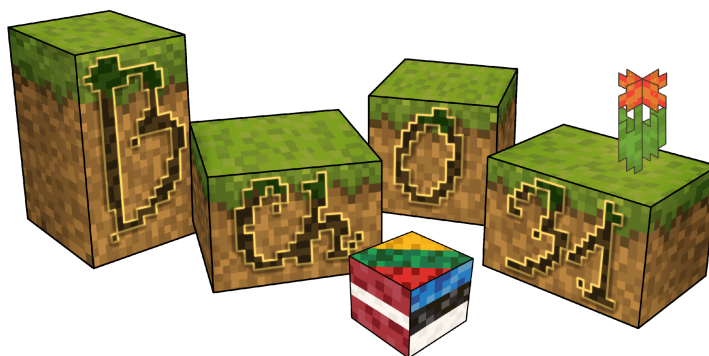




31st Baltic Chemistry Olympiad (2025)
Vilnius, 2025

Theoretical problems

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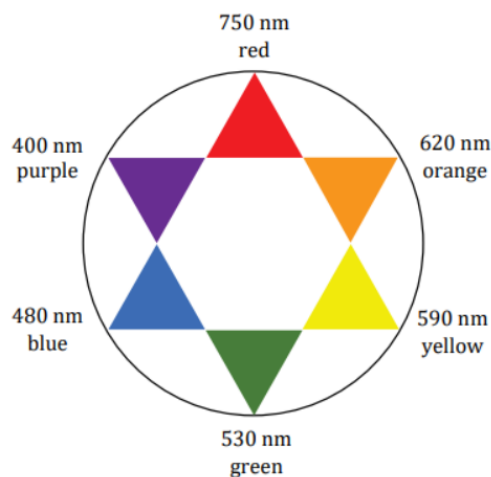
General instructions for theoretical part:

- You have 5 hours to complete the theoretical part.
- Use of calculator, ruler, periodic table of the elements is allowed.
- All answers must be clearly written with a pen.
Do not leave answers written with a pencil, they will not be graded!
- Drinks or light snacks during examinations are allowed.
- For drafts use separate white sheets.
- Even if not directly required in the question, always include necessary calculations in your answer.
- Collaboration during examination is strictly prohibited!
- If you need to leave the exam room (to use the toilet or have a drink or a snack), raise your hand and the supervisor will come to accompany you.
- Do not forget to write your participant code in the box on the first page.
- Mobile phones and electronic devices must be in the bags or backpacks.
Use of them is strictly prohibited!
- Supervisors will inform you how much time is left 2 h, 1 h, 30 min., 10 min. until the end of examination.
- If you have any questions, raise your hand and the supervisor will come to help.

Periodic table of the elements

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 l	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -



 Constants and formulae

Avogadro constant	$N_A = 6,02214 \cdot 10^{23} \text{ mol}^{-1}$	Rate law	$v = k [A]^m [B]^n \dots$
Universal gas constant	$R = 8,3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 0,083145 \text{ L} \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	1st order integrated rate law	$\ln \frac{[A]_t}{[A]_0} = -kt$
Standard pressure	$p^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$	1st order half-life	$t_{1/2} = \frac{\ln 2}{k}$
1 atm pressure	$760 \text{ mmHg} = 101325 \text{ Pa}$	2nd order integrated rate law	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$
Ideal gas equation	$pV = nRT$	2nd order half-life	$t_{1/2} = \frac{1}{k[A]_0}$
	$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2}$	Arrhenius equation	$k = A \cdot \exp\left(-\frac{E_A}{RT}\right)$
$\chi_1 = \frac{n_1}{n_1 + n_2 + \dots} = \frac{p_1}{p_1 + p_2 + \dots}$		$\ln \frac{k_2}{k_1} = \frac{E_A}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$	
Work of gas expansion against constant pressure	$A = -p\Delta V$	Enthalpy change	$\Delta H = \Delta U + p\Delta V$
Work of reversible gas expansion	$A = nRT \ln \frac{p_2}{p_1}$	Gibbs free energy change	$\Delta G = \Delta H - T\Delta S$
Lambert-Beer law	$A = \lg \frac{I_0}{I} = \epsilon c l$	$\Delta_r H^\circ = \sum \nu \Delta_f H^\circ(\text{prod}) - \sum \nu \Delta_f H^\circ(\text{reag})$	
Atomic mass unit	$1 \text{ u} = 1,66054 \cdot 10^{-27} \text{ kg}$	$\Delta_r G^\circ = \sum \nu \Delta_f G^\circ(\text{prod}) - \sum \nu \Delta_f G^\circ(\text{reag})$	
Electron mass	$m_e = 9,10938 \cdot 10^{-31} \text{ kg}$	$\Delta_r S^\circ = \sum \nu S^\circ(\text{prod}) - \sum \nu S^\circ(\text{reag})$	
Planck constant	$h = 6,62608 \cdot 10^{-34} \text{ J s}$	$a \text{ A(aq)} + b \text{ B(aq)} \rightleftharpoons c \text{ C(aq)} + d \text{ D(aq)}$	
Speed of light	$c = 2,99793 \cdot 10^8 \text{ m s}^{-1}$	$Q_r = \frac{[C]^c [D]^d}{[A]^a [B]^b}$	
Boltzmann constant	$k_B = 1,38065 \cdot 10^{-23} \text{ J K}^{-1}$	$\Delta_r G = \Delta_r G^\circ + RT \ln Q_r$	
Photon energy	$E = h\nu$	$\Delta_r G^\circ = -RT \ln K = -nFE^\circ_{\text{cel}}$	
Wavelength and frequency relationship	$\lambda \cdot \nu = c$	Nernst equation	$E = E^\circ - \frac{RT}{nF} \ln Q_r$
Wavenumber	$\tilde{\nu} = \frac{1}{\lambda}$	Faraday constant	$F = 96485 \text{ C mol}^{-1}$
1 eV 1 eV/atom	$1,60218 \cdot 10^{-19} \text{ J}$ $96,4853 \text{ kJ/mol}$	$\ln \frac{k_2}{k_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$	
$pH = -\lg[H^+]$	$pH = pK_a + \lg \lg \frac{[B]}{[R]}$	$K_a \times K_b = K_w$	$K_p = K_c (RT)^{\Delta \nu_{\text{duj\ddot{u}}}}$

Problem 1. Thermodynamics of fuel cells

The following data might be helpful in the task. Assume that the given quantities are independent of temperature.

	$\Delta_f H^\circ$ [kJ mol ⁻¹]	S° [J mol ⁻¹ K ⁻¹]	MW [g mol ⁻¹]	ρ [g L ⁻¹]
HCOOH(l)	-425.51	131.84	46.03	1220
H ₂ O(l)	-285.83	69.95	18.02	-
CO ₂ (g)	-393.52	213.79	44.01	-
O ₂ (g)	-	205.15	32.00	-
H ₂ (g)	-	130.68	2.02	0.090

The overall reaction in a hydrogen fuel cell is:



- a)** Calculate the standard potential (E°) for the reaction at 298 K.

The thermal energy efficiency of the fuel cell is defined as the amount of useful electrochemical energy produced ($|\Delta G|$) relative to the change in stored chemical energy ($|\Delta H|$).

- b)** Calculate the efficiency of an ideal hydrogen fuel cell.

A real hydrogen fuel cell operates at a potential (E) of 0.80 V.

- c)** Calculate the energy efficiency for the real hydrogen fuel cell.

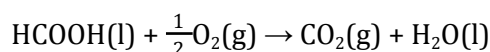
Besides efficiency, to determine the applicability of fuel cells, useful quantities are the gravimetric energy density ($\Delta G/m$) and volumetric energy density ($\Delta G/V$), describing the total electrochemical energy released per mass or volume of the reactant, respectively. The commonly used units for these quantities are kWh kg⁻¹ for the gravimetric energy density, and kWh L⁻¹ for the volumetric energy density.

- d)** Calculate the gravimetric energy density expressed in kWh kg⁻¹ for hydrogen at 298 K. 1 W = 1 J s⁻¹.
e) Calculate the volumetric energy density expressed in kWh L⁻¹ for hydrogen at 298 K.

To achieve higher volumetric energy density, the hydrogen can be pressurised. A typical pressurized H₂ cylinder has a pressure of 700 bar.

- f)** Calculate the volumetric energy density for the pressurised hydrogen. Assume that hydrogen behaves as an ideal gas.

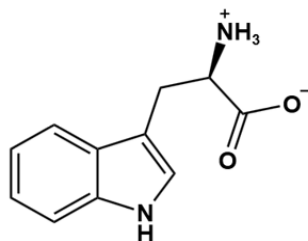
One of the alternatives to the hydrogen fuel cell is a formic acid fuel cell, with the overall reaction:



- g)** Calculate the standard Gibbs free energy ($\Delta_r G^\circ$) and the standard potential (E°) for the reaction at 298 K.
h) Calculate the gravimetric energy density expressed in kWh kg⁻¹ for formic acid at 298 K.
i) Calculate the volumetric energy density expressed in kWh L⁻¹ for formic acid at 298 K.

Problem 2. From tryptophan to melatonin

L-tryptophan (Trp) is an essential amino acid. It plays a crucial role in the production of niacin (vitamin B₃), the synthesis of the neurotransmitter serotonin, as well as the hormone melatonin. The acid dissociation constant values of Trp: $pK_{a1} = 2.38$ and $pK_{a2} = 9.39$ at 25 °C.



Tryptophan

a) Calculate the following molar fractions of *L*-tryptophan at its isoelectric point, where the overall charge of the molecule is zero:

- i)
- ii)
- iii)

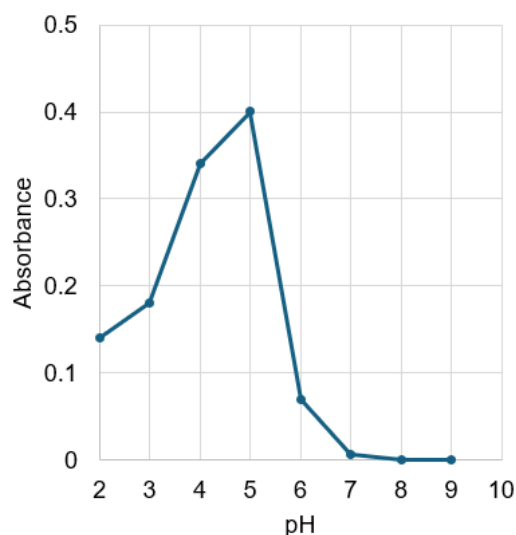
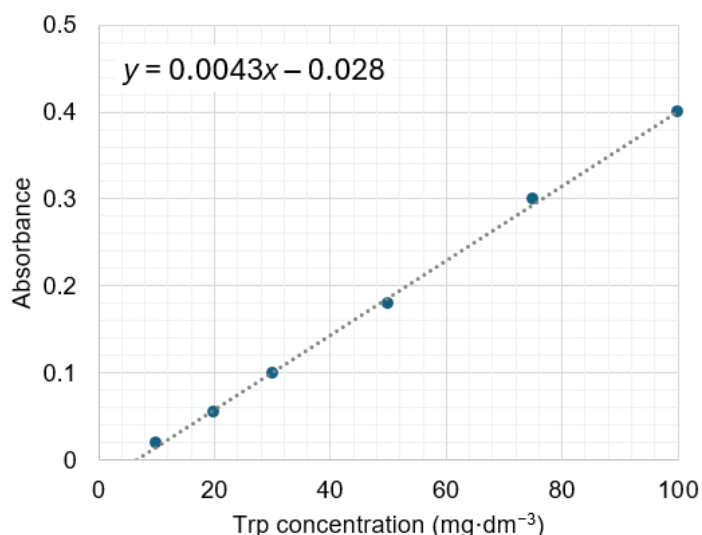
α_{carboxyl} of the ionogenic carboxyl group;

α_{amino} of the ionogenic amino group;

α_{neutral} of the completely neutral (uncharged) form of Trp.

b) A 1.00 g sample of Trp is dissolved in 50.0 cm³ of deionized water. Calculate the equilibrium concentrations (mol·dm⁻³) of all forms of *L*-tryptophan [Trp⁺], [Trp⁰], and [Trp⁻] present in the solution.

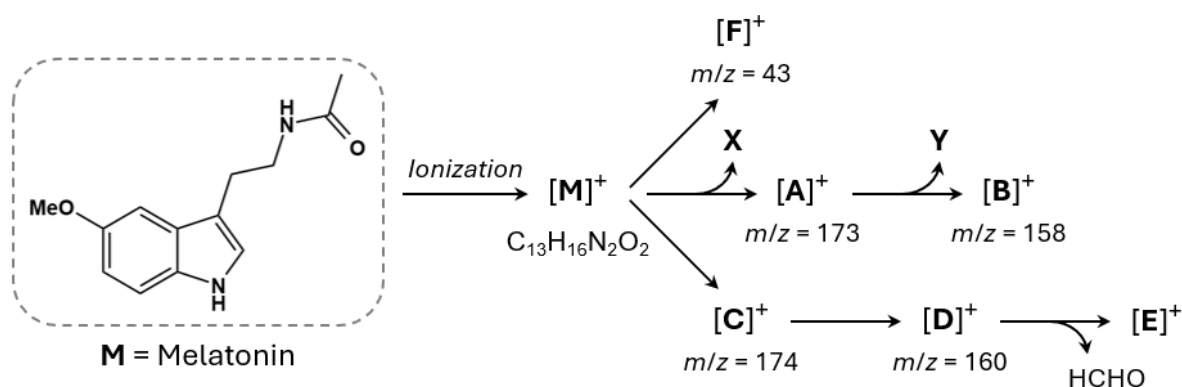
The concentration of Trp can be determined spectrophotometrically. In the chromogenic Hopkins-Cole reaction, a crimson-coloured, light-absorbing product is formed when Trp reacts with glyoxylic acid in a 2 : 1 molar ratio in the presence of an oxidizing agent. The left graph shows the linear correlation between different Trp concentrations and absorbance at 525 nm. The right graph illustrates the change in absorbance at 525 nm of a 50 mg·dm⁻³ Trp solution at different pH levels. The measurements were taken using a cuvette with an optical path length of exactly 1 cm.



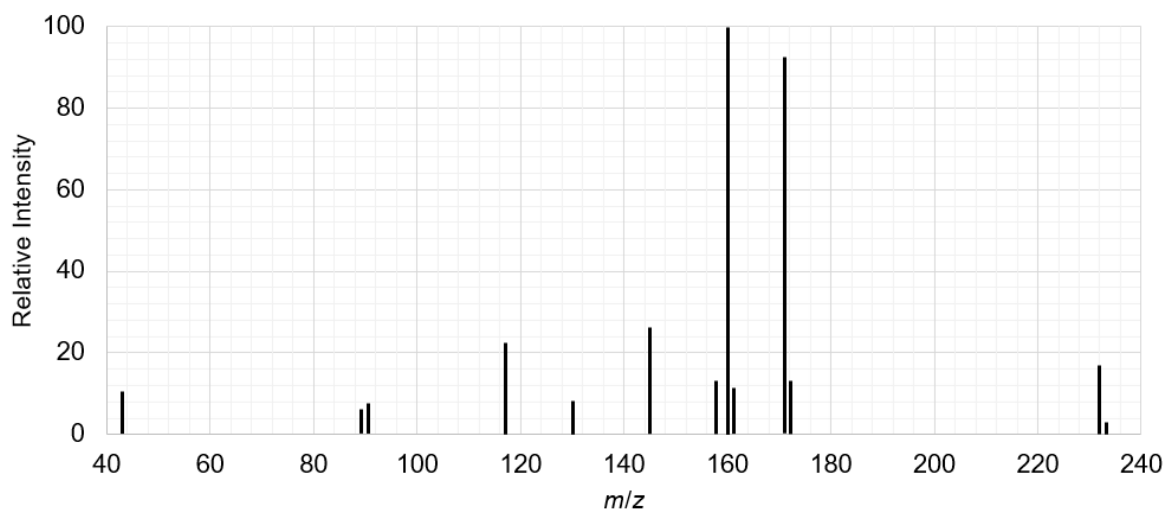
c) Calculate:

- i) the concentration (g·dm⁻³) of a Trp solution, given that its measured absorbance is 0.785.
- ii) the theoretical molar absorption coefficient ϵ (dm³·mol⁻¹·cm⁻¹) of the crimson-coloured Trp solution at pH 5.

Melatonin, produced by the pineal gland, plays a key role in regulating the sleep-wake cycle. The possible EI (electron ionization) fragmentation pathways of the melatonin's molecular ion [M]⁺ are shown in the following scheme:



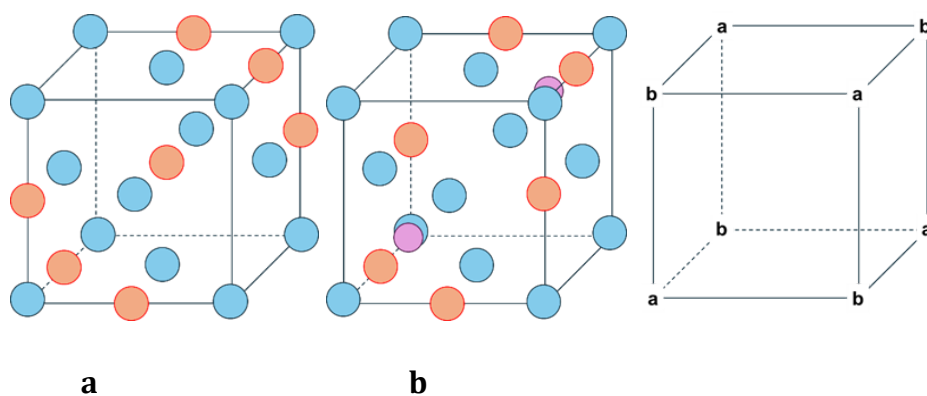
The corresponding mass spectrum of melatonin with some additional fragment peaks is given below. Note that the mass spectrum does not display all possible fragment peaks.



- d) Draw the structural formulas of fragments **A–F** and the molecule **X**.
- e) Draw the possible non-radical reaction mechanisms showing the transformations **i)** from $[M]^+$ to $[A]^+$ and **ii)** from $[D]^+$ to $[E]^+$. Provide the structures of all the products for both reactions!

Problem 3. Spinel structures

Spinel are naturally occurring crystals. Most commonly they exist as binary metal oxides (AB_2O_4). The crystal structure of normal spinels is characterized by a cubic lattice comprising 8 cubic subunits **a** and **b** in which oxygen atoms form a face-centered cubic (FCC) lattice. In **b** structure A metal ion occupies two tetrahedral voids, while in both subunits B ion occupies octahedral voids. Some compounds adopt an inverse spinel structure in which half of ions in octahedral voids occupy tetrahedral voids and all tetrahedrally coordinated ions occupy octahedral voids.



- a) How many AB_2O_4 formula units are in the spinel unit cell?
- b) What percentage of tetrahedral and octahedral voids A and B ions occupy in normal structure?
- c) What percentage of tetrahedral and octahedral voids are occupied by A and B in inverse spinel structure?
- d) Express smallest A–O distance in normal spinel in terms of unit cell length l . Assume that the structure is ideal.

$MgAl_2O_4$ is a prototype compound of the spinel structural family. It can form solid solutions with an excess of MgO . When Mg^{2+} cations, which have a lower valency, substitute Al^{3+} cations, two main mechanisms help maintain electrical balance. The first mechanism involves addition of cations to interstitial sites, while the second involves the creation of oxygen vacancies.

- e) At what ratio Mg^{2+} ions substitute Al^{3+} ions, when charge balance is preserved by adding cations to interstitial sites?
- f) How many oxygen ion vacancies per substitutional Mg^{2+} are needed to preserve electroneutrality? Hint: the ratio is not necessarily a whole number
- g) Write formulas in terms of x for $Mg_{1+x}Al_yO_z$ solid solution when cation addition to interstitial sites or oxygen ion vacancy formation mechanisms preserve the charge balance.
- h) MgO is mixed with $MgAl_2O_4$ and reaction takes place to form solid solution. Express the MgO/Al_2O_3 molar ratio in the resulting solid solution as a function of the added MgO molar fraction in the initial mixture. Assume that reaction goes to full completion and charge balance is maintained by adding forming cations to interstitial sites.

In spinel structures a metal ion preference for tetrahedral or octahedral sites can be determined by Crystal Field Theory (CFT). The coordination environment that provides greater crystal field stabilization energy (CSFE) is preferred for the metal ion to occupy. Crystal field stabilization energy can be expressed in terms of the crystal field splitting energy (Δ). The crystal field splitting energy in octahedral and tetrahedral environments can be compared by using this equation:

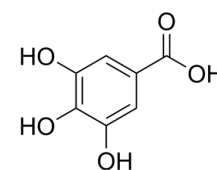
$$\Delta_t \approx \frac{4}{9}\Delta_o$$

where Δ_t and Δ_o are crystal field splitting energy in tetrahedral and octahedral coordination environments, respectively.

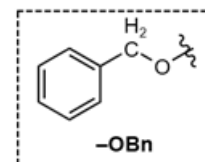
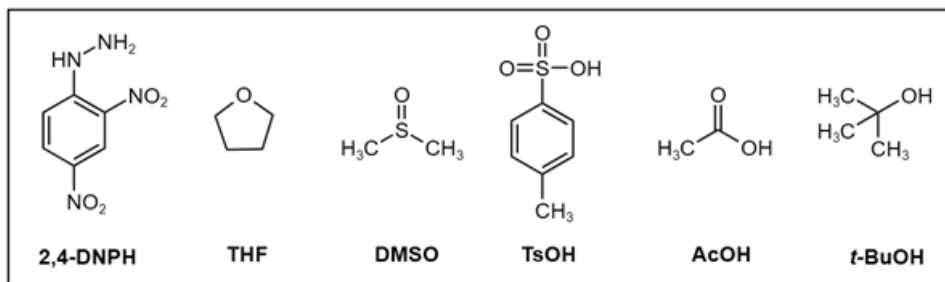
- i) Chromite ($FeCr_2O_4$) is another oxide which adopts spinel structure. Draw energy splitting diagrams of Fe^{2+} and Cr^{3+} ions in tetrahedral and octahedral coordination environments. Which spinel structure for this binary oxide is expected: normal or inverse? Crystal field splitting energy (Δ) for Cr^{3+} ion in octahedral coordination environment is greater than for Fe^{2+} and O^{2-} is weak field ligand.
- j) The length of the unit cell of chromite is $8.34 \text{ \AA}$. What is the density of chromite?
- k) Chromite is particularly used for production of ferrochrome alloy by carbothermic reduction process. Write a balanced equation for the reduction process of chromite. How much chromium can be extracted from 1 ton of this ore? Hint: the main gaseous product of reaction is CO .
- l) Crystal field splitting energy for Cr^{3+} ion in chromite is $17\,390 \text{ cm}^{-1}$. What wavelength of photon does this energy correspond to?

Problem 4. Relax, take it easy!

Alkaloids are a broad class of naturally occurring nitrogen-containing compounds. Most of them have found use in traditional medicine due to diverse and important physiological effects on humans. The first alkaloid to be ever isolated from a plant was morphine, which in 1806 German chemist Friedrich Sertürner extracted from opium. However, since we are here not for history class, today we will focus on one of the first laboratory syntheses of morphine except we will do it without getting our hands wet and in a simplified manner.



Gallic acid

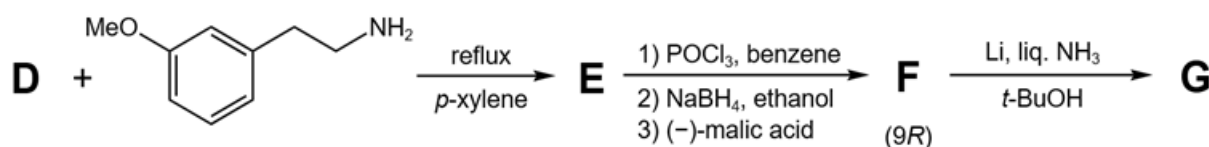


The synthesis begins with gallic acid that is easily accessible from hydrolysis of oak bark tannins. Firstly, esterification and selective etherification is done and few transformations of protected gallic acid ester are performed as shown below.



a) Draw structural formulas of compounds **A–D**.

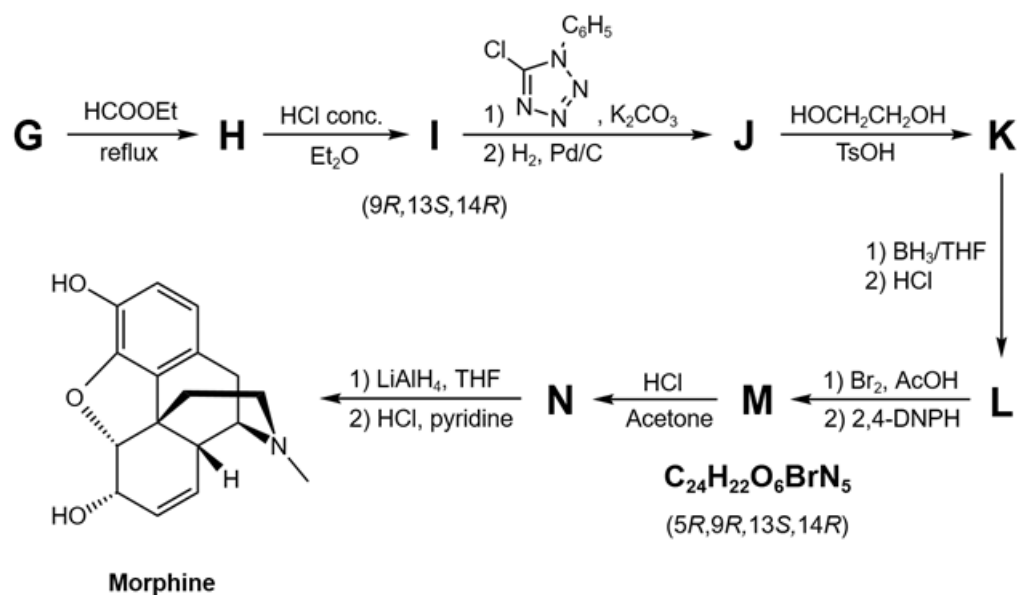
The condensation of **D** with 3-methoxyphenylethylamine yields compound **E** which consequently undergoes Bischler-Napieralski reaction and reduction to afford racemic **F**. After optical resolution enantiopure (*R*)-**F** undergoes Birch reduction producing **G** which is known to contain a double bond between carbons that hold two rings fused together.



- Explain why and how the use of (–)-malic acid enables chiral separation of **F** enantiomers.
- Draw structural formulas of compounds **E–G** with appropriate stereochemistry.
- Interestingly, if **D** is condensed with 4-methoxyphenylethylamine rather than 3-methoxyphenylethylamine and the product undergoes identical subsequent reactions as **E**, the same racemic **F** can be obtained. Propose a mechanism which provides an explanation for this abnormality. *Hint: Somewhere in the mechanism nitrilium intermediate should be formed.*

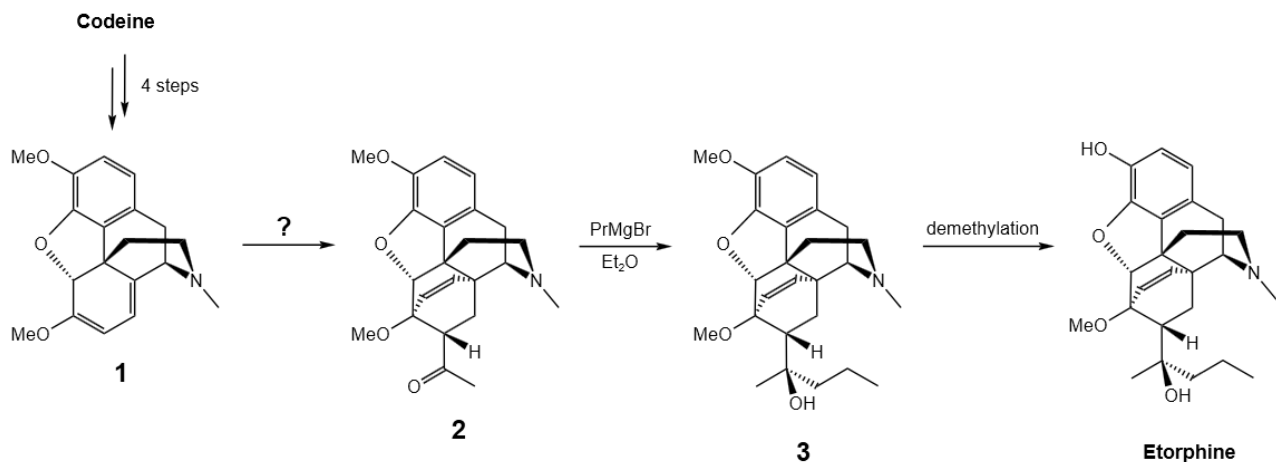
Even though the next sequence of transformations involves few reactions that are poorly stereoselective, conversion of stereoisomers to each other is possible with additional steps. For the sake of clarity, we will ignore optical purification procedures and assume that only enantiopure substances are allowed to react. Below stereochemical information is indicated *only when at least one new chiral center arises*.

Useful hints: Transformations **H** → **I** and **L** → **M** involve cyclization; **M** is an orange crystalline substance which has bromo and methoxy substituents meta to each other.

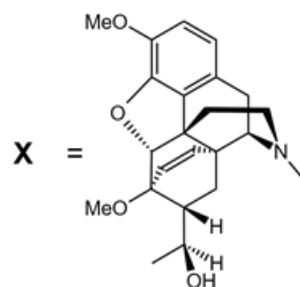


- e) Draw structural formulas of compounds **H–N** with appropriate stereochemistry.
 f) Show and briefly comment why the reaction of **N** with LiAlH_4 is highly stereoselective, yielding a morphine-like stereoisomer.

If morphine synthesis is stopped just before the last step, about ten thousand times more potent drug, etorphine, could be obtained by subjecting the product (codeine) to a sequence of straightforward reactions.

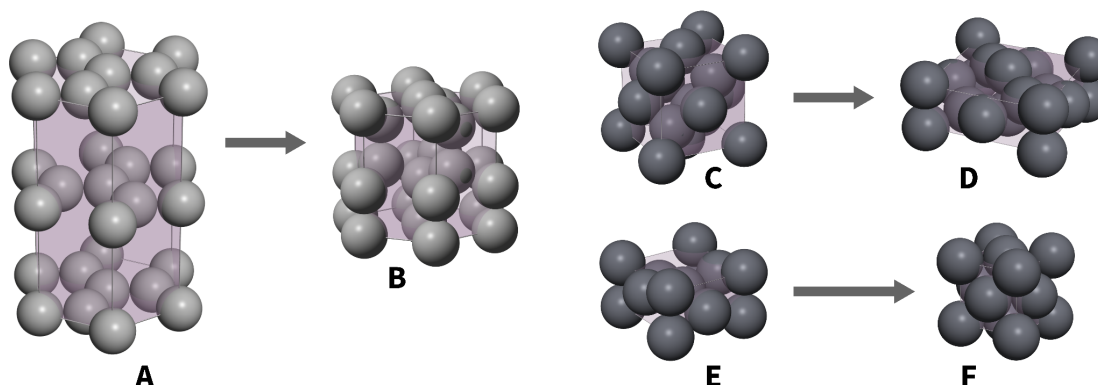


- g) Draw a simple reagent that could be used to achieve stereoselective conversion **1** → **2** in one step.
 h) Unfortunately, reaction of **2** with PrMgBr yields **X** as the major product. What coproduct is produced when **X** forms?
 i) Methoxy group having a 1,3-relationship with carbonyl group in **2** severely impacts stereoselectivity of Grignard reaction. Show preferred addition pathway which explains why particular diastereomer is formed in reaction **2** → **3**. *Hint: Newman projections may help you to provide an explanation. For simplicity use of labels –Me, –Pr, –CH₂R, –CR₂–OMe is recommended.*



Problem 5. From diatomics to solids

Elements of the 14th group are especially rich in allotropes. Graphite, diamond, nanotube, and β -tin are even used to label similar structures of other elements. The periodic trend in transformation of predominant forms of the 14th group elements – from graphitic structure carbon (**A**) to diamond-like structure (**C**) of silicon to β -tin structure of tin (**D** and **E**), and finally to face-centered cubic (FCC) structure of lead (**F**) – can be presented in the form of elongating a unit cell and/or shifting atoms' positions as illustrated below.



a) Determine the parameters of unit cells **A–F**. Here **B** is a hexagonal diamond structure.

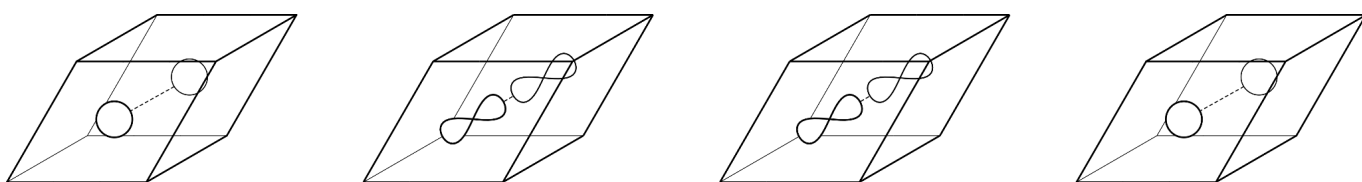
None of the 14th group elements are present in nature as diatomic molecules. Yet, you can see the emission of photons from the excited $^3\Pi_g$ state of C_2 formed in a flame of burning hydrocarbons. The ground state of the C_2 molecule ($^1\Sigma_g$) differs from the ground state of other 14th group diatomics ($^3\Sigma_g$).

b) Draw schematically and fill the MO diagrams of C_2 and Si_2 .

c) Circle the correct options in the following text about C_2 .

C_2 is a rare molecule without $\{\sigma, \pi, \delta\}$ -bonds, yet with two $\{\sigma, \pi, \delta\}$ -bonds. That is because the 2p orbital has $\{0, 1, 2\}$ radial nodes, which gives the best orbital overlap (S) in forming π -bonds compared to np orbitals, with $n > 2$. Also, as the energy of atomic orbitals (ϵ_{AO}) is proportional to n^{-2} , the bonding MO energy (ϵ_{MO}) is approximately $\epsilon_{AO} \cdot (1 + S)$, the π -bonds of C are much stronger than those of other 14th group elements. When excited to $^3\Pi_g$ – a state with a bond order of $\{1, 2, 3\}$ – C_2 relaxes by emitting a photon with 2.4 eV energy, which corresponds to $\{\text{red, orange, yellow, green, blue, purple}\}$ light. Eventually, C_2 produced in flame polymerizes into soot consisting of $\{\text{diamond, fullerene, graphene, graphite, lonsdaleite, nanotube}\}$ entities.

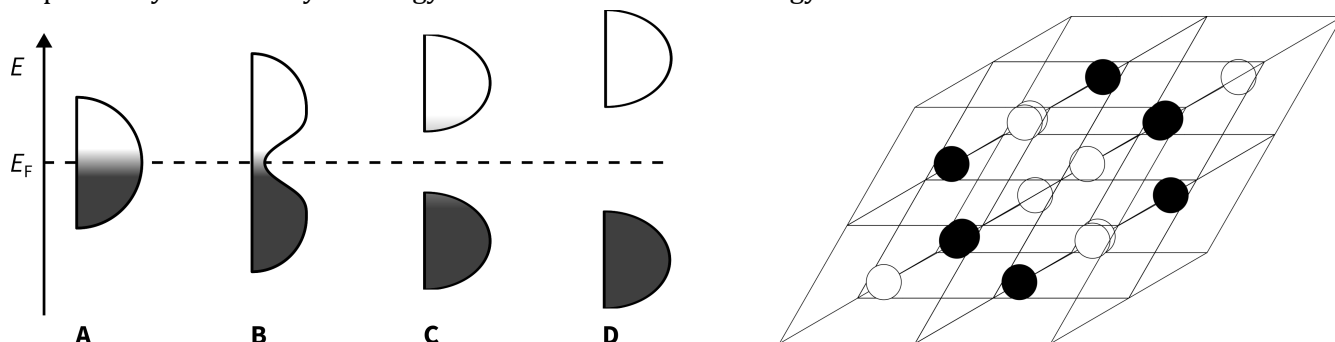
For many solid structures, it is possible to choose a unit cell that contains two atoms, resembling a diatomic molecule. In the following figure, the orbitals are embedded into a unit cell of the diamond-type structure.



d) Color in black-and-white the phase of the diatomic's MO, so that the orbital energy of the resulting periodic orbitals increases from left to right.

In solids, combinations of N orbitals give a so-called band, which corresponds to a range of allowed N energy levels. Periodic repetition of the orbitals shown below corresponds to extreme energy levels. Similarly to how MOs are constructed in diatomic molecules, it is possible to use a diatomic's MOs to form periodic orbitals for intermediate energy levels in bands. Namely, inverting half of the antibonding diatomics' MOs in a $2 \times 2 \times 2$ unit cell gives the shown non-bonding periodic orbital. The inverted and non-inverted periodic

orbitals set the upper and lower energy values for the corresponding antibonding s-band. The energy value between (or the average energy of) the highest occupied and lowest unoccupied orbitals is called the Fermi energy. Depending on whether the Fermi energy is within a band or in a band gap, an element can be a non-metal: an insulator (diamond) or a semiconductor (silicon); or a conductor: a semimetal (graphite) or a metal (lead). Electrical conductivity is the ability of electrons to move through a material, which depends on the proximity and density of energy levels above the Fermi energy.



- e) Assign the above listed material types to the shown electronic band structures **A–D**.
- f) Estimate the band gap in diamond-type structure of C, Ge, and Pb solids, assuming that the highest occupied periodic orbital is due to the bonding p-orbital (from question **d**) and the lowest unoccupied orbital is the shown non-bonding s-orbital. Assume that the energy of the bonding p-orbital is given by $\varepsilon_p \cdot (1 + 2 \cdot S)$ and $S \approx 4/9$. Take that orbital energies ε_s and ε_p equal to the negative value of ionization energies given in the table (in eV). *Hint: This model predicts that Pb has a negative band gap, which means it is a metallic solid with zero band gap. The estimation yields reasonable agreement with known values, particularly for semiconducting silicon, whose band gap is closest to 1.1 eV for optimal performance of solar cells.*

In terms of orbitals, a linear chain of carbon atoms – carbyne – has much in common with the FCC structure of lead, where atoms are also aligned. In both structures, pairs of p-orbitals combine in a similar way to form continuous π -bands with bonding and antibonding levels.

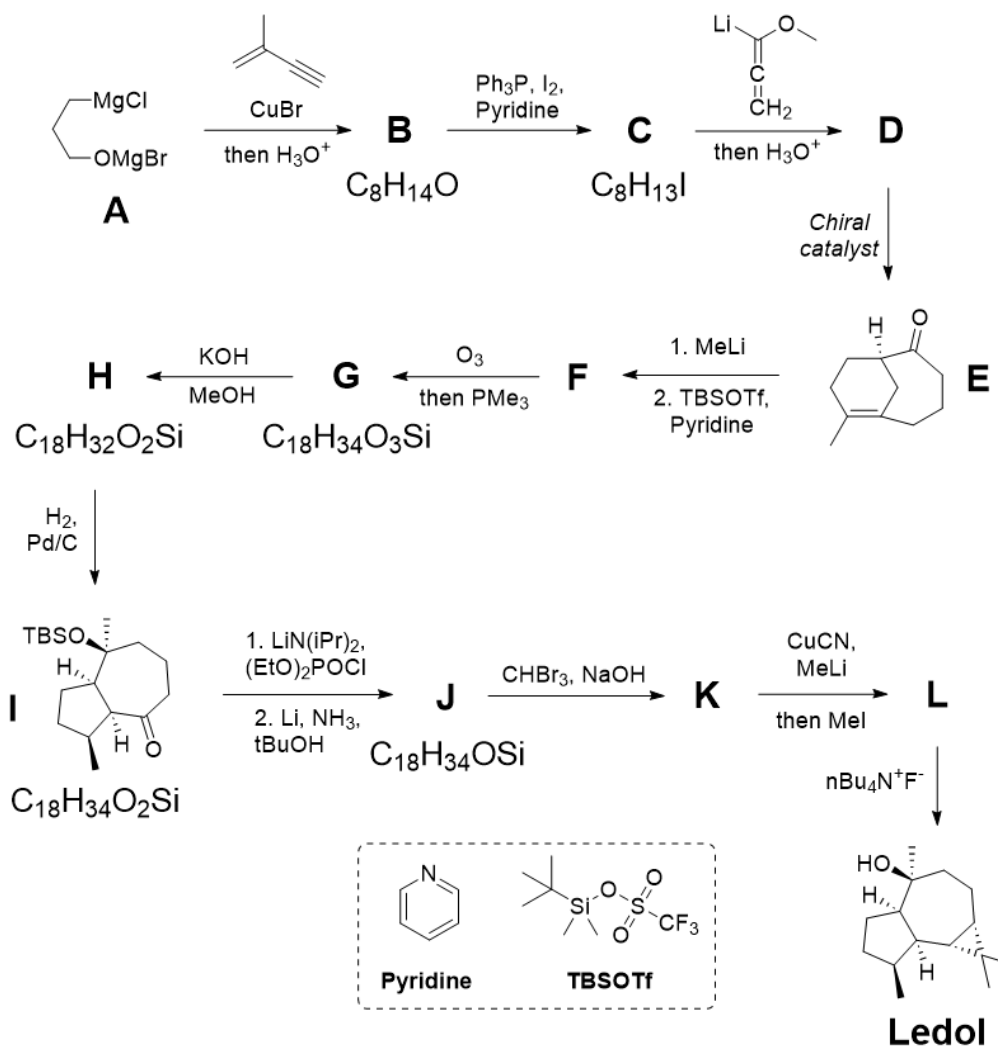
- g) Show that combinations of bonding and antibonding MOs can give identical periodic orbitals, which means there is no band gap between bonding and antibonding bands. *Hint: the drawing must have the same number of angular nodes, which (dis)appear upon inversion of MOs.*
- h) Circle the correct options in the following text about Pb.

In high-coordinated solids, the overlap (S) of a given orbital with neighboring orbitals is {lower, higher} than in low-coordinated ones. In the FCC structure, the overlap is {lower, higher}, leading to a {wider, narrower} p-band, in comparison to the diamond-type structure. Thus, the FCC structure is {stabilized, destabilized} by occupying the bonding p-orbitals. In the diamond-type structure, the antibonding {s, p, d}-band crosses the Fermi energy. Thus, the diamond-type structure is {stabilized, destabilized} by occupying the antibonding s-orbitals.

- i) Generalize the explanation of why some group 14 elements are semiconductors with low coordination numbers, while others are conductors with higher coordination numbers.
- ☐ The crystal structure is favored when its geometry allows orbital overlap that maximizes bonding interactions and minimizes the filling of antibonding levels.
 - ☐ The energy gap between s- and p-orbitals becomes smaller for heavier elements, which favours metallic bonding.
 - ☐ The larger atomic radius of heavier elements prevents directional bonding, making the diamond structure geometrically unstable.
 - ☐ Heavier elements have lower electronegativity, which favors metallic bonding.

Problem 6. What doesn't kill you makes you stronger?

Ledol is a sesquiterpene found in plants from eucalyptus to American ginseng. Beyond its biological effects, ledol-rich plants have long been utilized in shamanistic rituals. In this problem, we'll explore an enantioselective synthesis of ledol via an elegant intramolecular Diels–Alder (IMDA) reaction that creates an anti-Bredt bicyclic structure as a key intermediate. *Hints: IMDA reaction is formally an isomerization reaction; The first step in transformation $C \rightarrow D$ is an S_N2 reaction.*



- Draw the structures of compounds **B–D**, **F–H** and **J–L**, clearly indicating relevant stereochemistry.
- In the reaction from **J** to **K**, CHBr_3 first reacts with NaOH and creates a reactive intermediate. Draw a **Lewis** structure of this intermediate.
- Determine the role of PMe_3 in the reaction from **F** to **G**.

The specific catalyst, which acts as a chiral Lewis acid, used in the IMDA reaction is shown in the picture on the right side.

- By drawing a structure, show how the catalyst interacts with **D** (or a general substrate for such a reaction). Use R groups as abbreviations for simplification, if required.

