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26th CHEMISTRY OLYMPIAD OF THE BALTIC STATES

Riga, Latvia
April 13th-15th, 2018

THEORETICAL EXAMINATION



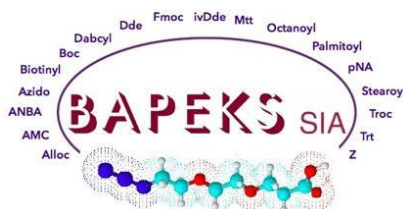
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“Back to where it all began”

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Periodic table of elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18													
1 H Hydrogen 1.008	2 He Helium 4.0026	3 Li Lithium 6.94	4 Be Beryllium 9.0122	5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180	11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 Al Aluminum 26.982	14 Si Silicon 28.085	15 P Phosphorus 30.974	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948													
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798													
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29													
55 Cs Caesium 132.91	56 Ba Barium 137.33	57-71 Lanthanum series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)													
87 Fr Francium (223)	88 Ra Radium (226)	89-103 Actinium series	104 Rf Rutherfordium (267)	105 Db Dubnium (268)	106 Sg Seaborgium (269)	107 Bh Bohrium (270)	108 Hs Hassium (277)	109 Mt Meitnerium (278)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (282)	112 Cn Copernicium (285)	113 Nh Nihonium (286)	114 Fl Flerovium (289)	115 Mc Moscovium (290)	116 Lv Livermorium (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)													
6 La Lanthanum 138.91	57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.05	71 Lu Lutetium 174.97	7 Ac Actinium (227)	89 Th Thorium 232.04	90 Pa Protactinium 231.04	91 U Uranium 238.03	92 Np Neptunium (237)	93 Pu Plutonium (244)	94 Am Americium (243)	95 Cm Curium (247)	96 Bk Berkelium (247)	97 Cf Californium (251)	98 Es Einsteinium (252)	99 Fm Fermium (257)	100 Md Mendelevium (258)	101 No Nobelium (259)	102 Lr Lawrencium (266)

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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General information

This exam contains 26 pages for theoretical exam tasks (including the answer sheets). There are a total of 6 problems.

Write your code on each answer sheet.

You will have a total of 5 hours to complete six theoretical tasks. You must begin as soon as the **“Start Command”** is given.

All answers must be written in answer boxes provided. Answer written in other places will not be graded. You can use other side of page as a draft paper.

When it is necessary, provide your calculations in the answer boxes. You will get full marks for correct answers (numbers and units) only if the calculations will be shown.

You must stop your work immediately (including filling answer sheets) when the **“Stop Command”** is announced.

Do not leave examination room before assistant allows to do it.

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Probably useful constants and formulas

Avogadro's constant, $N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$

Boltzmann constant, $k_B = 1.3807 \times 10^{-23} \text{ J K}^{-1}$

Universal gas constant, $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08205 \text{ atm L K}^{-1} \text{ mol}^{-1}$

Speed of light, $c = 2.9979 \times 10^8 \text{ m s}^{-1}$

Planck's constant, $h = 6.6261 \times 10^{-34} \text{ J s}$

Faraday constant, $F = 9.64853399 \times 10^4 \text{ C}$

Mass of electron, $m_e = 9.10938215 \times 10^{-31} \text{ kg}$

Standard pressure, $P = 1 \text{ bar} = 10^5 \text{ Pa}$

Atmospheric pressure, $P_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg} = 760 \text{ torr}$

Zero of the Celsius scale, 273.15 K

1 picometer (pm) = 10^{-12} m ; $1 \text{ \AA} = 10^{-10} \text{ m}$; nanometer (nm) = 10^{-9} m

1 eV = $1.6 \times 10^{-19} \text{ J}$

1 amu = $1.66053904 \times 10^{-27} \text{ kg}$

Ideal gas equation: $PV = nRT$

Enthalpy: $H = U - PV$

Gibbs free energy: $G = H - TS$ $\Delta G = \Delta G^\circ + RT \ln Q$

$$\Delta G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$$

Entropy change: $\Delta S = \frac{q_{\text{rev}}}{T}$, where q_{rev} is heat for the reversible process

$$\Delta S = nR \ln \frac{V_2}{V_1} \quad (\text{for isothermal expansion of an ideal gas})$$

Nernst equation: $E = E^\circ + \frac{RT}{nF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$

Energy of a photon: $E = \frac{hc}{\lambda}$ Lambert-Beer law: $A = \log \frac{I_0}{I} = \epsilon bC$

Integrated rate law

Zero order $[A] = [A]_0 - kt$ First order $\ln [A] = \ln [A]_0 - kt$

Second order $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

Arrhenius equation

$$k = Ae^{-E_a/RT}$$

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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 $\text{Na}_2\text{S}_2\text{O}_5$ 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 remoulded into Nobel medals, which were presented back to their rightful owners in 1952.

1. Write formulas of **A-G**! Write down all aforementioned reactions with correct coefficients:

A:	B:	C:	D:
E:	F:	G:	H:

2. Draw Lewis structures for compounds **B**, **C** and **D** indicating the formal charges! Use VSEPR to determine their geometry at N centres and overall geometry if appropriate.

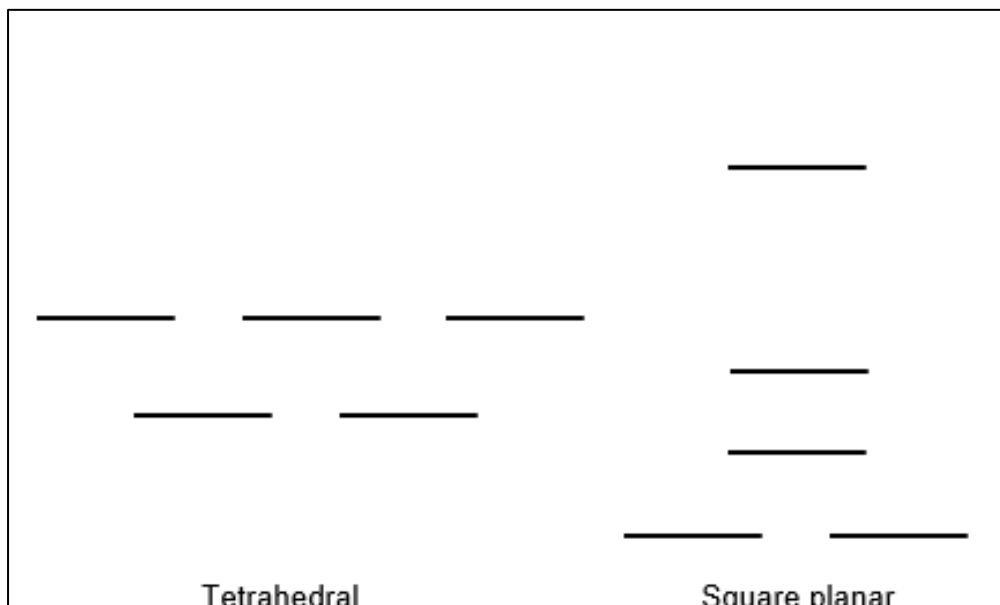
B:	C:	D:
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Geometry at N centre: (check correct answer) <input type="radio"/> Linear <input type="radio"/> Bent <input type="radio"/> Trigonal planar <input type="radio"/> Pyramidal	Geometry at N centre: (check correct answer) <input type="radio"/> Linear <input type="radio"/> Bent <input type="radio"/> Trigonal planar <input type="radio"/> Pyramidal	Geometry at N centre: (check correct answer) <input type="radio"/> Linear <input type="radio"/> Bent <input type="radio"/> Trigonal planar <input type="radio"/> Pyramidal
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Tetracoordinate compounds can be either tetrahedral or square planar, with their respective d orbital splitting diagrams provided below.

3., Fill in the splitting tetrahedral and square planar diagrams for gold in ion **A**

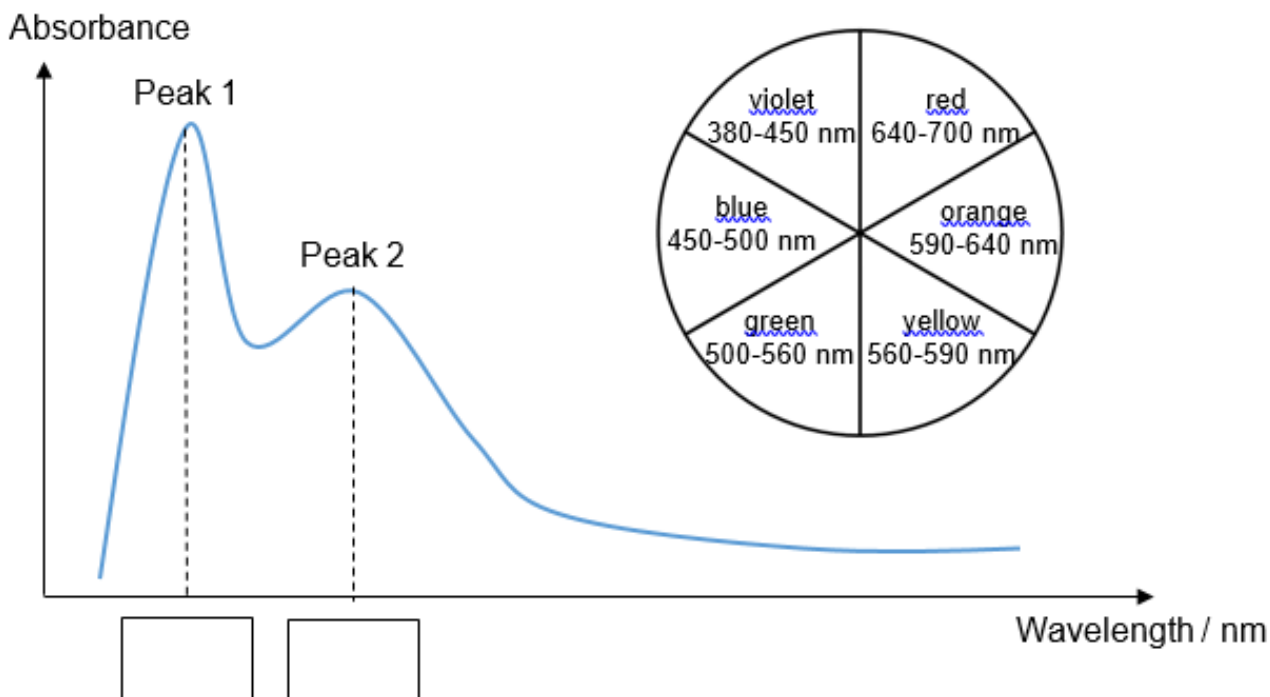


When Niels Bohr was not helping refugees of Nazism, he contributed massively to the field of chemistry. The unit of magnetic moment, Bohr magneton (μ_B), was named after him. A compound's spin-only magnetic moment in Bohr magnetons can be estimated with the formula $\mu = \sqrt{n(n+2)}$, where n is the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

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

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5. 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 estimated wavelength for peaks 1 and 2 in nanometres. Use the colour wheel provided.



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.

<p>Peak 1:</p>	<p>Peak 2:</p>
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The standard reduction potential of 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 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 Me^{3+} cation.

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+} , Fe^{3+} , and Sc^{3+} .

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

$$E^\circ(\text{X}^{3+}/\text{X}) =$$

$$E^\circ(\text{Z}^{3+}/\text{Z}) =$$

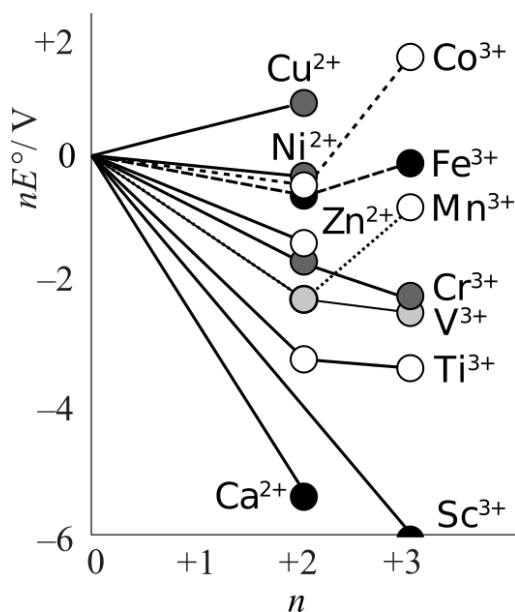
$$E^\circ(\text{Fe}^{3+}/\text{Fe}) =$$

$$E^\circ(\text{Sc}^{3+}/\text{Sc}) =$$

Reactivity series: _____

The experimental nE° values 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.

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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:

rel. low 3rd IE:

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).

- Larger radius of Y^{2+} than of Cu^{2+}
- 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):

- 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 of the elements in the 6th row.

h) Write the reactions between 3+ cations of X, Z, Fe, and Sc with iodide anion (I^-).
 $E^\circ(I_2) = +0.54 \text{ V}$.

X³⁺:

Z³⁺:

Fe³⁺:

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Sc³⁺:

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

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

$[\mathbf{X}(\text{H}_2\text{O})_6]^{3+}$	$[\mathbf{Z}(\text{H}_2\text{O})_4]^{3+}$	$[\mathbf{XF}_6]^{3-}$
$[\mathbf{XF}_4]^-$	$[\mathbf{ZF}_4]^-$	$[\mathbf{ZF}_6]^-$

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 \mathbf{Z} atom is 4. Solid \mathbf{XCl}_3 consists of 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		
\mathbf{ZF}_3		
\mathbf{XCl}_3		
\mathbf{ZCl}_3		

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

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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:

Answer:

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

Calculations:

Answer:

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

Calculation:

Answer:

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:

Answers: Rate constant:

half-life:

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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:

Answer:

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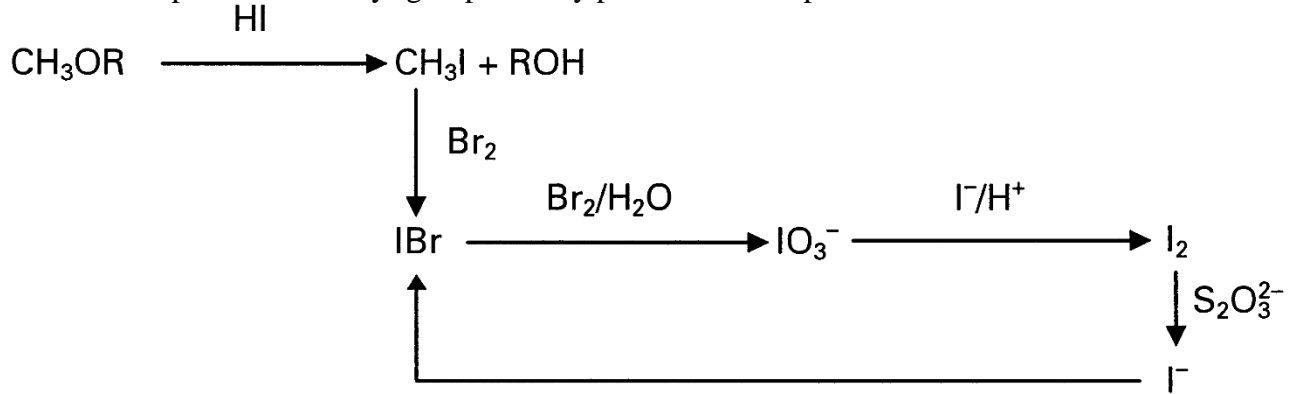
PROBLEM 4 (8 POINTS) - Titrimetric determination of methoxyl groups

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:

$$\begin{array}{l}
 \text{IBr} + __\text{Br}_2 + __\text{H}_2\text{O} \rightarrow __\text{IO}_3^- + __\text{H}^+ + __\text{Br}^- \\
 \text{IO}_3^- + __\text{I}^- + __\text{H}^+ \rightarrow __\text{I}_2 + __\text{H}_2\text{O} \\
 \text{I}_2 + __\text{S}_2\text{O}_3^{2-} \rightarrow __\text{I}^- + __\text{S}_4\text{O}_6^{2-}
 \end{array}$$

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

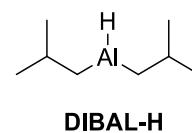
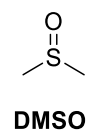
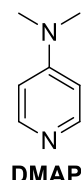
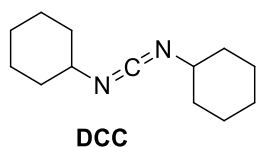
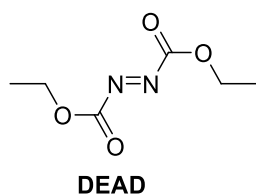
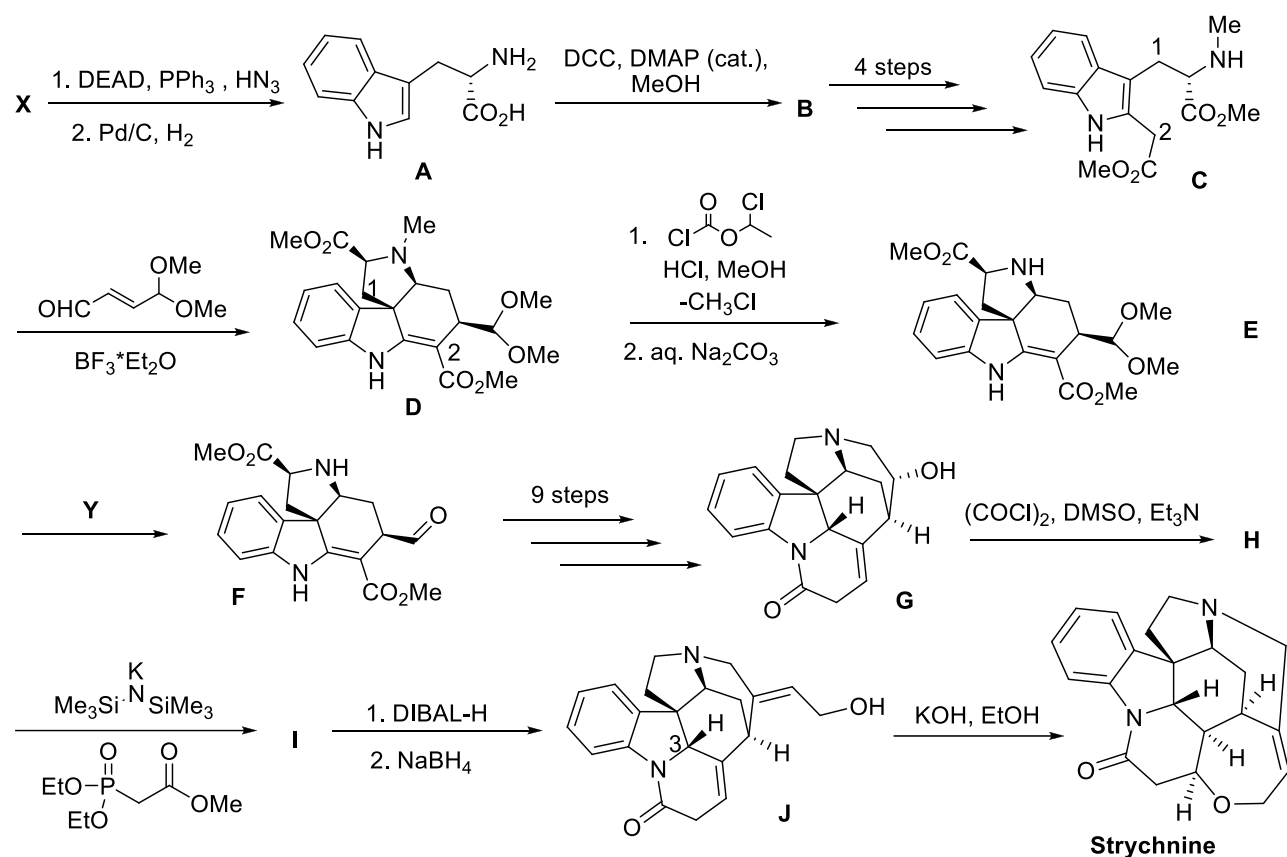
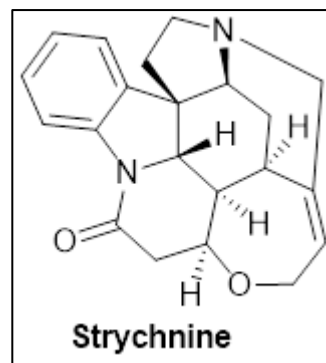
d) The minimum volume of 0.1000 M $\text{Na}_2\text{S}_2\text{O}_3$ solution that can be quantified in a titration is one drop of approximately 0.03 cm^3 . Estimate the minimal theoretical number of multiplication cycles needed to be repeated in order to detect a single molecule of R-O-CH_3 per 10 g 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 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.

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.



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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 in both structures (before and after the reaction).

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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.

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

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

H	I
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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***.

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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

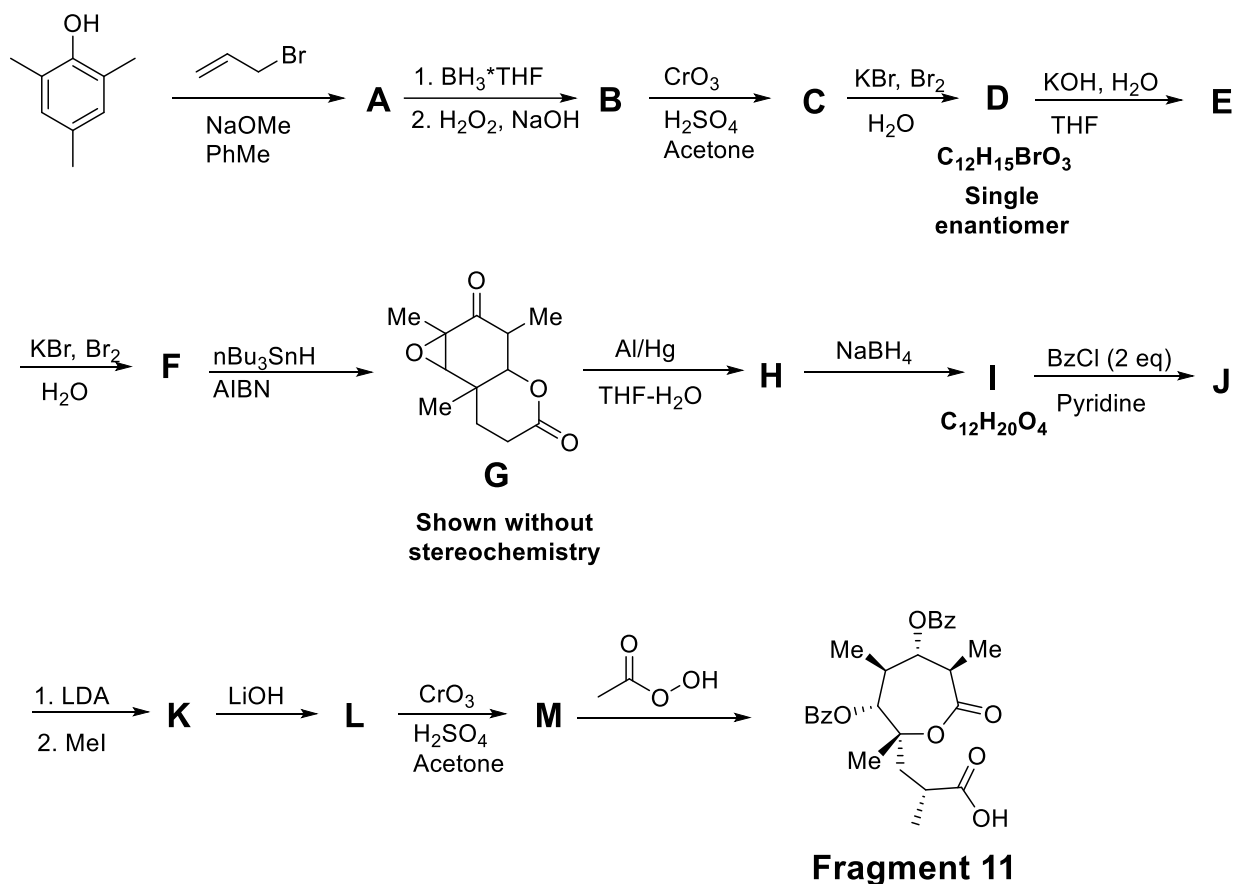
11. Which property does **Strychnine** exhibit? (Circle the correct answer.)

- a) acidic;
- b) basic;
- c) amphoteric;
- d) none.

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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** \rightarrow **Fragment 11**. You can do a schematic mechanism, as long as you show all the necessary features that describe the selectivity.

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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).

A	B
C	D
E	F
G (with stereochemistry)	H

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I	J
K	L
M	

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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.*