

## 26th BChO 2018, Riga, Latvia

### Problem 1 – ABC, INORG – Nobel medals

In the 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-colored solution was labeled "*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 colorless 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 a yellow mixture of two gases, **D** and **E**. **D** undergoes further decomposition into **E** and **F**, which spontaneously oxidizes 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 pyrosulfite  $\text{Na}_2\text{S}_2\text{O}_5$  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 remolded into Nobel medals, which were returned to their rightful owners in 1952.

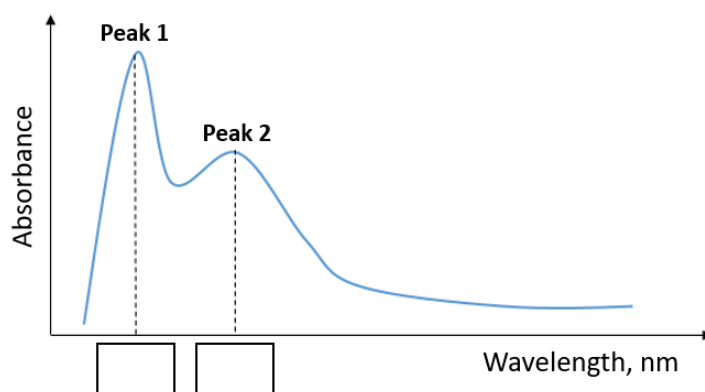
- Write the formulas of **A–G**. Write the equations for all mentioned reactions.
- Draw Lewis structures for compounds **B**, **C**, and **D**. Use VSEPR to determine their geometry at N centers and overall geometry if appropriate.

Tetracoordinate compounds can be either tetrahedral or square planar, with their respective d orbital splitting diagrams provided below.

- Draw in the splitting tetrahedral and square planar diagrams for gold in ion **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 ( $\mu_{\text{B}}$ ), 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.

- Given that **A** is diamagnetic, determine its geometry. What is the spin-only magnetic moment of the other isomer?
- A sketch of the UV-vis spectrum of **A** in solution is provided. Given that a fresh solution of the compound is pale yellow, label the boxes on the abscissa with the estimated wavelength for peaks 1 and 2 in nanometres.

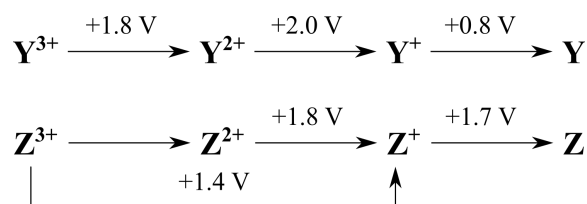


- f) Suggest electronic structures of the excited states corresponding to peaks 1 and 2 using the appropriate  $d$ -orbital splitting pattern from sub-question 3. Note: the overall spin of the molecule has to be preserved upon optical excitation.

### Problem 2 - ELECTRO, STRUCT - Chemistry of metals in oxidation number of +3

Atoms of 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 cm<sup>-3</sup>, respectively. The typical oxidation numbers of **X**, **Y**, and **Z** are +3, +1, and +3, respectively.

- a) Calculate the molar masses of the metals **X**, **Y**, and **Z**.  
 b) Using the data from the Latimer diagram, prove by calculations that the most stable oxidation numbers of **Y** and **Z** in aqueous solution are +1 and +3, respectively.



The standard reduction potential of  $\text{Me}^{n+}$  can be estimated as:  $E^{\circ} = (\Delta H_{\text{atom}} + \Delta H_{\text{ion}} + \Delta H_{\text{hydr}})/(nF) - 4.52 \text{ V}$ , where  $\Delta H_{\text{atom}}$  is the atomization enthalpy change of Me,  $\Delta H_{\text{ion}}$  is the sum of ionization energies, and  $\Delta H_{\text{hydr}}$  is the hydration energy of  $\text{Me}^{3+}$  cation.

- c) Using the provided thermodynamic data, calculate  $E^{\circ}$  values for  $\text{X}^{3+}$ ,  $\text{Z}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Sc}^{3+}$ .

Write a reactivity series for **X**, **Z**, Fe, and Sc.

Ion	$\Delta H_{\text{atom}}$ [kJ mol <sup>-1</sup> ]	$\Delta H_{\text{ion}}$ [kJ mol <sup>-1</sup> ]	$\Delta H_{\text{hydr}}$ [kJ mol <sup>-1</sup> ]
$\text{X}^{3+}$	326	5139	-4525
$\text{Z}^{3+}$	368	5763	-4420
$\text{Fe}^{3+}$	415	5281	-4265
$\text{Sc}^{3+}$	378	4257	-3795

The experimental  $nE^{\circ}$  values are summarized below in the form of a Frost diagram. As can be seen, elements have different preferences in the oxidation numbers. In part,  $E^{\circ}$  is determined by the  $\Delta H_{\text{ion}}$  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.

d) Write symbols of the 4<sup>th</sup> period elements which have lower  $n$ -th ionization energy (IE) values than their left neighbor.

e) The 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> IEs of **Y** and Cu are almost the same. Choose the factor(s) that disfavors oxidation number of +2 for **Y** in comparison to Cu (in aqueous solution):

- i) Larger radius of  $Y^{2+}$  than of  $Cu^{2+}$ ;
- ii) Lower atomization energy of **Y** than of Cu;
- iii) Higher electric conductivity of **Y** than of Cu.

f) Choose the reason(s) explaining why **Z** has considerably lower 3<sup>rd</sup> IE than **Y** (as well as why **Z** is yellow while **Y** is gray):

- Inert pair effect, i.e. the contraction of the  $6s^2$  orbital due to relativistic effect.
- 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.

g) Write the reactions between +3 cations of **X**, **Z**, Fe, and Sc with  $I^-$ .  $E^\circ(I_2) = +0.54$  V.

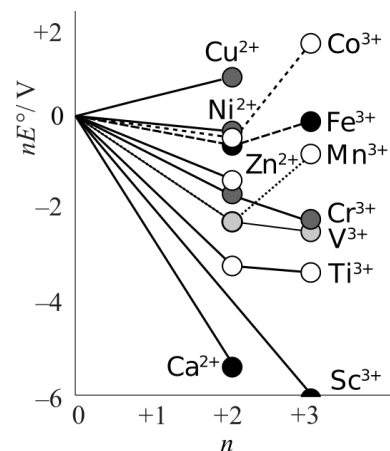
Cations do not occur in solution as bare ions but in a hydrated state as aqua complexes. Other ligands may take the place of water molecules. This way, complex ions are formed in melts and solids.

h) Draw  $[X(H_2O)_6]^{3+}$ ,  $[Z(H_2O)_4]^{3+}$ ,  $[XF_6]^{3-}$ ,  $[XF_4]^-$ ,  $[ZF_4]^-$ , and  $[ZF_6]^-$  complex structures.

Solid  $XF_3$  structure is cubic, with **X** at each corner of the unit cell and one F atom in the middle of each edge. In solid  $ZF_3$ , the coordination number of the **Z** atom is 4. Solid  $XCl_3$  consists of close-packed layers, where the coordination number of the **X** atom is 6. Molecular  $ZCl_3$  solid consists of dimers.

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

j) Draw structures of  $X_2Cl_6$ ,  $Z_2Cl_6$ , and  $W_2Cl_6$ . All have distinct geometry.



### Problem 3 – EQUIL, THERMO – Don't cry

Sulfuryl chloride  $SO_2Cl_2$  acts as a 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 and normal boiling point  $69.4$  °C.

Sulfuryl chloride reacts with water:  $SO_2Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$  (reaction 1)

Above boiling point sulfuryl chloride decomposes:  $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$  (reaction 2)

Standard thermodynamic properties (1 atm and 25 °C):

	$\Delta H_f^\circ$ [kJ mol <sup>-1</sup> ]	$\Delta G_f^\circ$ [kJ mol <sup>-1</sup> ]	$S^\circ$ [J mol <sup>-1</sup> K <sup>-1</sup> ]
$SO_2Cl_2$ (l)	-394.1	-314.0	?
$SO_2Cl_2$ (g)	-364.0	-320.0	311.9
$SO_2$ (g)	-296.8	-300.2	248.2
$Cl_2$ (g)	0.0	0.0	223.1

When solving this problem, assume that all gases are ideal and that enthalpy and entropy changes of processes under consideration are temperature-independent.

- a) 0.10 mol of  $\text{SO}_2\text{Cl}_2$  was dissolved in water and the solution was diluted to  $1.0 \text{ dm}^3$  volume. Calculate the pH of the obtained solution. Ionization constants are:  $\text{p}K_a(\text{HCl}) = -6.3$ ,  $\text{p}K_{a1}(\text{H}_2\text{SO}_4) = -3.0$ ,  $\text{p}K_{a2}(\text{H}_2\text{SO}_4) = 1.92$ .
- b) In the table above, the absolute entropy  $S^\circ$  of  $\text{SO}_2\text{Cl}_2$  (l) is missing. Calculate this parameter.
- c) Calculate the equilibrium constant of **reaction 2** at temperature 350 K.
- d) Indicate a correct statement about the equilibrium constant  $K$  in case of increasing temperature: **i)**  $K$  will increase; **ii)**  $K$  will decrease; **iii)**  $K$  will remain the same.
- e) Decomposition of sulfuryl chloride (**reaction 2**) is a first-order reaction. When considering the kinetics of this reaction at high temperatures, the backward reaction may be neglected because: **i)** the value of  $K$  is high or **ii)** the value of  $K$  is small.

When the decomposition reaction proceeds in a closed vessel, total pressure increases. In the table below, the total pressure change in time is presented (at temperature 600 K, at 0 s, only sulfuryl chloride is present in the vessel):

Time [s]	0	11000	24000	40000
Total pressure [Pa]	$1.00 \cdot 10^5$	$1.215 \cdot 10^5$	$1.41 \cdot 10^5$	$1.58 \cdot 10^5$

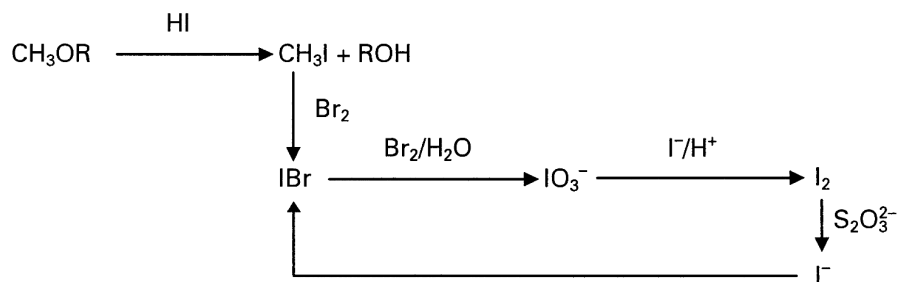
- f) Calculate the rate constant and half-life for this reaction at a given temperature.
- g) When temperature is increased from 600 to 610 K, the rate of the decomposition reactions increases 2.0 times. Calculate how many times the rate of the decomposition reaction at temperature 740 K is faster than at temperature 720 K.

#### Problem 4 - CALC, ELECTRO - Titrimetric determination of methoxyl groups

The 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 oxidized to iodate, and excess bromine is removed ( $E^\circ(\text{Br}_2/2\text{Br}^-) = +1.1 \text{ V}$ ).

- a) Which acid is suitable for removing bromine from the 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) Write the ionic equations of all the reactions depicted in the scheme.
- c) Show that after one cycle of multiplication, six iodide ions are formed per one methoxyl group initially present in a sample.

The minimum volume of 0.1000 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution that can be quantified in titration is one drop of approximately  $0.03 \text{ cm}^3$ .

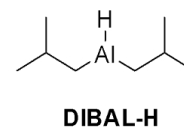
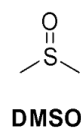
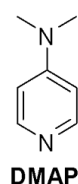
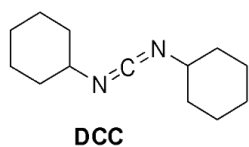
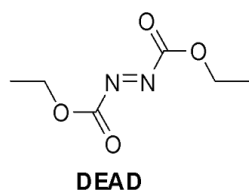
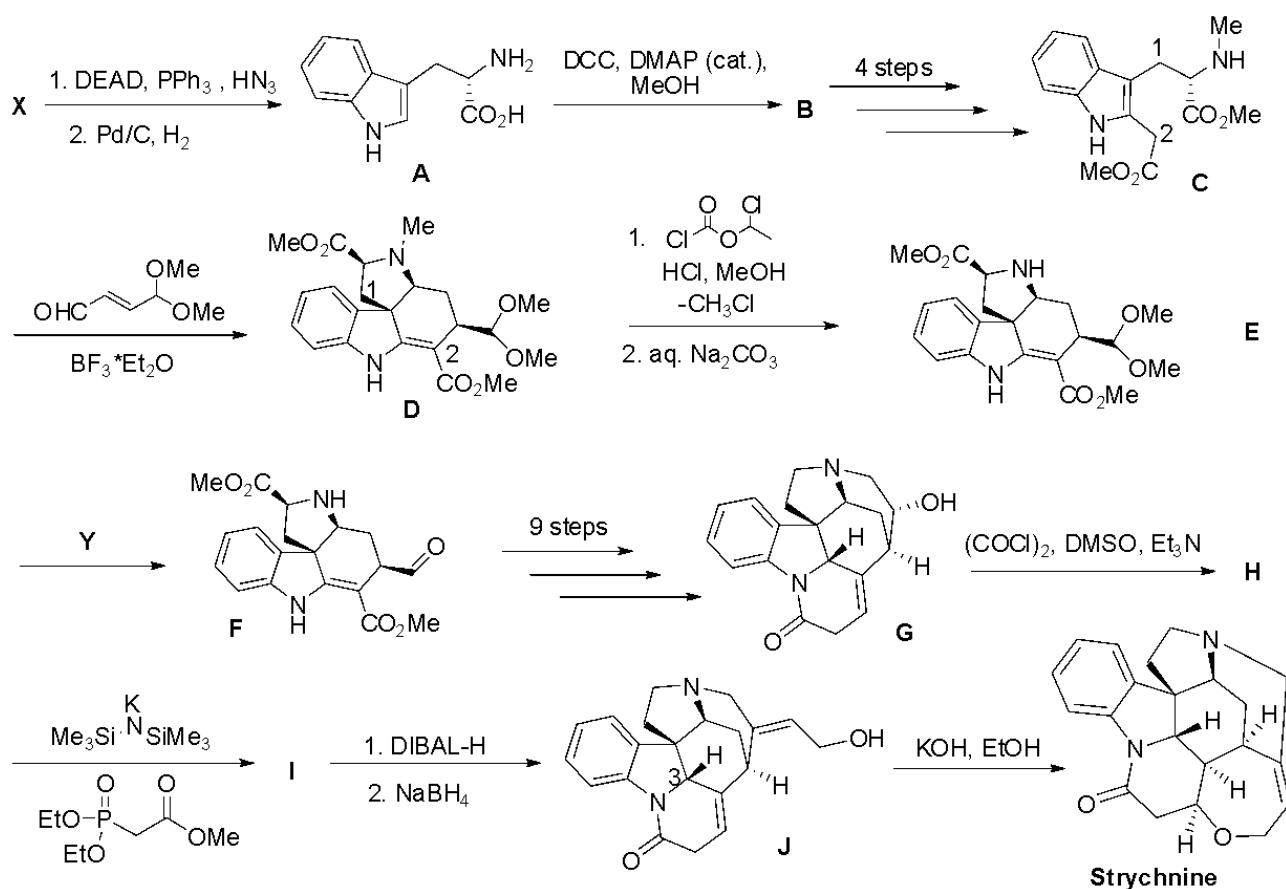
d) Estimate the minimal theoretical number of multiplication cycles needed to be repeated in order to detect a single molecule of  $\text{R-O-CH}_3$  per 10 g of a sample.

The methoxyl groups in the lignin mass (a biopolymer) were quantified according to the Zeisel-Vieböck-Schwappach method. A basswood sample was analyzed.  $11.60 \text{ cm}^3$  of 0.1000 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution was required to titrate the  $\text{I}_2$  produced from 0.100 g of the sample (after one Zeisel-Vieböck-Schwappach multiplication cycle).

e) Calculate the mass percent of  $\text{CH}_3\text{O}$  in the basswood sample.

### Problem 5 - STEREO, SYNTH - 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 have been 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.



- a) Draw the structure of compound **X** with stereochemistry. Identify the stereocenter(s) using the *R/S* nomenclature.
- b) 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.
- c) Write the suitable mechanism for the formation of compound **D**. During this reaction, the role of  $\text{BF}_3$  is to chelate to the 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 in both structures (before and after the reaction).
- d) After the first step of amine demethylation (from **D** to **E**), the intermediate **D1** forms which, after aqueous  $\text{Na}_2\text{CO}_3$  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.
- e) What reagent(s) **Y** is/are required for acetal hydrolysis?
- f) Draw the structures of **H** and **I** with stereochemistry.
- g) The reaction from **H** to **I** is called the 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**.
- h) In the reaction from **H** to **I**, two products are actually obtained. One of them is the target compound **I** and the other one is a side product **I\***. Draw the structural formula of **I\***.
- i) Draw the structure of the compound that would be theoretically acquired from **I** if we used  $\text{LiAlH}_4$  instead of DIBAL-H/ $\text{NaBH}_4$  reduction system.
- j) Define the stereochemistry of the carbon atom marked 3 in the compound **J** using *R/S* nomenclature (circle the correct answer).
- k) Which property does Strychnine exhibit: **i)** acidic; **ii)** basic; **iii)** amphoteric; **iv)** none?

### Problem 6 – STEREO, SYNTH – Synthesis of Erythronolide B

Natural product synthesis is an important part of organic chemistry. These products usually exhibit high biological activity and thus are extremely interesting from a medicinal standpoint. However, syntheses of these molecules are not trivial since they tend to have many stereocenters and a 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 the antibiotic Erythromycin. Many famous organic chemists, like Woodward, Evans, Carreira, Hoffmann and Danishefsky, have succeeded at synthesizing it. In this problem, we will discuss Elias Corey's 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 a racemic mixture, is purified to a single enantiomer. The conversion **F** → **G** proceeds with inversion of the stereochemistry at the reaction center, but conversion **G** → **H** proceeds with retention of the stereochemistry at the reaction center.

- a) Draw the structural formulas of the compounds **A–M** with stereochemistry.
- b) Draw a mechanism for the conversion **M** → **Fragment 11**.

