

24th Baltic Chemistry Olympiad



Theoretical Problems

1	2	3	4	5	6

9 April 2016
Tartu, Estonia

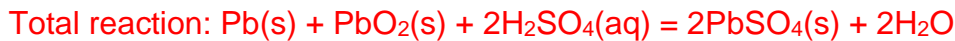
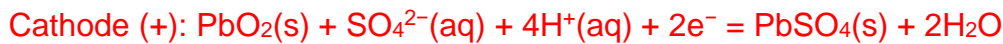
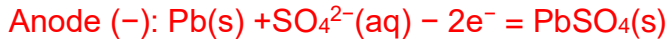
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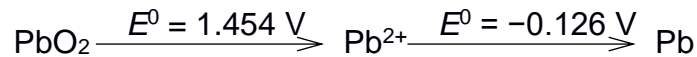
Problem 1. Lead-Acid Battery (10 points)

The lead-acid rechargeable battery is still one of the most common batteries used in cars at the beginning of 21st century. It has some superior characteristics, and it could be almost completely recycled. During the discharge process lead of one electrode and lead(IV) oxide of the other electrode is converted into lead sulphate. The sulphuric acid is used as the electrolyte.

- a) Write the anode, cathode and total reactions of the lead-acid battery during the discharge process.

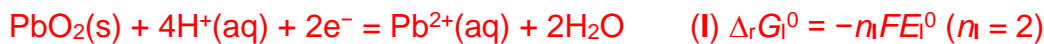


The solubility product of PbSO_4 is $K_{\text{sp}} = 1.6 \cdot 10^{-8}$. The Latimer diagram of lead (in acid) is:

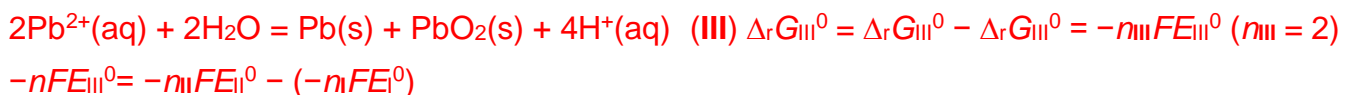


- b) Is the disproportionation reaction of lead(II) ions spontaneous process? Justify the answer using calculations.

Half reactions:



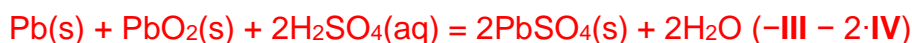
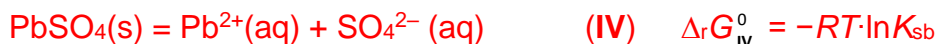
Disproportionation reaction of lead(II) ions:



$$E_{\text{III}}^0 = E_{\text{II}}^0 - E_{\text{I}}^0 = -0.126 \text{ V} - 1.454 \text{ V} = -1.580 \text{ V} < 0 \quad (\Delta_r G_{\text{III}}^0 \gg 0)$$

The disproportionation reaction of lead(II) ions **is not spontaneous**.

- c) Calculate the open circuit potential E_{cell}^0 of **one cell** of the fully charged battery.



$$\Delta_r G^0 = -(\Delta_r G_{\text{III}}^0 + 2 \Delta_r G_{\text{IV}}^0) = -n F E_{\text{cell}}^0 \quad (n = 2)$$

$$-n F E_{\text{cell}}^0 = n_{\text{III}} F E_{\text{III}}^0 + 2 RT \cdot \ln K_{\text{sb}}$$

$$E_{\text{cell}}^0 = -(n_{\text{III}}/n \cdot E_{\text{III}}^0 + 2 RT/(nF) \cdot \ln K_{\text{sb}})$$

$$E_{\text{cell}}^0 = -[2/2 \cdot (-1.580 \text{ V}) + \frac{2 \cdot 8.314 \text{ J}/(\text{mol} \cdot \text{K}) \cdot 298.15 \text{ K}}{2 \cdot 96485 \text{ C/mol}} \ln(1.6 \cdot 10^{-8})] = \mathbf{2.041 \text{ V}}$$

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- d) Calculate the open circuit potential (E_{cell}) of **one cell** of the fully charged lead-acid battery (at 25°C) which contains sulphuric acid with density 1.275 g/cm³.

	%wt	$\rho / \text{g cm}^{-3}$	%wt	$\rho / \text{g cm}^{-3}$	%wt	$\rho / \text{g cm}^{-3}$
$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{2F} \ln \frac{1}{[\text{H}_2\text{SO}_4]^2} = E_{\text{cell}}^0 + \frac{RT}{F} \ln [\text{H}_2\text{SO}_4]$	2	1.0104	34	1.2479	66	1.5602
$[\text{H}_2\text{SO}_4] = E_{\text{cell}}^0 + 0.02569 \text{ V} \cdot \ln [\text{H}_2\text{SO}_4]$	4	1.0234	36	1.2647	68	1.5829
$\%_{\text{wt}}(\text{H}_2\text{SO}_4) = 36 + \frac{38 - 36}{(1.2818 - 1.2647) \text{ g/cm}^3} \cdot (1.275) \text{ g/cm}^3 = 37.20$	6	1.0367	38	1.2818	70	1.6059
$[\text{H}_2\text{SO}_4] = \frac{100 \text{ g} \cdot 0.3720}{98.08 \text{ g/mol} \cdot \frac{1 \text{ dm}^3}{1000 \text{ cm}^3}} = 4.836 \text{ M}$	8	1.0502	40	1.2991	72	1.6292
$E_{\text{cell}} = 2.041 \text{ V} + 0.02569 \text{ V} \cdot \ln 4.836 = 2.081 \text{ V}$	10	1.0640	42	1.3167	74	1.6526
	12	1.0780	44	1.3346	76	1.6761
	14	1.0922	46	1.3530	78	1.6994
	16	1.1067	48	1.3719	80	1.7221
	18	1.1215	50	1.3911	82	1.7437
	20	1.1365	52	1.4109	84	1.7639
	22	1.1517	54	1.4310	86	1.7818
	24	1.1672	56	1.4516	88	1.7968
	26	1.1829	58	1.4726	90	1.8091
	28	1.1989	60	1.4940	92	1.8188
	30	1.2150	62	1.5157	94	1.8260
	32	1.2314	64	1.5378	96	1.8305

The open circuit potential of one cell of a lead-acid battery is $E_{\text{cell}}^0 = 2.033 \text{ V}$ at 5 °C.

- e) Calculate the temperature coefficient (dE_{cell}^0/dt) of one cell of the lead-acid battery in this temperature region.

$$dE_{\text{cell}}^0/dt = (2.041 \text{ V} - 2.033 \text{ V}) / (25 \text{ °C} - 5 \text{ °C}) = 0.0004 \text{ V/°C} = +0.4 \text{ mV/°C} > 0$$

At higher temperature the open circuit potential is higher.

- f) Calculate the reaction enthalpy of the discharging process in the battery.

$$\ln K = nFE_{\text{cell}}^0/RT$$

$$\ln K_{25 \text{ °C}} = 2 \cdot 96485 \text{ C/mol} \cdot 2.041 \text{ V} / (8.314 \text{ J/(mol}\cdot\text{K)} \cdot 298.15 \text{ K}) = 159$$

$$\ln K_{5 \text{ °C}} = 170$$

$K_{5 \text{ °C}} > K_{25 \text{ °C}}$ – at higher temperature the equilibrium is shifted towards reagents

The reaction is exothermic ($\Delta_r H^0 < 0$) according to the Le Chatelier' principle.

- g) During the discharging of the battery:

- The temperature of the battery increases;
- The temperature of the battery decreases;
- The temperature of the battery does not change;
- The water could evaporate from the battery because of the overheating.

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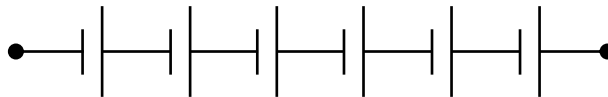
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The output voltage of the usual lead-acid battery is 12 V, and it consists of several cells.

h) How many cells should be used to get 12 V battery?

$N = 12 \text{ V} / 2.081 \text{ V} = 5.8$
Six cells should be used.

i) Draw electrical circuit demonstrating how the individual cells are connected in the 12 V lead-acid battery.



j) Calculate the theoretical output voltage of 12 V lead-acid battery *i.e.* use the open circuit potential E_{cell} calculated in d).

$E_{\text{max}} = 6 \cdot 2.081 \text{ V} = 12.49 \text{ V}$

The weight of the commercial lead acid battery is 4.05 kg (9.75x9.8x15.1 cm), the capacity is 12 A·h, and the internal resistance of the battery is 100 mΩ.

k) Calculate the charge which could be withdrawn from the battery fully charged.

$q = 12 \text{ A} \cdot 1 \text{ h} \cdot 3600 \text{ s/1 h} = 43\,200 \text{ C} = 43.2 \text{ kC}$

The battery was discharged, and the density of the electrolyte measured was 1.195 g/cm³. The fully charged battery contained 580 cm³ sulphuric acid.

l) Calculate how much hours would it take to fully charge the battery using average current 3 A. The efficiency of charging process is 65 %. Assume that the amount water is constant.

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$$m_{\text{charged}}(\text{H}_2\text{SO}_4 \text{ solution}) = 580 \text{ cm}^3 \cdot 1.275 \text{ g/cm}^3 = 739.5 \text{ g}$$

$$m_{\text{charged}}(\text{H}_2\text{SO}_4) = 739.5 \text{ g} \cdot 0.3720 = 275.09 \text{ g}$$

$$m(\text{H}_2\text{O}) = 739.5 \text{ g} - 275.09 \text{ g} = 464.40 \text{ g}$$

$$\rho = 1.195 \text{ g/cm}^3$$

$$\%_{\text{wt, discharged}}(\text{H}_2\text{SO}_4) = 27.51$$

$$m_{\text{discharged}}(\text{H}_2\text{SO}_4) = 27.51 / (100 - 27.51) \cdot 464.40 \text{ g} = 176.24 \text{ g}$$

$$\Delta m_{\text{discharged}}(\text{H}_2\text{SO}_4) = 275.09 \text{ g} - 176.24 \text{ g} = 98.85 \text{ g}$$

$$n_{\text{discharged}}(\text{H}_2\text{SO}_4) = 98.85 \text{ g} / 98.08 \text{ g mol}^{-1} = 1.008 \text{ mol}$$

$$q = 1.008 \text{ mol} \cdot 96485 \text{ C/mol} \cdot 1/0.65 = 149\,600 \text{ C}$$

$$t = 149\,600 \text{ C} / 3 \text{ A} \cdot 1 \text{ h} / 3\,600 \text{ s} = \mathbf{13.9 \text{ h}}$$

m) During the discharging the internal resistance of the battery:

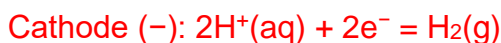
- Increases;
- Decreases;
- Decreases drastically;
- Does not change.

n) The open circuit potential of the battery:

- Does not change during charging;
- Does not change during discharging;
- Increases during discharging;
- Increases during charging;
- Decreases during charging.

The efficiency of the charging process is much lower than 100 % because high overvoltage is applied to the electrodes and instead of charging also the side reactions could occur: hydrogen evolution and oxygen evolution.

o) Write the equations of side reactions on the anode and cathode during the charging process.



The performance of various energy storing devices could be compared using maximum energy density $W_{\text{max}} = qE/m$, where q is charge stored in the device, E – operation voltage window and m – weight of the device. Maxwell ultracapacitor BCAP3000 has the following characteristics: capacitance – 3000 F, voltage window – 2.7 V and mass of the device – 510 g

p) For which energy storage device the maximum energy density (Wh/kg) is higher. During the discharge of the battery the potential does not change but during the discharge of capacitor the potential decreases almost linearly i.e. the average potential should be used.

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$$W_{\max}(\text{battery}) = 12 \text{ A} \cdot 12 \text{ V} / 4.05 \text{ kg} = 36 \text{ Wh/kg}$$

$$W_{\max}(\text{ultracapacitor}) = 3000 \text{ F} \cdot 2.7 \text{ V} \cdot 2.7 \text{ V} / 2 / 0.510 \text{ kg} \cdot 1 \text{ h} / 3600 \text{ s} = 6.0 \text{ Wh/kg}$$

The battery has higher maximum energy density.

q) The energy density of the lead-acid battery:

- Increases with the temperature;
- Decreases with the temperature;
- Does not change with the temperature;
- Increases during discharging;
- Increases during charging.

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Problem 2. Superconducting fullerides (10 points)

Some of the alkali metal doped fullerenes have a superconducting state. In these compounds, the alkali metal atoms fill the holes in a face-centred cubic lattice formed by the molecules of fullerene. Molecules in the fullerene crystal are also arranged in the face-centred cubic lattice.

- a) Calculate the lattice parameter (a) of the fullerene crystal with a density of 1.67 g cm^{-3} .

$$a = (nM/\rho/N_A)^{1/3} = (4 \cdot 720.66 \text{ g mol}^{-1} / 1.67 \text{ g cm}^{-3} / 6.022 \cdot 10^{23} \text{ mol}^{-1})^{1/3} = 1.42 \cdot 10^{-7} \text{ cm} = \mathbf{14.2 \text{ \AA}}$$

- b) Estimate the radius of the fullerene molecule, assuming that the distance between the neighbouring molecular spheres is $d = 1.42 \text{ \AA}$, *i.e.* one C–C bond length.

$$r(\text{C}_{60}) = \sqrt{2} \cdot a/4 - d/2 = 0.502 \text{ nm} - 0.071 \text{ nm} = \mathbf{4.31 \text{ \AA}}$$

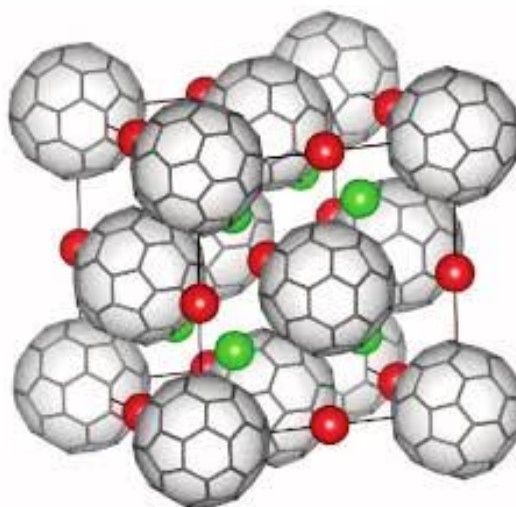
- c) Estimate the radii of spheres (r_{oct} and r_{thd}) that can fit the octahedral and tetrahedral holes of the fullerene crystal. Hint: Radius of a tetrahedron circumsphere is given as $r_{\text{thd}} = \sqrt{3}/8 \cdot t$, where t is the length of tetrahedron edge.

$$r_{\text{oct}} = a/2 - r(\text{C}_{60}) = \mathbf{2.79 \text{ \AA}}$$

$$t = a/\sqrt{2}$$

$$r_{\text{thd}} = \sqrt{3}/8 \cdot a/\sqrt{2} - r(\text{C}_{60}) = \mathbf{1.84 \text{ \AA}}$$

In the figure below is shown the crystal structure of face-centred cubic A_nC_{60} , where $\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$, and n is an integer number.



- d) Prove that $n = 3$ for the illustrated crystal structure. Note that all tetrahedral and octahedral holes are occupied by the alkali metal atoms.

In the A_nC_{60} crystal lattice, 8 A atoms fill the tetrahedral holes, 1 A atom occupies the central octahedral hole, and 12 A atoms are situated at the edges, in the octahedral holes. In total, there are $8 + 1 + 12/4 = 12$ A atoms in the unit cell which also contains 4 C_{60} molecules.

$$\text{Thus } n = 12/4 = 3.$$

In the Table below are given atomic ($r(\text{A}^0)$) and ionic ($r(\text{A}^+)$) radii of Li, Na, K, Rb and Cs, metal vaporisation enthalpies ($\Delta H_{\text{vap}}(\text{A})$) and ionisation energies ($\text{IP}(\text{A})$), as well as lattice parameters of corresponding fullerides.

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	$r(\mathbf{A}^0) / \text{\AA}$	$r(\mathbf{A}^+) / \text{\AA}$	$\Delta H_{\text{vap}}(\mathbf{A}) / \text{kJ mol}^{-1}$	$\text{IP}(\mathbf{A}) / \text{kJ mol}^{-1}$	$a(\mathbf{A}_n\text{C}_{60}) / \text{\AA}$
Li	1.52	0.76	136	520	–
Na	1.86	1.02	108	496	14.191
K	2.27	1.38	90	419	14.240
Rb	2.48	1.52	69	403	14.384
Cs	2.65	1.67	66	376	14.761

- e) Calculate r_{thd} values for each of the alkali metal doped fullerenes. Compare the calculated values with the $r(\mathbf{A}^0)$ and $r(\mathbf{A}^+)$ values from the table and prove that the alkali metal atoms are charged.

The largest radius of \mathbf{A} that can fit to a tetrahedral hole of the corresponding $\mathbf{A}_3\text{C}_{60}$ equals:

$$r_{\text{thd}}(\text{Na}_3\text{C}_{60}) = \sqrt{3/8} \cdot a(\text{Na}_3\text{C}_{60}) / \sqrt{2} - r(\text{C}_{60}) = 1.83 \text{ \AA}$$

$$r_{\text{thd}}(\text{K}_3\text{C}_{60}) = \sqrt{3/8} \cdot a(\text{K}_3\text{C}_{60}) / \sqrt{2} - r(\text{C}_{60}) = 1.86 \text{ \AA}$$

$$r_{\text{thd}}(\text{Rb}_3\text{C}_{60}) = \sqrt{3/8} \cdot a(\text{Rb}_3\text{C}_{60}) / \sqrt{2} - r(\text{C}_{60}) = 1.92 \text{ \AA}$$

$$r_{\text{thd}}(\text{Cs}_3\text{C}_{60}) = \sqrt{3/8} \cdot a(\text{Cs}_3\text{C}_{60}) / \sqrt{2} - r(\text{C}_{60}) = 2.08 \text{ \AA}$$

In all cases $r(\mathbf{A}^+) < r_{\text{thd}}(\mathbf{A}_3\text{C}_{60}) < r(\mathbf{A})$. Thus, we may conclude that the holes may contain only charged \mathbf{A} atoms, *i.e.* \mathbf{A}^+ ions.

- f) Calculate the lattice energy for Li_3C_{60} compound using the Kapustinskii equation: $\Delta U_{\text{lattice}} = -107000 \cdot v \cdot |z_+| \cdot |z_-| / (r_+ + r_-)$, where v is the total number of ions in the empirical formula, z_+ and z_- are the charges of the individual ions, r_+ and r_- are the ionic radii in pm, and the result is given in kJ mol^{-1} . Assume, $r_+ + r_- \approx r_{\text{thd}}(\text{Li}_3\text{C}_{60}) + 4.31 \text{ \AA}$.

Let us assume that $r_{\text{thd}}(\text{Li}_3\text{C}_{60}) = 1.52 \text{ \AA}$.

$$a(\text{Li}_3\text{C}_{60}) = (1.52 + 4.31) \cdot \sqrt{2} / \sqrt{3/8} \text{ \AA} = 13.46 \text{ \AA}$$

$$\Delta U_{\text{lattice}}(\text{Li}_3\text{C}_{60}) = -107000 \cdot 4 \cdot 3 \cdot 1 / 583 = -2202 \text{ kJ mol}^{-1}$$

$$\Delta U_{\text{lattice}}(\text{Na}_3\text{C}_{60}) = -107000 \cdot 4 \cdot 3 \cdot 1 / 614 = -2091 \text{ kJ mol}^{-1}$$

$$\Delta U_{\text{lattice}}(\text{K}_3\text{C}_{60}) = -107000 \cdot 4 \cdot 3 \cdot 1 / 617 = -2081 \text{ kJ mol}^{-1}$$

$$\Delta U_{\text{lattice}}(\text{Rb}_3\text{C}_{60}) = -107000 \cdot 4 \cdot 3 \cdot 1 / 623 = -2061 \text{ kJ mol}^{-1}$$

$$\Delta U_{\text{lattice}}(\text{Cs}_3\text{C}_{60}) = -107000 \cdot 4 \cdot 3 \cdot 1 / 639 = -2009 \text{ kJ mol}^{-1}$$

The first reported superconductor in the fulleride family was K_3C_{60} . In a year, Rb_3C_{60} and Cs_3C_{60} were synthesised. Preparation of Na_3C_{60} was more difficult and took longer. So far it has not been possible to produce Li_3C_{60} . There is a correlation between the formation enthalpy values and the sequence of the $\mathbf{A}_3\text{C}_{60}$ studies.

- g) Write the $\mathbf{A}_3\text{C}_{60}$ formula in an ascending order of the corresponding formation enthalpy **absolute** values. You may estimate the relative values using the data from the table.

Name:

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Cs₃C₆₀

Rb₃C₆₀

K₃C₆₀

Na₃C₆₀

Li₃C₆₀

$$\Delta H_f(\mathbf{A}_3\text{C}_{60}) \approx 3\Delta H_{\text{vap}}(\mathbf{A}) + \Delta H_{\text{vap}}(\text{C}_{60}) + 3IP(\mathbf{A}) + E(\text{C}_{60} \rightarrow \text{C}_{60}^{3-}) + \Delta U_{\text{lattice}}(\mathbf{A}_3\text{C}_{60})$$

$$\text{Relative formation energy: } \Delta H_f(\mathbf{A}_3\text{C}_{60})^* = 3\Delta H_{\text{vap}}(\mathbf{A}) + 3IP(\mathbf{A}) + \Delta U_{\text{lattice}}(\mathbf{A}_3\text{C}_{60})$$

$$\Delta H_f(\text{Li}_3\text{C}_{60})^* = [3 \cdot (136 + 520) - 2202] \text{ kJ mol}^{-1} = -234 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{Na}_3\text{C}_{60})^* = [3 \cdot (108 + 496) - 2091] \text{ kJ mol}^{-1} = -279 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{K}_3\text{C}_{60})^* = [3 \cdot (90 + 419) - 2081] \text{ kJ mol}^{-1} = -554 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{Rb}_3\text{C}_{60})^* = [3 \cdot (69 + 403) - 2061] \text{ kJ mol}^{-1} = -645 \text{ kJ mol}^{-1}$$

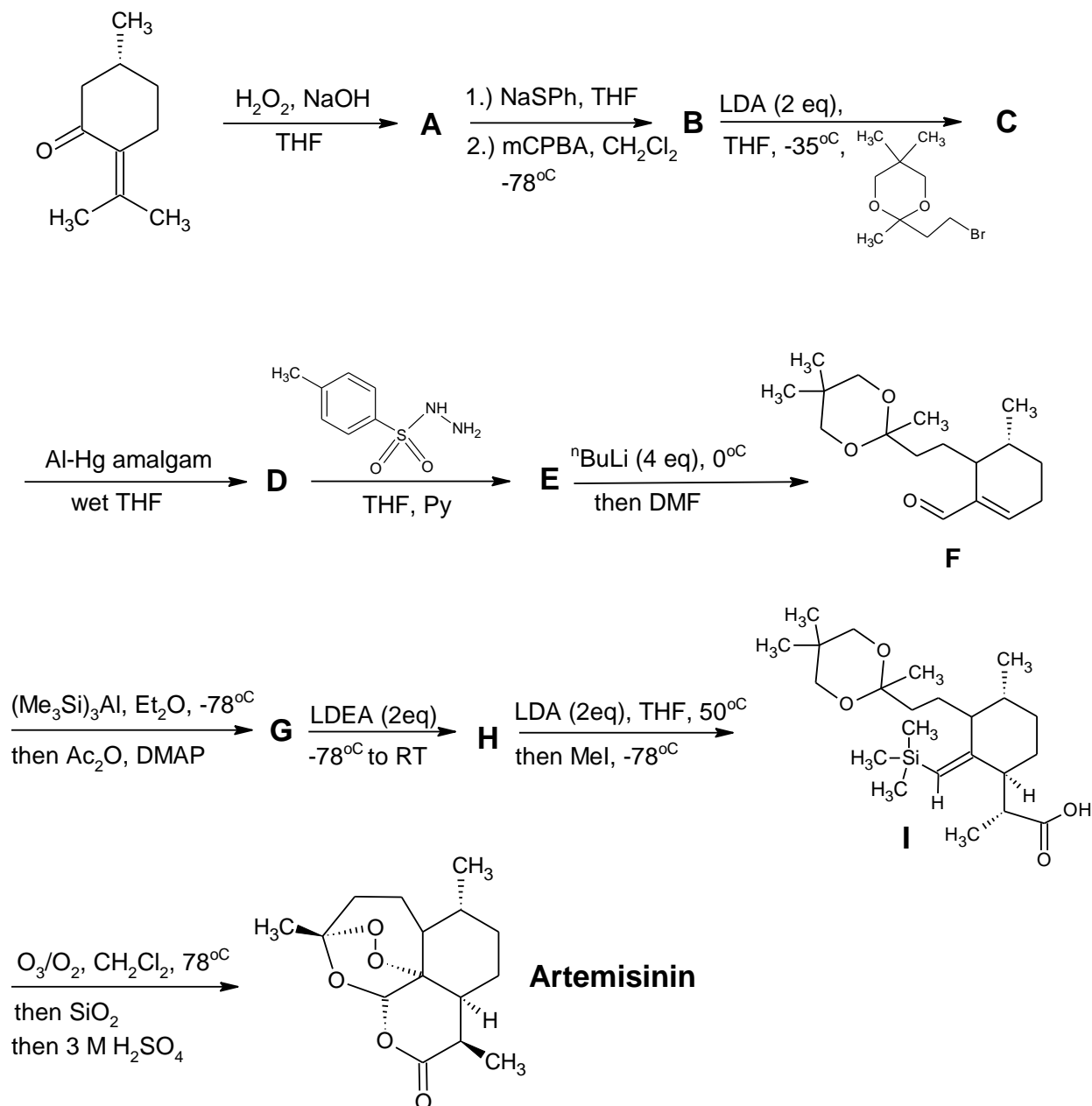
$$\Delta H_f(\text{Cs}_3\text{C}_{60})^* = [3 \cdot (66 + 376) - 2009] \text{ kJ mol}^{-1} = -683 \text{ kJ mol}^{-1}$$

To calculate the true formation energy let us take $E(\text{C}_{60} \rightarrow \text{C}_{60}^{3-}) = 51 \text{ kJ mol}^{-1}$ (theoretical estimation) and $\Delta H_{\text{vap}}(\text{C}_{60}) = 180 \text{ kJ mol}^{-1}$. Thus, $\Delta H_f(\text{Li}_3\text{C}_{60}) = +27 \text{ kJ mol}^{-1} > 0$ and $\Delta H_f(\text{Na}_3\text{C}_{60}) = -48 \text{ kJ mol}^{-1} < 0$. Among other alkali metal fullerides Li_3C_{60} is probably thermodynamically unstable.

Overall, K_3C_{60} , Rb_3C_{60} , and Cs_3C_{60} have markedly lower formation energies than Na_3C_{60} and Li_3C_{60} . These alkali metal fullerides were synthesised earlier.

The Great Drug of China

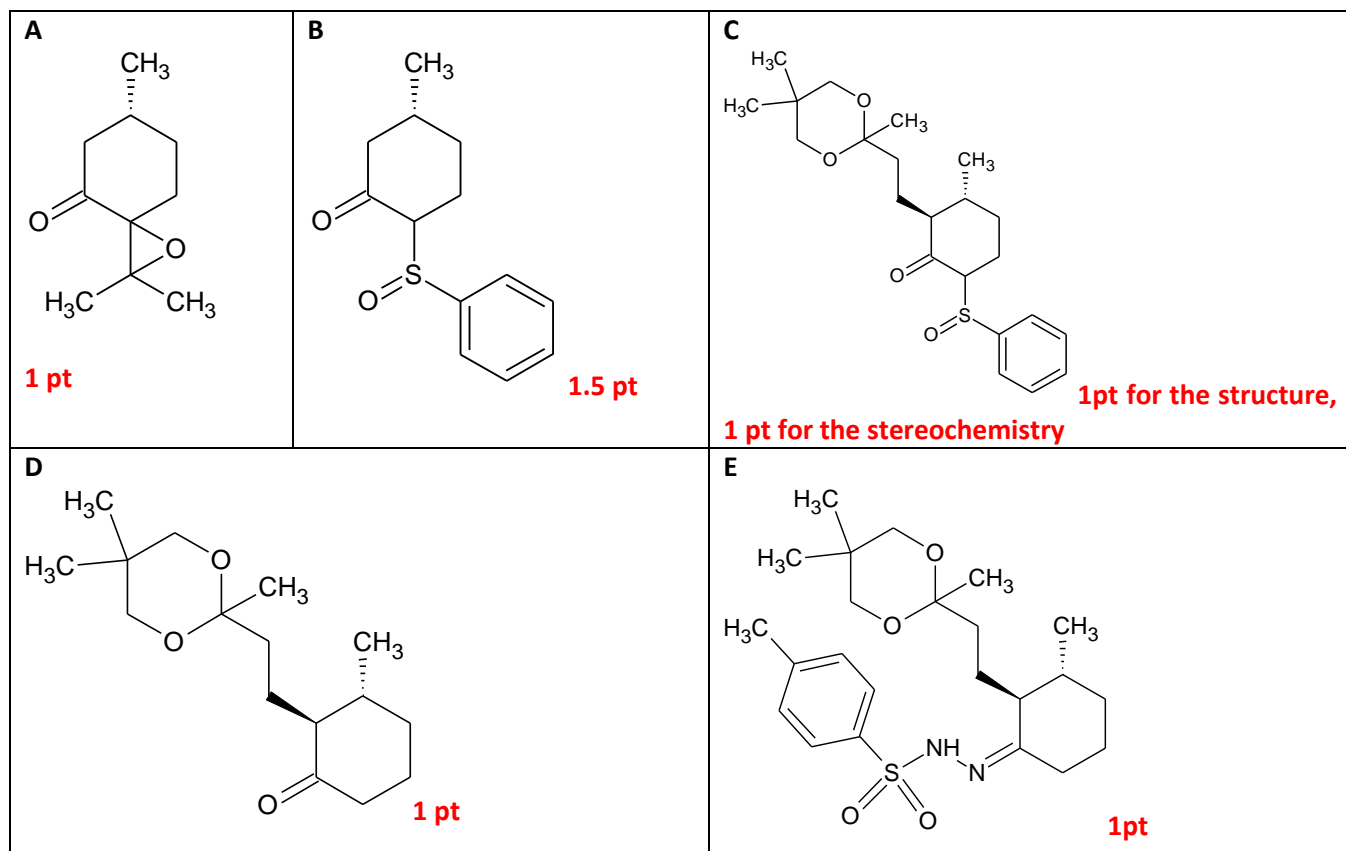
Artemisinin is a drug, that possesses most rapid action of all of the drugs used to treat Malaria. It was discovered in the 1970's by Tu Youyou, a Chinese scientist, who was awarded a Nobel Prize in 2015. She was the first Chinese Nobel Prize laureate. Initially artemisinin was obtained by isolation from the plant *Artemisa Annua*. Unfortunately, no significant quantities of this plant are being grown, so in 1992 Avery et al published a synthetic route to the Artemisinin shown below.



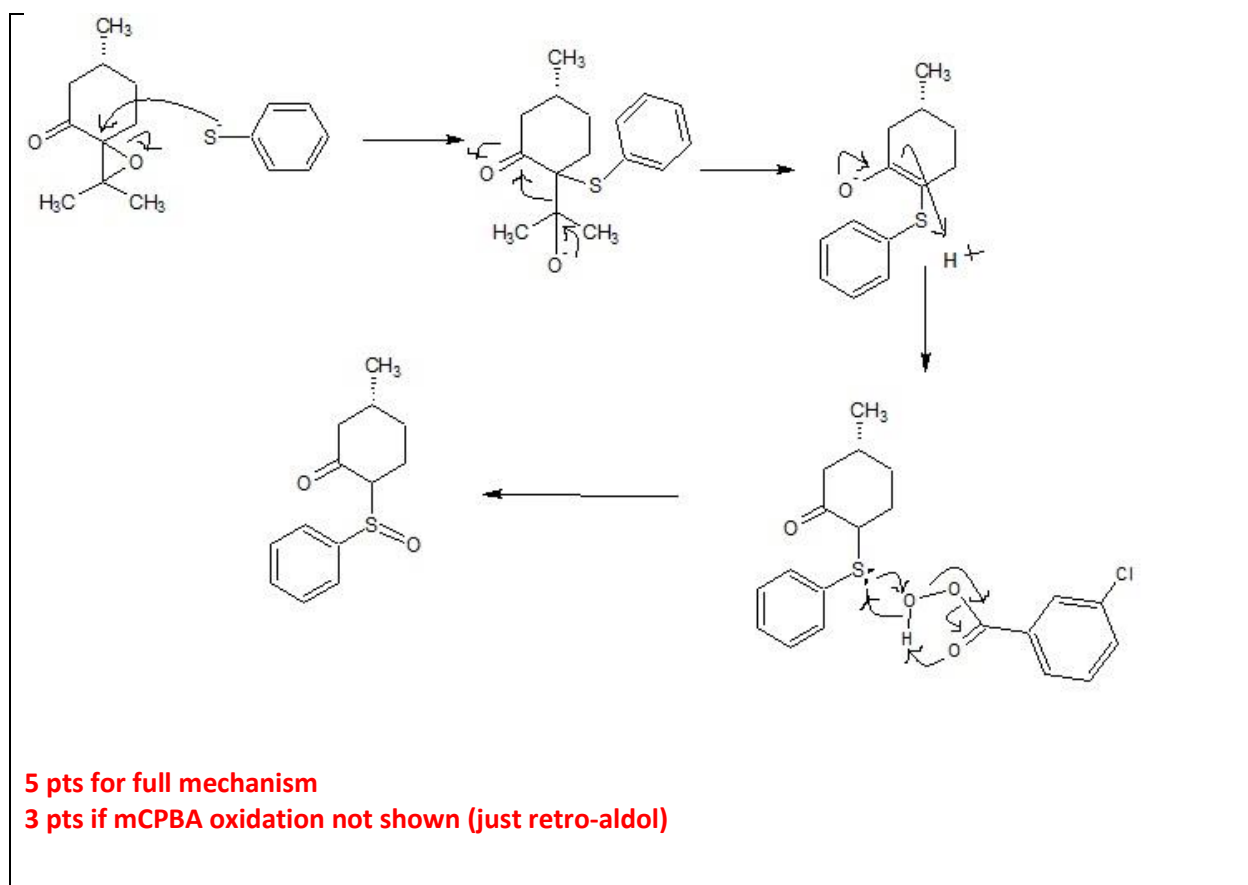
Notes:

- The empirical formulae of compounds are:
 - B** – $\text{C}_{13}\text{H}_{16}\text{O}_2\text{S}$
 - D** – $\text{C}_{16}\text{H}_{28}\text{O}_3$
 - G** – $\text{C}_{22}\text{H}_{40}\text{O}_4\text{Si}$
- All steps from **B** → **I** are stereoselective (reactions leading to **A** and **B** are not) thus you must draw the major enantiomers of all of the intermediates from **C** to **I**!
- LDA and LDEA are bulky bases.
- Conversion **G** to **H** is a very well known rearrangement reaction.

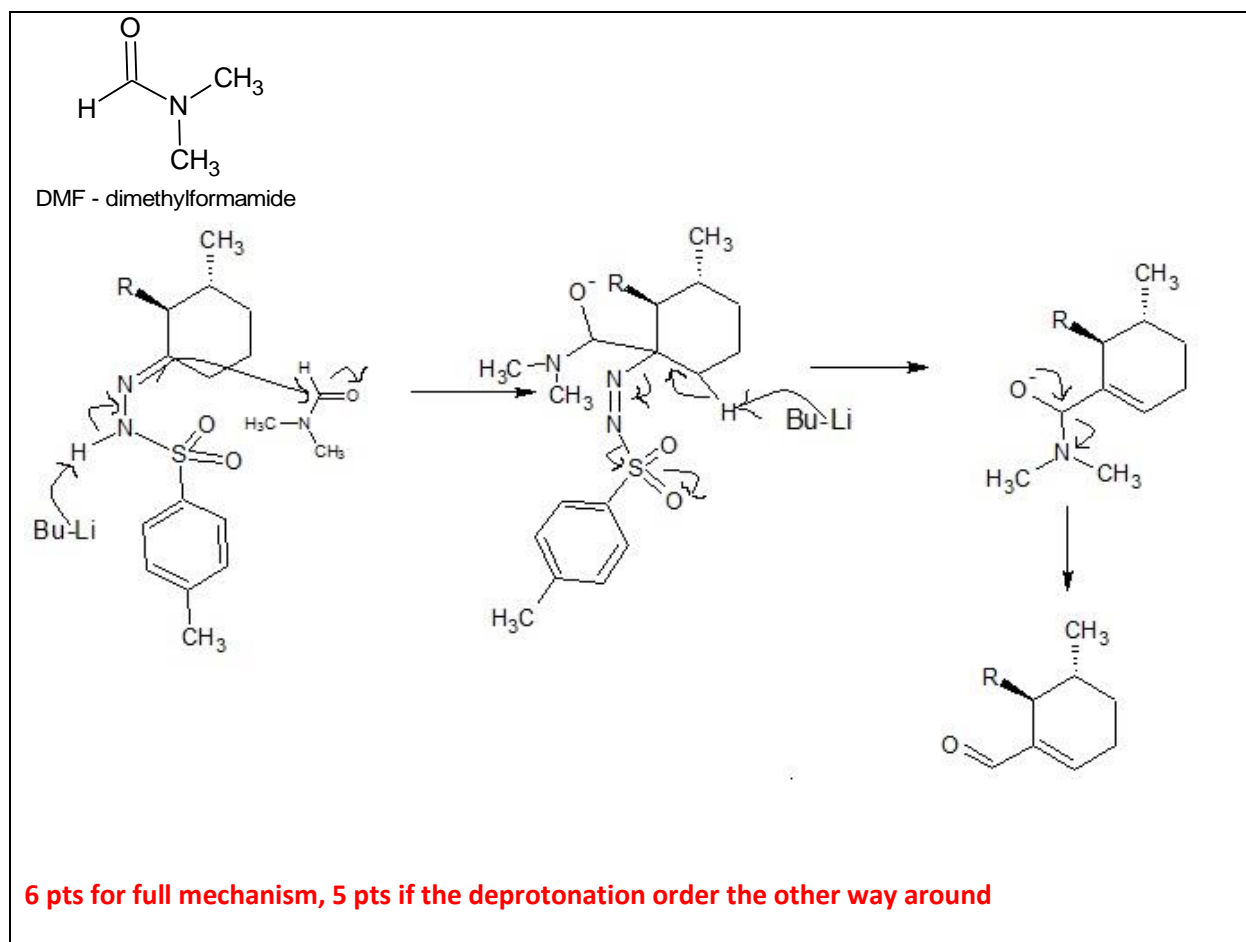
1. Draw the structures of the compounds **A** to **E**, paying particular attention to the stereochemistry of the compounds **C**, **D** and **E**.



2. Propose a mechanism for the conversion **A** to **B**!



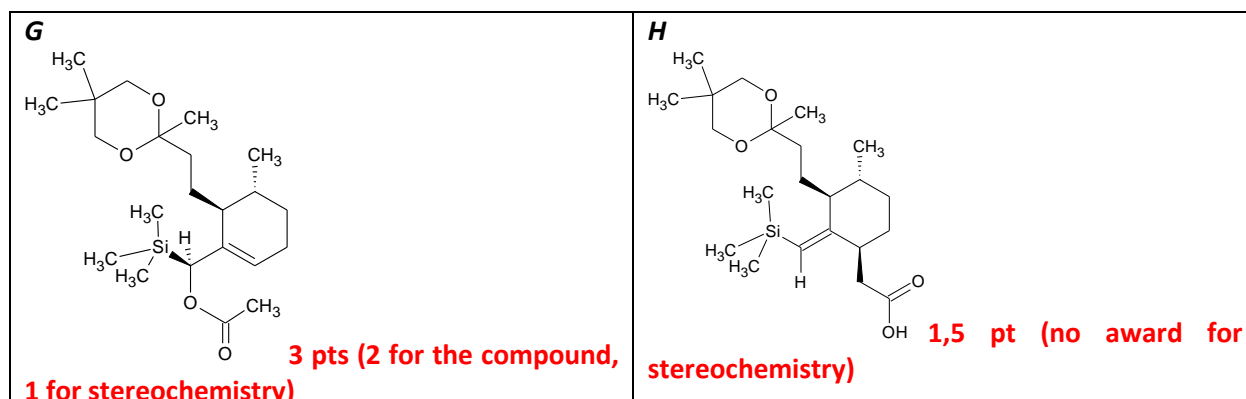
3. Propose a mechanism for the conversion **E** to **F**! Note, that DMF is **not** the solvent of the reaction and that there is no racemisation. You can use abbreviations for the mechanistically unimportant structural features.



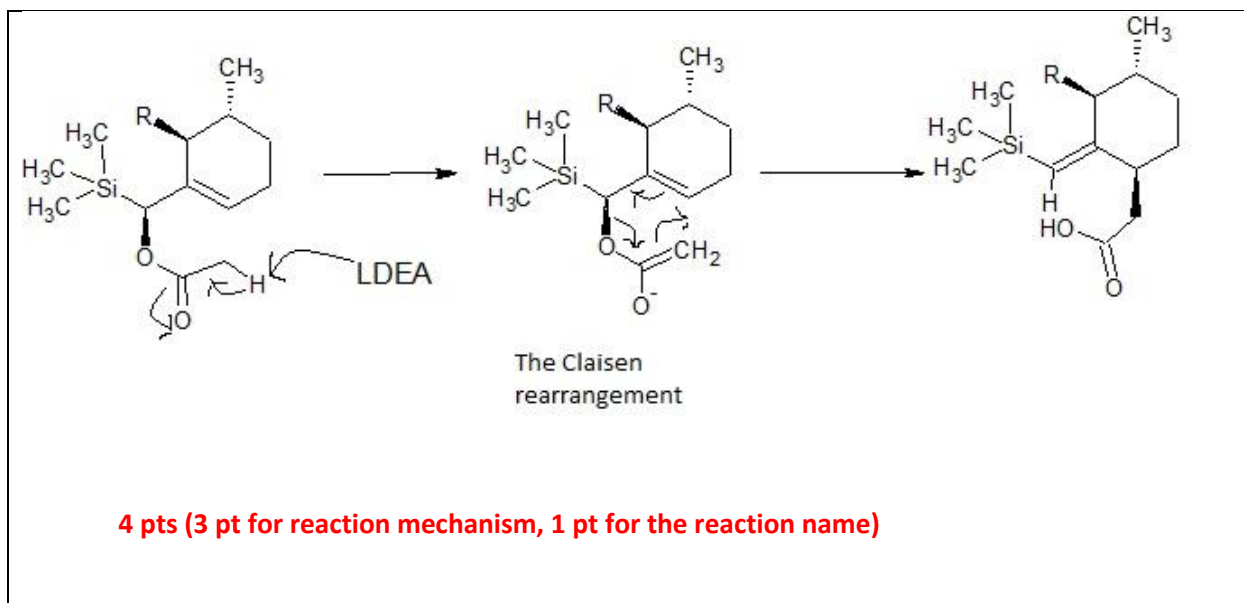
4. What is the **major** driving force of the reaction **E** -> **F**? Circle the most likely answer!

- There is a relief of the steric bulk upon the formation of the product.
- Product can form hydrogen bonds with the solvent.
- Having three oxygens in the molecule is better than having two.
- Nitrogen is produced and released during the reaction. **1pt**
- Product is more conjugated than the starting material
- Compound E is harmful, compound F is not.

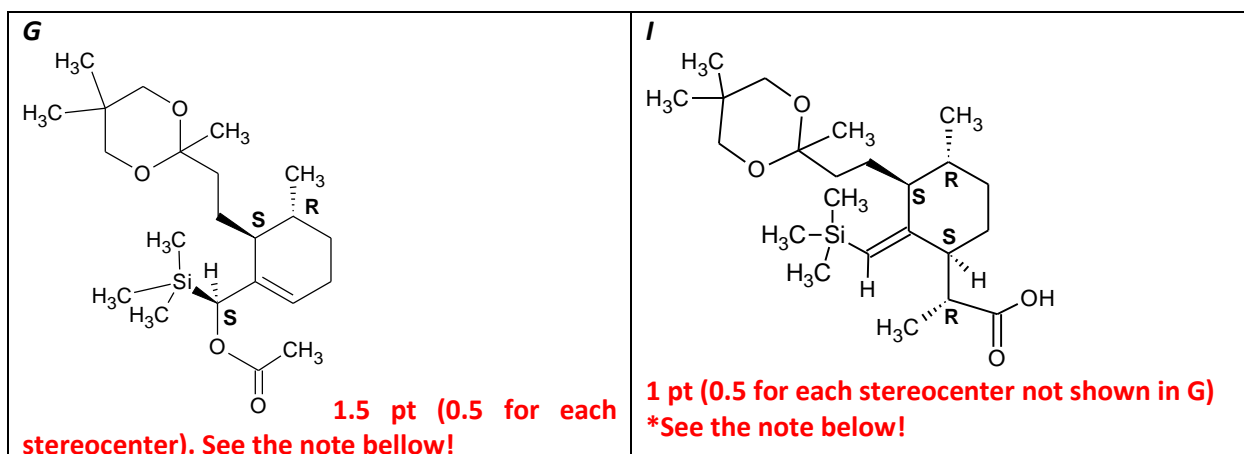
5. Draw the structures of the compounds **G** and **H**. Pay attention to the stereochemistry! Use abbreviation if necessary!



6. Propose the mechanism for the conversion **G** → **H**. Use abbreviations for the mechanistically unimportant structural features! What is the name of this reaction?



7. Assign the relative configuration (*R* or *S*) of all of the stereocentres for the compounds **G** and **I**!



*** Note: There are two stereocenters in common for both **G** and **I**. The student is awarded for the right assignment only once!**

Problem 4. The biggest coins in the world (10 points)

Beginning of 17th century was turn point in Sweden economics as it lost control over silver mines in Norway but added Baltic region (including Tartu and Riga) to their territories. The Mine of Falun had rich stores of the raw material and Swedish king decided to produce copper coins (plates) of value close to value of silver coins. The first copper coins were issued in 1624, the weight of one coin was 19.7 kg and the volume of 2205 cm³. Copper has face centred cubic lattice (fcc) with the lattice parameter of 361.5 pm. In nature copper usually is found as sulphide minerals, for example – chalcopyrite (contains 35% of copper by mass and iron) and chalcocite (contains 80% of copper by mass).

a) Calculate chemical formula of chalcopyrite and chalcocite.

Chalcopyrite calculations: CuFeS₂ 2 points	Chalcocite calculations: CuFeS₂ 2 points
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Nowadays copper is extracted even from ores where copper content is as small as 0.60%.

b) Write balanced reaction equations showing extraction of copper from ore containing chalcocite, if it is known that copper(I) oxide is formed as intermediate.

2Cu₂S + 3O₂ → 2Cu₂O + 2SO₂ 1 point
2Cu₂O + Cu₂S $\xrightarrow{t^o}$ 6Cu + SO₂... 1 point
if reaction is Cu₂O reaction with reducing agent (H₂, C, CO, active metal or electrolysis of molten oxide), then 0.5 points

c) Calculate mass of ore to be recycled to produce copper, which is necessary for production of one Swedish coin.

$m(\text{ore}) = \frac{m(\text{Cu})}{w} = \frac{19700}{0.006} = 3.3 \text{ tons} \quad (1 \text{ point})$

Copper(I) oxide is reddish-brown substance, it is used as component of some antifouling paints. Copper(I) oxide is reduced when it is mixed with chalcocite, free copper and sulphur dioxide is formed.

Substance and its state	Cu ₂ O(s)	Chalcocite(s)	Cu(s)	SO ₂ (g)
Standard enthalpy of formation / kJ mol ⁻¹	-168.6	-79.5		-296.8
Molar standard entropy / Jmol ⁻¹ K ⁻¹	93.1	120.9	33.2	248.2
Melting point / °C	1232	1130	1084	
Enthalpy of fusion / kJ mol ⁻¹			13	

- d) Use data in table and calculate Gibbs energy of copper(I) oxide reduction reaction at standard conditions (25°C)

$$\Delta H = -296,8 + 79,5 + 2 \times 168,6 = 119,9 \text{ kJ} \quad 1 \text{ point}$$

$$\Delta S = 248.2 + 33.2 \times 6 - 120.9 - 2 \times 93.1 = 140 \text{ J/K} \dots 1 \text{ point}$$

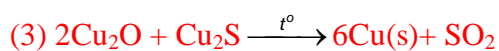
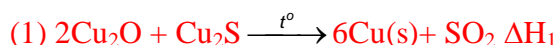
$$\Delta G = 119900 - 298 \times 140 = \underline{78,1 \text{ kJ}} \dots 1 \text{ point}$$

- e) Fill table below indicating sign of thermodynamic function of copper(I) oxide reduction reaction.

Temperature	0°C	500°C	1000°C
Sign of ΔH	+	+	+
Sign of ΔS	+	+	+
Sign of ΔG	+	+	-

(2 points)

- f) Use thermodynamic data in table and calculate Gibbs energy of copper(I) oxide reduction reaction at 1100°C temperature.



$$\Delta H_3 = \Delta H_1 + 6 \times \Delta H_2 = 197.9 \text{ kJ} \dots 1 \text{ point}$$

Entropy change for phase transition:

$$\Delta S = \Delta H / T = 9.6 \text{ J/K} \dots 1 \text{ point}$$

$$S(\text{Cu,l}) = \Delta S + S(\text{Cu,s}) = 9.6 + 33.2 = 42.8 \text{ J/K} \dots 1 \text{ point}$$

$$\Delta S = 248.2 + 42. \times 6 - 120.9 - 2 \times 93.1 = 197.8 \text{ J/K} \quad 1 \text{ point}$$

$$\Delta G = \Delta H - T \times \Delta S = - \underline{78.6 \text{ kJ}} \dots 1 \text{ point (total 5 points)}$$

Young chemist Grzegorz decided to reuse copper coin; he made up electrolytic cell, and attached Swedish copper coin and almost pure copper wire as electrodes and used copper(II) nitrate as electrolyte.

- g) Which electrode (anode / cathode) was made from Swedish copper coin? Write corresponding half reaction.

Circle the correct answer: **anode** / cathode

Half-reaction: $\text{Cu} - 2\text{e}^- \rightarrow \text{Cu}^{2+}$ (1 + 1 = 2 point)

- h) How long (in hours) does, it takes to recycle all Swedish coin if electrolysis is performed with 1.00 A current?

$$m = \frac{M \cdot I \cdot t}{z \cdot F} \quad 19700 = \frac{63,5 \cdot 1 \cdot t}{2 \cdot 96500}$$

... $t = 700 \text{ days} (\pm 20 \text{ days}) = 1.9 \text{ years}$ (2 points)

- i) Copper nowadays is used for preparation of internet cables. Calculate length of copper fiber of diameter 0.1 mm which can be produced from Swedish copper coins.

Volume of coin is 2205 cm^3 , if wire is cylinder, then: $V = \pi \cdot R^2 \cdot h$

$$2205 = 3.14 \cdot \left(\frac{0.01}{2}\right)^2 \cdot h \text{ and } h = 280 \text{ km} \text{ (1 point)}$$

- j) How many copper coins it is necessary to recycle to produce copper fibre with length of 600 km (distance from Tallinn to Vilnius via Riga).

Number of Swedish coins = 3; (1 point), if answer was 2.1.. coins, then max. = 0.5 points

If question i was wrong but j was according to answer in i, then max = 0.5 points (Error carried forward, ECF)

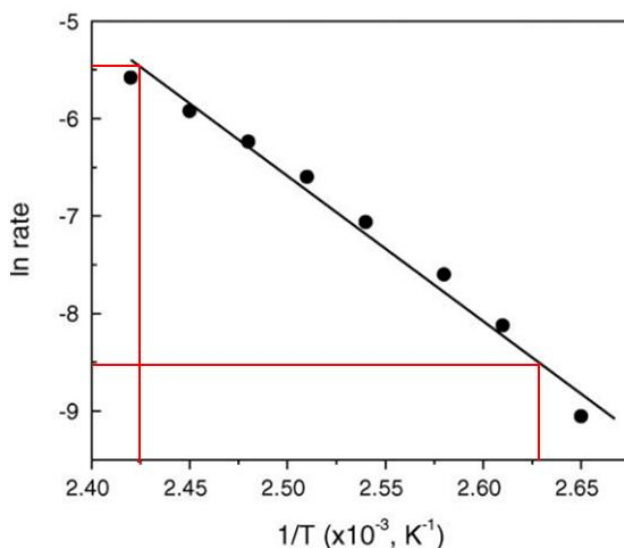
Most part of copper used in nowadays is recycled. Another method used in recycling process is dissolution of copper in nitric acid. Nitric acid reacts with copper in two ways given bellow

- k) Complete and balance both oxidation-reduction reaction equations.



$\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$ (4 points, 1 p. for products and 1 p. for coefficients in oxidation reduction reaction)

Scientific papers state that complete oxidation of carbon monoxide can be achieved at room temperature over unsupported copper(II) oxide catalyst by a careful and controlled generation of the oxide. Figure below is shows natural logarithm of oxidation reaction rate as function of $1/T$, where T is temperature in Kelvin (K).



- l) Use data in figure and estimate activation energy for oxidation of carbon monoxide.

$$\text{tg } \alpha = 3 / ((2.627 - 2.425) \times 10^{-3}) = 14850$$

$E(A) = 123 \text{ kJ}$ (scientific paper gives value 124 kJ)

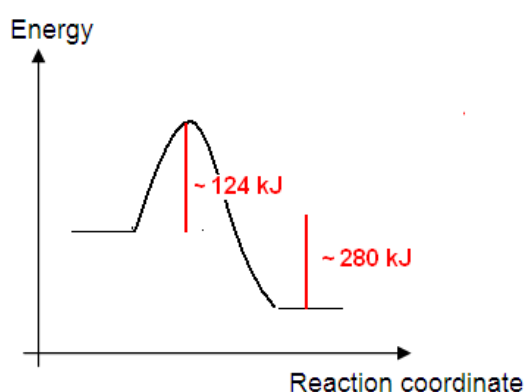
$124 \pm 5 \text{ kJ}$ is acceptable interval

If answer was $124 \pm 12 \text{ kJ}$, then 1 point.

If Arrhenius equation was used in transformed form (comparing to formula page), then 0.5 points.

<http://www.sciencedirect.com/science/article/pii/S0926337305004030>

- m) Enthalpy of complete combustion of carbon (in solid state as graphite) is -393 kJ/mol , but standard enthalpy of formation of carbon monoxide is -111 kJ/mol . Sketch energy diagram of carbon monoxide oxidation reaction and state exact energy difference values where possible.



3 points = 1 for activation energy + 1 for enthalpy + 1 for form of curve

Copper is still used in production of coins. Young chemist decided to prove it and analysed 2 EUR coin by x-ray diffraction. Diffraction pattern for analysed coin is shown below.

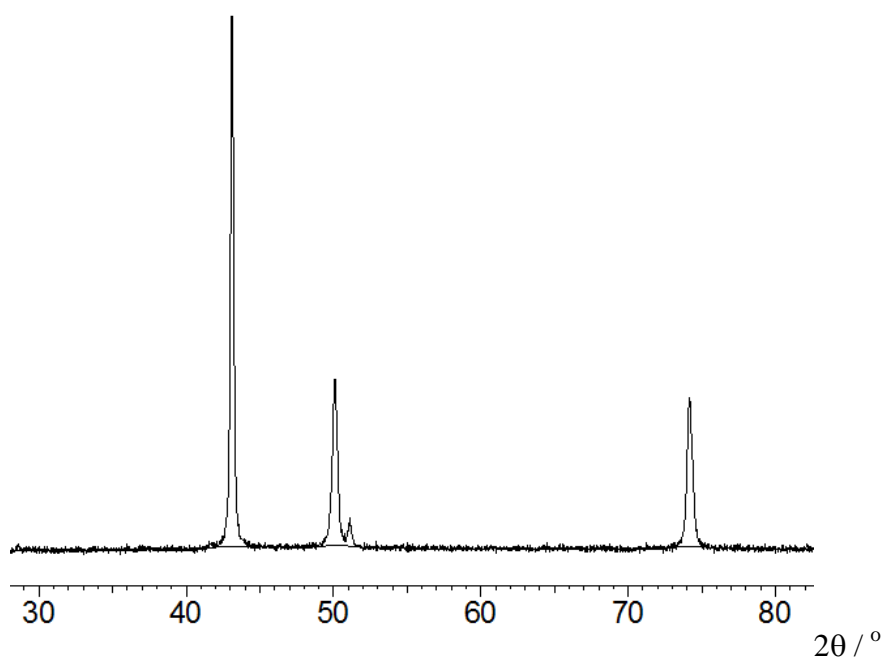


Figure Diffraction pattern of 2 EUR coin

Use Bragg equation

$$d = \frac{\lambda}{2 \cdot \sin \frac{2\theta}{2}}$$

where d – distance between diffraction planes (nm); λ - wavelength of x-rays (0.15408 nm), 2θ - diffraction angle.

and

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where d – distance between diffraction planes (nm), a – lattice parameter, h , k and l – Miller indices. For facecentred cubic lattice (fcc) only diffraction peaks where all Miller indices are odd numbers or all Miller indices are even numbers are allowed.

n) Indicate in diffraction pattern which peak(s) correspond to copper and state at least one set of Miller indices for each of the copper peaks.

Peak 2θ , °	43	50	51	74
d, nm	0.210	0.182	0.178	0.128
h, k, l	1,1,1	2,0,0 or 0,2,0 or 0,0,2 or	none	2,2,0 or 2,0,2 or 0,2,2
Conclusion	YES	YES	NO	YES

1 point for each column, total 4 points

Name:

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Problem 5. “My precious” (10 points)

Silver jewellery is seldom made of absolutely pure silver. Different alloys are usually used instead of pure silver. Chemistry student Grzegorz decided to analyse his mom’s silver ring and find out how much copper it contains because he knew that this ring had some copper impurity. So, Grzegorz dissolved 1.00 g of that ring in a small volume of concentrated nitric acid and diluted the solution to 25 ml. Let’s call it solution **A**. It was coloured, because of that the student decided to calculate the amount of copper in the solution using its feature to absorb visible light. He measured the absorbance of the solution using the photometer. Usually, molar extinction coefficients of metals salts solutions are less than $1000 \text{ M}^{-1}\text{cm}^{-1}$. In this problem use Bouguer–Beer–Lambert law:



$$\log(I_0/I) = A = \epsilon c l$$

In his measurements, Grzegorz used the photometer, which can measure the smallest value of absorption $A=0.001$.

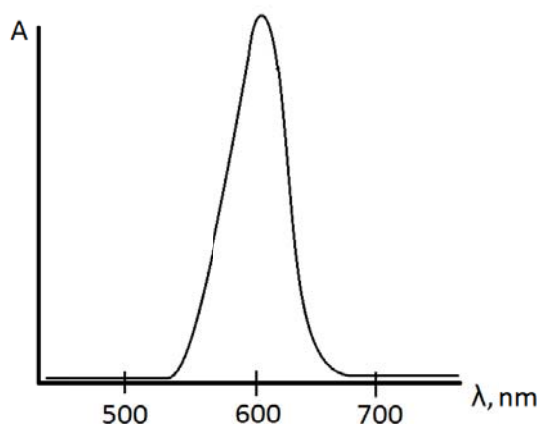
- a) Calculate the smallest concentration of hypothetical substance **X** that can be measured by this device when $\lambda=600 \text{ nm}$, $\epsilon_{600}=3.25 \text{ M}^{-1}\text{cm}^{-1}$ and $l=1 \text{ cm}$?

$$c = 0.001 / 3.25 \text{ M}^{-1} \text{ cm}^{-1} / 1 \text{ cm} = 3.08 \cdot 10^{-4} \text{ M}$$

- b) Light filters are usually used in photometers to generate the monochromatic light beam. What is the colour of the filter if it absorbs only violet (390 nm) light?

- blue
- green**
- violet
- red

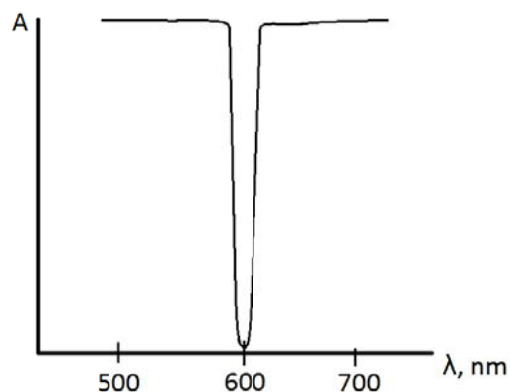
The absorbance spectrum of hypothetical substance **X** is given in the figure below.



- c) Draw the absorbance spectrum of the best suitable filter for the substance **X** analysis. “Best suitable” means that, when that filter is used, Lambert–Beer law holds, the smallest possible substance **X** concentrations can be measured, and the most accurate results are obtained.

Name:

Code:



4 points

To find out copper concentration in solution **A**, he used “addition method”. In the beginning, Grzegorz measured the absorbance of solution **A** in 3.00 cm cuvette at $\lambda = 700$ nm wavelength. The photometer showed 0.240. Assume that silver ions do not absorb visible light.

- d) Calculate, what fraction (in percent) of initial light intensity is transmitted through the sample.

$$T = 10^{-0.24} \cdot 100\% = 57.5\%$$

After that, Grzegorz weighed 5.12 g of copper sulphate pentahydrate, dissolved it in a 20 ml volumetric flask and diluted to the mark (let's call it solution **B**). Then he mixed 15 ml of solution **A** and 1 ml of solution **B** and also measured the absorbance of this mixture in 1.00 cm cuvette at $\lambda = 700$ nm wavelength. The photometer showed the value $A = 0.694$.

- e) Calculate the mass fraction (in percent) of copper in the ring.

$$c_a = \frac{5.12}{250 \cdot 0.02} = 1.024 M$$

2 points

$$c_{x+a} = \frac{c_a V_a + c_x V_x}{V_a + V_x}$$

2 points

$$\frac{A_x}{A_{x+a}} = \frac{c_x l_x}{c_{x+a} l_{x+a}}$$

2 points

$$\frac{A_x}{A_{x+a}} = \frac{c_x l_x (V_a + V_x)}{(c_a V_a + c_x V_x) l_{x+a}}$$

$$A_x c_a V_a l_{x+a} + A_x c_x V_x l_{x+a} = A_{x+a} c_x l_x (V_a + V_x)$$

$$c_x = \frac{A_x c_a V_a l_{x+a}}{A_{x+a} l_x (V_a + V_x) - A_x V_x l_{x+a}}$$

2 points

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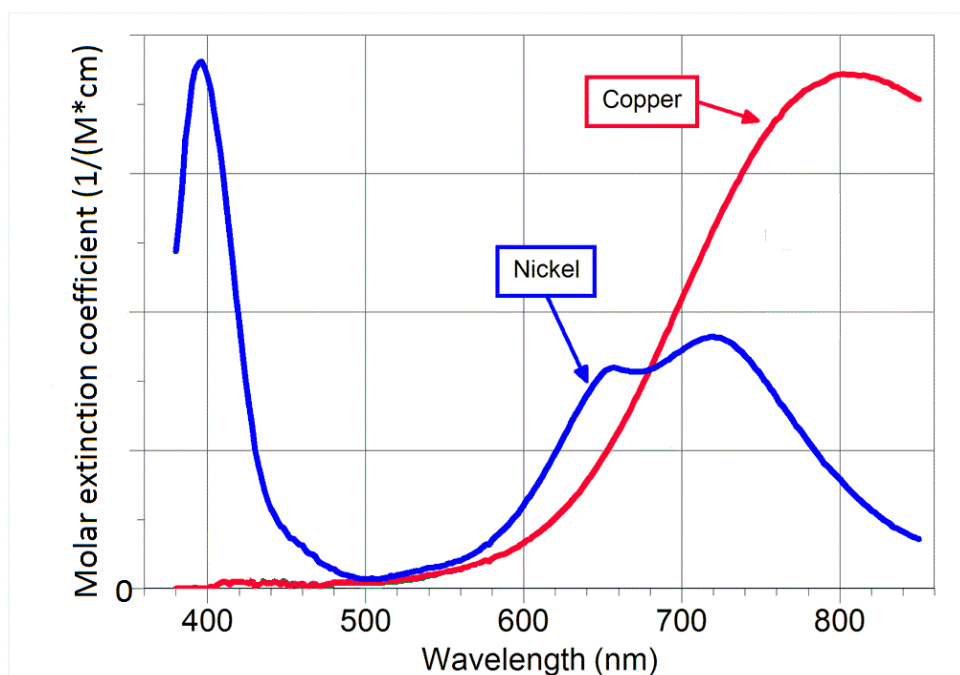
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$$c_x = \frac{0.24 * 1.024 * 0.001 * 1}{0.694 * 3 * 0.016 - 0.24 * 0.015 * 1} = 8.27 * 10^{-3} M$$

$$\omega = \frac{8.27 * 10^{-3} * 0.025 * 64}{1} * 100\% = 1.32\%$$

1 point

Grzegorz was so interested in his mom's jewellery analysis that he decided to measure the quantitative composition of mom's earring, which was made from monel metal (copper-nickel alloy). So the student dissolved a piece of that earring in concentrated nitric acid (let's call it solution **C**) and measured the absorbance of solution **C** in 1.00 cm cuvette at $\lambda_1 = 400$ nm wavelength and at $\lambda_2 = 800$ nm wavelength. He also measured the absorbance of earlier prepared standard solution **D** in which $[\text{Cu}^{2+}] = 0.025$ M and $[\text{Ni}^{2+}] = 0.055$ M. The results he got are listed in the Table below. The Figure below shows the molar extinction coefficient dependence on wavelength for copper and nickel. Molar extinction coefficient for nickel at wavelength 800 nm $\epsilon_{800} = 4.41 \text{ M}^{-1}\text{cm}^{-1}$.

Table. Absorbance dependence on solution and λ

λ , nm \ Solution	400	800
C	0.765	0.548
D	0.894	0.638

Name:

Code:

f) Using data given above, find out the composition (in mass percent) of the earring.

$$\varepsilon_{400}(\text{Cu}^{2+}) = 0 \text{ M}^{-1} * \text{cm}^{-1}$$

1 point

$$\varepsilon_{400}(\text{Ni}^{2+}) = \frac{0.894}{0.055} = 16.25 \text{ M}^{-1} * \text{cm}^{-1}$$

1 points

$$\varepsilon_{800}(\text{Ni}^{2+}) = 4.41 \text{ M}^{-1} * \text{cm}^{-1}$$

$$\varepsilon_{800}(\text{Cu}^{2+}) = \frac{0.638 - 0.055 * 4.41}{0.025} = 15.82 \text{ M}^{-1} * \text{cm}^{-1}$$

2 points

$$[\text{Ni}^{2+}] = \frac{0.765}{16.25} = 0.0471 \text{ M}$$

2 points

$$[\text{Cu}^{2+}] = \frac{0.548 - 0.0471 * 4.41}{15.82} = 0.0215 \text{ M}$$

Assume that we have 1 L of solution **C**

$$\omega(\text{Ni}) = \frac{0.0471 * 64}{0.0471 * 64 + 0.0215 * 59} * 100\% = 70.4\%$$

2 points

$$\omega(\text{Cu}) = 100 - 70.4 = 29.6\%$$

Grzegorz's friend Piotr told Grzegorz about metal complexes. Piotr pointed out that it is better to evaluate metal concentrations in solutions using organic compounds that make complexes with metal ions. Due to recent changes in safety rules Grzegorz's school was trying to get rid of carcinogenic cobalt (II) chloride. So Grzegorz waited for the right moment and deliberately took the salt as he came up with an idea to analyse cobalt (II) complex formation reaction.

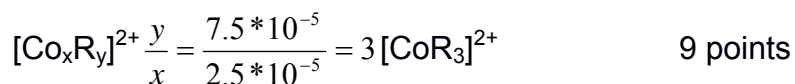
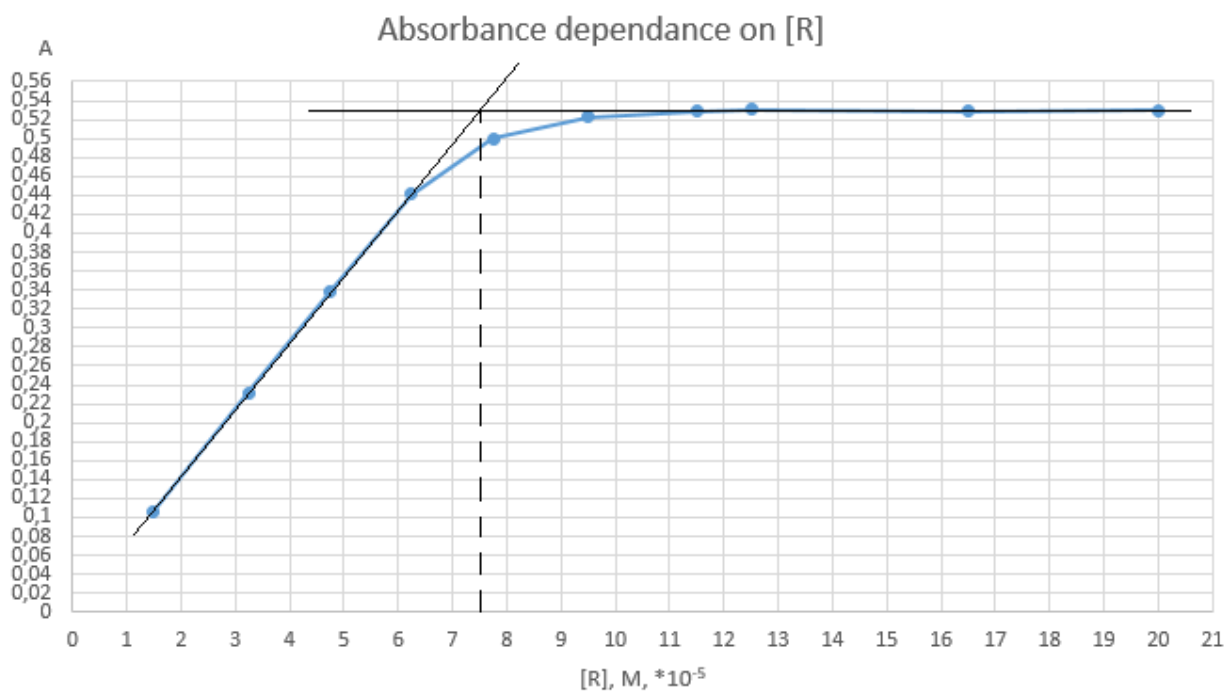
The complex between Co(II) and the ligand **R** was investigated photometrically. A green filter at 550 nm (the wavelength of absorbance maximum for the complex) was used for the measurements. Assume that only the complex absorbs the light. The initial cation concentration was $2.5 \cdot 10^{-5}$ mol/L in solutions with different concentrations of **R**. The absorbance data (1 cm cell) were obtained as follows:

g) Draw a graph of absorbance versus **R** concentration and determine the ligand to cation ratio for the complex.

Conc. R (mol/L) $\times 10^{-5}$	Absorbance (A)
1.50	0.106
3.25	0.232
4.75	0.339
6.25	0.441
7.75	0.500
9.50	0.523
11.5	0.529
12.5	0.531
16.5	0.529
20.0	0.530

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h) Determine the value of molar extinction coefficient ϵ_{550} for the complex from g) question.

It can be found in two ways:

from horizontal line of the graph

$$\epsilon_{550} = \frac{0.530}{2.5 \cdot 10^{-5}} = 21200 \text{ M}^{-1} \cdot \text{cm}^{-1}$$

or from the increasing line of the graph:

$$\epsilon_{350} = \frac{0.339 - 0.232}{\frac{1}{3} \cdot (4.75 \cdot 10^{-5} - 3.25 \cdot 10^{-5})} = 21400 \text{ M}^{-1} \cdot \text{cm}^{-1}$$

Both answers are correct. And other similar answers are correct. 4 points

i) Which one of the following statements best describes the advantage of using complexes in photometry?

- to increase the molecular mass of analyst;
- to enhance the solubility of the analyst;
- to increase molar extinction coefficient of the analyst;
- all of the above

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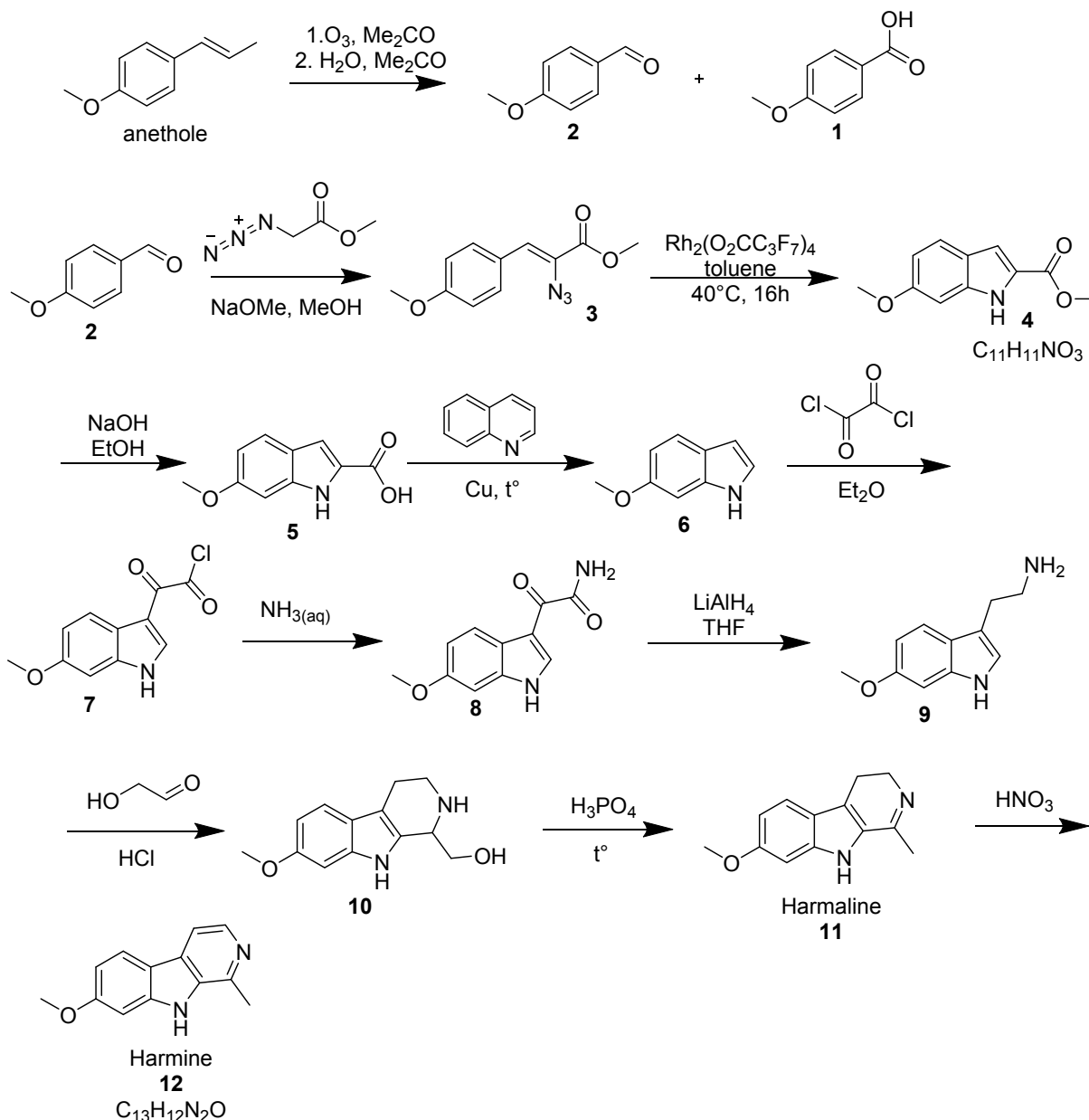
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Ayahuasca

Ayahuasca is a brew made out of *B. caapi* vine. This brew is used orally as a traditional spiritual medicine in ceremonies in South America. It can be mixed with leaves containing DMT for a significantly different – psychedelic effect. *N,N*-dimethyltryptamine (DMT) is a psychedelic compound of the tryptamine family and it is a structural analog of serotonin and melatonin. It is interesting to notice that DMT taken orally is broken down by the enzyme monoamine oxidase through a process called deamination and is quickly inactivated orally unless combined with a monoamine oxidase inhibitor.



Harmala alkaloids are monoamine oxidase-inhibiting *beta*-carboline. Two of the three most studied harmala alkaloids in the *B. caapi* vine are harmine and harmaline. In this problem you have to complete the synthesis of harmine and harmaline given below.

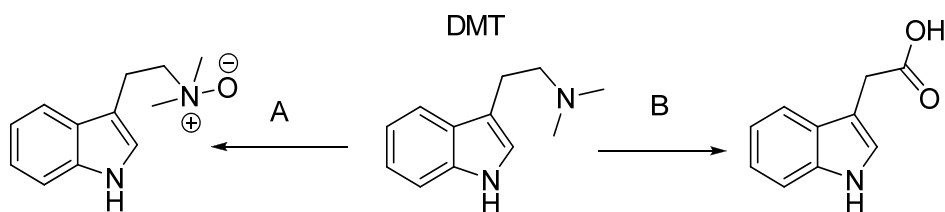


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4. Identify compounds **1-10** and **12** and draw their structures.
The answers are in the scheme of synthesis above.

DMT in one's mouth can be metabolized in at least two different ways. One pathway is governed by a monoamine oxidase and aldehyde dehydrogenase enzyme activity (MAO-ADH). Other product is obtained through other modifications. Two products are given bellow.



5. MAO-ADH enzyme is hidden under the letter (mark the right one):

- A
 B
 both
 none of these are right