Baltic Chemistry Competition

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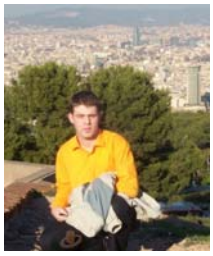
3rd round, Problems

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 21.02.2010. 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)

Liquid ice (5 points)

All required constants can be found in data books or online. References must be given to sources of information.
The following experiments are carried out at standard conditions.

A is a 0.4M NH_4OH solution.

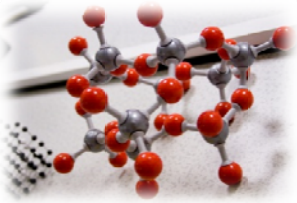
1) In order to obtain a solution of 0.1M NH_4Cl , a solution of HCl can be added to 400 mL of the solution **A**. Calculate the required concentration and volume of HCl solution.
2) What is the pH of 0.1 NH_4Cl aqueous solution at 25°C?

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad K_b$$

$$H_2O \rightarrow H^+ + OH^- \qquad K_w$$

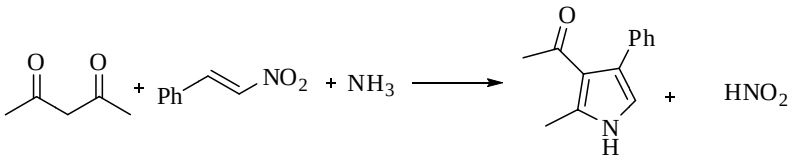
3) How do K_b and K_w vary with temperature? (Tables of thermodynamic properties can be consulted)
4) Can a solution of 0.1M NH_4Cl be neutral (pH=7)? If so, what is the required temperature?
5) What are minimum and maximum pH values of 0.1M NH_4Cl solution?

Problem 2 (Lithuania)

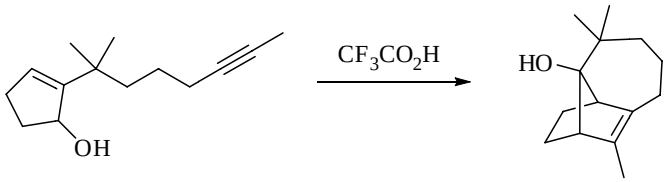


Are you hungry for organic chemistry? (9 points)

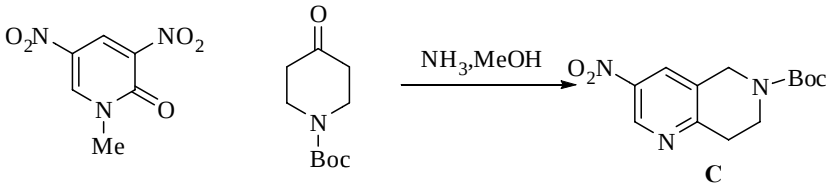
1. What are the mechanisms of the following transformations? *(Boc acts as a protecting group)*



A

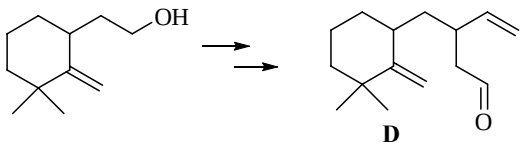


B

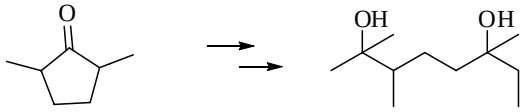


C

2. Provide plausible synthesis plans (reagents and intermediate compounds) for compounds **D** and **E**. You may use other simple carbon containing compounds to make reagents. *N.B. You do not have to provide the mechanisms.*



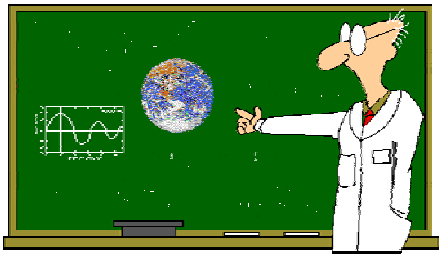
D



E

Problem 3 (Estonia)

Unknown compound chemistry (5 points)

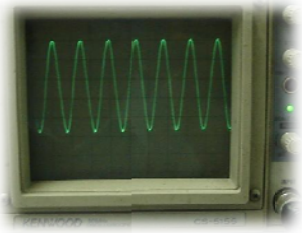


For the first time compound **X** was obtained in the middle of the XX century. This achievement proved the existence of a new class of compounds. Gas **Y** was used as one of the reagents in the synthesis of **X**. Interestingly, until the end of the XX century there was no pure-chemical method to synthesize **Y**. The following reaction sequence shows the synthesis of compound **X** starting from the synthesis of **Y**, using a common chemical reagents scheme.

1) $KMnO_4$ + H_2O_2 + mineral acid **A** and respective mineral salt **B**→ metal complex **C (22.2% Mn)** + H_2O + O_2
2) Semimetal **D** + elemental gas **E**→ liquid **F (40.7% D)**
3) **F** + **A**→ liquid**G (56.2% D)** + mineral acid **H**
4) **C** + **G**→ metal complex **I (44.3% D)** + salt **J (49% Mn)** + elemental gas **Y**
5) **Y** + **K**→ **M** (**K** is a noble metal)
6) **M** + **L** (1:1) →**X**

*a) Write formulae for **A–M, X** and **Y**.*

b) Write equations of the reactions mentioned above.



Problem 4 (Lithuania)

Chemical oscillator (8 points)

Chemical kinetics is one of the most exciting areas of chemistry and, as a matter of fact, it deals with a lot of thermodynamics too. You are free to use every source you need, however, you **must** reference from where the specific information was taken (books, websites, chemistry camps.)

Part 1

In the beginning let's start with some experimental techniques as it is the life of a true chemist. Although properly designed experiments are a must for nowadays scientist, the equipment during the experiment might fail and there is nothing more to do than just to modify the procedure.

Let's assume there is a reaction:

$$\mathbf{A + B \rightarrow C + D}$$

The experiment is designed so that the order of the reaction with respect to the reactant **A** and **B** could be determined. The change of concentration in time was measured with *spectrophotometer.* However, due to malfunctioning of the device, only the last two digits were visible. The folowing data was obtained.

*Table 1: data from 2 series of measurements. (1st), (2nd), (3rd) show how many times the shown digits were seen in the screen after they were written down. If *.*99 (2nd) is written, then it means, that only the measurement was made when *.*99 appeared in the screen for the second time.*

No.	Time (the 1st trial)	Absorbtion	Time (the 2nd trial)	Absobtion
0	0 s	*.*76	0 s	*.*76
1	16 s	*.*90 (1st)	12 s	*.*39 (2nd)
2	39 s	*.*52 (2nd)	24 s	*.*09 (2nd)
3	69 s	*.*95 (2nd)	41 s	*.*44 (2nd)
4	110 s	*.*98 (2nd)	59 s	*.*61 (2nd)
5	160 s	*.*73 (3rd)	87 s	*.*89 (3rd)
6	222 s	*.*29 (3rd)	112 s	*.*29 (2nd)
7	280 s	*.*46 (2nd)	140 s	*.*12 (3rd)
8	357 s	*.*58 (3rd)	179 s	*.*64 (3rd)
9	458 s	*.*94 (3rd)	230 s	*.*89 (3rd)
10	572 s	*.*43 (3rd)	297 s	*.*01 (3rd)

Although spectrophotometer was malfunctioning, some exact values were still known:

- The concentration of **B** reactant remained approximately constant during the reaction. In the 1st series of measurements it was equal to 1 *M*, while in the 2nd series – twice the magnitude.
- The width of the cell was equal to 1cm and the molar extinction coefficient was equal to 4530 $M^{-1}cm^{-1}$.
- The initial concentration of the reactant A is not known, yet, it is held constant during the whole experiment.

Questions:

1. What assumptions have you made in processing the given data. Please answer in English.
2. Determine the order of reaction with respect to each reactant.
3. Determine the overall order of the reaction
4. Determine the initial concentration of A_0.
5. Determine the real kinetic constant for the reaction.

In all cases above show your calculations and where appropriate, derivations of the mathematical formulas.

Part 2

In this part we will deal more with autocatalytic reactions. The reaction which we are going to investigate is as follows:

$$\mathbf{A + B \rightarrow 2B}$$

In the reaction above, the concentrations of **A** and **B** vary in time as:

- $$[A] = \frac{[A]_0 + [B]_0}{1 + \frac{[B]_0}{[A]_0} e^{([A]_0 + [B]_0)kt}}$$
- $$[B] = \frac{[A]_0 + [B]_0}{1 + \frac{[A]_0}{[B]_0} e^{-([A]_0 + [B]_0)kt}}$$

Questions:

1. Sketch the graph A(t) and B(t) on the same axes.
2. Mark the values of the asymptotes and y-intercepts.
3. What happens with the graph, if $[A_0] + [B_0]$ is increased/decreased? Please explain in English.
4. What happens if B_0 is increased/decreased? Please explain in English.

Part 3

Oscillating chemical reactions is yet another interesting example of autocatalytic reactions. The mathematics of these reactions in order to sketch the graphs of the concentrations of chemicals is rather too complicated, so we will take a glimpse from other perspective.

Let us examine the reaction:

$$A + B \Leftrightarrow 2B$$

Questions

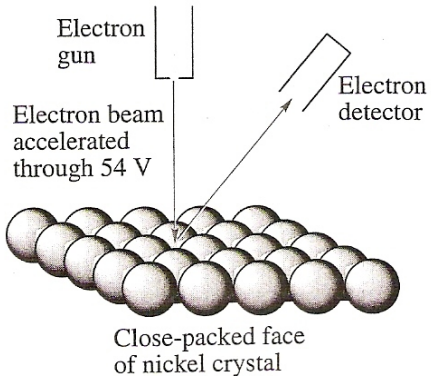
1. Sketch the graph "Reactants energy versus reaction time" of a non-autocatalytic reaction. How does the varying concentration of catalytic particles influence the curve of the graph? Please explain in English.
2. Using Le Chatelier's principle and knowledge from the first question, answer why the oscillating reactions may exist? Please explain in English.

Problem 5 (Latvia)

De Broglie heritage (3 points)

In 1927, Davison and Germer demonstrated that electrons can be diffracted from the surface of a nickel crystal, a result which can be explained only if electrons have wave-like properties. By applying the de Broglie relationship they were able to calculate the interatomic spacing between the nickel atoms, and their result agreed with value obtained from X-ray diffraction measurements.

Davisson and Germer used an electron beam that had been accelerated through a potential difference of 54.0 volts and the electrons approached the surface at normal incidence, i.e. perpendicularly, as shown in picture 1. The nickel sample had been heated to high temperatures before experiments began, and this had caused large crystals to form which produced the regular array of nickel atoms show in picture. Unlike X-rays, electrons do not penetrate very far into the metal crystal, and most of the scattering occurs form the top layer of metal atoms. Scattering of electrons was found to occur most strongly at an angle of 50^o to the surface normal, and this result can be explained in the terms of the constructive interference of electron waves scattered from neighboring nickel atoms.



Calculate the wavelength of electrons, spacing between the rows of nickel atoms and metallic radius of nickel. ***Hint****. Start with calculation of impulse momentum …*