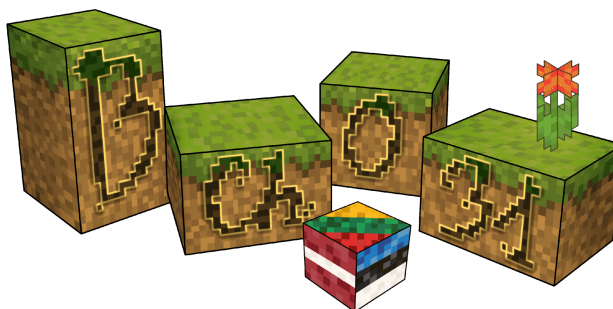


Participant code	
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Name																	
Surname																	

(Write in capital letters)



31st Baltic Chemistry Olympiad (2025)
Vilnius, 2025

Theoretical part

Answer sheets

For authors of problems:

Problem	1	2	3	4	5	6	Σ
Primary evaluation							
Appeal							
Final							

Problem 1. Thermodynamics of fuel cells

a)	b)	c)	d)	e)	f)	g)	h)	i)	Σ
1	1	2	2	1	2	4	2	1	16

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

$$E^\circ = -\Delta_r G^\circ / nF = -(-226080) / (2 \cdot 96485) = \mathbf{1.17 \text{ V}} \quad (1)$$

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

$$\eta = |\Delta G| / |\Delta H| = 226.08 / 285.83 = 0.79 = \mathbf{79\%} \quad (1)$$

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

$$\Delta G = -nFE = -2 \cdot 96485 \cdot 0.8 = -154.38 \text{ kJ mol}^{-1} \quad (1)$$

$$\eta = |\Delta G| / |\Delta H| = 154.38 / 285.83 = 0.54 = \mathbf{54\%} \quad (1)$$

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

$$\Delta G/W = 226.08 \text{ kJ mol}^{-1} / 2.02 \text{ g mol}^{-1} = 111.92 \text{ kJ g}^{-1} \quad (1)$$

$$1 \text{ W} = 1 \text{ J s}^{-1}; \text{ so } 1 \text{ Wh} = 1 \text{ J s}^{-1} * 1 \text{ h} = 1 \text{ J s}^{-1} * 3600 \text{ s} = 3600 \text{ J}; \text{ so } 1 \text{ kWh} = 3600 \text{ kJ}$$

$$\Delta G/W = 111.92 \text{ kJ g}^{-1} / 3600 \text{ kJ kWh}^{-1} = 0.031 \text{ kWh g}^{-1} = \mathbf{31 \text{ kWh kg}^{-1}} \quad (1)$$

- e) Calculate the volumetric energy density expressed in kWh L⁻¹ for hydrogen at 298 K.

$$\Delta G/V = \Delta G/W * \rho = 31 \text{ kWh kg}^{-1} * 0.000090 \text{ kg L}^{-1} = \mathbf{2.79 \cdot 10^{-3} \text{ kWh L}^{-1}} \quad (1)$$

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

At standard conditions, $P^\circ = 1 \text{ bar}$.

From the ideal gas law, density is proportional to pressure. (1)

$$\Delta G/V = 2.79 \cdot 10^{-3} * 700 = \mathbf{1.95 \text{ kWh L}^{-1}} \quad (1)$$

g) Calculate the standard Gibbs free energy ($\Delta_r G^\circ$) and the standard potential (E°) for the reaction at 298 K.

$$\Delta_r S^\circ = 49.33 \text{ J mol}^{-1} \text{ K}^{-1} \quad (1)$$

$$\Delta_r H^\circ = -253.84 \text{ kJ mol}^{-1} \quad (1)$$

$$\Delta_r G^\circ = \Delta_r H^\circ - \Delta_r S^\circ \cdot T = 253.84 - 49.33 \cdot 10^{-3} \cdot 298 = \mathbf{-268.539 \text{ kJ mol}^{-1}} \quad (1)$$

$$E^\circ = -\Delta_r G^\circ / nF = -(-268539) / (2 \cdot 96485) = \mathbf{1.39 \text{ V}} \quad (1)$$

h) Calculate the gravimetric energy density expressed in kWh kg⁻¹ for formic acid at 298 K.

$$\Delta G/W = 268.54 \text{ kJ mol}^{-1} / 46.03 \text{ g mol}^{-1} = 5.83 \text{ kJ g}^{-1} \quad (1)$$

$$\Delta G/W = 5.83 \text{ kJ g}^{-1} / 3600 \text{ kJ kWh}^{-1} = \mathbf{1.62 \text{ kWh kg}^{-1}} \quad (1)$$

i) Calculate the volumetric energy density expressed in kWh L⁻¹ for formic acid at 298 K.

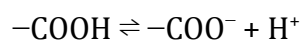
$$\Delta G/V = \Delta G/W \cdot \rho = 1.62 \text{ kWh kg}^{-1} \cdot 1.220 \text{ kg L}^{-1} = \mathbf{1.98 \text{ kWh L}^{-1}} \quad (1)$$

Problem 2. From tryptophan to melatonin

a)	b)	c)	d)	e)	Σ
4	4	2	6	2	18

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

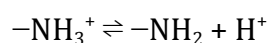
i) α_{carboxyl} of the ionogenic carboxyl group



$$K_{a1} = \frac{[\text{COO}^-] \cdot [\text{H}^+]}{[\text{COOH}]} \Rightarrow [\text{COO}^-] = [\text{COOH}] \cdot \frac{K_{a1}}{[\text{H}^+]} \quad (0.5)$$

$$\alpha_{\text{carboxyl}} = \frac{[\text{COOH}]}{[\text{COOH}] + [\text{COO}^-]} = \frac{[\text{COOH}]}{[\text{COOH}] + [\text{COOH}] \cdot \frac{K_{a1}}{[\text{H}^+]}} = \frac{1}{1 + \frac{10^{-\text{p}K_{a1}}}{10^{-\text{pH}}}} = \frac{1}{1 + 10^{(\text{pH} - \text{p}K_{a1})}} \approx \mathbf{3.1 \cdot 10^{-4}} \quad (1)$$

ii) α_{amino} of the ionogenic amino group



$$K_{a2} = \frac{[\text{NH}_2] \cdot [\text{H}^+]}{[\text{NH}_3^+]} \Rightarrow [\text{NH}_3^+] = [\text{NH}_2] \cdot \frac{[\text{H}^+]}{K_{a2}} \quad (0.5)$$

$$\alpha_{\text{amino}} = \frac{[\text{NH}_2]}{[\text{NH}_2] + [\text{NH}_3^+]} = \frac{[\text{NH}_2]}{[\text{NH}_2] + [\text{NH}_2] \cdot \frac{[\text{H}^+]}{K_{a2}}} = \frac{1}{1 + \frac{10^{-\text{pH}}}{10^{-\text{p}K_{a2}}}} = \frac{1}{1 + 10^{(\text{p}K_{a2} - \text{pH})}} \approx \mathbf{3.2 \cdot 10^{-4}} \quad (1)$$

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

Molar fraction of the completely uncharged form of Trp:

$$\alpha_{\text{neutral}} = \alpha_{\text{carboxyl}} \cdot \alpha_{\text{amino}} = (3 \cdot 10^{-4})^2 = \mathbf{9 \cdot 10^{-8}} \text{ (negligible amount)} \quad (0.5)$$

$$\alpha_{\text{carboxyl}} = \underline{\hspace{2cm}} \quad \alpha_{\text{amino}} = \underline{\hspace{2cm}} \quad \alpha_{\text{neutral}} = \underline{\hspace{2cm}}$$

b) Calculate the equilibrium concentrations ($\text{mol}\cdot\text{dm}^{-3}$) of all forms of *L*-tryptophan $[\text{Trp}^+]$, $[\text{Trp}^0]$, and $[\text{Trp}^-]$ present in the solution.

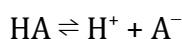
$$c_0 = \frac{n}{V} = \frac{m}{M \cdot V} = \frac{1.00 \text{ g}}{204.2 \text{ g}\cdot\text{mol}^{-1} \cdot 0.05 \text{ dm}^3} = 0.0979 \text{ mol}\cdot\text{dm}^{-3} \quad (0.5)$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-5.89} = 1.29 \cdot 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$$

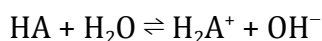
$$c_0 = [\text{Trp}^0] + [\text{Trp}^+] + [\text{Trp}^-] = [\text{Trp}^0]$$

$$[\text{Trp}^0] = [\text{HA}] = c_0 \cdot \frac{K_{a1}[\text{H}^+]}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} = \frac{0.0979 \cdot (4.17 \cdot 10^{-3} \cdot 1.29 \cdot 10^{-6})}{(1.29 \cdot 10^{-6})^2 + (4.17 \cdot 10^{-3} \cdot 1.29 \cdot 10^{-6}) + (4.17 \cdot 10^{-3} \cdot 4.07 \cdot 10^{-10})} =$$

$$= \frac{0.0979 \cdot 5.38 \cdot 10^{-9}}{5.38 \cdot 10^{-9}} = \mathbf{0.0979 \text{ mol}\cdot\text{dm}^{-3}} \quad (1)$$



$$[\text{Trp}^-] = [\text{A}^-] = \frac{[\text{HA}] \cdot K_{a2}}{[\text{H}^+]} = \frac{0.0979 \cdot 10^{-9.39}}{1.29 \cdot 10^{-6}} = \mathbf{3.09 \cdot 10^{-5} \text{ mol}\cdot\text{dm}^{-3}} \quad (1)$$



$$K_w = [\text{H}^+][\text{OH}^-] = 1 \cdot 10^{-14} \Rightarrow [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1 \cdot 10^{-14}}{1.29 \cdot 10^{-6}} = 7.75 \cdot 10^{-9} \text{ mol}\cdot\text{dm}^{-3} \quad (0.5)$$

$$[\text{Trp}^+] = [\text{H}_2\text{A}^+] = \frac{[\text{HA}] \cdot K_b}{[\text{OH}^-]} = \frac{[\text{HA}] K_w}{[\text{OH}^-] K_{a1}} = \frac{0.0979 \cdot 1 \cdot 10^{-14}}{7.75 \cdot 10^{-9} \cdot 10^{-2.38}} = \mathbf{3.03 \cdot 10^{-5} \text{ mol}\cdot\text{dm}^{-3}} \quad (1)$$

$$[\text{Trp}^+] = \underline{\hspace{2cm}}$$

$$[\text{Trp}^0] = \underline{\hspace{2cm}}$$

$$[\text{Trp}^-] = \underline{\hspace{2cm}}$$

c) Calculate:

i) the concentration ($\text{g}\cdot\text{dm}^{-3}$) of a Trp solution, given that its measured absorbance is 0.785

$$A = 0.785 = 0.0043x - 0.028 \Rightarrow x = c = \frac{0.785 + 0.028}{0.0043} \cdot \frac{1}{1000} \approx \mathbf{0.19 \text{ g}\cdot\text{dm}^{-3}} \quad (1)$$

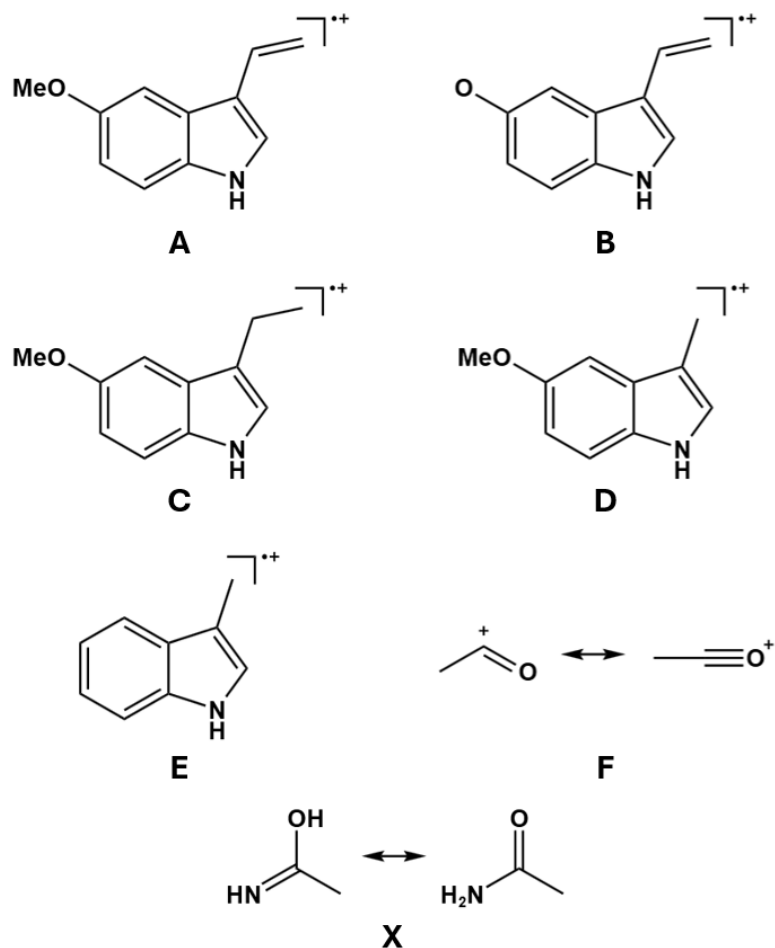
ii) the theoretical molar absorption coefficient ε ($\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) of the crimson-coloured Trp solution at pH 5

$$A = c\varepsilon l \Rightarrow \varepsilon = \frac{A}{c \cdot l} = \frac{0.4}{\left(\frac{1}{2} \cdot \frac{50 \text{ mg}\cdot\text{dm}^{-3}}{204.2 \text{ g}\cdot\text{mol}^{-1}} \cdot \frac{1 \text{ g}}{1000 \text{ mg}}\right) \cdot 1 \text{ cm}} \approx \mathbf{3300 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}} \quad (1)$$

$$c (\text{g}\cdot\text{dm}^{-3}) = \underline{\hspace{2cm}}$$

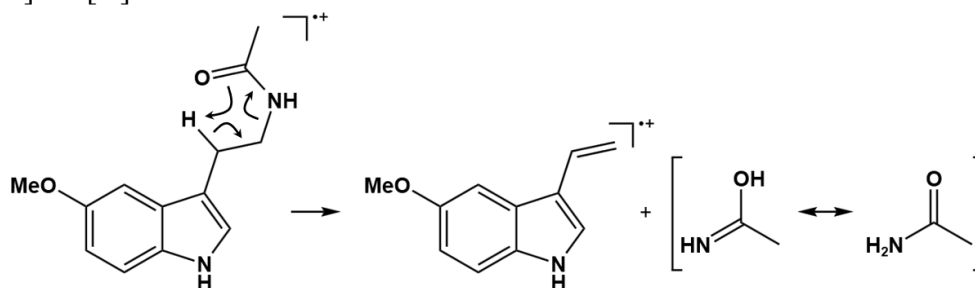
$$\varepsilon (\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}) = \underline{\hspace{2cm}}$$

d) Draw the structural formulas of fragments A–F and the molecule X.

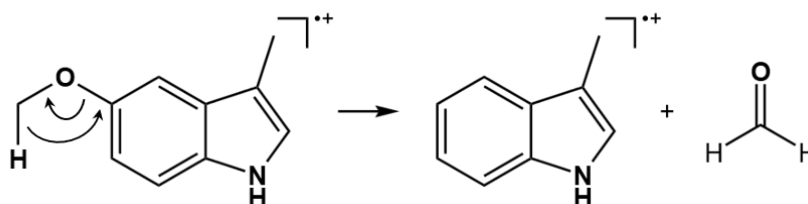


e) Draw the possible non-radical reaction mechanisms showing the transformations. Provide the structures of all the products for both reactions!

i) from $[\text{M}]^+$ to $[\text{A}]^+$



ii) from $[\text{D}]^+$ to $[\text{E}]^+$



Problem 3. Spinel structures

a)	b)	c)	d)	e)	f)	g)	h)	i)	j)	k)	l)	Σ
2	2	3	1	1	1	1	2	6	1	1	1	22

a) How many AB_2O_4 formula units are in the spinel unit cell?

In FCC structure there are 4 O^{2-} . Total number of oxygen ions is $8 \cdot 4 = 32$.
 There are 2 A metal ions per **b** subunit. Total A ions per unit cell is $4 \cdot 2 = 8$.
 There are $2\frac{1}{2}$ B metal ions per **a** subunit. There are $1\frac{1}{2}$ B ions per **b** subunit. The total B ions per unit cell is $\left(2\frac{1}{2} + 1\frac{1}{2}\right) \cdot 4 = 16$

Ratio of ions A:B:O in unit cell is 8:16:32. Hence, in the spinel unit cell there is 8 AB_2O_4 formula units.

2 p.

b) What percentage of tetrahedral and octahedral voids A and B ions occupy in normal spinel structure?

FCC unit cell has 8 tetrahedral voids and 4 octahedral voids. Spinel unit cell has 64 tetrahedral voids and 32 octahedral voids. 8 A ions take 8 tetrahedral voids. 16 B ions take 16 octahedral voids.

A ion occupies 8 tetrahedral voids or $\left(\frac{8}{64}\right) \cdot 100\% = 12.5\%$ of tetrahedral voids

B ion occupies 16 octahedral voids or $\left(\frac{16}{32}\right) \cdot 100\% = 50\%$ of octahedral voids

3 p.

c) What percentage of tetrahedral and octahedral voids are occupied by A and B in inverse spinel structure?

Half of B ions take tetrahedral position

A ion occupies 8 octahedral voids or $\left(\frac{8}{32}\right) \cdot 100\% = 25\%$ of octahedral voids

B ion occupies 8 tetrahedral voids or $\left(\frac{8}{64}\right) \cdot 100\% = 12.5\%$ of tetrahedral voids

B ion occupies 8 octahedral voids or $\left(\frac{8}{32}\right) \cdot 100\% = 25\%$ of octahedral voids

3 p.

d) Express smallest A–O distance in normal spinel in terms of unit cell length a . Assume that the structure is ideal.

Problem is solved by employing fractional coordinates. Length of **b** unit cell is:

$$b = \frac{a}{2}$$

Choosing one of vertex oxygen ions as origin of coordinate system. The coordinates of A ions in **b** cell can be expressed as such (0.75, 0.25, 0.25) and (0.25, 0.75, 0.75). Choosing A (0.75, 0.25, 0.25), we find that one of the four closest oxygen ions coincide with vertex of **b** cell (1, 0, 0).

$$|AO| = b\sqrt{(1 - 0.75)^2 + (0 - 0.25)^2 + (0 - 0.25)^2} = \frac{\sqrt{3}}{4}b = \frac{\sqrt{3}}{8}l$$

3 p.

e) At what ratio Mg^{2+} ions substitute Al^{3+} ions, when charge balance is preserved by adding cations to interstitial sites?

To preserve charge balance 3 Mg^{2+} substitute 2 Al^{3+} ions. 2 Mg^{2+} ions substitute 2 Al^{3+} and 1 Mg^{2+} adds to interstitial site to maintain charge balance.

1 p.

f) How many oxygen ion vacancies per substitutional Mg^{2+} are needed to preserve electroneutrality? *Hint: the ratio is not necessarily a whole number*

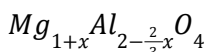
2 Mg^{2+} substitute 2 Al^{3+} . To maintain charge balance 1 O^{2-} vacancy must form.

1 p.

g) Write formulas in terms of x for $\text{Mg}_{1+x}\text{Al}_y\text{O}_z$ solid solution when cation addition to interstitial sites or oxygen ion vacancy formation mechanisms preserve the charge balance.

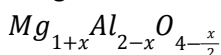
Cation interstitial mechanism:

x Mg^{2+} cations substitute $2 \cdot \frac{x}{3}$ Al^{3+} cations and O^{2-} ion count does not change. Therefore, the formula is



Oxygen ion vacancy mechanism:

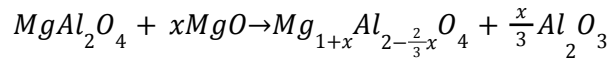
x Mg^{2+} ion substitute x Al^{3+} ions and $x/2$ O^{2-} vacancies must form. Therefore, the formula is



3 p.

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 cations to interstitial sites.

The reaction equation is:



η is molar fraction of MgO in initial mixture.

n is MgO/Al_2O_3 molar ratio in solid solution

η can be expressed as function of x :

$$\eta = \frac{x}{1+x}$$

Rearranging above equation yields:

$$x = \frac{\eta}{1-\eta}$$

MgO and Al_2O_3 moles in solid solution can expressed function of x :

$$MgO \text{ moles} = 1 + x$$

$$Al_2O_3 \text{ moles} = 1 - \frac{x}{3}$$

Therefore, the ratio n can be expressed as:

$$n = \frac{1+x}{1-\frac{x}{3}} = \frac{3+3x}{3-x}$$

where $0 \leq x < 3$

Substituting for x yields:

$$n = \frac{3+3\frac{\eta}{1-\eta}}{3-\frac{\eta}{1-\eta}} = \frac{3}{3-4\eta}$$

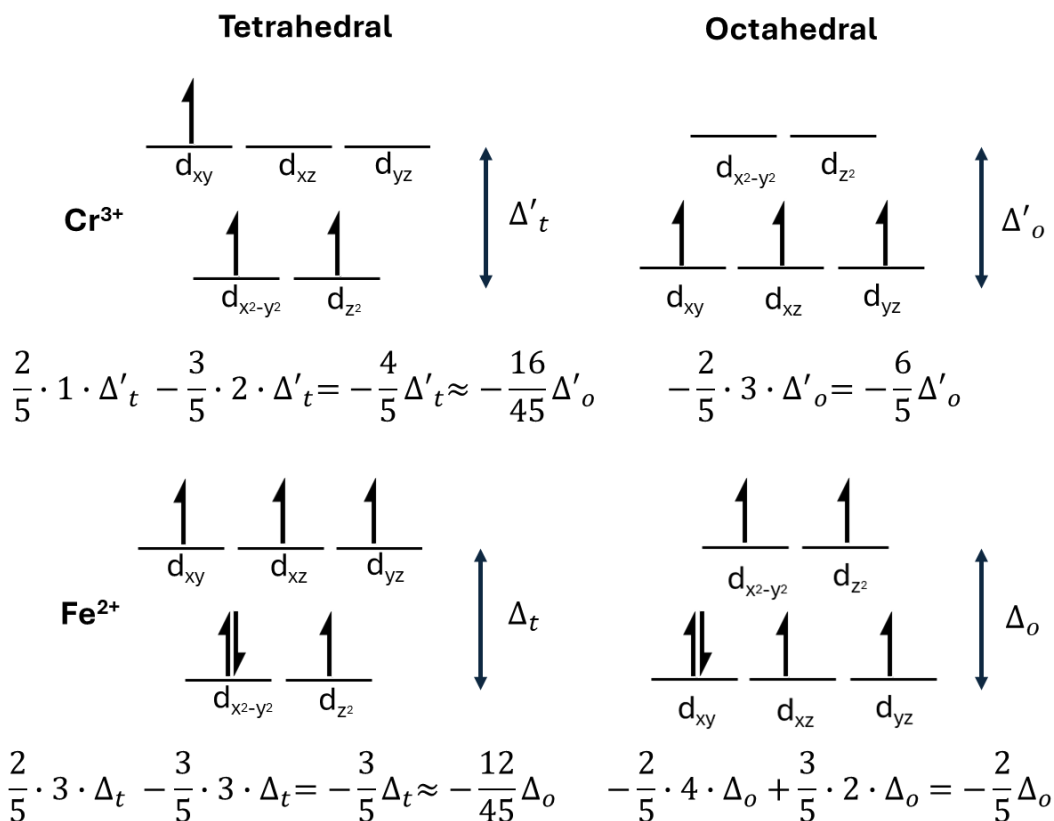
, where $0 \leq \eta < 0.75$

4 p.

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 an octahedral coordination environment is greater than for Fe^{2+} and O^{2-} is weak field ligand.

O^{2-} is weak field ligand, high-spin electronic configuration are expected. In high-spin complexes spin pairing energy cancels out.

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



Cr^{3+} shows strong preference for octahedral coordination ($-\frac{16}{45}\Delta'_o > -\frac{54}{45}\Delta'_o$)

Fe^{2+} shows also shows slight preference octahedral coordination ($-\frac{12}{45}\Delta_o > -\frac{18}{45}\Delta_o$)

Since $\Delta'_o > \Delta_o$, then $-\frac{54}{45}\Delta'_o < -\frac{18}{45}\Delta_o$. Therefore, normal spinel structure is expected.

5 p.

j) The length of the unit cell of chromite is $8.34 \text{ \AA}$. What is the density of chromite?

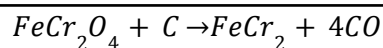
In unit cell there 8 FeCr_2O_4 units.

$M(\text{FeCr}_2\text{O}_4) = 223.833 \text{ g/mol}$

$$\rho = \frac{8 \cdot 223.833 \frac{\text{g}}{\text{mol}}}{6.022 \cdot 10^{23} \text{ mol}^{-1} \cdot (8.34 \cdot 10^{-8})^3 \text{ cm}^3} = 5.12 \frac{\text{g}}{\text{cm}^3}$$

3 p.

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 (in kg) can be extracted from 1 tone of this ore? Hint: the main gaseous product of reaction is CO.



$$\frac{2 \cdot 51.996}{223.833} \cdot 1000 \text{ kg} = 464 \text{ kg}$$

2 p.

Crystal field splitting energy for Cr^{3+} ion in chromite is 17390 cm^{-1} .

l) What wavelength of photon does this energy correspond to?

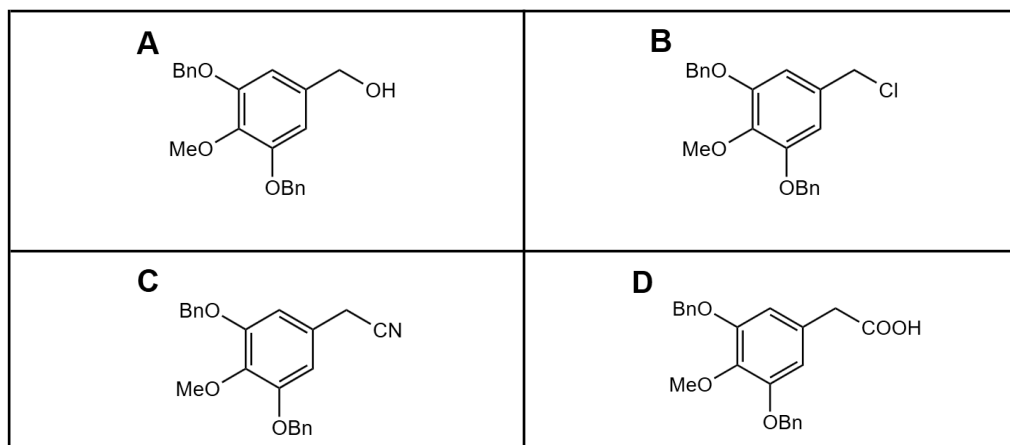
$$\lambda = \frac{1 \text{ cm}}{17,390} \cdot \frac{1 \text{ m}}{100 \text{ cm}} \cdot \frac{10^9 \text{ nm}}{1 \text{ m}} = 575 \text{ nm}$$

1 p.

Problem 4. Relax, take it easy!

a)	b)	c)	d)	e)	f)	g)	h)	i)	Σ
4	2	5	3	13	2	1	1	3	34

a) Draw structural formulas of compounds A–D.

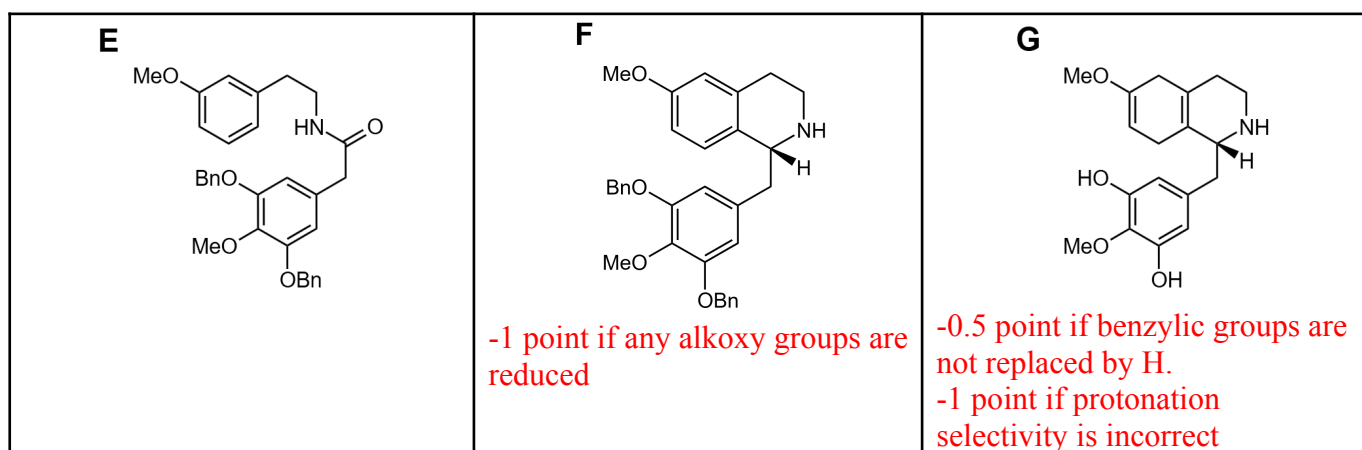


b) Explain how use of (-)-malic acid enables chiral separation of **F** enantiomers.

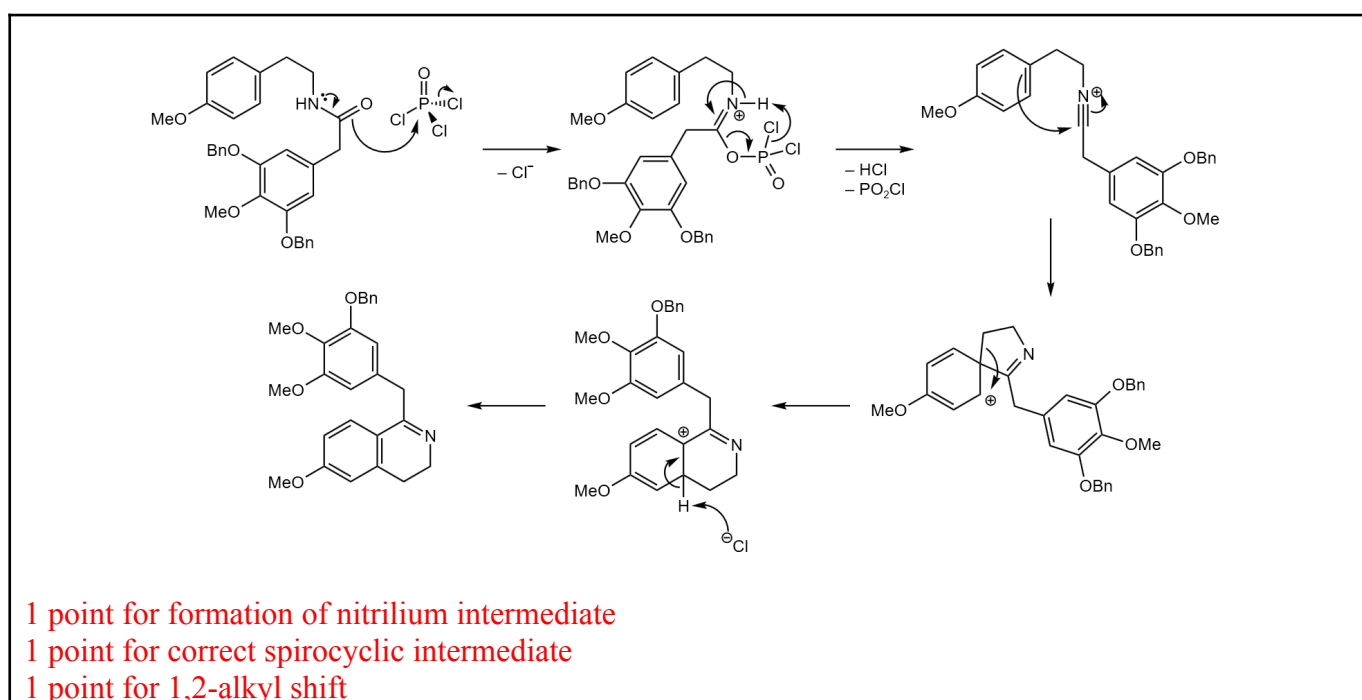
When a single enantiomer of malic acid is added to a racemic mixture of amine, salts that form are diastereomeric. The chirality centers of the acid portion of the salts are enantiomerically related to each other, but the chirality centers of the amine portion are not. Since diastereomers have different physical properties, these salts can be separated by careful crystallization. Separated salts are then basified and amines are freed from their ionic form.

Because too many students were talking about chiral chromatography it was also considered to be a possibility (the use of a chiral column packed with adsorbent that has mentioned (-)-malic acid in it). This is also accepted, however, the explanation should be more detailed and include different retention factors or elution times.

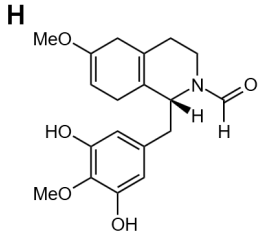
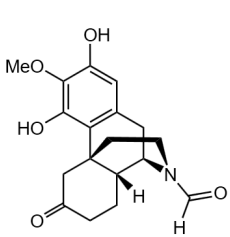
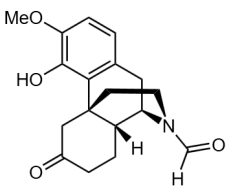
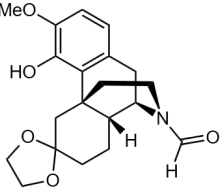
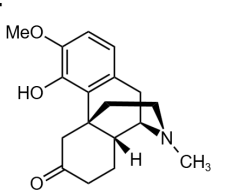
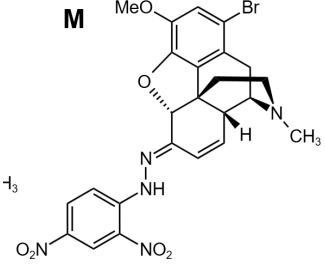
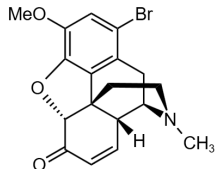
c) Draw structural formulas of compounds **E–G** with appropriate stereochemistry.



d) 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.*

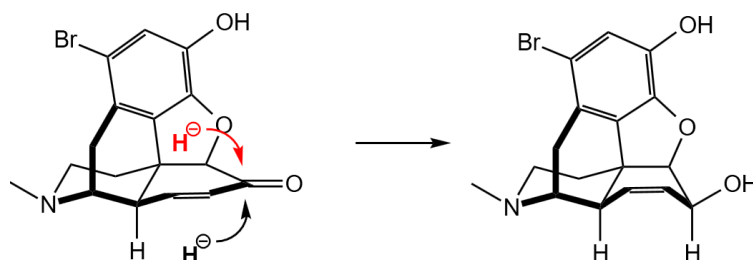


e) Draw structural formulas of compounds **H–N** with appropriate stereochemistry.

H 	I  -1 point if stereochemistry is incorrect
J  -1 point if both phenolic groups are reduced	K  -1 point if amide is also protected or protection is done inversely
L  -1 point if ketone is also reduced	M  -1 point if stereochemistry is incorrect
N  -1 point if bromine is lost -0.5 point if -OH is present instead of -OMe	

f) Show and briefly comment why the reaction of **N** with LiAlH_4 is highly stereoselective, yielding a morphine-like stereoisomer.

The top side of the semi-planar cyclic ketone part of **N** is heavily crowded by a system of fused rings. Bottom side, on the other hand, is almost free of steric hindrance because large substituents are absent. AlH_4 is treated as H^- here.

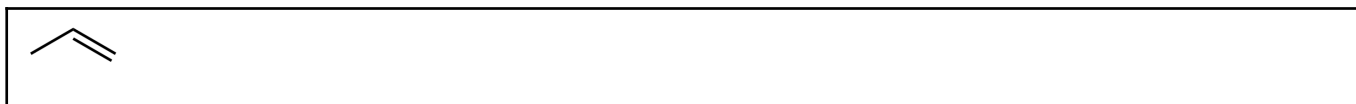


-1 point if explanation is not sufficient to account for stereoselectivity or schematic drawing is missing

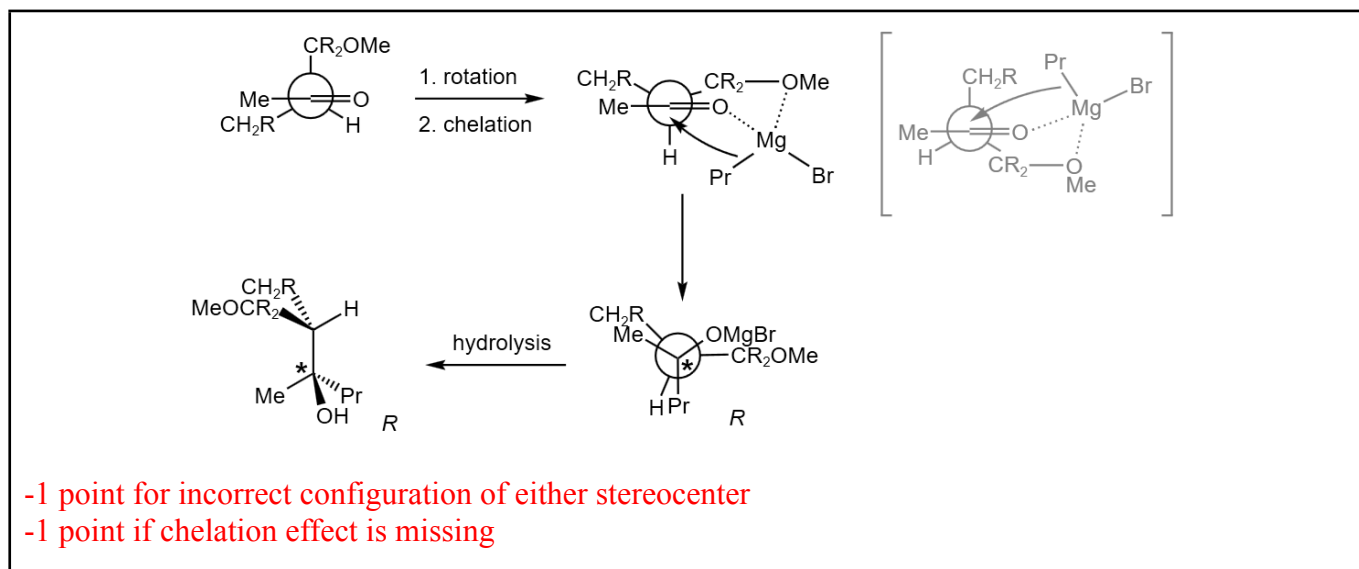
g) Draw a simple reagent that could be used to achieve stereoselective conversion **1** → **2** in one step.



h) Unfortunately, reaction of **2** with PrMgBr yields **X** as the major product. What coproduct is produced when **X** forms?

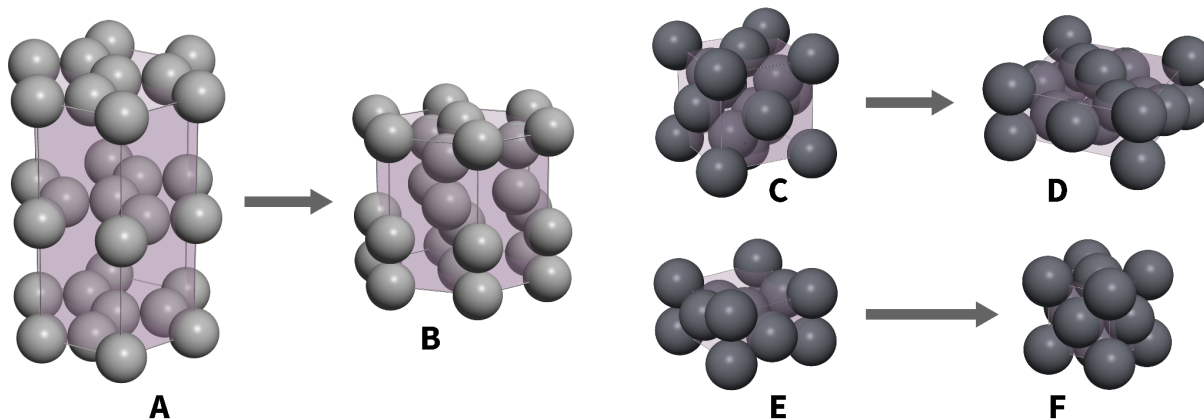


i) Methoxy group having a 1,3-relationship with carbonyl group in **2** severely impacts stereoselectivity of Grignard reaction. Show preferred addition pathway which explains why particular diastereomer is formed in reaction **2** → **3**. *Hint: Newman projections may help you to provide an explanation. For simplicity use of labels $-\text{Me}$, $-\text{Pr}$, $-\text{CH}_2\text{R}$, $-\text{CR}_2-\text{OMe}$ is recommended.*



Problem 5. From diatomic to solids

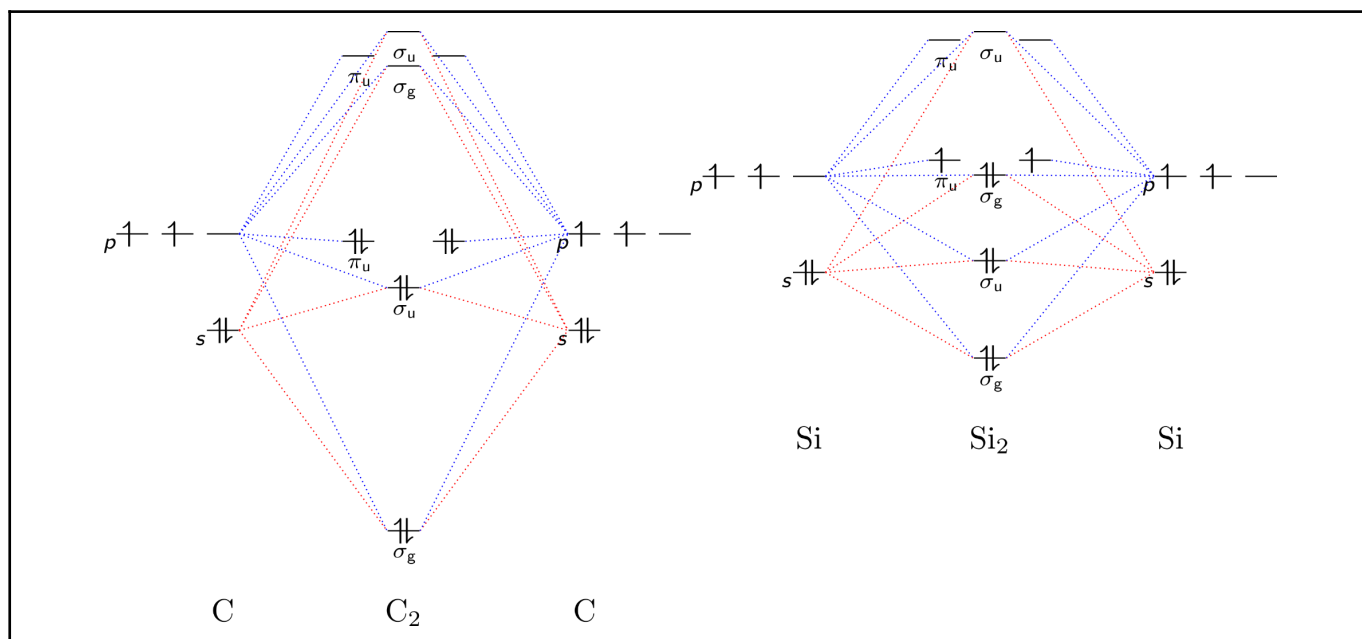
a)	b)	c)	d)	e)	f)	g)	h)	i)	Σ
6	4	4	4	3	3	2	3	1	30



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

	A	B	C	D	E	F
Number of atoms per unit cell	12	12	8	8	4	4
Coordination number of atoms	3	4	4	4 (6)	4 (6)	12

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

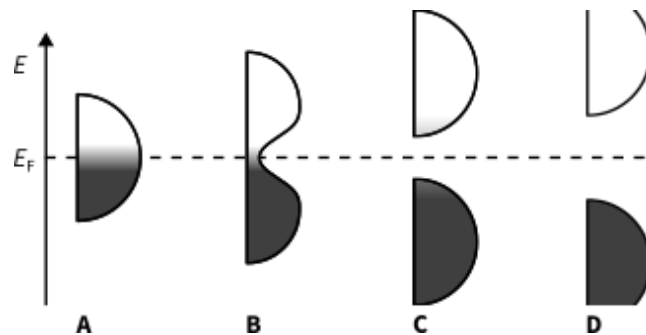
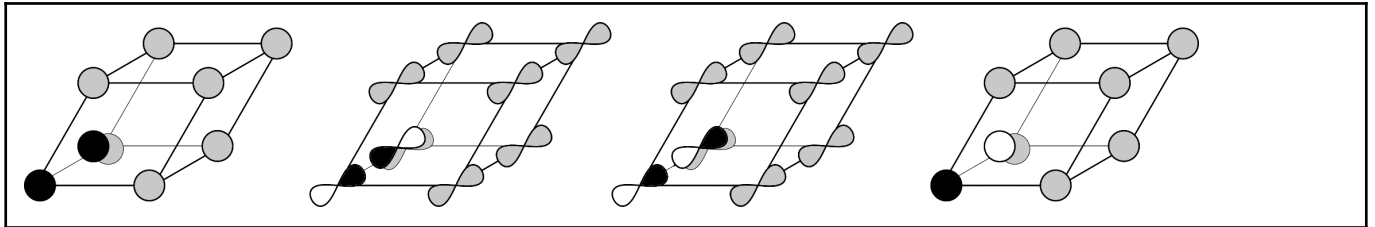


c) Circle the correct options in the following text about C_2 .

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 {red, orange, yellow, green, blue, purple} light. Eventually, C_2 produced in flame polymerizes into soot consisting of {diamond, fullerene, graphene, graphite, lonsdaleite, nanotube} entities.

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.



e) Assign the material type to the shown electronic band structures A–D.

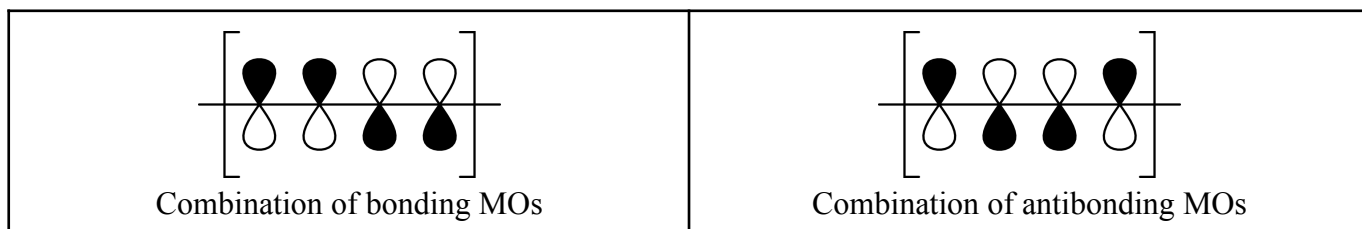
insulator	semiconductor	conductor	semimetal	metal
D	C	A, B	B	A

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 $\epsilon_p \cdot (1 + 2 \cdot S)$ 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.*

$E_g(C) = -16.59 \text{ eV} + 11.26 \text{ eV} \cdot (1 + 2 \cdot 4/9) = \mathbf{4.68 \text{ eV}}$ $E_g(Ge) = -14.29 \text{ eV} + 7.90 \text{ eV} \cdot (1 + 2 \cdot 4/9) = \mathbf{0.63 \text{ eV}}$ $E_g(Pb) = -14.60 \text{ eV} + 7.42 \text{ eV} \cdot (1 + 2 \cdot 4/9) = \mathbf{-0.58 \text{ eV}}$	5 – B	6 – C	7 – N	8 – O	9 – F	10 – Ne
	12.93	16.59	20.34	28.48	37.86	48.48
	8.30	11.26	14.53	13.62	17.42	21.57
	13 – Al	14 – Si	15 – P	16 – S	17 – Cl	18 – Ar
	10.62	13.46	16.15	20.20	24.54	29.24
	5.99	8.15	10.49	10.36	12.97	15.76
	31 – Ga	32 – Ge	33 – As	34 – Se	35 – Br	36 – Kr
	11.87	14.29	16.59	20.15	23.77	27.51
	6.00	7.90	9.79	9.75	11.81	14.00
	49 – In	50 – Sn	51 – Sb	52 – Te	53 – I	54 – Xe

	11.03	13.11	15.02	17.84	20.61	23.40
	5.79	7.34	8.61	9.01	10.45	12.13
81 – Tl	82 – Pb	83 – Bi	84 – Po	85 – At	86 – Rn	
12.24	14.60	15.86	19.83	20.90	26.17	
6.11	7.42	7.29	8.41	9.32	10.75	

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.

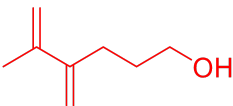
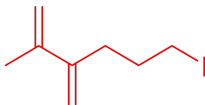
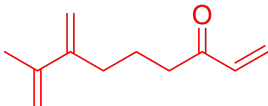
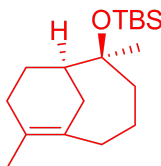
i) Generalize the explanation of why some group 14 elements are semiconductors with low coordination numbers, while others are conductors with higher coordination numbers.

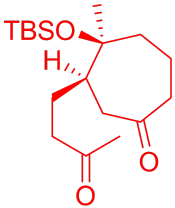
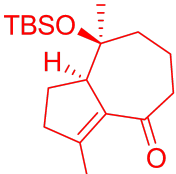
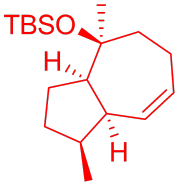
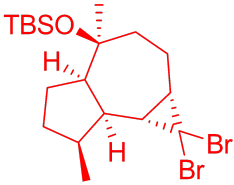
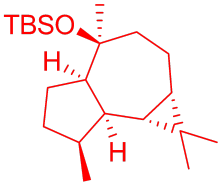
- ☒ The crystal structure is favored when its geometry allows orbital overlap that maximizes bonding interactions and minimizes the filling of antibonding levels.
- ☐ The energy gap between s- and p-orbitals becomes smaller for heavier elements, which favours metallic bonding.
- ☐ The larger atomic radius 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?

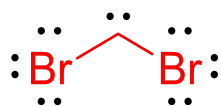
a)	b)	c)	d)	Σ
27	3	2	3	35

a) Draw the structures of compounds **B–D**, **F–H** and **J–L**, clearly indicating relevant stereochemistry.

B  -1 mark if drawn a isomer (of alkyne addition or alkene addition)	C 
D 	F  -1 point if stereochemistry not drawn (but no penalisation again if not drawn in other structures)

G  1 point if product drawn as carboxylic acid or aldehyde.	H  -1 point if product is condensation but a different regioisomer.
J 	K 
L 	corrections

b) 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. reactive intermediate.



-1 mark for not drawing electrons on Br, -1 mark for not drawing carbene electrons.
If drawn another carbene, even if Lewis structure is correct = 1 mark.

c) Circle the role of PMe_3 in the reaction from **F** to **G**.

- solvent
- acid
- base
- oxidant
- reductant
- catalyst

d) 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.

