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23rd Chemistry Olympiad of the Baltic States

Daugavpils, Latvia

April 24-26, 2015

University of Daugavpils
http://du.lv/en

University of Latvia
http://www.lu.lv/eng/

JSC OlainFarm
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THEORETICAL EXAMINATION, ENGLISH
(used for clarification only)

"ScientiaVinces"

" Through knowledge you win "

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Introduction

General information

• **You can only start to work once the START command is given.**

• **You are given 5 hours to complete your theoretical work and fill the answer sheets**. You will be notified 15 minutes before the end of theoretical examination. You must stop working once the “STOP” signal is given. If you are late 5 min or more, your work will be disqualified and you will be given 0 points for theoretical examination.

• **Write your code** (found on your working place, same as yesterday) **in designated areas on ALL of your answer sheets.**

• All results should be written in boxed areas in answer sheets. Information written in other parts of answer sheets will not be graded.White sheets provided are draft papers and it will not be graded. If you need more draft paper just ask assistants.

• Ask assistant if you need English version of problems. It can be used for clarification only.

• Do not leave the examination room without permission.

• Number of decimal places in calculations must be in accordance with significant figures (±1 significant figure is acceptable) error and data analysis principles. You will be penalized once with minus 1 point for inaccurate calculations in whole theoretical examination, even if your solution are correct in all other aspects.

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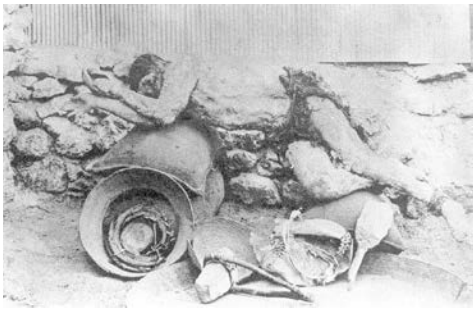
Problem 1. Copper Man (6 points)

"Copper Man" was a Chilean copper miner who was entrapped in a copper mine in 550 AD and subsequently copperized (coated in copper). The mummy has become a subject of interest in archeology, metallurgy, and more recently, art.



1. Under the right conditions, charcoal dust can promote reaction that could lead to Copper Man's coating. Assume that Copper Man is coated in Cu_2O and Cu^0, which originated from Cu^{2+} salts in the copper mine. State the role of charcoal in this reaction (mark correct answer with X):

   - ☐ reducing agent
   - ☐ oxidizing agent
   - ☐ catalyst
   - ☐ insulator
   - ☐ none of above

2. Consider the following reactions and reduction potentials:

$$Cu_2O + 2H^+ + 2e^- \rightarrow 2Cu + H_2O \qquad E^0_{red} = 0.471 - 0.059(pH)$$

$$CuO + 2H^+ + 2e^- \rightarrow Cu + H_2O \qquad E^0_{red} = 0.570 - 0.059(pH)$$

   a. For neutral (pH =7.0) environment, construct a Latimer diagram for the above couples and calculate the potential for the CuO/Cu_2O.

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3. Chalcanthite, the pentahydrate of copper sulfate, was the mineral that Copper Man was harvesting from the mine.

In order to extract copper from the chalcanthite, Copper Man heated the chalcanthite to >700 °C in the presence of Na_2O, at which point a violent explosion would occur due to the following reactions:

$$4CuSO_4 + 4Na_2O \rightarrow 4Na_2SO_4 + 2Cu_2O + O_2 \qquad \text{React. I}$$

$$Cu_2O + CO \rightarrow 2Cu^0 + CO_2 \qquad \text{React. II}$$

Calculate the Gibbs free change energy for these reactions using the half-reaction standard potentials. (Hint: For $CO_2 + 2e^- \rightarrow CO + O^{2-}$ you can use $E^0_{red} = 0.11$ V, and for $O_2 + 4e^- \rightarrow 2O^{2-}$ you can use $E^0_{red} = 1.23$ V)

ΔG for reaction I:
ΔG for reaction II:

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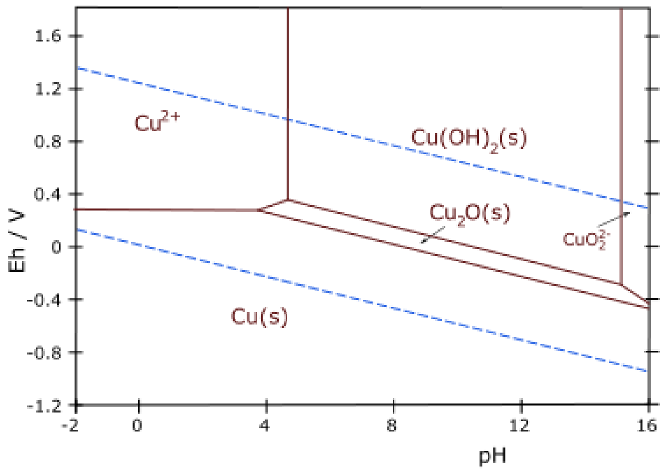
For an exhibition, you must recreate Copper Man using a galvanic cell. Consider thePourbaix diagram of copper.



4. Draw a diagram of a two-compartment galvanic cell that incorporates Copper Man as an electrode in solution X coupled to a metal Y electrode in a solution of same metal ions. Label all components including the electrodes (cathode and anode), the electrolyte species, and the reactions occurring at the electrodes.

a. Choose the main component of the solution X:

- ☐ $CuCl_2$
- ☐ Na_2CuO_2
- ☐ $Cu(OH)_2$
- ☐ CuCl

b. Choose metal Y suitable for copper plating in the galvanic cell?

- ☐ Zn
- ☐ Ag
- ☐ Na
- ☐ Au

c. Draw diagram and write labels here:

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d. Reaction on cathode:

e. Reaction on anode:

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Problem 2. Determination of water content (10 points)

Very small water quantities can be measured with different methods: Karl Fischer titration, nuclear magnetic resonance, infrared spectroscopy, gas chromatography, UV-Vis spectroscopy.

In Karl Fischer titration a mixture of iodine, pyridine (Py), sulfur dioxide and methanol is used. In the presence of water following reactions take place:

$$SO_2 + CH_3OH + H_2O + I_2 \rightarrow 2HI + CH_3OSO_3H$$

$$Py + HI \rightarrow PyH^+I^-$$

$$Py + CH_3OSO_3H \rightarrow PyH^+CH_3OSO_3^-$$

Usually, the limiting component of the reaction is iodine.

As Karl Fischer titrant is somewhat unstable, the practical titre (mass of analyte per volume of titrant) is often determined right before the analyses of a sample. An analyst weighted 260.3 mg of pure water and filled the 100 ml volumetric flask with acetonitrile that does not contain any water. 10.00 ml of the sample was taken for analyses and 6.20 ml of titrant was spent to reach the endpoint.

1.1 Calculate the titre (mg/ml) of the Karl Fischer titrant.

The same titrant was used to determine the water content of commercial acetonitrile. 20.00 ml of the commercial acetonitrile was titrated with 5.12 ml of titrant. Density of acetonitrile is 0.786 g/ml.

1.2 Determine the water content in commercial acetonitrile (% and ppm).

A coulometric Karl Fischer titration is used in a laboratory, where one of the reagents I_2 is generated electrochemically from I^-. It was of interest what the bias of the coulometric titration is. 4.113 g of acetonitrile (containing an unknown amount of water) was analyzed with coulonometric Karl Fischer method and 138.7 C was passed through coulometer (1 C = 1 A·s). 143.2 mg of water was weighted into

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100 ml volumetric flask and filled with the same acetonitrile to mark. 2.714 g of the sample was taken for analyses and 145.3 C was used for complete titration of the sample.

1.3 Calculate the bias for this titration. Faraday constant F = 96500 C/mol.

The same procedure was repeated with 1.356 g of water weighted into 100 ml volumetric flaks. For titrating 1.194 g of this sample 306.7 C was used.

1.4 Calculate the bias for this titration.

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1.5 Explain why can two titrations have a significantly different bias in this case.

Karl Fischer titration can also be used for water determination in solid samples if these can be dissolved in appropriate solvent. However, some building material such as cement, chalk, ceramic materials can not be analysed in this way due to occurring side reactions.

Therefore, infrared spectroscopy was used. Two chalk based reference materials containing 2.1 mg/kg and 17.2 mg/kg of H_2O were measured with attenuated total reflectance (ATR) method. At peak maximum absorptions observed were 0.045 and 0.371 AU (absorption units).

2.1 What side reaction occurs for these materials and how does it influence the bias of Karl Fischer method.

2.2 With IR-ATR method also a chalk sample was analysed and absorbance of 0.276 AU was recorded at the peak maximum. Based on the Lambert–Beer law calculate the water content in the chalk sample. Lamber Beer law: $A=\varepsilon lc$, where A is the absorption at wavelength λ, ε is the molar attenuation coefficient at wavelength λ, l is the optical path length and c is the analyte concentration. Assume that optical path length is the same for all three measured materials.

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Problem 3. Some simple physical chemistry (9 points)

1. An equilibrium is reached in 0.10 M $AgNO_3$ and *x* M $NH_3 \cdot H_2O$ solution:

$Ag^+ + NH_3 \Leftrightarrow [Ag(NH_3)]^+$, $K_1 = 2.09 \cdot 10^3\ M^{-1}$

$[Ag(NH_3)]^+ + NH_3 \Leftrightarrow [Ag(NH_3)_2]^+$, $K_2 = 8.32 \cdot 10^3\ M^{-1}$

At what *x* the concentration of $[Ag(NH_3)]^+$ is maximal? Calculate the value of *x*.

2. Equal amounts of KIO_3 and KI (0.10 M each) react in a solution of H_2SO_4 at an initial pH value of 3.00.

$\frac{1}{2}I_2 + e^- \Leftrightarrow I^-$ $E_1° = +0.54$ V

$IO_3^- + 6H^+ + 5e^- \Leftrightarrow \frac{1}{2}I_2 + 6H_2O$ $E_2° = +1.20$ V

Calculate the pH value of the solution at equilibrium.

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3. α-halogenation of aldehydes and ketones is autocatalytic reaction, *i.e.* the byproduct H^+ is the catalyst for that reaction:

$$R'COR + X_2 = RCORX + H^+ + X^-$$

The reaction rate is expressed as:

$$r = k[R'COR][X_2][H^+]$$

If the initial concentrations $[R'COR]_0 = [X_2]_0$, at what concentration $[X_2]$ is reached the maximum rate of the reaction? Hint: $d(x^n)/dx = nx^{n-1}$.

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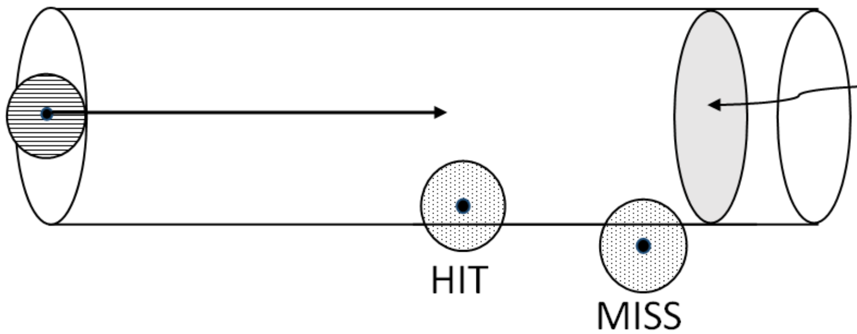
Problem 4. Harpoons and collisions (12points)

When modeling the path of a single atom A, it is useful to use it as a point of reference and "freeze" all the other species in their own places. Therefore, we only have to consider any other particles when they collide with the atom whose path we are modelling. If a centre of another species B is located in such a way that the atom A will hit it, it is said to be in the *collision tube* of the atom A.



1.Given that a golf ball with a radius of 2.3 cm is touching a basketball with a radius of 12.5 cm, calculate the distance between their centres.

2. Hence, calculate the radius (R, in meters) and area (σ, in square meters)of the cross section of the collision tubecreated by a gaseous potassium atom moving through bromine gas. The radius of a potassium atom is 243 pm and the "radius" of a bromine molecule is 165 pm.

The collision tube as a model is used in the kinetic theory of gases. By applying this model, a useful equation for the rate constant of second order reactions can be obtained:

$$k_2 = \sigma \bar{c} N_A e^{-\frac{E_A}{RT}},$$

where$\bar{c}$ is the average effective velocity of the gas molecules. The pre-exponential term describes the number of collisions occurring, while the exponential term describes the proportion of successful collisions

3. Write down the more popular form of this equation and name the scientist who proposed it

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4. A second order reaction has a rate constant of 1000 L mol^{-1} s^{-1}, an effective cross sectional area of the collision tube of 1.0*10^{-18} m^2, and average effective velocity of gas molecules of 100 m s^{-1} in standard conditions. What is the activation energy of the reaction in kJ mol^{-1}?

5. Consider a reaction whose activation energy is 0 J. Mark each correct statement with a + sign and each incorrect statement with a - sign. (Note: each incorrect answer will incur negative marks, with the total for this question not less than 0)

An appropriately selected catalyst would speed up this reaction	
Every reactantatom/molecule has sufficient energy for the reaction	
The reaction enthalpy change has to be zero or negative	
The reactants of such a reaction are likely to be charge free and only contain paired electrons	

6. Referring back to the beginning of the problem, calculate the k (L mol^{-1} s^{-1}) of the reaction between gaseous potassium and bromine at 800°C. Assume that the activation energy of the reaction is 0 J. $\bar{c} = \sqrt{\frac{8k_BT}{\pi\mu}}$, where k_B is the Boltzmann constant (1.38 × 10^{-23} m^2 kg s^{-2} K^{-1}) and μ is the reduced mass of the particles involved ($\mu = \frac{m_1m_2}{m_1+m_2}$).

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However, the measured *k* of the reaction is larger than the calculated value at 1.0×10^{12} L mol^{-1} s^{-1}, which seemingly suggests that *more* species react than actually collide. This is because of the so-called harpoon mechanism – the potassium atom "shoots" an electron into the bromine molecule even before the collision takes place. This occurs due to the fact that the cross-sectional area ignores the effect of the geometry of collisions on the reaction, as it assumes that all collisions in most cases are equal.

7. Assess how the transfer of the electron impacts the size of the particles and thus the cross-sectional area of the collision tube! (Note: each incorrect answer will incur negative marks, with the total for this question not less than 0)

7.1. What is the effect of ionisation of the K atom on its size?

A. It increases, as loss of the charge of one electron weakens the attraction between nucleus and the electron cloud
B. It increases, as loss of the 4s orbital weakens the shielding experienced by other orbitals, thus diffusing them
C. It decreases, as the lost electron is the only one in 4th energy level
D. It decreases, as the volume of the orbital the electron occupies is lost

7.2.What is the effect of electron transfer to the bromine molecule on its size?

A. It increases, as the new electron occupies a bonding molecular orbital
B. It increases, as the new electron occupies a anti-bonding molecular orbital
C. It decreases, as the new electron occupies a bonding molecular orbital
D. It decreases, as the new electron occupies a non-bonding molecular orbital

7.3. What is the net effect of the electron transfer on the cross-sectional area of the collision tube?

A. It increases
B. It decreases
C. Insignificant effect
D. Not enough data to assess

The modified reactive cross section area σ^* which should be used for reactions proceeding by a harpoon mechanism can be calculated from radius R_h^* using equation:

$$\sigma^* = \pi(R_h^*)^2.$$

R_h describes the separation of centres of reacting species. There are three contributions to the energy of interaction between the colliding species: ionization energy of potassium (abbreviated as *I*), electron affinity of bromine gas (E_{EA}) and Coulombic interaction (CI) energy between the ions when they have been formed given by equation:

$$\text{CI} = -\frac{e^2}{4\pi\varepsilon_0 R_h}.$$

R_h^* is a distance when all these three contributions to the energy are in balance and following equation is obeyed:

$$0 = I - E_{EA} + \text{CI}$$

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8. Calculate the radius R_h^* and reactive cross section area σ^*, if it is given that I = 420 kJ·mol^{-1}, E_{EA}= 250 kJ·mol^{-1}, and vacuum permittivity constant ε_0 = 8.854·10^{-12}C^2·N^{-1}·m^{-2} and elementary charge e =1.602·10^{-19}C.

Usually to describe such a reactions a steric factor P is introduced, which connects reactive cross section area σ^* with collision cross section area σ so that $\sigma^* = P\sigma$.

9. Calculate the steric factor P:

10. Now calculate the k (in L mol^{-1} s^{-1}) of the same reaction at 800°C using σ^* instead of σ:

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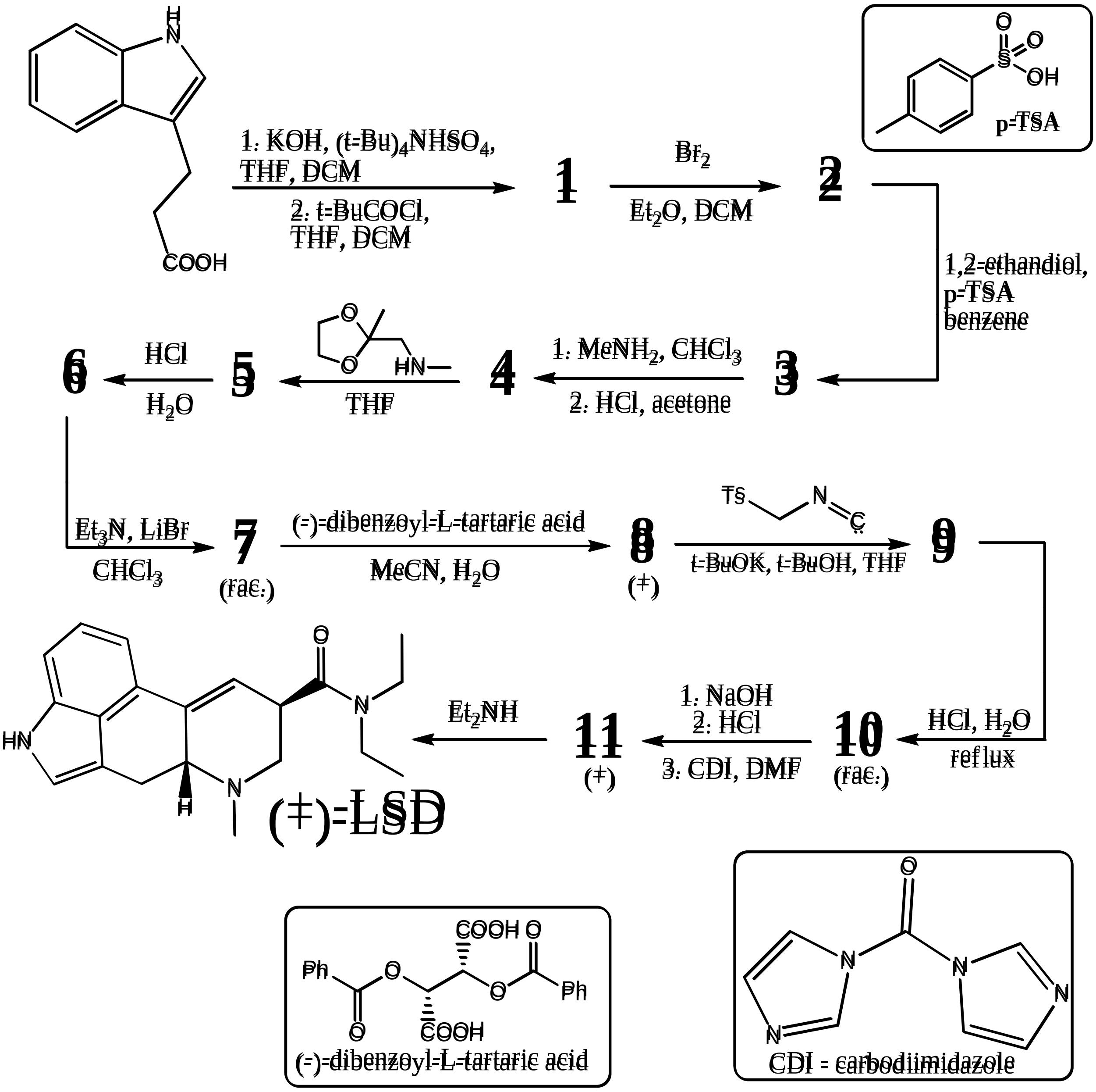
Problem 5. “Lucy in the Sky with Diamonds”(12points)

Back in the days of 1967, this famous song by the Beatles was released. It did not take long for hippies to notice that an abbreviation would be *LSD*. This, one of the most widely known chemical substances was first synthesized even earlier – in 1938 by a Swiss chemist Albert Hofmann and up to around 1980 it was used as a psychiatric drug or for research purposes.

Today you will have a chance to synthesize (on paper!) this highly biologically active compound, that boasts of a tetracyclic carboskeleton. Such an arrangement was and still is quite problematic if one tries to come up with a synthesis route from very simple starting materials, hence you will begin your synthesis from already bicyclic indole-3-propionic acid.



Hints: compound **1** is known to be tricyclic; compound **7** is known to be tetracyclic; (rac.) denotes *racemate*, compound **9** has one stereocenter.

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1. Draw structures of compounds (do not forget stereoisomerism, where necessary) **1-11**.

1	2	3
4	5	6
7	8	9
10	11	

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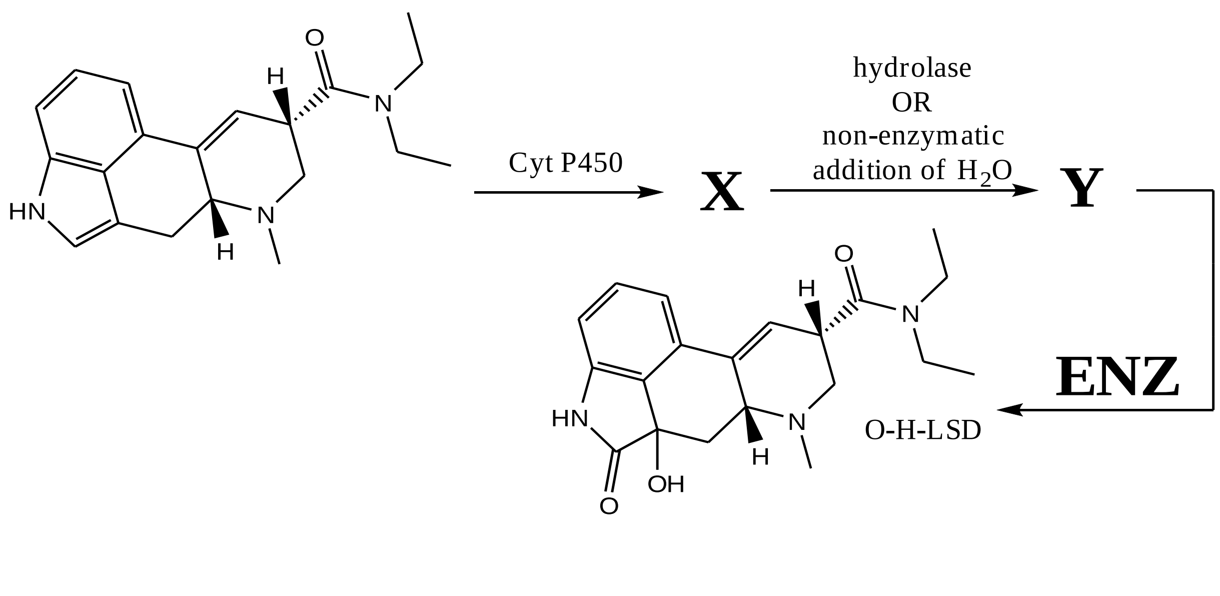
2. Draw reaction mechanism of **8** + $TsCH_2NC$: → **9**.

From a biochemical standpoint, lysergic acid diethylamide binds to the serotonin receptors in the body, but the hallucinogenic effect lasts for up to 6-8 hours, meaning that it's metabolism is quite fast. Studies have shown that metabolism in human organisms proceeds through *O-H-LSD* intermediate. A mechanism of *O-H-LSD* formation was proposed, but it seems that some information is missing.



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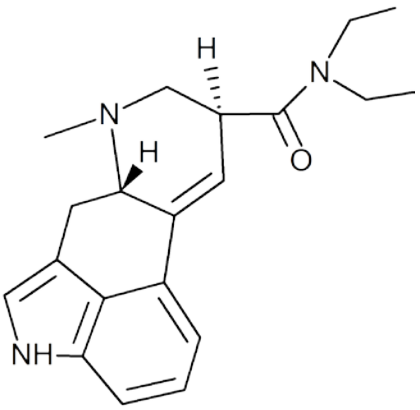
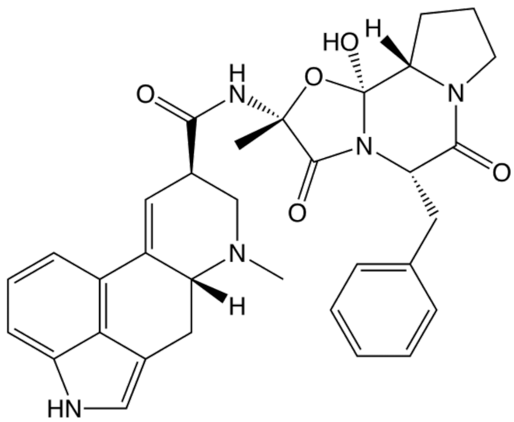
3. Decipher structures **X** and **Y** and suggest an enzyme (**ENZ**) for the final step. It is known, that **ENZ** should belong to Oxidoreductases. *Note:The substrate of the enzyme is not supposed to be specified, e.g. the answers deaminase or oxidase is specific enough.*

X	**Y**
ENZ	

Biochemists have shown that LSD and its precursor ergotamine ERG bind the same serotonin receptor to it's active site.

4. Taking into account that LSD and ERG bind the same receptor site, outline physiologically active part in each molecule.

 **LSD molecule** (depicted geometry is similar to geometry in 3D)	 **ERG molecule**

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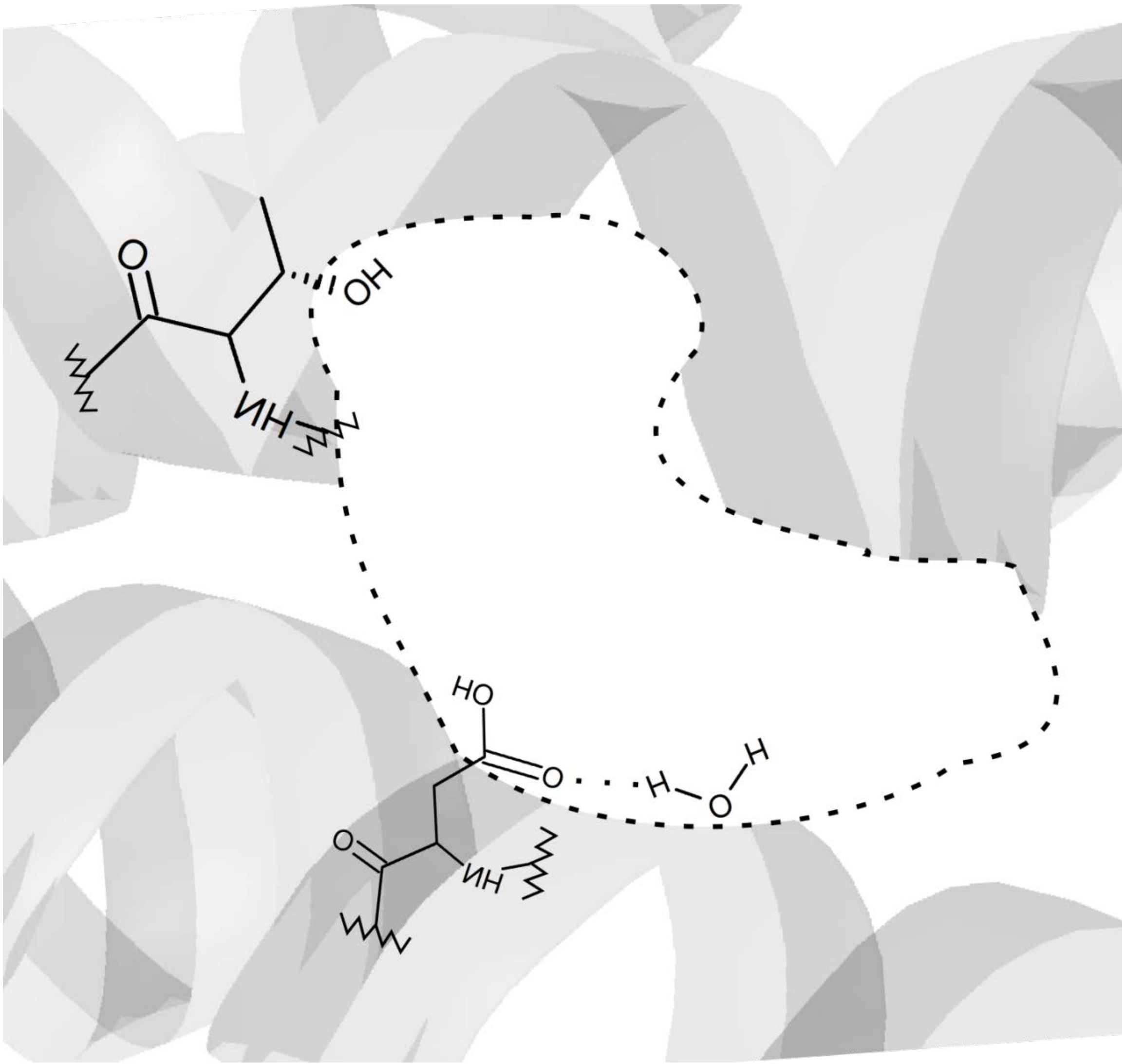
5. Fit LSD molecule into the active site of serotonin receptor and show molecular interactions.



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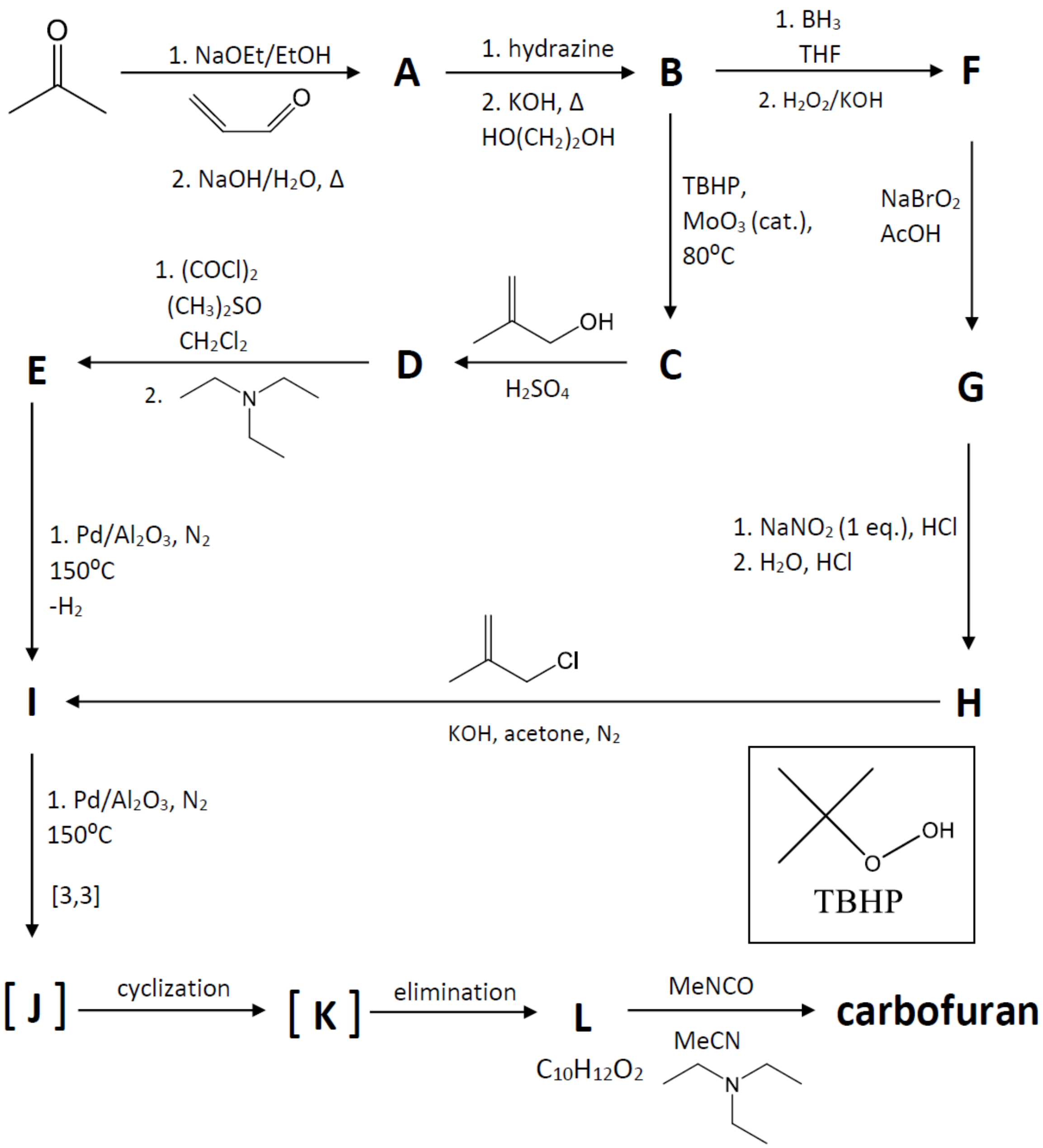
Problem 6. Easy grow, easy bloom (11points)

Carbofuran is one of the most toxic insecticides and, therefore, is banned in Canada and European Union. However, this pesticide is still widely used in other countries to control the amount of insects in potato, pumpkin, sunflower fields.

Carbofuran can be produced quite easily from many simple chemical substances, but the main drawbacks of these processes are the expense of production and the toxicity of chemicals involved in the syntheses. Although, in 1980s several alternative methods for carbofuran production were invented, which are relatively safe and require cheap starting materials (acetone in this case).The synthesis scheme of carbofuran, bicyclic compound, is given below.

(*cat.*) – catalyst, (*eq.*) – equivalent



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1. Draw the structures of compounds **A** and **B** and the mechanism of the reaction **A** → **B**.

A	**A** → **B**
B	

2. Draw the structures of **C** and **D**(**D** is a mixture of stereoisomers). Also write down all possible compound **D**stereoisomers,which can be produced in the reaction **C** → **D**, mark all the streocenters with '*' and indicate their configuration (R/S).

C	Stereoisomers of **D**
D	

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3. Draw the structure of compound **E**. Taking into account that the reaction **D** → **E** was carried out using only enantiomerically pure compound **D'**(one of **D** stereoisomers)with all the stereocenters having only R configuration,draw the stereoisomer(-s) of compound **E** which would be synthesized in the reaction **D** → **E**.

E	Stereoisomer(-s) of **E**

4. Write down the structures of compounds **F**, **G**, **H** and **I**.

F	**G**	**H**	**I**

5. Show the mechanism of the reaction **G** → **H**.

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6. Compound **E** heated with Pd/alumina catalyst in nitrogen atmosphere produces intermediate**I** which further heated under the same conditions gives more stable compound**J**and then, bicyclic compound**K**. These intermediates are not extracted in this synthesis but are further heated to produce compound **L**. Draw the structures of compounds **J**, **K** and **L**.

J	**K**	**L**

7. Write down the systematic name for the compound **J** using IUPAC nomenclature.

8. In the reaction from **J** to **K** a second ring is formed. How thisring could be named separately?
A) oxyfurane
B) dehydrofurane
C) benzofurane
D) dihydrofurane
E) ketofurane

9. Finally, the last step gives us the final product, carbofuran. Draw the structure of carbofuran.

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hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 * *	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

*Lanthanide series	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
* *Actinide series	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]