precursor of adrenaline. A molecule of adrenaline contains the same number of carbon atoms as tyrosine. Match the names to the formulas listed below.



Answer:

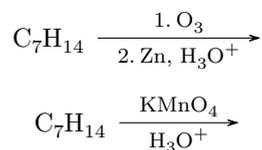
The complete reaction scheme is shown below:



Examples of 7th level questions

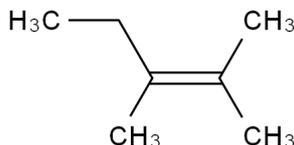
Question a)

Give the structure of an alkene C_7H_{14} that gives the same products upon oxidation by $KMnO_4$ and upon ozonolysis under the following conditions:



Answer:

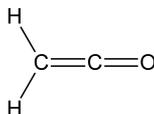
Ozonolysis under these conditions yields two ketones. Only a tetrasubstituted alkene will also give two ketones by a reaction with permanganate. There is only one possible formula for the alkene in question:



Question b)

A careless student dissolved a pre-weighted quantity of acetyl chloride in a larger amount of triethylamine. He was rewarded by a new, strongly unpleasant stench. The gas that was formed is toxic, strongly odorous, and reactive enough to undergo dimerization with itself. It readily reacts with water; the diluted product of this reaction is commonly used in kitchens. The rounded value of its molar mass is 42 g/mol. Give the structural formula of this gas.

Answer:



The product is ethenone, the simplest ketene. The reagents triethylamine and acetyl chloride both contain carbon chains of two atoms at most. The even molar mass of 42 g/mol precludes the presence of nitrogen in the molecule in question. Subtraction of two carbon atoms leaves a remainder of 18 g/mol that can only correspond to one oxygen atom and two hydrogen atoms, leading to a molecular formula of C_2H_2O . This fragment clearly originates from a molecule of acetyl chloride and, based on the difference in the molecular formulas, was produced by triethylamine acting as a base, eliminating a molecule of HCl. This must have left a second double bond. These cumulated double bonds are the reason for the extraordinary reactivity.

Examples of 8th level questions

Question a)

The periodic table invites students to make use of the trends that are present among the elements. However, it is not always possible to draw easy analogies between seemingly similar elements. A good example of this are halogens — regardless of whether we react chlorine with cold water or with a basic solution, it will disproportionate to hydrochloric acid and hypochlorous acid or their salts. On the other hand, reacting fluorine with cold water yields an acid containing fluorine (**A**), the other product, however, is a gaseous element slightly denser than air (**X**). A reaction analogous that of chlorine happens only at very low temperatures, when water ice at $-40\text{ }^{\circ}\text{C}$ is carefully fluorinated. The products of this reaction are **A** and **B**. Bubbling fluorine through a solution of sodium hydroxide yields (apart from water) a salt of acid **A** — this is compound **D**, and a very toxic binary compound **C** of the stoichiometry LM_2 , which is formally an anhydride of acid **B**.

Identify compounds **A**, **B**, **C**, **D** and element **X** described above.

Answer:

Compound **A** is hydrofluoric acid HF.

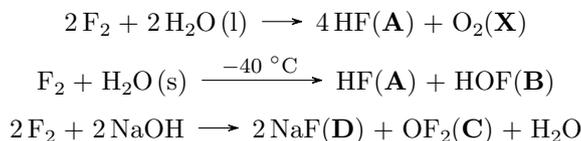
Compound **B** is HOF, or hypofluorous acid. This name is a bit misleading, however, since the fluorine atom has an oxidation state of -1 and the oxygen atom has an oxidation state of zero.

Compound **C** is oxygen difluoride OF_2 .

Compound **D** is sodium fluoride NaF.

Element **X** is oxygen O_2 .

These are the reactions that are described in the questions



Question b)

For many students, biochemistry is mostly about memorising biological pathways (which is partially correct). However, many biochemical problems require using logic, and one of them is determination of primary structure of proteins. Determine the primary structure of a peptide using the following information

1. After treatment with Sanger's reagent (1-fluoro-2,4-dinitrobenzene, DNFB) and a subsequent hydrolysis the peptide gives $1\times\text{Met-DNP}$, $1\times\text{Ser-DNP}$, $2\times\text{Cys}$, $1\times\text{Lys}$, $1\times\text{Leu}$, $1\times\text{Met}$, $1\times\text{Arg}$, and $1\times\text{Val}$.
2. Reaction with 2-mercaptoethanol gives two smaller chains, A and B.
3. Reaction of peptide A with cyanogen bromide gives free Met and a tripeptide.
4. Cleavage of peptide A with trypsin gives free Leu and a tripeptide.
5. Reaction of peptide B with cyanogen bromide gives a tripeptide and the dipeptide Arg-Val.
6. A second cycle of Edman degradation of peptide B gives a cysteine derivative.

Write down the primary structure of the peptide using three-letter amino acid abbreviations starting from the N-terminus and ending with the C-terminus. Label the chains of peptides A and B, and show any disulfide bridges if present.

Hint: Sanger's reagent labels the N-terminus of peptides with dinitrophenyl (DNP). 2-Mercaptoethanol reduces disulfide bridges. Cyanogen bromide (BrCN) cleaves the peptide bond at the C-terminus of methionine residues. Trypsin cleaves the peptide bond at the C-terminus of lysine and arginine. Edman degradation cleaves off amino acids one by one from the N-terminus.

Answer:

Treatment with Sanger's reagent followed by hydrolysis tells us what amino acids are present in the peptide and we learn that there are 2 N-terminal amino acids – Met and Ser.

Reaction with mercaptoethanol reveals that the protein is composed of two peptide chains connected by a disulfide bridge.

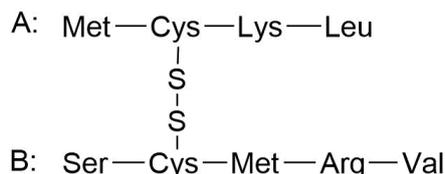
Reaction of peptide A with cyanogen bromide shows that peptide A has an N-terminal Met, and that overall A has 4 amino acid residues (i.e. A is of the form Met-X-X-X). This means that peptide B has 5 amino acids and Ser at its N-terminus (based on the earlier Sanger's reagent experiment). Therefore, B must be of the form Ser-X-X-X-X.

The trypsin experiment tells us that the A terminus has -Lys-Leu in this order, since trypsin cleaves after lysine residues. Thus, peptide A must be Met-X-Lys-Leu.

From the reaction of B with cyanogen bromide, we learn that peptide B consists of a tripeptide that ends with Met, followed by the dipeptide Arg-Val. Peptide B, therefore, has to be of the form Ser-X-Met-Arg-Val.

Edman degradation of peptide B shows that the second amino acid (counting from the the N-terminus) is Cys. Therefore, Peptide B is Ser-Cys-Met-Arg-Val. The last unknown amino acid is the second acid in A. This must be the last remaining acid from the hydrolysis, which means that A has the sequence Met-Cys-Lys-Leu.

Therefore, the primary structure of the peptide is:



Examples of 9th level questions

Question a)

It is often the case that similar chemical substances dissolve in each other, react in similar ways and behave similarly to pure substances when mixed. For example, the mixture of hexane and heptane behaves from the physical point of view almost ideally. Calculate the composition of the gas phase over a mixture composed of 50 g of liquid hexane and 50 g of liquid heptane at 50 °C at equilibrium. The saturated vapour pressure of pure compounds can be calculated from the Antoine equation

$$\ln p_s = A - \frac{B}{T + C}$$

where T is the temperature in the units of K, and p_s is the saturated vapour pressure in the units of kPa. A , B and C are experimentally determined coefficients that are given below.

Hexane:

$$A_6 = 13.8216 \qquad B_6 = 2697.55 \qquad C_6 = -48.78$$

Heptane:

$$A_7 = 13.8744 \qquad B_7 = 2895.51 \qquad C_7 = -53.97$$

Answer:

The first step is to calculate the saturated vapour pressure of each pure substance at 50 °C.

$$p_{s6} = \exp\left(A_6 - \frac{B_6}{T + C_6}\right) = \exp\left(13.8216 - \frac{2697.55}{323.15 - 48.78}\right) = 54.04 \text{ kPa}$$

$$p_{s7} = \exp\left(A_7 - \frac{B_7}{T + C_7}\right) = \exp\left(13.8744 - \frac{2895.51}{323.15 - 53.97}\right) = 22.59 \text{ kPa}$$

Assuming ideal behaviour of the mixture, we can use Raoult's law for each of the components

$$py_6 = p_{s6}x_6$$

$$py_7 = p_{s7}x_7$$

where x_i is the molar fraction of the component i in liquid phase and y_i is the molar fraction in the gas phase. We know that the composition of the liquid phase in terms of masses is 50 g of hexane and 50 g of heptane, so we have to calculate the molar composition.

$$x_6 = \frac{n_6}{n_6 + n_7} = \frac{\frac{m_6}{M_6}}{\frac{m_6}{M_6} + \frac{m_7}{M_7}}$$

$$x_6 = \frac{\frac{50}{86.18}}{\frac{50}{86.18} + \frac{50}{100.21}} = 0.538$$

$$x_7 = 1 - x_6 = 0.462$$

We can substitute for one of the gas phase molar fractions using the summation $y_6 + y_7 = 1$. This yields two equations for two unknowns y_6 and p .

$$py_6 = p_{s6}x_6$$

$$p(1 - y_6) = p_{s7}x_7$$

Substituting p from the first equation into the second allows us to express y_6 .

$$\frac{p_{s6}x_6}{y_6}(1 - y_6) = p_{s7}x_7$$

$$p_{s6}x_6\left(\frac{1}{y_6} - 1\right) = p_{s7}x_7$$

$$\frac{1}{y_6} - 1 = \frac{p_{s7}x_7}{p_{s6}x_6}$$

$$\frac{1}{y_6} = \frac{p_{s7}x_7}{p_{s6}x_6} + 1$$

$$y_6 = \frac{1}{\frac{p_{s7}x_7}{p_{s6}x_6} + 1} = \frac{1}{\frac{22.59 \times 0.462}{54.04 \times 0.538} + 1} = 0.736$$

$$y_7 = 1 - y_6 = 1 - 0.736 = 0.264$$

The composition of the gaseous phase is 73.6 % hexane and 26.4 % heptane.

Examples of 10th level questions

We shall leave these as a surprise.