

52 International Chemistry Olympiad



52nd IChO 2020
International Chemistry Olympiad

Russian Training Olympiad Theoretical tour

Department of Chemistry, Moscow State University Lomonosov
November 23, 2019

60 Points total
5 hours

2019 Camp Page

<http://www.chem.msu.ru/rus/olimpiad/intl-winter-2019/>

Original questions (in Russian) can be found at the following link:

<http://www.chem.msu.ru/rus/olimpiad/intl-winter-2019/theor-olymp.pdf>

Solutions can be found at the following link:

<http://www.chem.msu.ru/rus/olimpiad/intl-winter-2019/theor-olymp-resh.pdf>

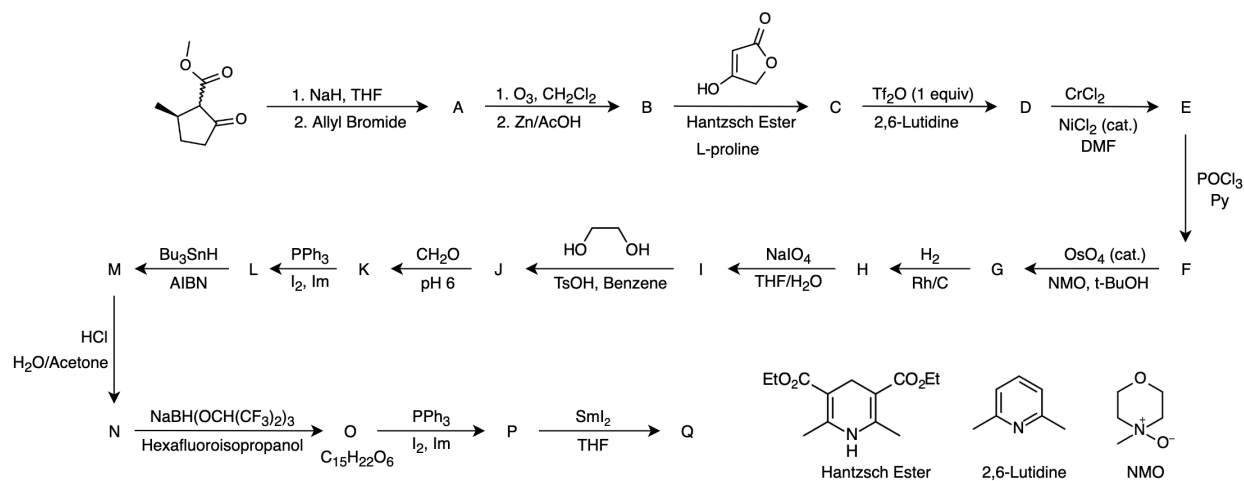
Results of the theoretical exam can be found at the following link:

<http://www.chem.msu.ru/rus/olimpiad/intl-winter-2019/rezultat.pdf>

Task 1. Synthesis of a terpenoid (10 points)

Question	1	2	3	Amount
Total	17	1	2	20
Earned				

Shown below is the total synthesis of one fragment of a terpenoid, carried out in 2006 by a group of Swiss scientists.



1. Identify unknown substances **A – Q**, if it is known that the Hantzsch ester in the third step reduces the Knoevenagel condensation product.

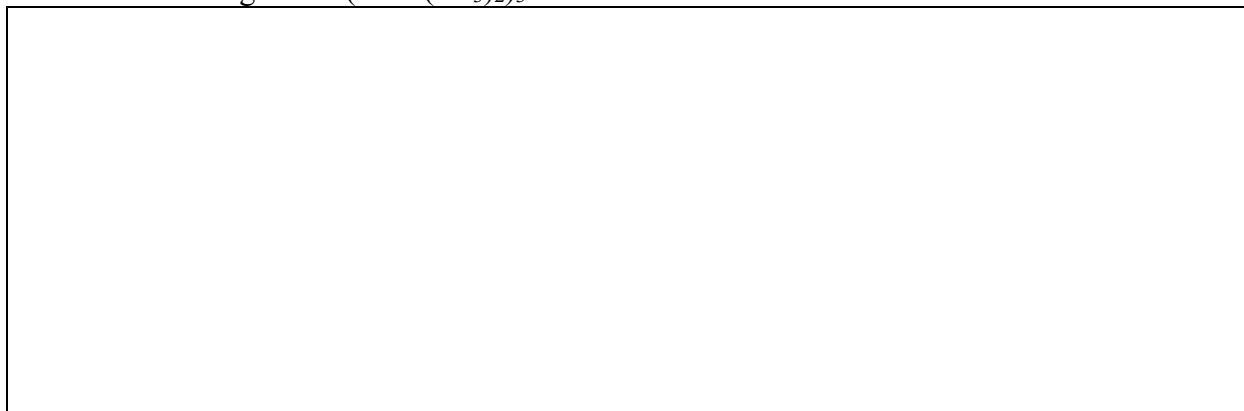
2. In the **N**→**O** step, a rather specific reducing agent is used. Why can't more common borohydride reducing agents (i.e. $NaBH_4$, $NaBH_3CN$, $NaBH(OAc)_3$) be used instead?

3. Propose a mechanism for **D**→**E**.

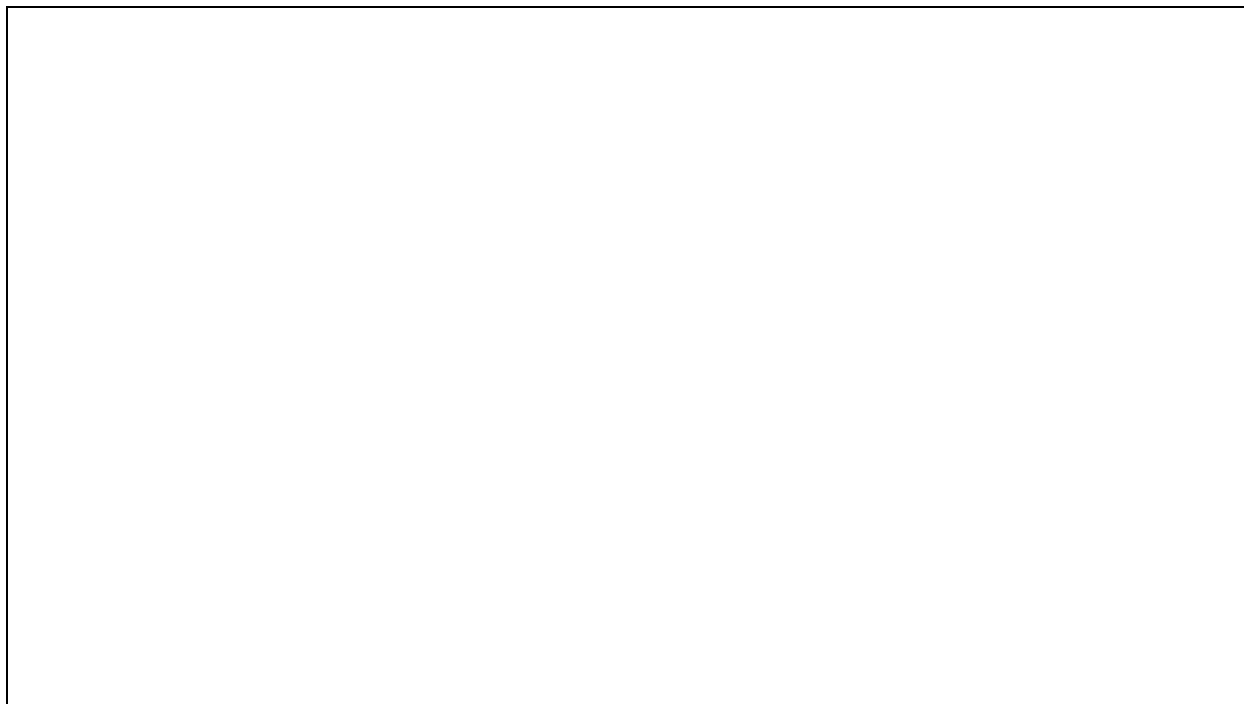
Answer Form*Write structural formulas below*

A	B	C
D	E	F
G	H	I
J	K	L
M	N	O
P	Q	

2. Reason for using $\text{NaBH}(\text{OCH}(\text{CF}_3)_2)_3$



3. Mechanism for **D** → **E**



Task 2. Uranium hydride (8 points)

Question	1	2	3	Amount
Total	3	1	4	8
Earned				

Uranium forms the stoichiometric hydride UH_3 , which decomposes on heating into its elements. The temperature dependence of the equilibrium pressure of hydrogen over a mixture of solid uranium and UH_3 has the following form:

$$\ln p_{\text{H}_2} = 69.32 - \frac{14.64 \cdot 10^3}{T} - 5.65 \ln T$$

where pressure is expressed in pascals and temperature in kelvins.

1. Calculate ΔG° , ΔH° , ΔS° of the reaction $2\text{UH}_3(\text{s}) \rightleftharpoons 2\text{U}(\text{s}) + 3\text{H}_2(\text{g})$ at 500 K.

2. Calculate the heat capacity of uranium hydride at the same temperature.

Reference information: $C_p(\text{U}(\text{s})) = 27.67 \text{ J}/(\text{mol}\cdot\text{K})$, $C_p(\text{H}_2(\text{g})) = 29.26 \text{ J}/(\text{mol}\cdot\text{K})$.

It turned out that uranium deuteride (UD_3) has slightly different thermodynamic characteristics, which makes it possible to use uranium to separate and enrich mixtures of hydrogen and deuterium. The separation coefficient for UD_3 is:

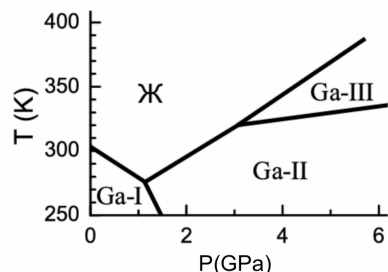
$$S = \frac{(n_{\text{D}}/n_{\text{H}})_{\text{g}}}{(n_{\text{D}}/n_{\text{H}})_{\text{s}}} = 1.33$$

where n_{D} and n_{H} are the number of deuterium and hydrogen atoms in the corresponding phase.

3. Hydrogen gas containing equal amounts of protium and deuterium atoms was introduced into an evacuated 30 ml vessel containing solid uranium such that the final pressure was 1 atm at 298 K. After heating to 600 K and establishing equilibrium, the solid phase was a mixture of U and $\text{UH}_{1.64}\text{D}_{1.36}$, and the gas was an equilibrium mixture of H_2 , HD, and D_2 . The equilibrium constant of the reaction $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ at 600 K is 3.73. Calculate the molar fractions of protium and deuterium atoms and the amounts of H_2 , HD, and D_2 in the gas phase.

Task 3. Phase diagram of gallium (5 points)

Question	1	Amount
Total	5	5
Earned		



At moderate temperatures, gallium can exist in the form of four condensed phases: liquid and three solid, indicated as Ga-I, Ga-II and Ga-III in the phase diagram. In the vicinity of the triple point g - Ga-I - Ga-II (with coordinates 277 K and 1.24 GPa), the pressure (in GPa) of the equilibrium phase transition on temperature (in K) has the form:

$$\text{Ж} - \text{Ga-I} \quad p = 1.24 - 0.0856 (T - 277)$$

$$\text{Ж} - \text{Ga-II} \quad p = 1.24 + 0.0657 (T - 277)$$

$$\text{Ga-I} - \text{Ga-II} \quad p = 1.24 - 0.0143 (T - 277)$$

Calculate ΔH of the Ga-I \rightarrow Ga-II phase transition. The gallium melting enthalpy at normal pressure is 5.59 kJ / mol.

Problem 4. Kinetics of Ester Hydrolysis (8 points)

Question	1	2	3	4	5	6	Amount
Total	1	2	1	1.5	1	1.5	8
Earned							

Esters are hydrolyzed in an aqueous medium, and this process is catalyzed by both acids and bases.

1. Write down the equations for the hydrolysis of R_1COOR_2 ester in the presence of acid and base.

The table shows the dependence of the concentration of methyl acetate in water on time. The initial solution was obtained by mixing ~ 20 ml of ester ($\rho_{ester} = 0.933$ kg/L), 980 ml of water and a catalytic amount of sulfuric acid (pH ~ 2, maintained constant, neglect the volume of acid).

Time (min)	10	150	400	720	1010
[MeCOOMe], M	0.269	0.246	0.211	0.173	0.144

2. Determine the reaction order in ester and calculate the effective rate constant (with units)

Note: calculate k_{obs} for each point, and then average.

Order in Ester = _____

$k_{obs} =$ _____

When methyl acetate is replaced by methyl butyrate ($C_4H_7O_2CH_3$) 25 ml of ether, ($\rho_{ester} = 0.90$ kg /L), 975 ml of water and acid), the situation changes qualitatively: in the first 14.5 hours, the concentration of ester in water was found to be 0.157 M and does not change, and then decreases.

3. Briefly explain why this occurs

4. Calculate the rate constant of hydrolysis of methyl butyrate, as well as its concentration a day after the start of the experiment.

If the pH of the solution is ~ 1.5 , the concentration of methyl butyrate remains constant for 4.5 hours.

5. How does the observed rate constant depend on the acidity of the medium?

$k_{obs}([H^+]) =$

Upon hydrolysis of methyl acetate in the presence of a base (50% excess), the following data were obtained:

Time, min	0	0.5	1	1.75
[MeCOOMe]	0.500	0.338	0.246	0.165
r , M/s	$7.39 \cdot 10^{-3}$	$3.91 \cdot 10^{-3}$	$2.4 \cdot 10^{-3}$	$1.35 \cdot 10^{-3}$

6. Find the reaction order of ester in this case and calculate the rate constant (with units)

Order in Ester = _____

k_{obs} = _____

Problem 5. Structures of Oligosaccharides (8 points)

Question	1	2	3	4	5	Amount
Total	3	6	6	3	8	26
Earned						

In the chemistry of carbohydrates, various approaches have been developed to establish the structure of oligosaccharides, mainly using the size of the rings in monosaccharide residues and the positions through which they are connected to each other. One method is exhaustive methylation followed by hydrolysis of all glycosidic bonds.

1. What position should the monosaccharide residue be in the oligosaccharide if, as a result of complete methylation and subsequent hydrolysis, a methyl derivative of the monosaccharide is formed in which:

- A) there is not a single non-methylated alcohol group (not counting the hemiacetal hydroxyl)
- B) one unmethylated alcohol group
- C) two unmethylated alcohol groups?

A)	_____
B)	_____
C)	_____

Trisaccharide **X** consists of sequentially (from left to right) connected units **A**, **B** and **C**. Complete methylation of **X** and its subsequent hydrolysis lead to 2,3,4,6-tetra-O-methyl-D-glucose, 3,4,6-tri-O-methyl-D-glucose and 1,2,3,6-tetra-O-methyl-D-galactose. The data obtained do not allow an unambiguous conclusion about the structure of **X**.

2. Draw all possible structures of **X** corresponding to the set of products described above. Note that all linkages in **X** are β -glycosidic bonds.

To unambiguously determine the structure, **X** was previously subjected to reduction, followed by complete methylation and hydrolysis. The result was 2,3,4,6-tetra-O-methyl-D-glucose, 3,4,6-tri-O-methyl-D-glucose and 1,2,3,5,6-penta-O-methyl-D-galactitol (galactitol is a product of galactose reduction).

3. Draw 1,2,3,5,6-penta-O-methyl-D-galactitol and the final established structure **X**

1,2,3,5,6-penta-O-methyl-D-galactitol	X
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The α -galactosidase enzyme, which cleaves terminal α -galactosyl residues from oligosaccharides, is practically absent in the gastrointestinal tract of most animals and humans which complicates the digestion of compounds such as oligosaccharide **Y**. After treatment of **Y** with α -galactosidase, two products **E** and **F** (which are now easily absorbed by the body) are formed in a 2:1 molar ratio.

F does not react with the Tollens reagent, and with moderate heating in a weakly acidic medium the products **G** and **H** form in an equimolar ratio, with **G** being the main unit of the polysaccharide forming the cell wall of plants. **H** can be formed from **G** in the presence of a dilute base through an enol intermediate. Oxidation of **E** (which belongs to the hexose family) with concentrated nitric acid leads to an optically inactive dicarboxylic acid.

4. Write the equation for the formation of **G** and **H** from **F** (use structural formulas)

5. Draw the structures of **E** and **Y**

E	Y

Problem 6. Cations of hydrides of noble gases (7 points)

Question	1	2	3	4	5	6	Amount
Total	1	2	4	2	3	1	13
Earned							

Noble gas hydride cations (such as HeH^+ , NeH^+ and ArH^+) are of great interest in astrophysics and astrochemistry. It is believed that one of these hydride cations was one of the first diatomic particles that formed after the Big Bang.

1. Which of these cations is being referred to above? Why was it one of the first to form? What particles could be formed simultaneously with it?

More recently, lines corresponding to the vibrational and rotational transitions of the $^{36}\text{Ar}^1\text{H}^+$ isotope have been discovered in the Crab nebula.

2. Suggest mechanisms for the formation and destruction of this particle. Note that the nebula is predominantly composed of atoms of noble gases, H_2 molecules, as well as atoms of some light elements, such as O and C.

It was determined that the vibrational transition energy from the zero to first state for $^{36}\text{Ar}^1\text{H}^+$ is $E_{01} = 2592.7 \text{ cm}^{-1}$, and from the first to the second is $E_{12} = 2473.5 \text{ cm}^{-1}$.

3. Calculate the wave number ω_e and the anharmonicity constant $\omega_e x_e$ for the $^{36}\text{Ar}^1\text{H}^+$ particle. Give your answer in cm^{-1} .

$\omega_e =$	$\omega_e x_e =$
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4. Calculate the energies of the transition from the second to the third vibrational state, E_{23} , and from the third to the fourth, E_{34} . Give your answer in cm^{-1} .

$E_{23} =$	$E_{34} =$
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The dissociation energy of $^{36}\text{Ar}^1\text{H}^+$ in the zero vibrational state is $D_0 = 31,309 \text{ cm}^{-1}$. Compute the dissociation energy if the cation is in the first (D_1) or in the second vibrational state (D_2). What is the wavelength of light that can cause a particle to dissociate in the first or second vibrational state? Give your answers in cm^{-1} and nm respectively.

$D_1 =$	$D_2 =$
$\lambda_1 =$	$\lambda_2 =$

5. Argon has three stable isotopes: ^{36}Ar , ^{38}Ar , ^{40}Ar . The table shows the transition energies from the zero to first vibrational states for various isotopomers of ArH^+ . Determine which isotopes of argon and hydrogen correspond to each of the energies.

E_{01}, cm^{-1}	Ar Isotope	H Isotope
2589.3		
1880.9		
1883.5		
2590.9		
1878.6		

Anharmonic Oscillator Energy

$E_n = \omega_e (n + 1/2) - \omega_e x_e (n + 1/2)^2$, where n is the number of the vibrational level ($n = 0, 1, \dots$)
 ω_e (cm^{-1}) is the wave number, $\omega_e x_e$ (cm^{-1}) is the anharmonicity constant.

The wave number ω_e is inversely proportional to the root of the reduced mass of the molecule, and the anharmonicity constant $\omega_e x_e$ is inversely proportional to the reduced mass μ :

$$\omega_e \sim \frac{1}{\sqrt{\mu}} \quad \omega_e x_e \sim \frac{1}{\mu}$$

Reference Information

$$m(^1\text{H}) = 1.008 \text{ amu}$$

$$m(^2\text{D}) = 2.014 \text{ amu}$$

$$m(^{36}\text{Ar}) = 35.968 \text{ amu}$$

$$m(^{38}\text{Ar}) = 37.963 \text{ amu}$$

$$m(^{40}\text{Ar}) = 39.962 \text{ amu}$$

$$h = 6.626 \cdot 10^{-34} \text{ J}\cdot\text{s}$$

$$c = 2.998 \cdot 10^8 \text{ m/s}$$

Task 7. About zinc and iron (8 points)

Question	A.1	A.2	A.3	A.4	A.5	A.6	B.1	B.2	B.3	B.4	Amount
Total	12	10	16	10	12	2	4	4	26	4	100
Earned											

A. Zinc Hydroxide

The solubility product of zinc hydroxide is $K_{SP} = 1.80 \cdot 10^{-17}$.

A.1. Calculate the molar solubility of zinc hydroxide in water.

A.2. Calculate the pH of a saturated zinc hydroxide solution, without considering the possible formation of complexes.

The standard potentials of the following reactions are given:



A.3. Calculate the formation constant of tetrahydroxozincate

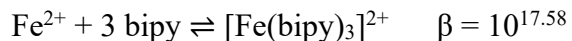
A.4. Calculate the molar solubility of zinc hydroxide at pH = 9.58, not taking into account the possible formation of tetrahydroxozincate.

A.5. Now calculate the molar solubility of zinc hydroxide at pH = 9.58, taking into account the possible formation of tetrahydroxozincate.

A.6. Briefly compare the results from A.4 and A.5

B. Determination of Iron

For the quantitative determination of Fe^{2+} , the formation of its complex with 2,2'-bipyridine (bipy) is often used.



The complex absorbs at $\lambda_{\text{max}} = 520 \text{ nm}$ and its molar absorption coefficient is $\epsilon = 8.377 \cdot 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

For spectrophotometric determination, a cuvette with a thickness of 1.00 cm which was accurate for absorbances between 0.12 and 1.2 was used. The initial concentrations in the solution for measurement until equilibrium were reached were: $c(\text{Fe}^{2+}) = 1.000 \cdot 10^{-4} \text{ mol / L}$ and $c(\text{bipy}) = 2.667 \cdot 10^{-4} \text{ mol / L}$.

B.1. Ignoring the absorbance of uncomplexed Fe^{2+} , will the selected concentrations produce results within the accurate range of the spectrophotometer? Justify with calculation.

B.2. Using the data given, roughly approximate the concentration of the complex without doing any equilibrium calculations.

B.3. Write down the expression for the stability constant, denoting the unknown concentration of the complex as x . The solution to the resulting expression is possible by approximation:

- a) Isolate one of the x terms on the left hand side of your expression (write as $x = \dots$)
 - b) Compute the value of x using an estimated value for x on all terms on the right-hand side and thus produce a new approximate value which you can use to repeat this step until x converges
- Follow the two steps of iteration and thereby try to calculate the concentration of the colored complex with the highest possible accuracy.

B.4. Now calculate the absorbance using the result of part B.3.

Task 8. Lithium fluoride (6 points)

Question	1	2	3	4	Amount
Total	4	1	2	5	12
Earned					

1. Using the data below ($T = 298 \text{ K}$), calculate $E^\circ (\text{Li}^+ (\text{aq}) / \text{Li} (\text{s}))$.

$$\Delta H_f^\circ (\text{LiF}(\text{s})) = -612.1 \text{ kJ/mol}$$

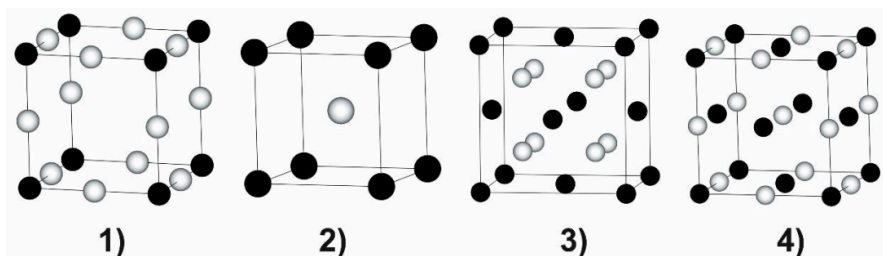
$$E^\circ (\text{F}_2(\text{g})/\text{F}^-(\text{aq})) = 2.87 \text{ V}$$

$$K_{\text{sp}} (\text{LiF}) = 1.7 \cdot 10^{-3}$$

$$\Delta S_r^\circ (\text{Li}(\text{s}) + \frac{1}{2} \text{F}_2(\text{g}) \rightleftharpoons \text{LiF}(\text{s})) = -94 \text{ kJ/K}$$

The change in enthalpy when diluting the solution is neglected.

2. Which of the following unit cells (1-4) could be LiF ? Explain your answer.



3. State the coordination numbers and polyhedra of the cation and anion in the LiF unit cell

The interaction of a lithium fluoride melt with barium titanate produces (among other products) a colorless gas **b**, a binary crystalline substance **B** with a fluorite structure and crystalline substance **A** with a spinel structure. The reflection spectrum of substance **A** contains a band at 430 nm. Dissolving 0.87 g of substance **A** in one liter of water produces a solution with pH approximately 12.

4. Determine the formulas of the unknown substances **A**, **B**, and **b** (justify with calculations) and write the equations of both reactions.