



53 Chemistry Olympiad

Final competitions (24.03.2007)

PROBLEM 1

Standard addition method in potentiometric analysis

A. Cu(II) ions concentration was assessed in solution A (c_A), using the standard addition method. Initially, potential of a copper wire electrode immersed in this solution was measured. The measurement was carried out at the temperature 25 °C, against a reference electrode. Then a portion of a standard solution of $\text{Cu}(\text{NO}_3)_2$ of volume $v = 2$ mL and concentration $c_{st} = 0.1$ mol/L was added to a sample of solution A of volume $V = 50$ mL. After mixing of the solution, potential increase $\Delta E = 13$ mV was recorded (in relation to the initial value prior to standard addition).

Problems:

- a1.** Derive the equation expressing the unknown concentration, c_A , as a function of ΔE , c_{st} , V and v .
- a2.** Using the obtained equation, calculate the concentration c_A .
- a3.** Calculate the concentration c'_A directly from Nernst equation, knowing that prior to standard addition the potential of the electrode (copper wire immersed in solution A) was 36 mV, and the standard potential of this electrode, measured using the same reference electrode, is $E^0 = 115$ mV. Compare the concentration values c_A and c'_A .

B. For real samples, results obtained from a direct measurement (i.e. from the Nernst equation) and calculated using the method of standard addition can differ significantly. This is the influence of “matrix” effect, resulting e.g. from interactions of analyzed ions with various components of the sample.

The role of a “matrix” in this problem is played by a complexing ligand, EDTA, present in large excess in relation to copper ions.

Potential of the copper wire described above and immersed in 50 mL of solution B containing EDTA of concentration 0.05 mol/L and Cu(II) ions of unknown total concentration c_B (free and complexed ions) was -514 mV. After addition of 0.1 mL of 0.1 mol/L $\text{Cu}(\text{NO}_3)_2$ solution to this solution, the potential increase was equal to 11 mV (change of EDTA concentration resulting from the standard addition can be neglected).

Problems:

- b1.** Prove that determination of total Cu(II) ions concentration in the initial solution requires application of the standard addition method. Calculate this concentration (c_B) and determine the value of stability constant of the complex Cu^{2+} with EDTA, β .
- b2.** Check, how does the „matrix” effect influence the dependence of potential on sample dilution. Therefore calculate change of the electrode potential, when two initial solutions of $\text{Cu}(\text{NO}_3)_2$ (of a given concentration) are ten-fold diluted. One of the initial solution did not contain EDTA, while the second one contained excess of this ligand.

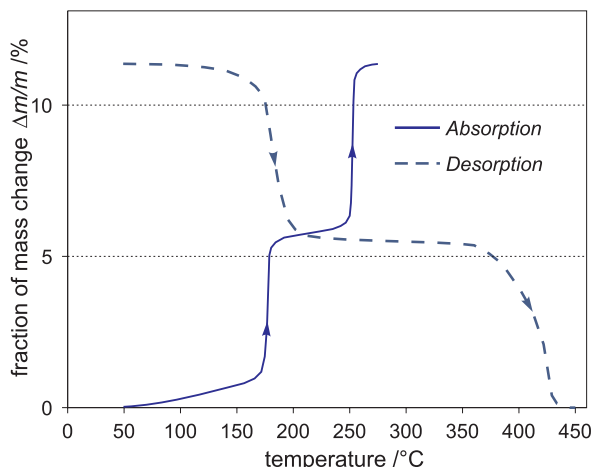
$R = 8.314$ J/(mol·K), Faraday’s constant, $F = 96484$ C.

PROBLEM 2

Future hydrogen storage

As early as in 1910, F. W. Dafert and R. Miklauz revealed that hydrogen readily reacts with lithium nitride Li_3N . However, they did not study this reaction in detail and only the reaction stoichiometry was established. Recently the detailed study of the reaction course was reported in the prestigious journal *Nature*.

It was revealed, that the absorption of hydrogen in lithium nitride proceeds at temperatures above 50°C and under pressure of about $3 \cdot 10^5$ Pa. Almost all absorbed hydrogen can be subsequently desorbed if the hydrogenated sample is evacuated to 1 Pa and heated up to 450°C (see figure). Adsorption and desorption processes are associated with chemical reactions between lithium nitride and hydrogen, and were investigated for the wide range of temperature. It was stated that these reactions may be used for the hydrogen storage. The mass changes (% m/m) of the Li_3N and the hydrogenated lithium nitride samples during heating and cooling, respectively, are presented in figure. The absorption and desorption profiles show that both reactions proceeds in two stages.



The sample of lithium nitride was placed in the furnace under hydrogen and heated for 1 h at temperature of 260°C . The reaction products were characterized by X-ray diffraction and three crystalline phases were identified: compound **A** of structure isotypic with NaCl , tetragonal compound **B** and small amounts of cubic compound **C**. No traces of substrate were found. The sample of reaction products of 2.6674 g was treated carefully with an excess amounts of 0.5M hydrochloric acid. The evolving colorless gas was passed through the cupric oxide at 180°C , the weight of which was decreased by 2.096 g as a result of the reaction between the gas and CuO . For further analysis, two thin tubes were filled with compound **A** and compound **B** in 1:1 molar ratio as given in scheme below. Both tubes were heated at 350°C and simultaneously the carrier gas (He) was passed through. The outlet gas was absorbed in water with addition of phenolphthalein.



In the first experiment the carrier gas was passed firstly through the **A** layer and then through the **B** layer. The X-ray measurement showed that during heating the compound **A** did not react, whereas the compound **B** was converted into compound **C**. Moreover, the water was pink-colored.



In the second experiment the direction of the gas flow was inverted. In this case, in both layers mainly crystalline product **C** was formed and the water remains colorless.

Problems:

- a) Considering the plots in Figure 1 write down the chemical equations for each step of the hydrogen absorption and desorption reactions proceeding in lithium nitride.

- b) Calculate the maximum volume of hydrogen (under normal conditions) that may be stored in 1kg of lithium nitride.
- c) Write the chemical equations for reactions between hydrochloric acid and the hydrogenation reaction products formed at 260°C. Determine molar fractions of the solid products.
- d) Provide the chemical formula of compounds **A**, **B** and **C** along with the chemical equations of the reactions occurring during heating of **A** and **B** in the presence of carrier gas.
- e) Draw the crystal unit cell of compound **A**.

For calculations use the following molar masses:

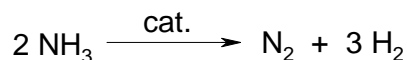
Li – 6.94 g/mol; H – 1.008 g/mol; N – 14.01 g/mol; O – 16.00 g/mol

PROBLEM 3

Kinetics and mechanism of reactions on solid-state catalysts

Reactions on solid-state catalysts are the basis of many important technological processes extensively used in a modern chemical industry. Examples include cracking and reforming of crude oil distillation products, various oxidation and hydrogenation processes. The mechanism of these reactions is complex and involves an initial adsorption of substrates on a catalyst surface. The kinetics of a catalytic reaction (and of any multistep reaction in general) are dictated by the rate of the slowest step.

A. Ammonia undergoes decomposition on a solid-state catalyst according to the equation:



The adsorbed form of ammonia (it can be depicted as $\text{NH}_3\text{-S}$) is involved in the rate determining step. The rate of the decomposition is directly proportional to the surface coverage of ammonia.

- a1. Write the expression for the rate of the reaction (kinetic equation) if the adsorption of products is negligible and the ammonia pressure is high.
- a2. What is the reaction order for the given conditions?

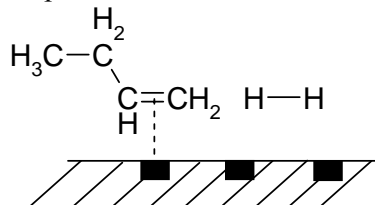
Assume that the adsorption of ammonia can be described using the Langmuir adsorption theory.

B. In some cases adsorption can be dissociative, i.e., the molecule is split into isolated parts when binding to a catalyst surface. For instance, a two-atomic molecule is split homolytically and single atoms bind to active sites of a catalyst independently. Hydrogen can undergo dissociative adsorption on some catalysts. This is important for many hydrogenation reactions.

- b1. Write the chemical equation for the dissociative adsorption of hydrogen.
- b2. Write the expression for the equilibrium constant of adsorption. K_{ads} .
- b3. Write the expression for the surface coverage of the atomic hydrogen
 $\theta_H = f(p_{H_2})$

C. Hydrogenation of alkenes. The first step of a multistep mechanism of but-1-ene hydrogenation is shown schematically below:

Step 1.



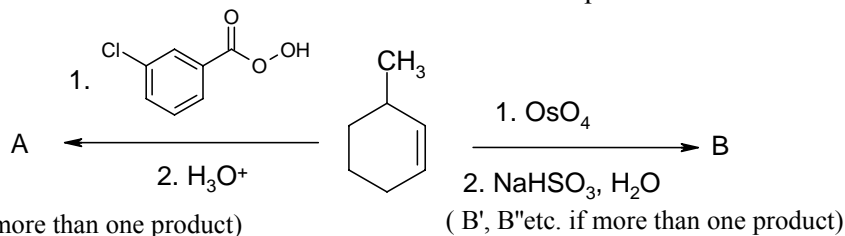
Adsorption of but-1-ene due to the interaction of π -electrons with an active site of a catalyst.

- c1.** Draw remaining steps analogously in a proper order. Assume that hydrogen undergoes dissociative adsorption.
- c2.** Explain the formation of isomeric but-2-enes (byproducts). Advice: hydrogenation of but-1-ene is reversible.

PROBLEM 4

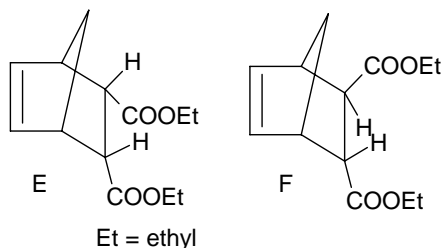
Stereoisomerism in cyclic compounds

An example of the isomerism phenomenon is isomerism cis-trans in cyclic compounds. The discovery of such isomerism in numerous natural compounds, drugs and other biologically active compounds cause dynamic development of organic synthesis methods leading to the compounds with appropriate arrangement of the substituents in respect to ring plane. Consider the problems described below, that refer to cis-trans isomerism and answer the questions.



- A.** Two reactions of 3-methylcyclohexene are shown in the scheme.
- a1.** Draw structural formulas of all products formed during the reactions. Be aware that racemic mixture of 3-methylcyclohexene was taken for the reactions
 - a2.** Assign the absolute configuration of all asymmetric carbon atoms which are present in the product.
 - a3.** Draw a chair formula of the product in which all asymmetric carbon atoms possess the R configuration
 - a4.** Draw the structural formulas of the intermediates in both reactions. (omit the stereochemistry)
- B.** Geometric isomers of 3,4 - dimethylcyclopentanone, C and D (Warning: one of them is in a form of racemate) were reacted with NaBH_4 in ethanol, and after that were hydrolyzed in acidic conditions. In ^1H NMR one set of signals was obtained for product coming from isomer C, whereas in NMR spectrum of the products from D a mixture of two distinguishable compounds was observed.
- b1.** Draw the structural formulas of C and D and the related final products of the reactions.
 - b2.** How many signals are present in ^1H NMR of compounds C and D? Label the groups of protons on structural formulas of C and D which have the same chemical shifts.

C. Isomeric compounds E and F (formulas on the scheme below) were obtained in Diels-Alder reaction.



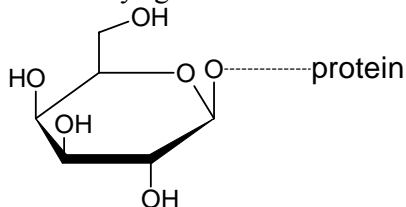
c1. Draw the structural formulas of the compounds allowing to synthesize E and F.

PROBLEM 5

Blood groups

In the routine blood transfusion it is necessary to determine the blood group. Mixing incompatible blood types can cause agglutination of red blood cells and the death of the patient. There are known four types of blood groups: A, B, AB and 0. The type of the blood group depends on the composition of the oligosaccharide bounded with surface protein of red blood cells.

The central part of the saccharide is always galactose which is bounded with the protein:

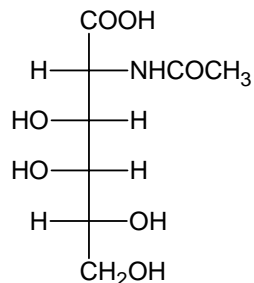


Galactose is also bounded with:

- sugar **C** by bond α -1,2' in blood type 0
- sugar **C** by bond α -1,2' and sugar **A** by bond α -1,3' in blood type A
- sugar **C** by bond α -1,2' and sugar **B** by bond α -1,3' in blood type B

Identification of sugar A:

Isolated sugar **A** reacted with Tollens reagent (silver mirror test) to give bellow compound:

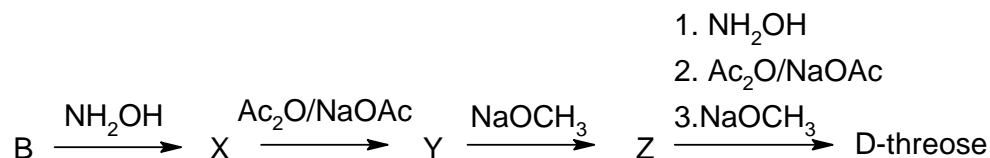


Identification of sugar B:

Sugar **B** reacted with hydroxylamine to form compound **X**, which was next heated with acetyl anhydride in the presence of sodium acetate to give compound **Y** as the product of that reaction. Basic hydrolysis of compound **Y** provided to sugar **Z** which was one carbon atom shorter than

parent sugar **B**. Sugar **Z** treated with the same reagents as sugar **B** gave D-threose as the result of those reactions.

Transformations described in the text are given on the bellow scheme:



Percentage composition of compound **Y** is: 49,6% of C, 41,3% of O, 3,6% of N and the rest is hydrogen.

There is also known that the oxidation of sugar **B** with HNO_3 provides to the product which is optically inactive.

Identification of sugar C:

Sugar **C** belongs to the L-row. The absolute configuration of the third carbon atom (C-3) was assignment as *R*. When sugar **C** was reduced in such conditions that CHO group was converted into the methyl group, the *meso* compound was formed. The reaction between 1 mol of **C** and HIO_4 gave 1 mol of CH_3CHO and 4 moles of HCOOH .

Problems:

a. Give Fischer projections of:

- a1.** sugar **A**
- a2.** sugar **B** and **X**, **Y**, **Z** derivatives
- a3.** sugar **C**

Explain the structures of compounds **B**, **Y** and **C**.

b. Monosaccharides form 6-membered pyranose rings. Give Haworth projections of:

- b1.** disaccharide from blood type 0
- b2.** trisaccharide from blood type A
- b3.** trisaccharide from blood type B

SOLUTIONS

SOLUTION OF PROBLEM 1

a1. Before the standard addition $E_1 = E^0 + S \log c_A$ ($S = 2.3RT/2F = 29.5$ mV). After standard addition, the new potential $E_2 = E^0 + S \log \{(Vc_A + \nu c_{st})/(V + \nu)\}$. Subtracting these equations and taking $\Delta E = E_2 - E_1$, one obtains: $\Delta E = S \log [\{(Vc_A + \nu c_{st})\}/\{c_A(V + \nu)\}]$. After rearrangement:

$$\frac{c_A V + c_{st} \nu}{c_A V + c_A \nu} = 10^{\frac{\Delta E}{S}} \quad (1R)$$

the final form can be obtained:

$$c_A = \frac{c_{st} \nu}{(V + \nu) \cdot 10^{\Delta E/S} - V} \quad (2R)$$

a2. After incorporating the values $c_{st} = 0.1$ mol/L, $V = 50$ mL, $\nu = 2$ mL, $\Delta E = 13$ mV and $S = 29.5$ mV into equation 2R, one obtains $c_A = 2.14 \cdot 10^{-3}$ mol/L.

a3. Using the Nernst equation: $E = E^0 + 2.3RT/(2F) \log[\text{Cu}^{2+}]$ (T : temperature in K) and numerical data, one obtains: $36 = 115 + 2.3 \cdot 1000 \cdot 8.314 \cdot 298 / (2 \cdot 96484) \log c_A = 115 + 29.5 \log c_A$; thus $c_A = 2.10 \cdot 10^{-3}$ mol/L (pre-logarithmic 1000-coefficient is introduced to express the potential in mV). Similar values of c_A and c_A were obtained.

b1. The total concentration of copper (II) ions cannot be determined in this case from a direct measurement, for the given E^0 , because the measured potential gives information about concentration of free (non-complexed) Cu^{2+} ions. The concentration of free Cu^{2+} ions and EDTA is coupled with concentration of the complex, $\text{Cu}(\text{EDTA})$, by expression for the stability constant, β :

$$\beta = \frac{[\text{Cu}(\text{EDTA})]}{[\text{Cu}^{2+}][\text{EDTA}]} \quad (3R)$$

This equation can be transformed to expression describing free $[\text{Cu}^{2+}]$ ions concentration:

$$[\text{Cu}^{2+}] = \frac{[\text{Cu}(\text{EDTA})]}{\beta[\text{EDTA}]} \quad (4R)$$

After substituting $[\text{Cu}^{2+}]$ in Nernst equation by equation 4R, one obtains:

$$E = E^0 + 29.5 \log[\text{Cu}^{2+}] = E^0 + 29.5 \log \frac{[\text{Cu}(\text{EDTA})]}{\beta[\text{EDTA}]} \quad (5R)$$

and for a constant EDTA concentration

$$E = \text{const} + 29.5 \log[\text{Cu}(\text{EDTA})] \quad (6R)$$

where $\text{const} = E^0 - 29.5 \log(\beta[\text{EDTA}])$.

Since we assume that practically all copper (II) ions are complexed, the measured potential is a linear function of the total copper (II) ions concentration. To determine this concentration, the standard addition method can be applied (in such a case const value is not necessary in calculations). Then, by using $c_{st} = 0.1$ mol/L, $V = 50$ mL, $\nu = 0.1$ mL, $\Delta E = 11$ mV and $S = 29.5$ mV in eq. 2R (c_B was replaced by c_A), one obtains $c_B = 1.47 \cdot 10^{-4}$ mol/L = $[\text{Cu}(\text{EDTA})]$. By using $E = -514$ mV, $E^0 = 115$ mV, $S = 29.5$ mV, $[\text{EDTA}] = 0.05$ mol/L and $[\text{Cu}(\text{EDTA})] = 1.47 \cdot 10^{-4}$ mol/L in eq. 5R, one obtains $\beta = 6.2 \cdot 10^{18}$.

b2. Ten-fold dilution of $\text{Cu}(\text{NO}_3)_2$ solution of concentration c results in potential change $\Delta E = 29.5 \log(c/10) - 29.5 \log c = -29.5 \log 10 = -S = -29.5 \text{ mV}$.

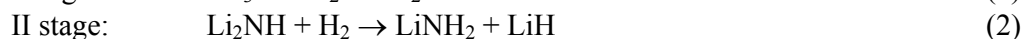
In the presence of EDTA excess, the potential is dependent on free Cu^{2+} ions concentration. This concentration is described by eq. 4R. Ten-fold dilution results in ten-fold decrease of concentration, both $\text{Cu}(\text{EDTA})$ and EDTA. Consequently:

$$[\text{Cu}^{2+}] = \frac{[\text{Cu}(\text{EDTA})]/10}{\beta[\text{EDTA}]/10} \quad (7R)$$

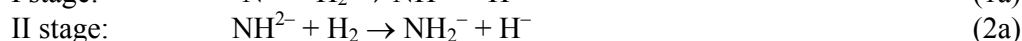
i.e. free Cu^{2+} ion concentration does not change. This means, that dilution does not affect the potential value. The “matrix” effect results in either decreasing or elimination of potential dependence on sample dilution.

SOLUTION OF PROBLEM 2

- a)** Li_3N reacts with hydrogen in two stages and for both the amounts of the hydrogen absorbed (desorbed) are nearly the same. The hydrogen is too weak reducing agent to reduce lithium cation, on the other hand it is also too weak oxidizer to oxidize the nitride anion. Thus, the reaction with Li_3N is a *red-ox* disproportionation reaction: $\text{H}_2 \rightarrow \text{H}^+ + \text{H}^-$, due to strongly basic character of nitride anions, which readily bind the hydrogen cations:



or in ionic form:



Such a reaction scheme can be confirmed by the relative mass change of Li_3N , calculated for the reaction (1):

$$\Delta_1 = \frac{M_{\text{H}_2}}{M_{\text{Li}_3\text{N}}} \cdot 100\% = \frac{2.016}{34.83} \cdot 100\% = 5.79\%$$

and for the total reaction (1)+(2): $\Delta_2 = 2 \cdot \Delta_1 = 11.6\%$

Desorption reactions are reverse to reactions presented above.

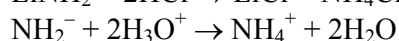
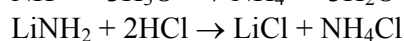
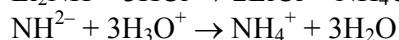
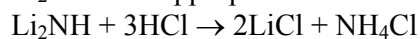
- b)** Assuming a yield of the hydrogenation reaction:



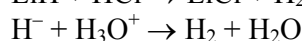
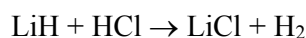
is equal to 100% than 1kg of Li_3N may store:

$$V = 2 \cdot \frac{1000 \text{ g}}{M_{\text{Li}_3\text{N}}} \cdot 22.4 \text{ dm}^3 \cdot \text{mol}^{-1} \approx 1286 \text{ dm}^3 \text{ of H}_2.$$

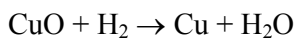
- c)** The product of hydrogenation at 260°C is composed of: LiNH_2 , LiH and small amounts of Li_2NH . The appropriate reactions with the hydrochloric acid are as follows:



Reaction between LiH and HCl is a synproportionation *red-ox* reaction:



The only gaseous product is H_2 , which reacts with heated CuO according to the following equation:



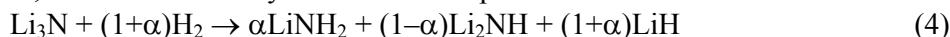
From the mass loss one may calculate the amounts of formed LiH (n_{LiH}) and H₂ (n_{H_2}) adsorbed:

$$n_{\text{LiH}} = n_{\text{H}_2} = n_{\text{Cu}} = \frac{\Delta m}{M_{\text{O}}} = \frac{2.096}{16.00} \approx 0.1310 \text{ moles of LiH (H}_2\text{)}$$

as well as the amount of Li₃N before hydrogenation.

$$n_{\text{Li}_3\text{N}} = \frac{m_{\text{Li}_3\text{N}}}{M_{\text{Li}_3\text{N}}} = \frac{m - n_{\text{H}_2} \cdot M_{\text{H}_2}}{M_{\text{Li}_3\text{N}}} = \frac{2.6674 - 0.2641}{34.83} \approx 0.0690 \text{ moles of Li}_3\text{N}$$

Since the fraction $n_{\text{H}_2}/n_{\text{Li}_3\text{N}} \approx 1.9$ is less than 2, the yield of hydrogenation reaction was less than 100%, hence the summary reaction can be put as follows:



where $\alpha \approx 0.9$

The amounts of LiNH₂ and Li₂NH can be readily obtained from eq (4):

$$n_{\text{LiNH}_2} = n_{\text{LiH}} - n_{\text{Li}_3\text{N}} = 0.1310 - 0.0690 = 0.0620$$

$$n_{\text{Li}_2\text{NH}} = n_{\text{Li}_3\text{N}} - n_{\text{LiNH}_2} = 0.0690 - 0.0620 = 0.0070$$

The corresponding molar fractions are equal to:

$$x_{\text{LiH}} = \frac{0.1310}{0.1310 + 0.0620 + 0.0070} = \frac{0.1310}{0.2000} = 0.655$$

$$x_{\text{LiNH}_2} = \frac{0.0620}{0.2000} = 0.310$$

$$x_{\text{Li}_2\text{NH}} = \frac{0.0070}{0.2000} = 0.035$$

- d*) Compound **C**, occurring only in small amounts in the hydrogenated sample is formed in the first reaction step and it is lithium imide Li₂NH. Compound **B** decomposes during heating and evolves gaseous product soluble in water. The solid product of the reaction is lithium imide (comp. **C**). From the facts mentioned above, it may be concluded that the compound **B** is the lithium amide, which decomposes as follows:

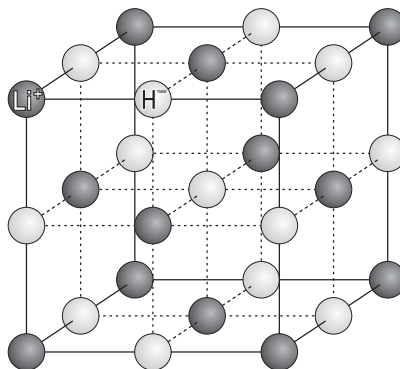


Thus, compound **A** is LiH, which is stable at 350°C (experiment 1), but readily reacts with NH₃ in experiment 2:



Reaction (6) explains formation of salt **C** (Li₂NH) and the lack of ammonia in gaseous products.

- e*) Since the compound **A** (LiH) is isotopic with sodium chloride, the unit cell can be drawn as presented below:



SOLUTION OF PROBLEM 3

A. The rate of adsorption is higher than the rate of decomposition on a catalyst surface. Hence, the system is able to reach the equilibrium of adsorption; the surface coverage is given by the Langmuir isotherm equation.

a1. This results in a following kinetic equation (we exclude in this case the adsorption of products).

$$v = k\theta_{NH_3}$$

$$v = k \frac{K_{NH_3} p_{NH_3}}{1 + K_{NH_3} p_{NH_3}}$$

If the ammonia pressure is high, then $K_{NH_3} p_{NH_3} \gg 1$, hence

$$\frac{K_{NH_3} p_{NH_3}}{1 + K_{NH_3} p_{NH_3}} \cong 1$$

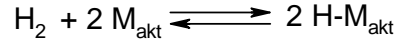
The kinetic equation takes a simplified form:

$$v = k$$

a2. This is a zero order reaction.

B. The dissociative adsorption of hydrogen can be interpreted as a reversible reaction of H_2 molecules with active sites of a catalyst producing adsorbed atoms.

b1. The reaction is represented by the chemical equation:



b2. The dissociative adsorption is characterized by the equilibrium constant.

$$K_d = \frac{\theta_H^2}{p(1-\theta_H)^2}$$

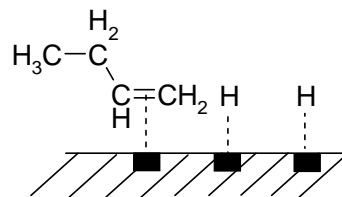
b3. It transforms into the following expression:

$$\pm \sqrt{K_d p} = \frac{\theta_H}{1-\theta_H}$$

Only the positive root has the physical sense as in this case $\theta_H \in \langle 0,1 \rangle$. Further transformations lead to the isotherm equation:

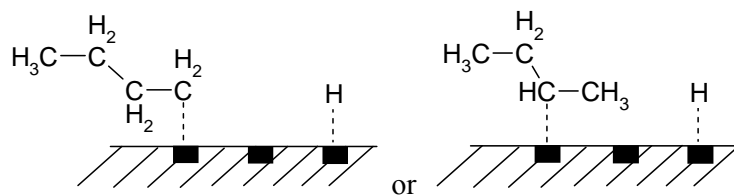
$$\theta_H = \frac{\sqrt{K_d p}}{1 + \sqrt{K_d p}}$$

c1. Step 2.



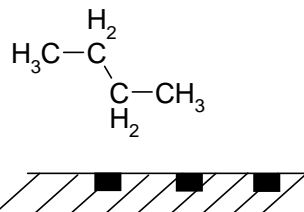
Dissociative adsorption of hydrogen.

Step 3.



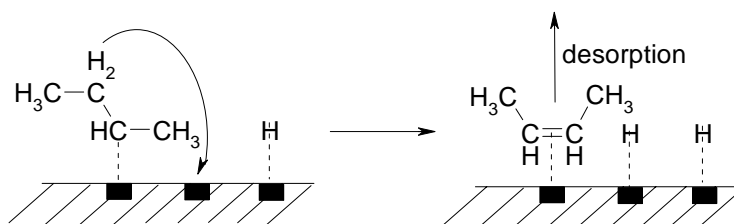
Addition of single hydrogen atom to the double bond of but-1-ene and formation of an adsorbed semi-hydrogenated form (primary or secondary).

Step 4.



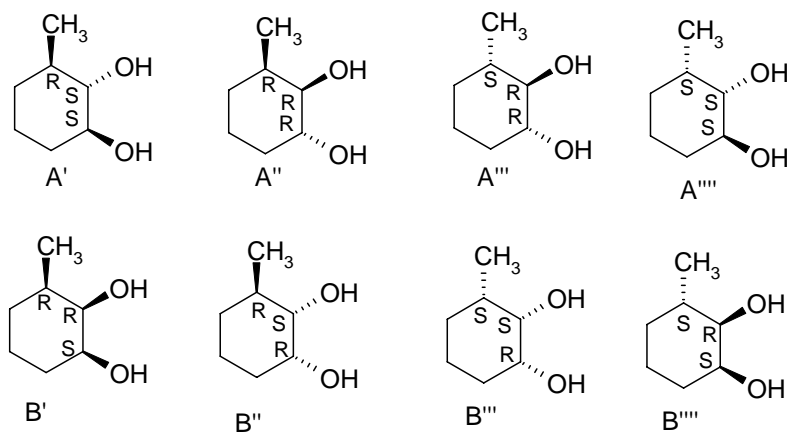
Addition of a second hydrogen atom and formation of butane.

c2. Elimination of a hydrogen atom from an adsorbed semi-hydrogenated secondary form gives but-2-ene (*E* or *Z*), which subsequently undergoes desorption.

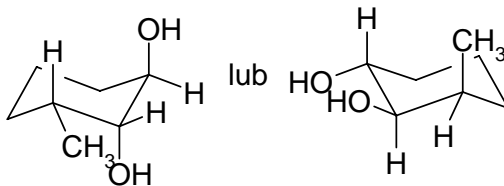


SOLUTION OF PROBLEM 4

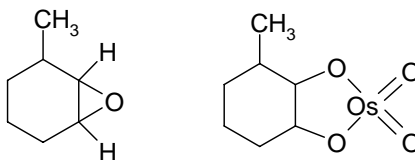
a1. and a2.



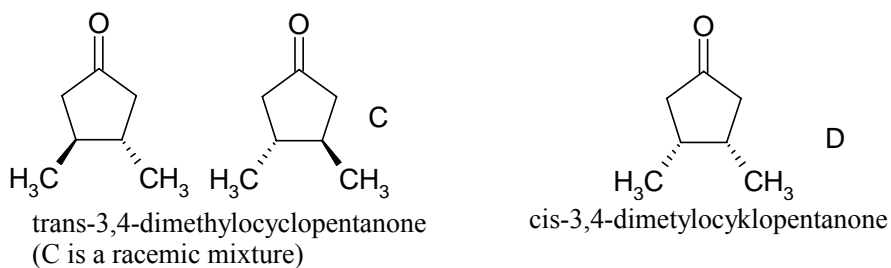
a3.



a4.

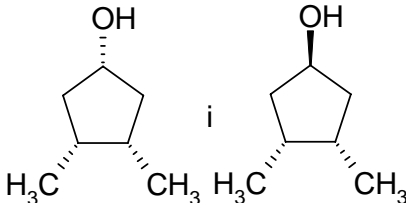


b1.



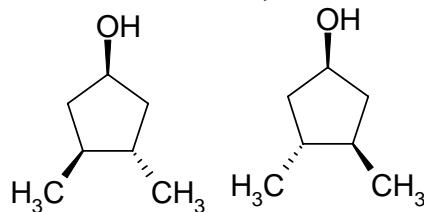
Reduction of the isomers leads to following alcohols.

Reduction of isomer D gave two distinct compounds in ^1H NMR



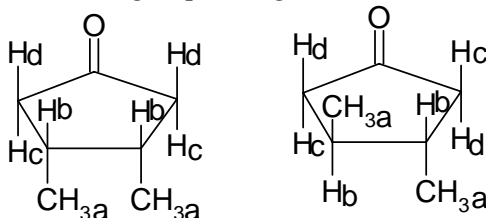
two diastereoisomers

Isomer C gave mixture of two enantiomers, which have the same ^1H NMR spectra.

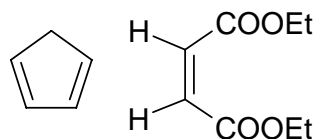


enantiomers (non-distinct in ^1H NMR)

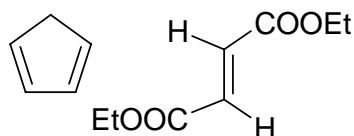
b2. Isomers cis and trans, both show 4 groups of signals in ^1H NMR spectra.



c. Compound E was obtained using reagents depicted below:

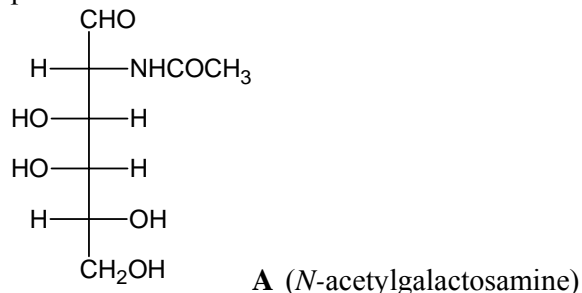


Whereas compound F was obtained using following reagents:

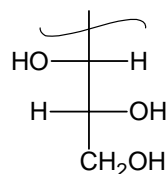


SOLUTION OF PROBLEM 5

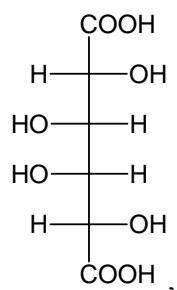
a1. In the Tollens reaction the aldehyde group is oxidized to the carboxylic one. The structure of the product of the silver mirror test is known, so the structure of compound **A** must be as presented bellow:



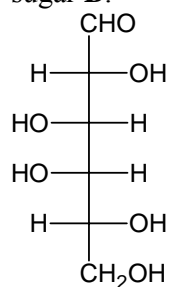
a2. The product of the doubled degradation of sugar **B** is D-threose, so the structure of the terminal fragment is as followed:



Sugar **B** is oxidized to the optically inactive aldaric acid in the presence of nitric acid. An aldaric acid is optically inactive when it has the plane of symmetry. There is only one structure of the aldaric acid with the plane of symmetry for given above terminal fragment of the molecule:

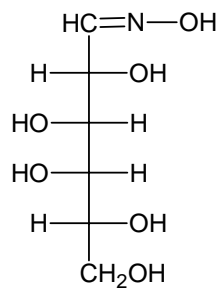


Because the structure of the aldaric acid is known, it is possible to determine the structure of sugar **B**:



B (galactose)

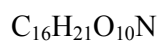
The product of the reaction of sugar **B** with hydroxylamine is an oxime **X**:



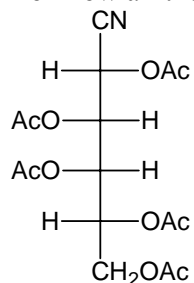
X

Molecular formula of compound **Y** is:

$$\text{C} : \text{O} : \text{N} : \text{H} = \frac{49,6}{12} : \frac{41,3}{16} : \frac{3,6}{14} : \frac{5,5}{1} = 4,13 : 2,58 : 0,26 : 5,5 = 16 : 10 : 1 : 21$$

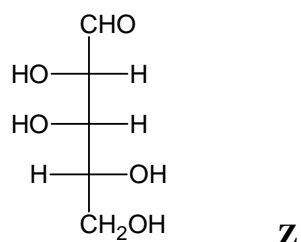


The number of carbon and oxygen atoms show that all hydroxyl groups were acetylated in the reaction with acetyl anhydride. Dehydration of oxime group into the nitrile was also observed. To know all those data we can determine the structure of compound **Y**:



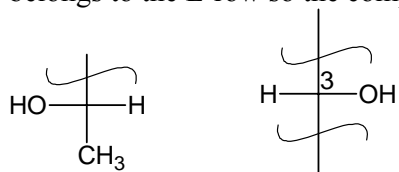
Y

Sugar **Z** is one carbon atom shorter than parent sugar **B**, so its structure must be as followed:

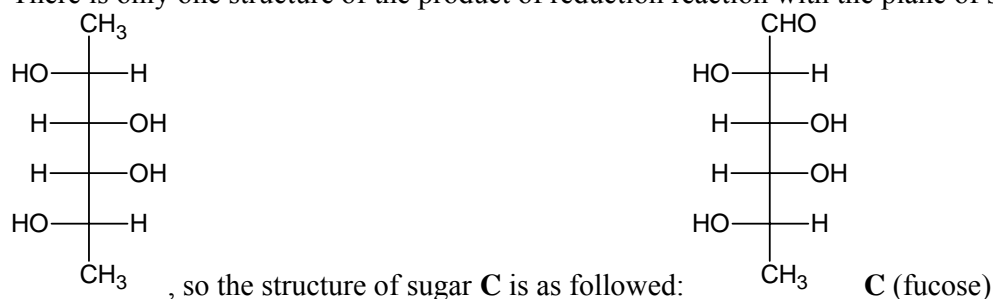


a3. In the reduction reaction CHO group is converted into CH₃ and *meso* compound is formed. It means that the last carbon atom of parent sugar **C** is incorporated in CH₃ group. It was proven by reaction with HIO₄, because CH₃CHO was identified as one of the products.

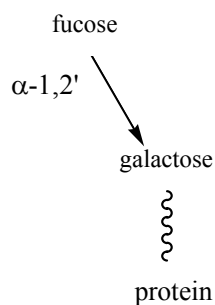
The absolute configuration of the third carbon atom (C-3) was assignment as *R* and sugar belongs to the L-row so the compound has to contain fragments presented below:



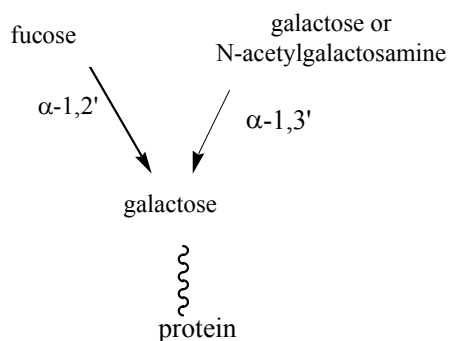
There is only one structure of the product of reduction reaction with the plane of symmetry:



b. General scheme of saccharide connections:

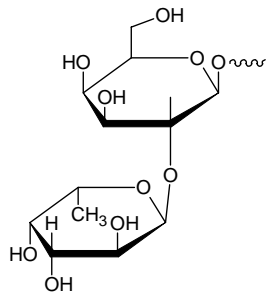


Blood type 0

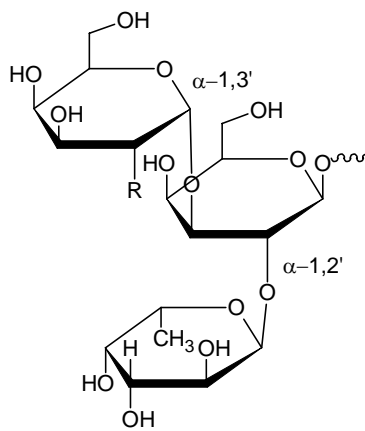


Blood type A or B

Saccharides in the blood group 0:



Saccharides in the blood groups A and B:



Blood group A: substituent R= NHCOCH₃

Blood group B: substituent R= OH