



26th CHEMISTRY OLYMPIAD OF THE BALTIC STATES

Riga, Latvia
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ANSWERS AND SOLUTIONS OF THEORETICAL EXAMINATION



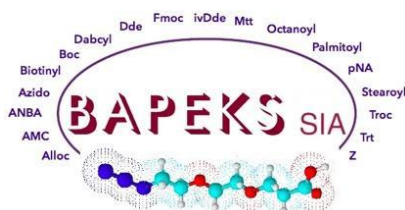
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“Back to where it all began”

PROBLEM 1 (8 POINTS) - Nobel medals

In 1930s the German-resident Jewish scientist James Franck and Hitler critic Max von Laue smuggled their Nobel medals over the Danish border for safekeeping in Niels Bohr's lab. When Copenhagen fell to the Nazis in April 1940, the medals and their keeper were no longer secure, so a Hungarian scientist from the lab, George de Hevesy, took it upon himself to hide them. He decided against burying them in the garden, and instead used a chemical trick.

He dissolved the medals in aqua regia (3:1 mixture of concentrated hydrochloric and nitric acids) forming a tetracoordinate gold-containing monovalent anion **A** and a gas **B**, as well as a hydronium ion and water. The vessel containing this orange-coloured solution was labelled "aqua regia" and hidden in the lab among the other chemicals. Though Nazis thoroughly searched the lab, they found no evidence of medals, which were kept in their dissolved state for years. It is also known that **B** coexists with a colourless liquid **C**, which starts to predominate upon cooling.

To recover the gold, excess aqua regia was boiled off and residue was obtained. It was then redissolved in hydrochloric acid to reduce the remaining nitric acid and the acid mixture was boiled off again. Each reduction step forms water and yellow mixture of two gasses: **D** and monoelemental **E**. **D** undergoes further decomposition into **E** and **F**, which spontaneously oxidises to gas **B** in atmospheric oxygen. The cycle of adding more hydrochloric acid and evaporation is repeated until a strong acid **G** is formed as a yellow-orange crystalline solid, which liberates **A** upon dissolution in water. **G** was then reacted with a solution of sodium pyrosulphite in water to precipitate gold as a brown powder, creating hydrochloric acid and **H** ($w_{\text{Na}} < 40\%$) as side products. The gold precipitate was remoulded into Nobel medals, which were presented back to their rightful owners in 1952.

1. Identify compounds A-G! Write down all aforementioned reactions with correct coefficients:

A: $[\text{AuCl}_4]^-$	B: NO_2	C: N_2O_4	D: NOCl
E: Cl_2	F: NO	G: HAuCl_4	H: NaHSO_4

(8*1p)

If H = Na_2SO_4 or $\text{Na}_2\text{S}_2\text{O}_6$, then 0.5 points for question H.

$\text{Au} + 3 \text{HNO}_3 + 4 \text{HCl} \rightarrow [\text{AuCl}_4]^- + 3 \text{NO}_2 + [\text{H}_3\text{O}]^+ + 2 \text{H}_2\text{O}$ (1 mark correct species, including hydronium ion + 1 mark coefficients = 2 marks)

$2 \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$ (1 mark)

$3 \text{HCl} + \text{HNO}_3 \rightarrow \text{NOCl} + \text{Cl}_2 + 2 \text{H}_2\text{O}$ (1 mark)

$2 \text{NOCl} \rightarrow 2 \text{NO} + \text{Cl}_2$ (1 mark)

$2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$ (1 mark)

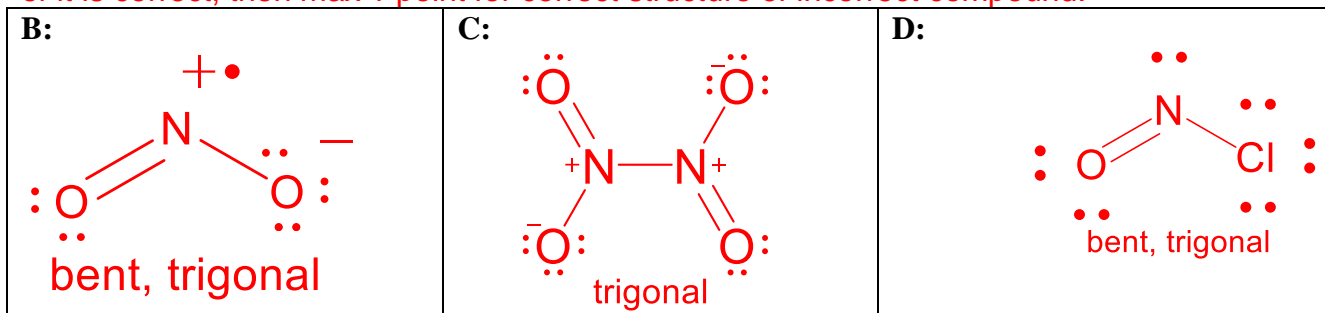
$[\text{AuCl}_4]^- + \text{H}^+$ (or $[\text{H}_3\text{O}]^+$) $\rightarrow \text{HAuCl}_4$ (+ H_2O) (0.5 marks).

$\text{HAuCl}_4 + \text{H}_2\text{O} \rightarrow [\text{H}_3\text{O}]^+ + [\text{AuCl}_4]^-$ (0.5 marks)

$3 \text{Na}_2\text{S}_2\text{O}_5 + 9 \text{H}_2\text{O} + 4 \text{HAuCl}_4 \rightarrow 4 \text{Au} + 16 \text{HCl} + 6 \text{NaHSO}_4$ (1 mark correct species + 2 marks correct coefficients = 3 marks) (10 marks total. Award 0.5 marks per reaction in case a reasonable reaction with an incorrectly identified compound is proposed instead)

2. Predict the full structures for compounds **B**, **C** and **D**! Use VSEPR to determine their geometry at N centres and overall geometry if appropriate.

(3*2 = 6p). In each example 0.5 marks for each of: correct bond orders, correct placement of non-bonding electrons (pairs and radicals), correct valence of N with appropriately placed charges, and correctly shown geometry (not linear structures). Award full marks for correctly drawn delocalised structures. If compound is incorrect in 1st question, but structure of it is correct, then max 1 point for correct structure of incorrect compound.

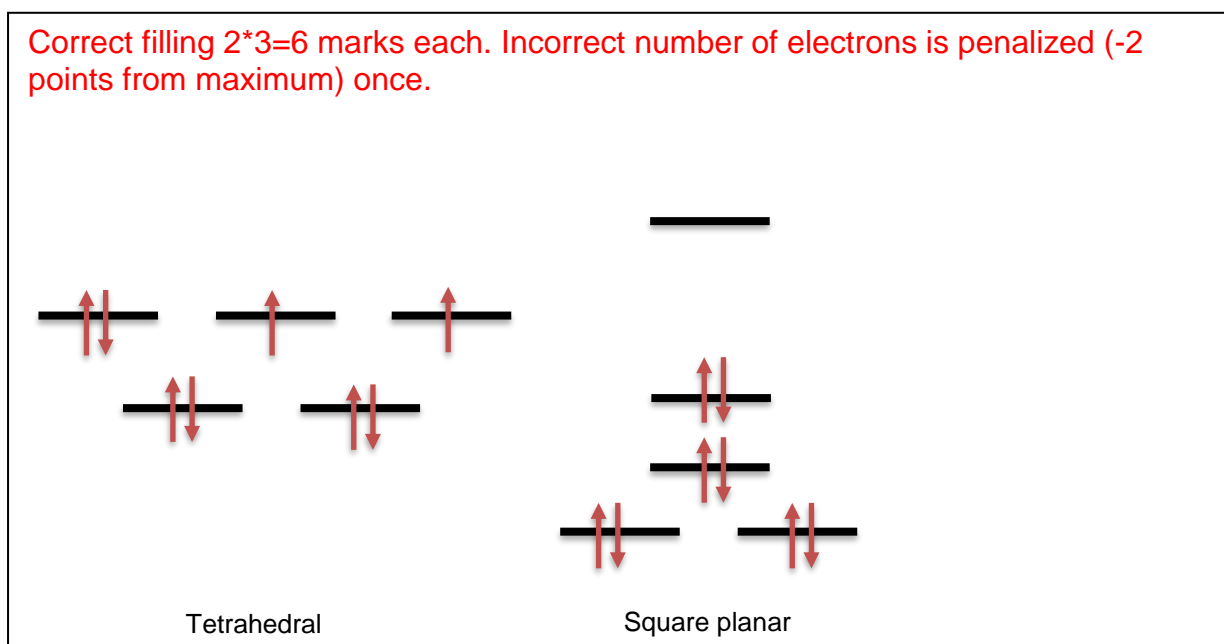


<p>Geometry at N centre: (check correct answer)</p> <ul style="list-style-type: none"> <input type="radio"/> Linear <input checked="" type="radio"/> Bent <input type="radio"/> Trigonal planar <input type="radio"/> Pyramidal 	<p>Geometry at N centre: (check correct answer)</p> <ul style="list-style-type: none"> <input type="radio"/> Linear <input type="radio"/> Bent <input checked="" type="radio"/> Trigonal planar <input type="radio"/> Pyramidal 	<p>Geometry at N centre: (check correct answer)</p> <ul style="list-style-type: none"> <input type="radio"/> Linear <input checked="" type="radio"/> Bent <input type="radio"/> Trigonal planar <input type="radio"/> Pyramidal
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1.5 points

Tetracoordinate compounds can be either tetrahedral or square planar, with their respective d orbital splitting diagrams provided below together with a visual representation of electron pairing energy.

3. Assuming that the 6s electrons can also occupy these orbitals in addition to 5d electrons, fill in the splitting tetrahedral and square planar diagrams for gold in compound **A**!



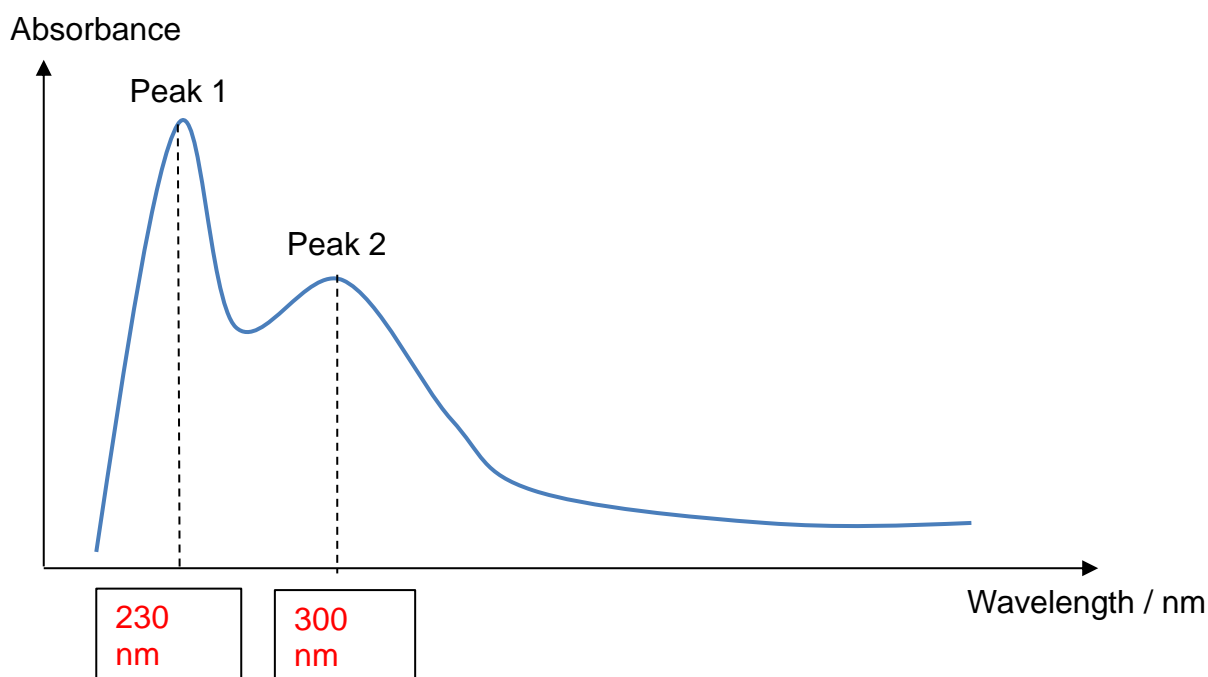
When Niels Bohr was not helping refugees of Nazism, he contributed massively to the field of chemistry. The unit of magnetic moment, Bohr magneton (μ_B), was named after him. A compound's spin-only magnetic moment in Bohr magnetons can be estimated with the formula $\mu = \sqrt{n(n+2)}$, where n is the number of unpaired electrons.

4. Given that compound A is diamagnetic, determine its geometry. What is the spin-only magnetic moment of the other isomer?

Square planar (1 mark)

For tetrahedral: $\mu = (2 \times (2+2))^{1/2} = 2.83$ (μ_B) (1 mark, only awarded if units present; if there are no units, then 0.5 points for calculated number).

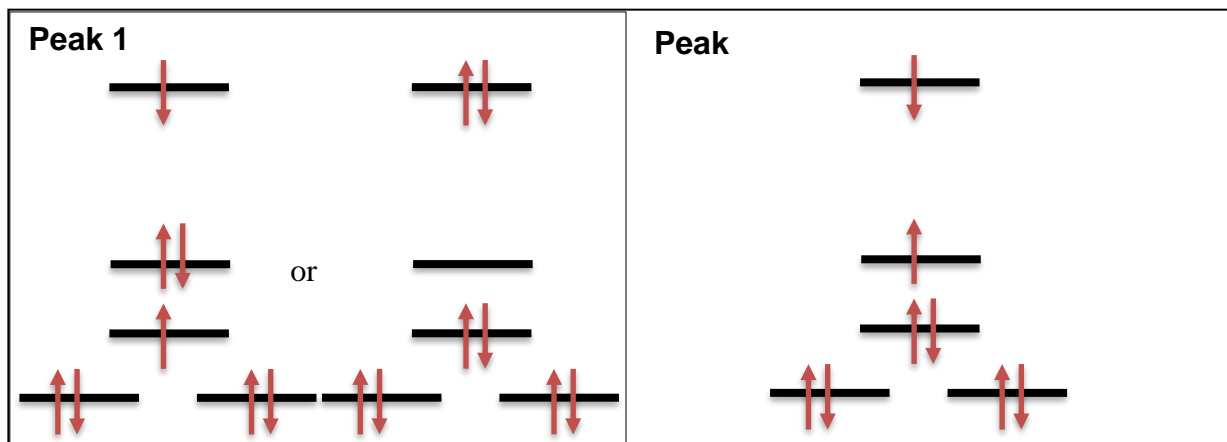
5. A sketch of the UV-vis spectrum of compound A in solution is provided. Given that a fresh solution of the compound is pale yellow, label the boxes on the abscissa with estimated wavelength for peaks 1 and 2 in nanometres. Use the colour wheel provided.



For Peak 1 award 2 marks for being in the range of 100-380 nm AND 20-100 nm lower than the proposed Peak 2; otherwise award 0 marks. Units not necessary, as they are already provided on the axis.

For Peak 2 award 1 mark if within violet range (380-470), as then compound would be bright yellow-orange, not pale. 2 marks if 351-380 nm, 3 marks if 250-350 nm (Peak 2 is broad and there is only some absorption in the violet region). 0 marks for other suggestions..

6. Offer electronic structures of the excited states that correspond to peaks 1 and 2 using the appropriate d orbital splitting pattern from sub-question 3. Note: overall spin of the molecule has to be preserved upon optical excitation. (3*2=6 marks)



Peak 2 is a reasonable lowest E transition AND both excited states have the same overall spin as the ground state provided for sub-question 3.

PROBLEM 2 (12 POINTS) - Chemistry of metals in oxidation state of +3

Metals **X**, **Y**, and **Z** have almost the same radius of approx. 0.144 nm as well as the same crystal packing. Densities of the **X**, **Y**, and **Z** metals equal 2.7, 10.5, 19.3 g/cm³, respectively. The typical oxidation state of **X**, **Y**, and **Z** is III, I, and III, respectively.

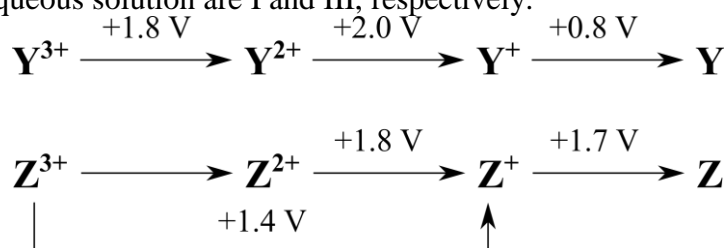
a) Calculate the molar masses of the metals and determine **X**, **Y**, and **Z**.

$$M(\mathbf{X}) = 2,7 \text{ g/cm}^3 \cdot (4/\sqrt{2} \cdot 1,44 \cdot 10^{-8} \text{ cm})^3 \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1} / 4 = 27 \text{ g/mol (Al)}$$

$$M(\mathbf{Y}) = 10,5 \text{ g/cm}^3 \cdot (4/\sqrt{2} \cdot 1,44 \cdot 10^{-8} \text{ cm})^3 \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1} / 4 = 107 \text{ g/mol (Ag)}$$

$$M(\mathbf{Z}) = 19,7 \text{ g/cm}^3 \cdot (4/\sqrt{2} \cdot 1,44 \cdot 10^{-8} \text{ cm})^3 \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1} / 4 = 196 \text{ g/mol (Au)}$$

b) Using the data from the Latimer diagram, prove by calculations that the most stable oxidation states of **Y** and **Z** in aqueous solution are I and III, respectively.



For the Latimer diagram, if the potential to the right of the species is higher than the potential on the left, it disproportionates. Therefore, Ag⁺ and Au⁺ are stable, while Ag²⁺ and Au²⁺ are unstable relative to disproportionation ($E^\circ(\text{Au}^{3+}/\text{Au}^{2+}) = 1.4 \text{ V} \cdot 2 - 1.8 \text{ V} = 1.0 \text{ V}$).
 $E^\circ(\text{Ag}^{3+}/\text{Ag}) = (1.8 \text{ V} + 2.0 \text{ V} + 0.8 \text{ V})/3 = 1.5 \text{ V} > E^\circ(\text{O}_2/\text{H}_2\text{O}) > E^\circ(\text{Ag}^+/\text{Ag})$. Thus Ag³⁺ is a much stronger oxidizing agent than Ag⁺. It can oxidize water to oxygen.
 $E^\circ(\text{Au}^{3+}/\text{Au}) = (1.4 \text{ V} \cdot 2 + 1.7 \text{ V})/3 = 1.5 \text{ V} < E^\circ(\text{Au}^+/\text{Au}) > E^\circ(\text{O}_2/\text{H}_2\text{O})$. Thus Au⁺ is a stronger oxidizing agent than Au³⁺. Both can oxidize water to oxygen unless they are bind in a complex, like AuCl₄⁻ ($E^\circ(\text{AuCl}_4^-/\text{Au}) = 1.0 \text{ V}$).

A more elegant explanation requires plotting a Frost diagram. Then it would be evident that Ag²⁺, Au²⁺, and Au⁺ disproportionate and that Ag³⁺ is thermodynamically least stable relative to Ag.

The standard reduction potential of Meⁿ⁺ can be estimated as:

$$E^\circ = (\Delta H_{\text{atom}} + \Delta H_{\text{ion}} + \Delta H_{\text{hydr}})/(nF) - 4.52 \text{ V},$$

where ΔH_{atom} is the atomization enthalpy change of Me, ΔH_{ion} is the sum of ionization energies, and ΔH_{hydr} is the hydration energy of Me³⁺ cation in water.

c) Tick the right assumption for the derivation of the given equation.

$\Delta G = -nFE^\circ$, $\Delta G = \Delta H - T\Delta S$, $|\Delta H| \ll |T\Delta S|$

$\Delta G = -nFE^\circ$, $\Delta G = \Delta H - T\Delta S$, $|\Delta H| \gg |T\Delta S|$

$\Delta G = -nFE^\circ$, $\Delta G = \Delta H - T\Delta S$, $|\Delta H| = |T\Delta S|$

d) Using the provided thermodynamic data, calculate E° values for **X**³⁺, **Z**³⁺, Fe³⁺, and Sc³⁺. Write a reactivity series for **X**, **Z**, Fe, and Sc.

Ion	ΔH_{atom} (kJ/mol)	ΔH_{ion} (kJ/mol)	ΔH_{hydr} (kJ/mol)
X ³⁺	326	5139	-4525

Z ³⁺	368	5763	-4420
Fe ³⁺	415	5281	-4265
Sc ³⁺	378	4257	-3795

$$E^\circ = (\Delta H_{\text{atom}} + \Delta H_{\text{ion}} + \Delta H_{\text{hydr}})/(nF) - 4.52 \text{ V}$$

$$E^\circ(\text{Sc}^{3+}/\text{Sc}) = (378 + 4257 - 3795) \text{ kJ}/3/96.485 \text{ C} - 4.52 \text{ V} = -1.62 \text{ V}$$

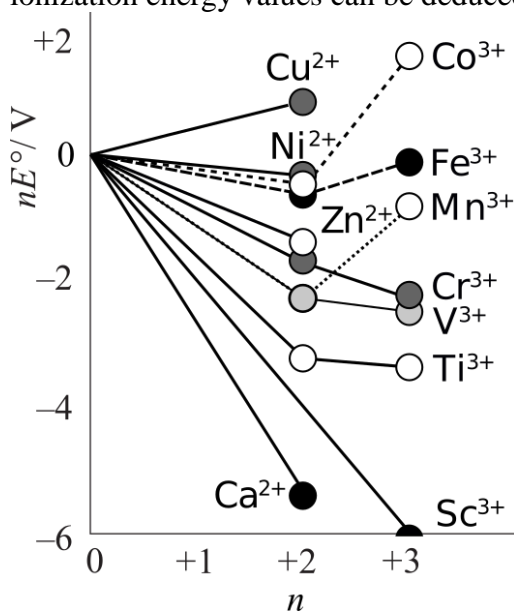
$$E^\circ(\text{Al}^{3+}/\text{Al}) = (326 + 5139 - 4525) \text{ kJ}/3/96.485 \text{ C} - 4.52 \text{ V} = -1.27 \text{ V}$$

$$E^\circ(\text{Fe}^{3+}/\text{Fe}) = (415 + 5281 - 4265) \text{ kJ}/3/96.485 \text{ C} - 4.52 \text{ V} = 0.42 \text{ V}$$

$$E^\circ(\text{Au}^{3+}/\text{Au}) = (368 + 5763 - 4420) \text{ kJ}/3/96.485 \text{ C} - 4.52 \text{ V} = 1.39 \text{ V}$$

Reactivity series: Sc, Al, Fe, Au

The experimental nE° are summarized below in the form of a Frost diagram. As can be seen, elements have a different preference in the oxidation states. In part, E° is determined by the ΔH_{ion} values. In general, due to the shielding effect, the ionization energy increases in a period from left to right. However, other regularities arise due to electron pairing and exchange. Overall, the relative ionization energy values can be deduced by analyzing the electronic configurations of atoms.



e) Write symbols of the 4th period elements which have lower n^{th} ionization energy (IE) values than their left neighbour.

rel. low 2nd IE: Ca, Mn, Zn, Ge

rel. low 3rd IE: Sc, Fe, Ga, As

f) The 1st, 2nd, and 3rd IEs of Y and Cu are almost the same. Tick the factor(s) that disfavours oxidation state of II for Y in comparison to Cu (in aqueous solution).

X Larger radius of Y²⁺ than of Cu²⁺

Lower atomization energy of Y than of Cu

Higher electric conductivity of Y than of Cu

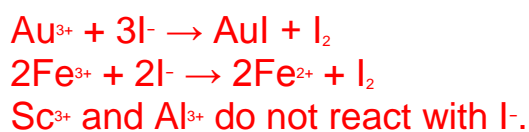
g) Tick the reason(s) explaining why **Z** has considerably lower 3rd IE than **Y** (as well as why **Z** is yellow while **Y** is gray):

Inner pair effect, *i.e.* the contraction of the 6s² orbital due to relativistic effect.

X Orbital splitting, *i.e.* shifts in orbital energy levels due to the spin-orbit interaction.

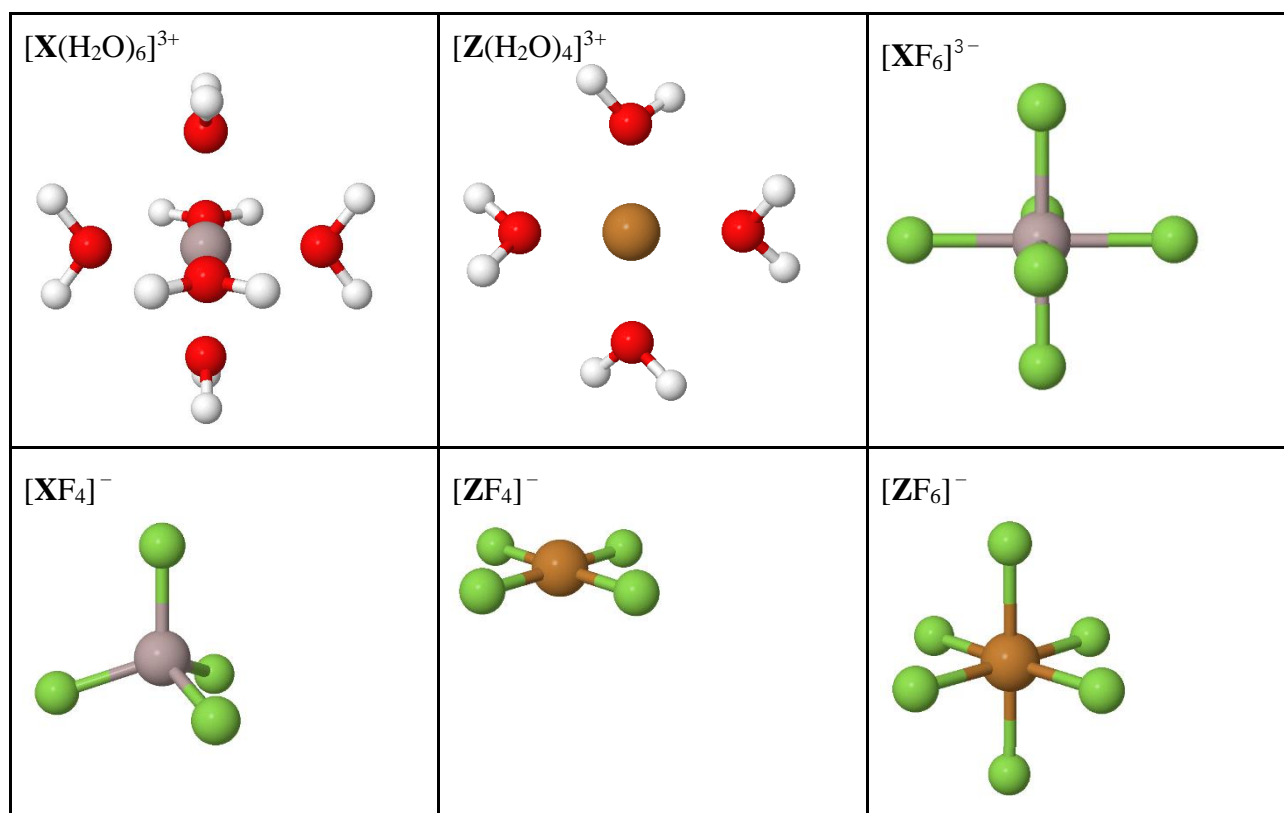
Lanthanide contraction, *i.e.* greater-than-expected decrease in ionic radii of the elements in the 6th row.

h) Write the reactions between 3+ cations of **X**, **Z**, Fe, and Sc with iodide anion (I⁻). $E^\circ(\text{I}_2) = +0.54 \text{ V}$.



Cations do not occur in solution as bare ions, but in a hydrated state as aqua complexes. If other ligands are present in solution, they may replace water molecules. Similarly, complex ions are formed in melts.

i) Draw $[\text{X}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Z}(\text{H}_2\text{O})_4]^{3+}$, $[\text{XF}_6]^{3-}$, $[\text{XF}_4]^-$, $[\text{ZF}_4]^-$, and $[\text{ZF}_6]^-$ complex structures.

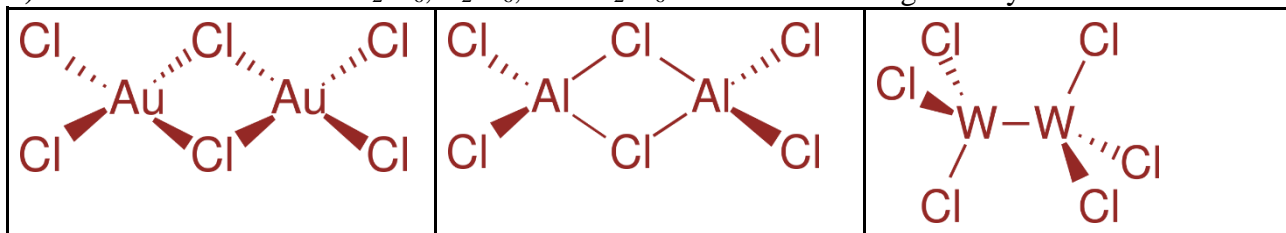


Solid \mathbf{XF}_3 structure is cubic with \mathbf{X} at each corner of the unit cell and one F atom in the middle of each edge. In solid \mathbf{ZF}_3 the coordination of metal atoms is 4. Solid \mathbf{XCl}_3 consists of cubic close-packed layers, where the coordination of \mathbf{X} atom is 6. Molecular \mathbf{ZCl}_3 solid consists of dimers.

j) Determine the coordination of F and Cl atoms in the compounds.

	F/Cl first type of atoms	F/Cl second type of atoms
\mathbf{XF}_3	2	
\mathbf{ZF}_3	2	1
\mathbf{XCl}_3	3	
\mathbf{ZCl}_3	2	1

k) Draw structures of $\mathbf{X}_2\text{Cl}_6$, $\mathbf{Z}_2\text{Cl}_6$, and $\mathbf{W}_2\text{Cl}_6$. All have distinct geometry.



PROBLEM 3 (10 POINTS) - Don't cry

Sulfuryl chloride SO_2Cl_2 acts as lachrymator – tears producing substance. In laboratory practice SO_2Cl_2 may be used as a chlorine source in organic synthesis.

Some properties of sulfuryl chloride:

Normal melting point -54.1°C

Normal boiling point 69.4°C

Sulfuryl chloride reacts with water: $\text{SO}_2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{HCl}$ (reaction 1)

Above boiling point sulfuryl chloride decomposes: $\text{SO}_2\text{Cl}_{2(\text{g})} \rightleftharpoons \text{SO}_{2(\text{g})} + \text{Cl}_{2(\text{g})}$ (reaction 2)

Standard thermodynamic properties (1 bar and 25°C)

	$\Delta_f H^\circ / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f G^\circ / \text{kJ}\cdot\text{mol}^{-1}$	$S^\circ / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$\text{SO}_2\text{Cl}_{2(\text{l})}$	-394.1	-314	?
$\text{SO}_2\text{Cl}_{2(\text{g})}$	-364.0	-320.0	311.9
$\text{SO}_{2(\text{g})}$	-296.8	-300.2	248.2
$\text{Cl}_{2(\text{g})}$	0.0	0.0	223.1

When solving this problem assume: i) all gasses are ideal; ii) enthalpy and entropy changes of processes under consideration are temperature independent.

1. 0,10 mol of SO_2Cl_2 was dissolved in water and solution diluted till $1,0 \text{ dm}^3$ volume. Calculate pH of the obtained solution.

Ionization constants are: $\text{p}K_a(\text{HCl}) = -6,3$, $\text{p}K_{a1}(\text{H}_2\text{SO}_4) = -3,0$, $\text{p}K_{a2}(\text{H}_2\text{SO}_4) = 1,92$.

Calculations:

HCl is fully ionized, H_2SO_4 ionizes only by the first step:

$$c(\text{H}^+) = 0,20 \text{ mol/L} + 0,10 \text{ mol/L} = 0,30 \text{ mol/L}$$

pH = 0.52

2. In table above absolute entropy S° of $\text{SO}_2\text{Cl}_{2(\text{l})}$ is missing. Calculate this parameter.

Calculations:

$$\text{SO}_2\text{Cl}_{2(\text{l})} \rightleftharpoons \text{SO}_2\text{Cl}_{2(\text{g})} \quad \Delta H^\circ = -364.0 - (-394.1) = 30.1 \text{ kJ/mol}$$

$$\Delta S^\circ = \frac{\Delta H^\circ}{T} = \frac{30.1 \cdot 10^3 \text{ J/mol}}{(273.15 + 69.4) \text{ K}} = 87.87 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$S^\circ = 311.9 - 87.87 = 224.0 \text{ J/mol}\cdot\text{K}$$

3. i) Calculate equilibrium constant of the reaction 2 at temperature 350 K.

Calculation:



$$\Delta H^\circ = -296.8 - (-364.0) = 67.2 \text{ kJ/mol}$$

$$\Delta S^\circ = 223.1 + 248.2 - 311.9 = 159.4 \text{ J/mol}\cdot\text{K}$$

$$\Delta G^\circ = 67.2 \cdot 10^3 \text{ J/mol} - 350 \text{ K} \times 159.4 \text{ J/mol}\cdot\text{K} = 11410 \text{ J/mol}$$

$$K = \exp(-11410 / (8.3145 \cdot 350)) = 0,02$$

ii) indicate correct statement about equilibrium constant in case of increasing temperature.

A K will increase B K will decrease C K will remain the same

4. Decomposition of sulfuryl chloride (reaction 2) is first order reaction.

i) When considering kinetics of this reaction at high temperature, backward reaction may be neglected, because:

A value of K is high B value of K is small

When decomposition reaction proceeds in closed vessel, total pressure increases. In table below, total pressure change in time is presented (at temperature 600 K):

Time /s	0	11000	24000	40000
Total pressure /bar	1.00	1.215	1.41	1.58

(at 0 s only sulfuryl chloride presented in the vessel)

ii) Calculate rate constant and half-life of this reaction at given temperature.

Calculation:

Partial pressure of SO_2Cl_2 changes: 1.0 0,785 0,59 0,42 bar

$$\ln \frac{0,785}{1} = -k \times 11000 \text{ s}$$

$$k = 2.2 \cdot 10^{-5} \text{ s}^{-1} \quad t_{1/2} = \ln 2 / 2.2 \cdot 10^{-5} \text{ s}^{-1} = 31500 \text{ s}$$

5. When temperature is increased from 600 to 610 K, rate of the decomposition reactions increases 2.0 times. Calculate how many times rate of the decomposition reaction at temperature 740 K is faster than in temperature 720 K.

Calculation:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad E_a = 211 \text{ kJ/mol}$$

$$k_4/k_3 = 2.59$$

PROBLEM 4 (8 POINTS) - Titrimetric determination of methoxyl groups

Zeisel–Vieböck–Schwappach method is used to determine methoxyl groups. The methoxyl compound reacts with hydroiodic acid to form iodomethane. The latter is distilled out and collected in bromine water which displaces the iodine. Produced iodine monobromide is then oxidised to iodate, and excess bromine is removed ($E^\circ(\text{Br}_2/2\text{Br}^-) = +1.1 \text{ V}$).

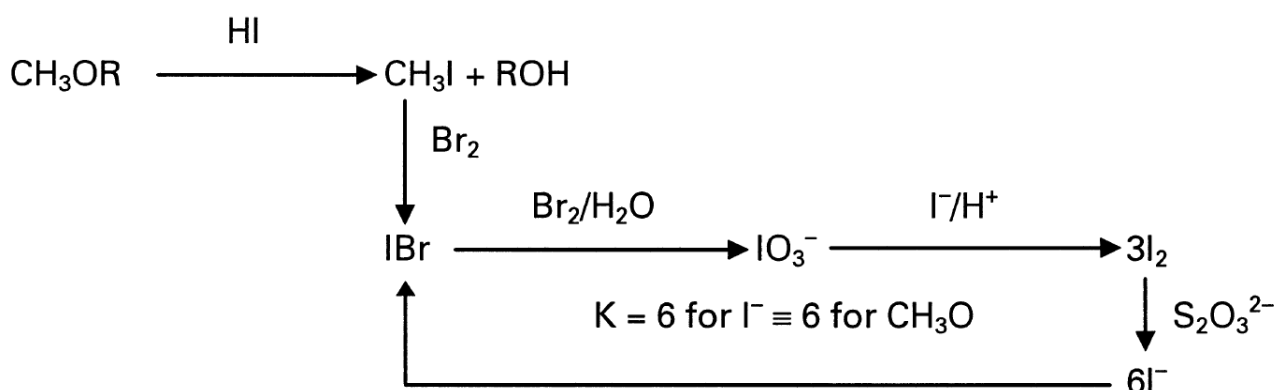
a) Tick the acid that is suitable for removing bromine from solution:

formic acid ($E^\circ(\text{CO}_2/\text{HCOOH}) = -0.1 \text{ V}$),

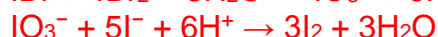
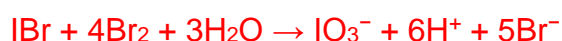
chlorous acid ($E^\circ(\text{ClO}_3^-/\text{HClO}_2) = +1.2 \text{ V}$)

hydrofluoric acid ($E^\circ(\text{F}_2/2\text{HF}) = +3.0 \text{ V}$).

The iodate is treated with iodide from an external source to form iodine, which can then be reduced back to iodide. The sequence of reactions can be repeated to multiply the ratio between the iodide ions formed per one methoxyl-group initially present in a sample.



b) Balance the reaction equations:



c) Show that after one cycle of multiplication, six iodide ions are formed per one methoxyl-group initially present in a sample.



d) The minimum volume of 0.1000 M $\text{Na}_2\text{S}_2\text{O}_3$ solution that can be quantified in a titration is one drop of approximately 0.03 cm^3 . Estimate the minimal theoretical number of multiplication cycles needed to be repeated in order to detect a single methoxyl-group per 10 g of a sample.

$$6^n \cdot (6.022 \cdot 10^{23} \text{ mol}^{-1})^{-1} = 0.03 \text{ cm}^3 \cdot 1 \text{ dm}^3/1000 \text{ cm}^3 \cdot 0.01000 \text{ M}$$

$$n = \log(0.03 \text{ cm}^3 \cdot 1 \text{ dm}^3/1000 \text{ cm}^3 \cdot 0.1000 \text{ M} \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1})/\log(6)$$

$$n = 24$$

The methoxyl groups in the lignin mass (a biopolymer) were quantified according to the Zeisel–Vieböck–Schwappach method. A basswood sample was analysed. 11.60 cm^3 of 0.1000 M $\text{Na}_2\text{S}_2\text{O}_3$

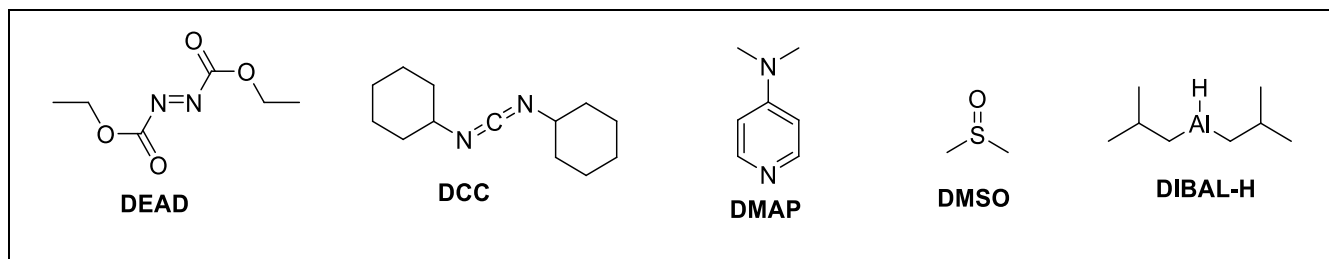
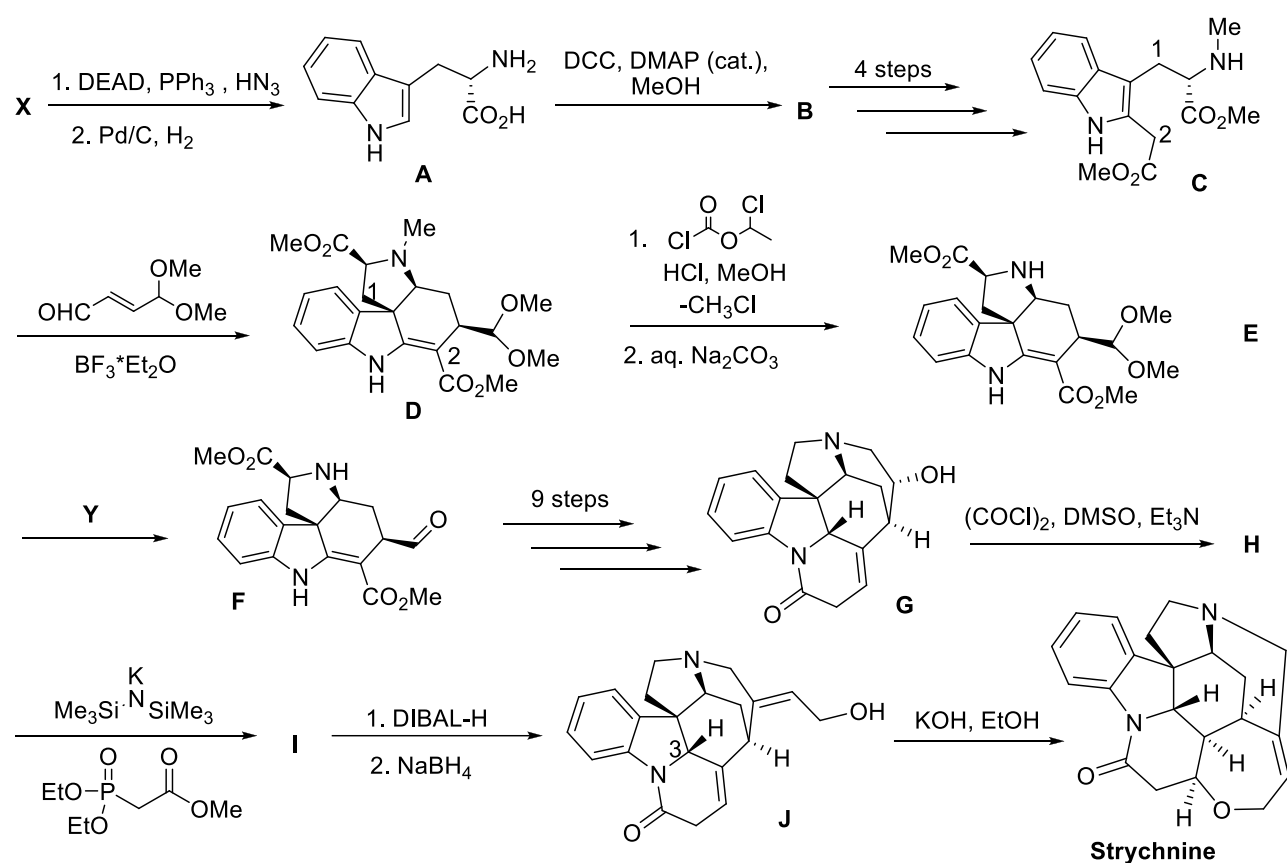
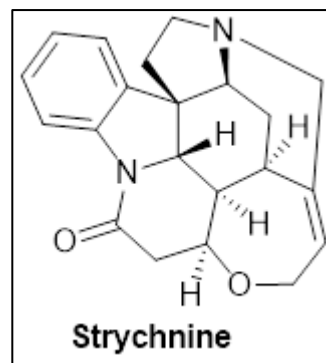
solution was required to titrate the I_2 produced from 0.100 g of the sample (after one Zeisel–Vieböck–Schwappach multiplication cycle).

e) Calculate the mass percent of CH_3O in the basswood sample.

$$\%(CH_3O) = 31.03 \text{ g/mol} / 0.100 \text{ g} \cdot 1/6 \cdot 11.60 \text{ cm}^3 \cdot 1 \text{ dm}^3 / 1000 \text{ cm}^3 \cdot 0.1000 \text{ M} = 6.00\%$$

PROBLEM 5 (10 POINTS) - Better do not eat

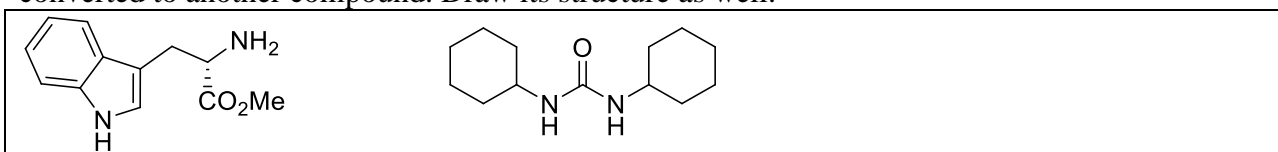
Strychnine is a highly toxic, bitter-taste, crystalline alkaloid used as a pesticide, particularly for killing small vertebrates such as birds and rodents. This chemical is naturally gathered from *Strychnos nux-vomica* tree. In organic chemistry enantiomerically pure strychnine is used for the resolution of organic molecules. Because of its complexity, pharmacological effects and high demand, synthetic chemists are looking for various routes to its total synthesis for many years. In this task you are given one of the shortest synthetic pathways of strychnine.



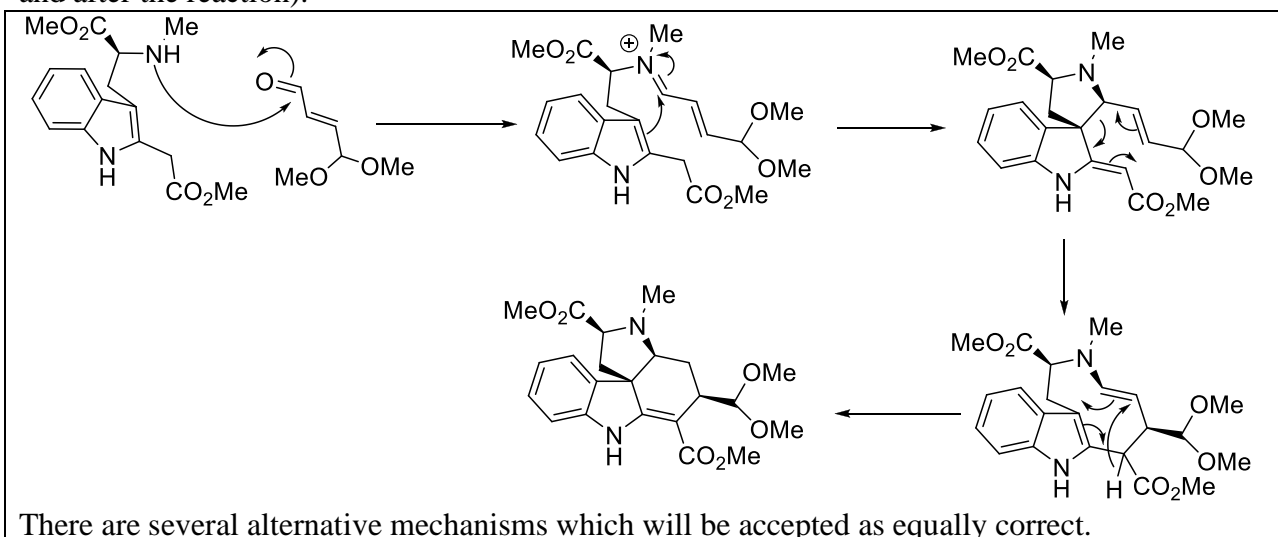
1. Draw the structure of compound **X**. Include proper stereochemical information. Identify the stereocenter(-s) using R/S nomenclature.



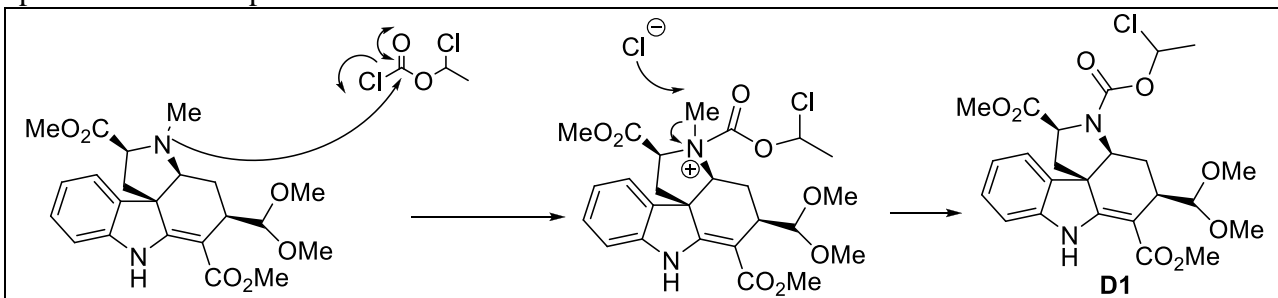
2. Draw the structure of compound **B**. During the reaction from **A** to **B**, the reagent DCC is converted to another compound. Draw its structure as well.



3. Write the suitable mechanism of the formation of compound **D**. During this reaction the role of BF_3 is to chelate to carbonyl group of the unsaturated aldehyde, but you do not need to show this in your mechanism. Keep in mind that during this formation [1,5] hydride shift occurs. Two numbered carbon atoms in the structures **C** and **D** indicate positions of these atoms (before and after the reaction).



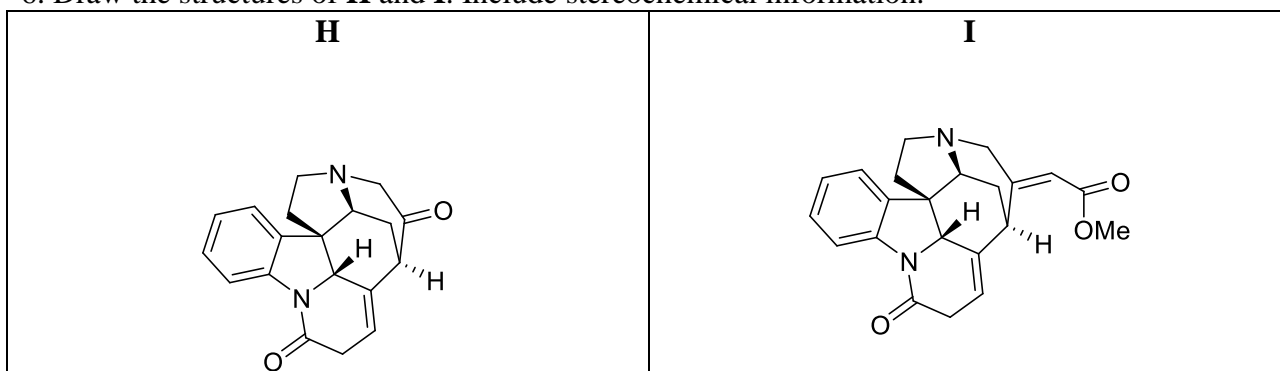
4. After the first step of amine demethylation (from **D** to **E**), the intermediate **D1** forms which after aqueous Na_2CO_3 workup becomes the compound **E**. Provide the detailed mechanism of the conversion from **D** to **D1**. Identify the compound **D1**. Keep in mind that chloromethane is a by-product of this step.



5. What reagent(-s) **Y** is(are) required for acetal hydrolysis?

Aqueous acid solution

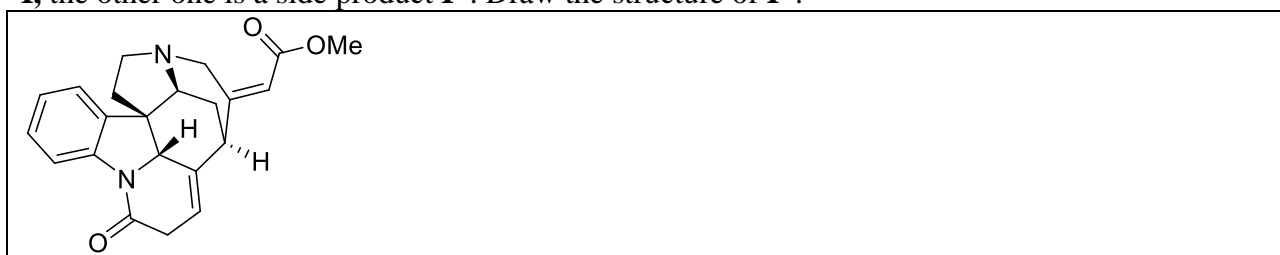
6. Draw the structures of **H** and **I**. Include stereochemical information.



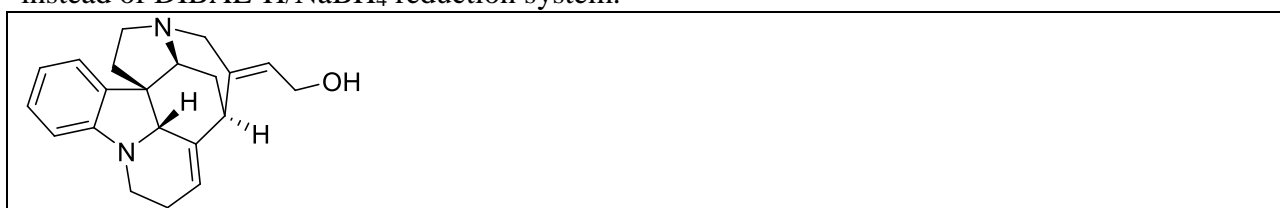
7. The reaction from **H** to **I** is called Horner-Wadsworth-Emmons reaction. Draw all the possible resonance structures of the main nucleophilic intermediate generated *in situ* (directly in the reaction mixture) which reacts with the compound **H**.



8. In the reaction from **H** to **I** actually two products are obtained. One of them is the target compound **I**, the other one is a side product **I***. Draw the structure of **I***.



9. Draw the structure of the compound that would be theoretically acquired from **I** if we used LiAlH_4 instead of DIBAL-H/ NaBH_4 reduction system.



10. Define the stereochemistry of the carbon atom marked 3 in the compound **J** using R/S nomenclature (circle the correct answer).

R

S

11. What properties does **Strychnine** exhibit? (Circle the correct answer.)

a) acidic;

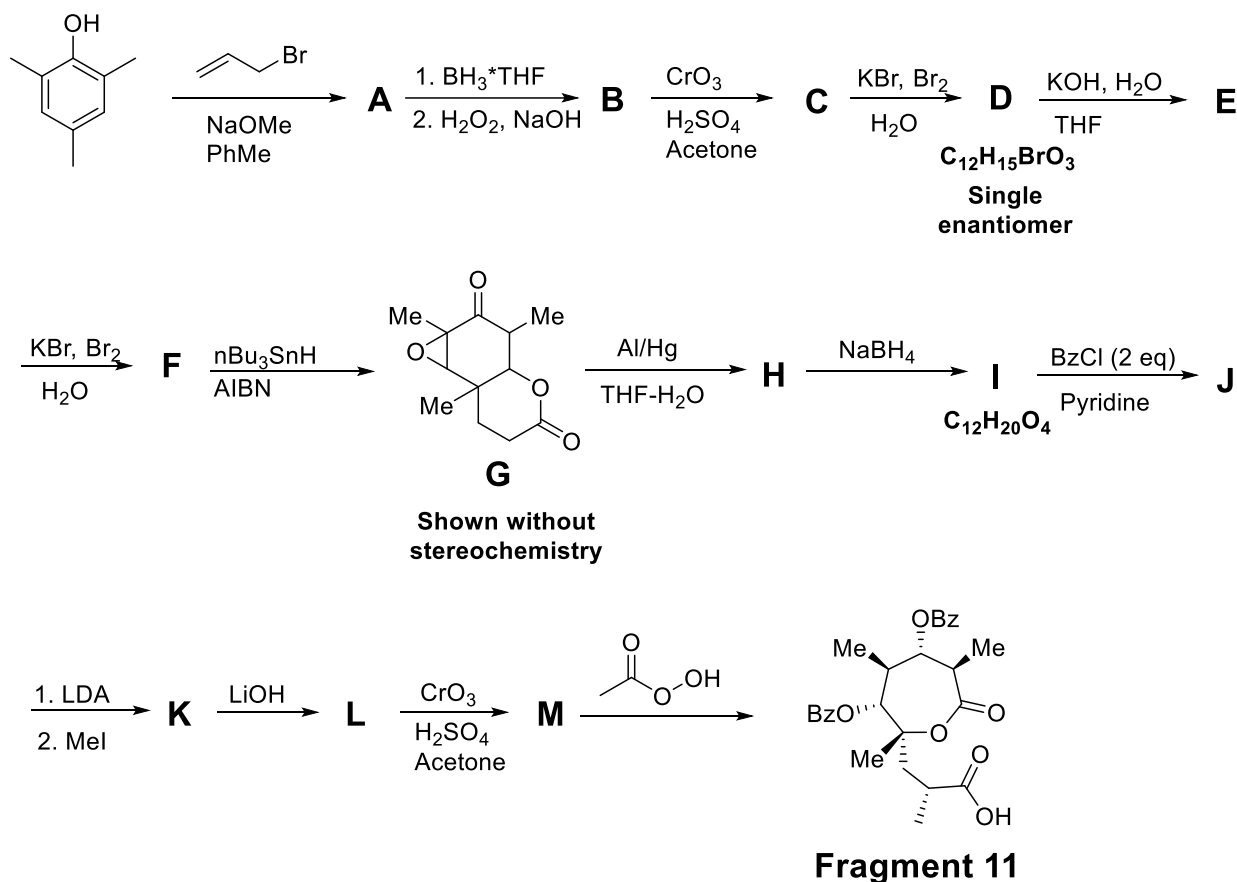
b) basic;

c) amphoteric;

d) none.

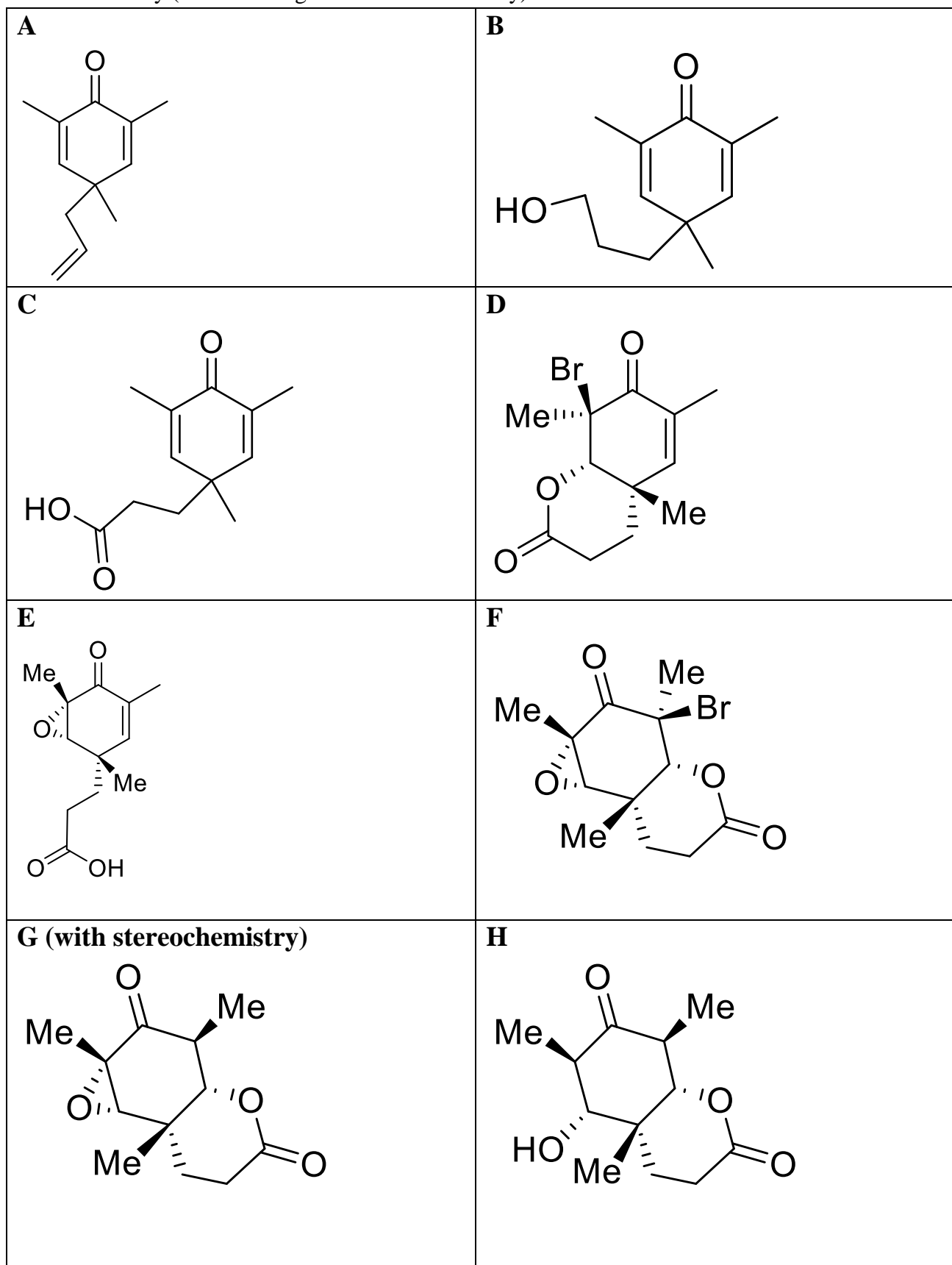
PROBLEM 6 (12 points) - Synthesis of Erythronolide B

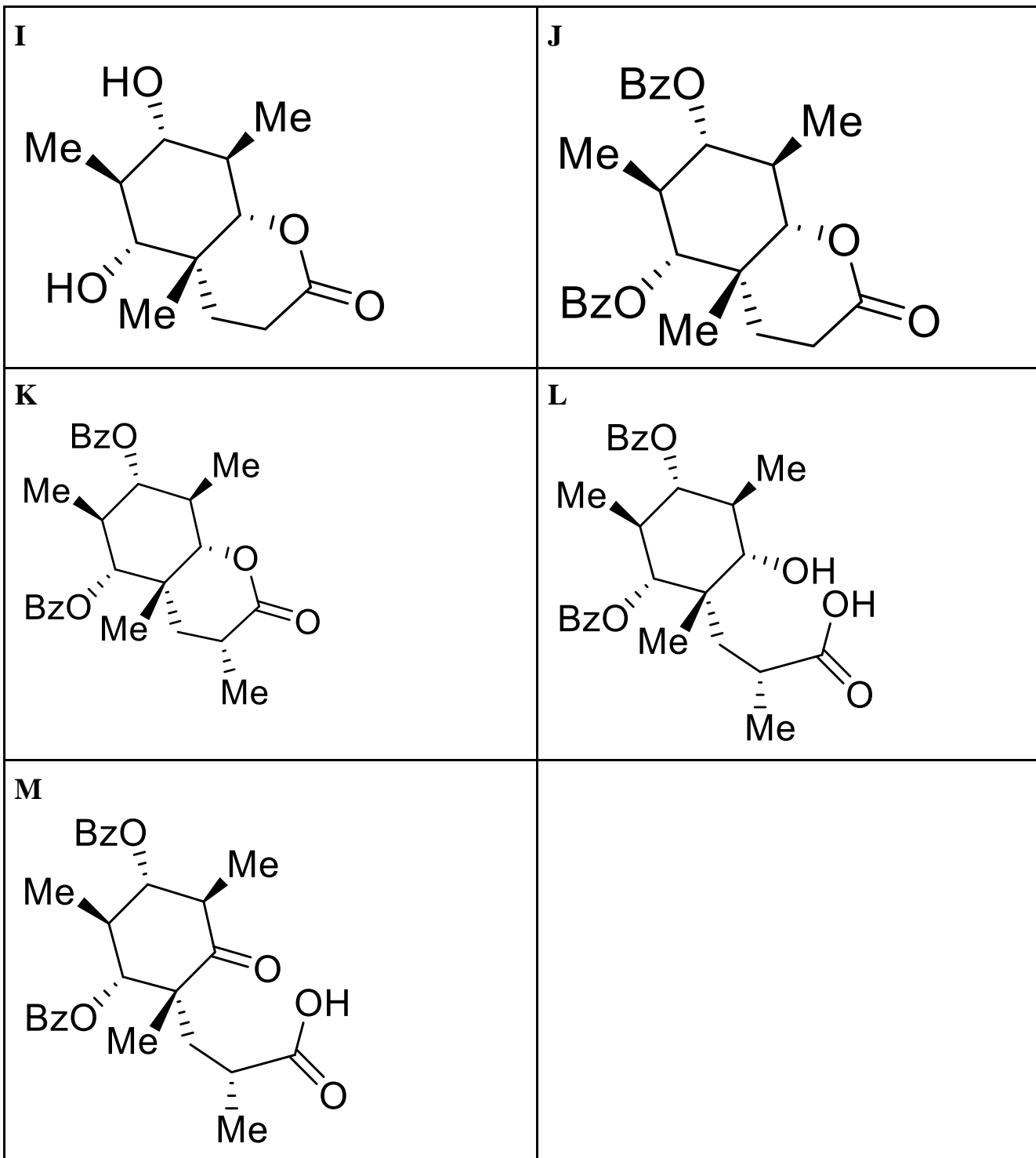
Natural product synthesis is an important part of the organic chemistry. These products usually show high biological activities and thus are extremely interesting from the medicinal standpoint. However, syntheses of these molecules are not trivial, since they tend to have many stereocentres and wide diversity of functional groups (which is what makes them so selective as potential drugs). One of these compounds is Erythronolide B, a biochemical precursor of an antibiotic Erythromycin. Many famous organic chemists, like Woodward, Evans, Carreira, Hoffmann and Danishefsky have succeeded at synthesizing it. In this problem we will discuss the Elias Corey synthesis of Erythronolide B. The full synthesis is not shown here, but the first part was synthesizing - what Corey called - **The Fragment 11**.



In this synthesis the compounds **A**, **B** and **C** are all non-aromatic meso-compounds. The compound **D**, although initially obtained as racemic mixture, is purified to a single enantiomer. The conversion **F** \rightarrow **G** proceeds with inversion of the stereochemistry at the reaction center, but conversion **G** \rightarrow **H** proceeds with retention of the stereochemistry at the reaction center.

1) Show the structures of the compounds **A** – **M**. For all the compounds **D** – **M**, show the stereochemistry (R and S assignment is not necessary).





2) Propose a mechanism for the conversion **M** -> **Fragment 11**. You can do a schematic mechanism, as long as you show all the necessary features that describe the selectivity.

