Baltic Chemistry Competition

1ST ROUND, PROBLEMS

Solve all or some of the four problems given on the next pages and write your answers in *MS Excel* answer sheets provided. If there are some explanations required, write them in English or Russian. Please, send your answers to: kimijas_olimpiades@inbox.lv **till 29.10.2009. at 24:00**. Answers which will be sent after this time will not be graded. Write all the answers in one workbook but in different worksheets for each problem. You should fill in the green spaces provided.

File name must consist from your name, surname (in English) and country, for example *John_Black_England.xls* (or *.xlsx). If you do not name the file as described you will receive 3 point penalty. For all correctly solved problems you can get the maximum of 30 points. The exact amount of points for each task is given at the top of each problem.

All students who will be taking part in at least one round will participate in the final round which will be held on the web on 27th of February. During the final round you will have to solve the multiple choice test.

Authors for problems in this round:

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Good luck with problem solving! ☺

If you have any questions, address them to us in English and send them to: kimijas_olimpiades@inbox.lv
Feel free to ask!

Problem 1 (Lithuania)

Self destructing paper (6 points)

Old books are a very important cultural heritage of nation's history. USA is losing this treasure, soon 40% of the books will be too fragile to handle. Problem of this fact hides in the paper of these books. In XIX century paper manufacturers found it useful to add $Al_2(SO_4)_3$ into paper in the manufacturing process but, unfortunately, this compound causes self destruction of the paper due to the formation of $Al(OH)^{2+}$ ions during the hydrolysis reaction.
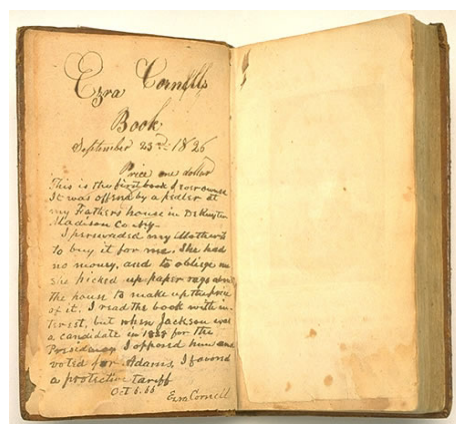
a) $Al(OH)^{2+}$ also forms in aqueous $Al(NO_3)_3$ solution. Ionization degree of this hydrated ion is 52.9% and pH of this solution is 5.00. Calculate pK_a of this ion.

b) One page of a book made from paper manufactured using $Al_2(SO_4)_3$ contains 0.86 mg of it. Book of 500 pages was dipped into 5.0 L volume of water and all alum dissolved. 1.0 ml of this solution was taken and pipetted into 1.0 L flask filled with distilled water. Calculate concentrations of all ions present in the resulting solution.

c) What compound causes destruction of the paper? Propose possible way to prevent destruction.

Problem 2 (Latvia)

Searching for secrets of Superman (10 points)

We all know what term *kryptonite* is related to; there is no clear definition for that. This material is usually shown as having been created from the remains of Superman's native planet of Krypton, and generally has detrimental effects on Superman and other Kryptonians. The name "Kryptonite" covers a variety of forms of the substance, but usually refers to the most common "green" form.

In one of "Supermans" episodes it is given as " element 126" in periodic table, which in reality corresponds to unbihexium/ekaplutonium and is called Kryptonium. Kryptonium has a radioactive half-life of 250 000 years.

1. Calculate radioactive decay rate constant of Kryptonium.
2. Calculate, after what time only 10% of starting kryptonium will remain.

In other episode there is another idea for what kryptonite is:
The chemical composition for the Kryptonite according to "Superman III" is Plutonium: 15.08%, Tantalum: 18.06%, Xenon: 27.71%, Promethium: 24.02%, Dialium: 10.62%, Mercury: 3.94%, Unknown: 0.57%.

3. Calculate the empirical formula of Kryptonite in "Superman III", assuming that Dialium is a particle that contains two aluminum atoms, and the unknown element is hydrogen. Is there is a possible mineral for this formula? Substantiate your answer.

Another version of what is kryptonite is mentioned in "Superman Returns". There are some screenshots from this movie that shows chemical composition and appearance of this mineral:
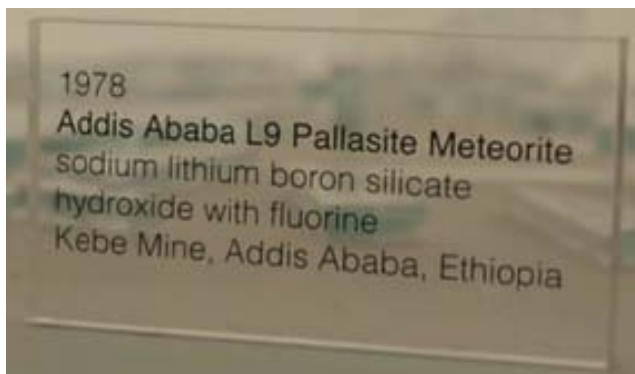
There was no mineral with such composition until the movie was presented, but after that, in November 2006, a mineral Jadarite was discovered in Serbia, Jadar Valley. Its chemical formula is *sodium lithium boron silicate hydroxide*: $LiNaSiB_3O_7(OH)$ or $Na_2OLi_2O(SiO_2)_2(B_2O_3)_3H_2O$. Although there is no fluorine in this mineral and it is white rather than green (see picture below), it made a small sensation due to its noticeable similarity with kryptonite. The jadarite fluoresces in a pinkish-orange color when exposed to UV light.

4. *Explain how fluorine can be bound in jadarite. In what other mineral same situation with fluorine is observed?*

Jadarite crystallizes in hard monoclinic crystals; space group is P2$_1$/c with lattice parameters a = 6.76421(7) Å, b = 13.8047(1) Å, c = 7.86951(9) Å, and β = 124.0895(5)° [1].

5. *Calculate the volume of jadarite unit cell and density of jadarite (in g/cm^3 if crystal structure [1] of it is shown on the right).*

The most intensive diffraction reflexes are shown in table (relative intensity, and d-spacing) [2].

d-spacing (Å)	Relative intensity
4.666	62
3.716	39
3.180	82
3.152	74
3.027	40
2.946	100
2.252	38
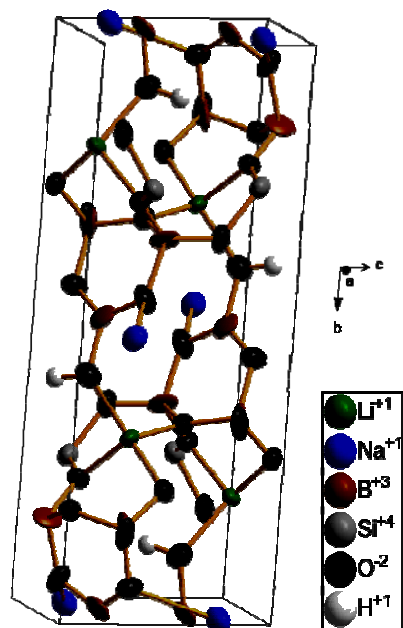
6. *Use Bragg's equation to calculate positions of 1st order diffraction reflexes in 2-Θ scale(^{o}) if Cu K$_\alpha$ radiation with the wavelength 0.15418 nm is used.*
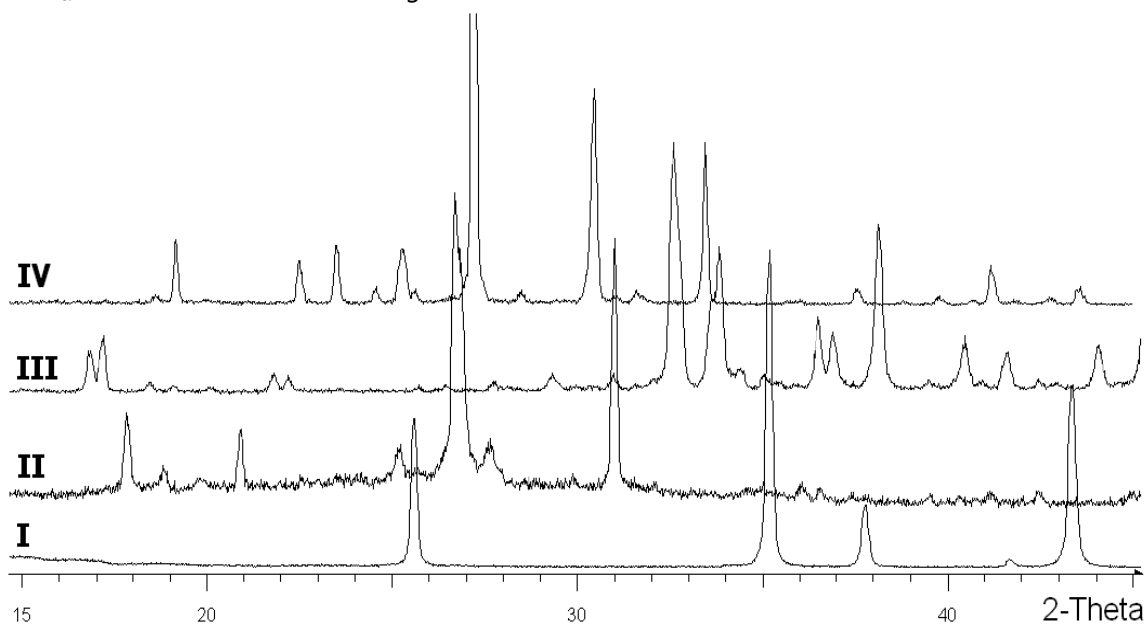
Possible jadarite PXRD patterns

7. *If it is possible from data given above, please, select the right powder diffraction (PXRD) pattern from figure in previous page which corresponds to jadarite. All patterns are done with Bruker D8 Advance diffractomter using Cu K$_\alpha$ radiation.*

Jadarite

Hydrated copper uranyl phosphate

There is a real mineral what is green and radioactive. Its chemical composition is: $Cu(UO_2)_2(PO_4)_2\cdot(8\text{-}12)H_2O$ (hydrated copper uranyl phosphate).

On the right side of the page the decay chain of uranium-238 (main isotope of natural uranium) is shown. Assume, that process $^{238}U \rightarrow {}^{234}U$ is one step process with the rate constant the same as for $^{238}U \rightarrow {}^{234}Th$. In natural uranium nowadays the abundance of isotopes is ^{238}U – 99.2742%, ^{235}U – 0.7204% and ^{234}U – 0.0054%.
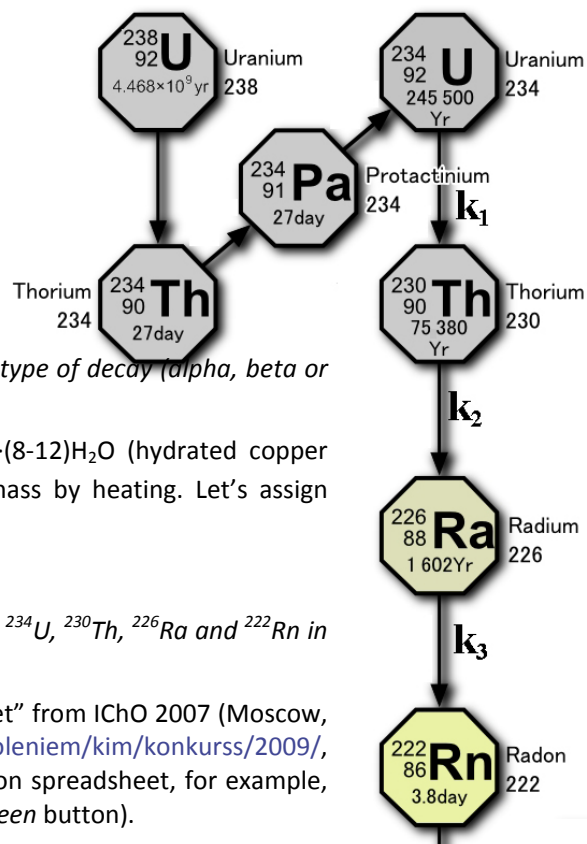
8. Write down all the reactions and classify them by the type of decay (alpha, beta or gamma).

Alchemist Daniel Rebuss took 5.00 g of $Cu(UO_2)_2(PO_4)_2\cdot(8\text{-}12)H_2O$ (hydrated copper uranyl phosphate) and determined that it loses 20.6% of mass by heating. Let's assign amount of uranium atoms in this ore with N_0.

9. Calculate N_0.

10. Construct the graph to show how the amounts of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra and ^{222}Rn in this sample will change during the next million years.

For your calculations you can use computer program "Kinet" from IChO 2007 (Moscow, Russia), program "Kinetics" (available in http://lu.lv/skoleniem/kim/konkurss/2009/, created by Mihails Arhangeļskis) or create your own calculation spreadsheet, for example, in *MS Excel*. Graphs can be saved as screenshots (use *Print Screen* button).

11. Find the time t_{max1}, when there is maximum number of ^{230}Th atoms in the sample of Daniel Rebuss.

Now, assume that you have pure ^{234}U isotope. In situations like this tone can use equations given below for calculation of the amount of particles in left (?) time:

$$N\left({}^{230}Th\right) = N\left({}^{234}U\right)_o \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

And its derivative:

$$\frac{dN\left({}^{230}Th\right)}{dt} = N\left({}^{234}U\right)_o \frac{k_1}{k_2 - k_1}\left(-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right)$$

12. Using formulas given above calculate the time t_{max2}, when there is the maximum number of ^{230}Th atoms in the sample.

13. Explain the differences between t_{max1} and t_{max2}!

Scientific references

1. **P. S. Whitfield, Y. Le Page, J. D. Grice, C. J. Stanley et.al.** LiNaSiB$_3$O$_7$(OH) - novel structure of the new borosilicate mineral jadarite determined from laboratory powder diffraction data, *Acta Cryst.* (2007). B**63**, 396-401
2. Web page: mindat.org - the mineral and locality database Available online: http://www.mindat.org/min-31570.html [07.07.2009.],Copyright Jolyon Ralph and Ida Chau 1993-2009

Problem 3 (Lithuania)

Push those arrows (8 points)

The study of the mechanisms of reactions in the modern organic chemistry is a field of a great scientific interest. In this problem you will have an opportunity to show your skills in predicting mechanisms of simple (and not so simple) organic and bioorganic reactions.
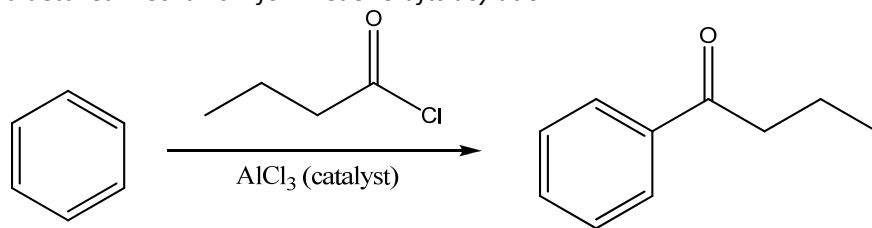
At first, let us explore a very handy reaction discovered by Charles Friedel and James Crafts in 1877.

1. *Provide a detailed mechanism for Friedel-Crafts alkylation.*
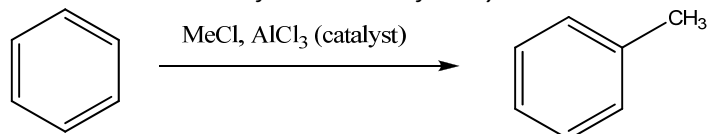
However, the Friedel-Crafts alkylation is usually replaced by Friedel-Crafts acylation.

2. *Provide a detailed mechanism for Friedel-Crafts acylation.*
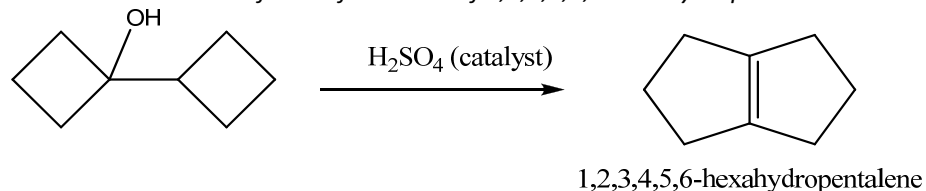

Product 1

3. *Predict the reagents for synthesis of the **Product 1** using Friedel-Crafts alkylation reaction. Predict the major products of this reaction along with mechanisms of their formation.*

*That is it for the easy part.* ☺

4. *Provide a detailed mechanism for the formation of 1,2,3,4,5,6-hexahydropentalene*

1,2,3,4,5,6-hexahydropentalene

Feeling bored already? Well, you should. Now, let us explore a basic bioorganic reaction. ☺

5. *Provide a plausible mechanism for the formation of a cyclic triterpene and spot the terpene subunits in the starting compound and the product. (Hint: -OPP group acts as a leaving group during the first step)*

6
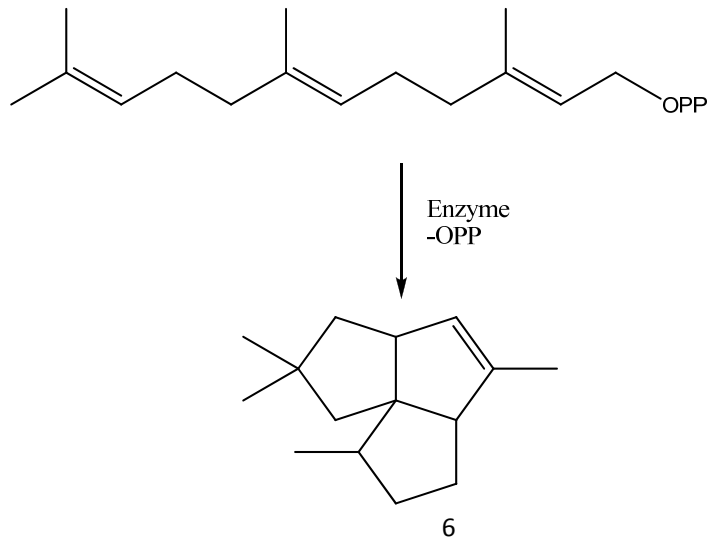
Problem 4 (Estonia)

Secrets of spectroscopy (6 points)

Nuclear magnetic resonance (NMR) spectroscopy is the preeminent technique for determining the structure of organic compounds. Chemists heavily rely on the spectroscopic methods of NMR, especially on ^{1}H-NMR, which is the most commonly used NMR method. In addition, some information about functional groups can be gained with Infrared (IR) spectroscopy analysis. The problem below demonstrates how NMR and IR can be used together to determine the structure of a given compound.

Compound of empirical formula $C_{12}H_{18}O_3$ contains two methyl groups one of which has a singlet in ^{1}H NMR spectrum and another a triplet. Reduction of the given compound by $NaBH_4$ gives compound $C_{12}H_{20}O_3$ containing two methyl groups one of which still has a triplet in ^{1}H NMR spectrum but another a doublet. In addition to that, the resulting compound has intensive maximums at 3400 and 1740 cm^{-1} in IR spectrum. Reduction of the given compound by $LiAlH_4$ gives compound $C_{10}H_{18}O_2$ which has doublet for methyl group in its ^{1}H NMR spectrum and intensive maximum at 3400 cm^{-1} in IR spectrum. Basic hydrolysis of the given compound gives compound $C_{10}H_{14}O_3$ which has singlet for methyl group in its ^{1}H NMR spectrum, two maximums in the interval 1700–1720 cm^{-1} and a broad maximum at 2500–3400 cm^{-1} in IR spectrum. Ozonolysis of this compound gives the following products: 4-oxopentanoic acid (Levulinic acid), propanedioic acid (Malonic acid), ethanedioic acid (Oxalic acid).

a) Draw the structure of the original compound.

b) Draw the mechanisms for all the mentioned reactions.