



## Theoretical problems from the Baltic Chemistry Olympiad

**1<sup>st</sup>–30<sup>th</sup> BChO**

**1993–2024**

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**Baltic Chemistry Olympiad**  
**Theoretical exams**

|                                                                                        |           |
|----------------------------------------------------------------------------------------|-----------|
| <b>Forewords.....</b>                                                                  | <b>9</b>  |
| <b>Constants and equations.....</b>                                                    | <b>11</b> |
| <b>Complementary colors of the visible light.....</b>                                  | <b>13</b> |
| <b>NMR chemical shifts.....</b>                                                        | <b>13</b> |
| <b>List of amino acids.....</b>                                                        | <b>14</b> |
| <b>Abbreviations for topics.....</b>                                                   | <b>15</b> |
| <b>1st BChO, 1993, Riga, Latvia.....</b>                                               | <b>16</b> |
| Problem 1 – ABC – A wet crystal.....                                                   | 16        |
| Problem 2 – ABC, CALC – So similar but not the same.....                               | 16        |
| Problem 3 – ABC – Do not drink it.....                                                 | 16        |
| Problem 4 – STRUCT – Organic siblings.....                                             | 16        |
| Problem 5 – ABC, SPECTRA – Organic riddle.....                                         | 16        |
| Problem 6 – BIO, STRUCT – Hemerythrin.....                                             | 17        |
| Problem 7 – INORG – Toxic gold.....                                                    | 17        |
| Problem 8 – EQUIL – Basic acid reactions.....                                          | 17        |
| <b>2nd BChO, 1994, Vilnius, Lithuania.....</b>                                         | <b>18</b> |
| Problem 1 – INORG – Famous for not just the wine.....                                  | 18        |
| Problem 2 – KINETICS – Unstable chemical.....                                          | 18        |
| Problem 3 – EQUIL, THERMO – All the kinds of soda.....                                 | 18        |
| Problem 4 – INORG – Copper nitrate.....                                                | 18        |
| Problem 5 – ELECTRO, EQUIL – A simple lead battery.....                                | 18        |
| Problem 6 – MECH, STEREO – Three children of cyclohexane.....                          | 19        |
| Problem 7 – ABC, BIO – The smell of Baltics.....                                       | 19        |
| Problem 8 – ABC, SPECTRA – Another fossil fuel.....                                    | 19        |
| <b>3rd BChO, 1995, Tartu, Estonia.....</b>                                             | <b>20</b> |
| Problem 1 – ABC, MECH, SPECTRA – Shapeshifting organics.....                           | 20        |
| Problem 2 – CALC, INORG – Oxidation of rhenium.....                                    | 20        |
| Problem 3 – ELECTRO – Silver energy.....                                               | 20        |
| Problem 4 – KINETICS – The kinetics of March test.....                                 | 20        |
| Problem 5 – ABC – A lot of heating.....                                                | 21        |
| Problem 6 – BIO – Don't starve.....                                                    | 21        |
| Problem 7 – ABC – Organic riddle.....                                                  | 21        |
| Problem 8 – EQUIL – Removal of iron from water.....                                    | 21        |
| <b>4th BChO, 1996, Riga, Latvia.....</b>                                               | <b>22</b> |
| Problem 1 – ABC – An unknown alloy.....                                                | 22        |
| Problem 2 – APPLIED, THERMO – Old-school hydrogen.....                                 | 22        |
| Problem 3 – ELECTRO – On cobalt and ammonia.....                                       | 22        |
| Problem 4 – EQUIL, THERMO – Combustion of acid vapors.....                             | 22        |
| Problem 5 – ABC, SPECTRA – Determining molecular mass without a mass spectrometer..... | 22        |

|                                                                             |           |
|-----------------------------------------------------------------------------|-----------|
| Problem 6 – STEREO, SYNTH – Chemical hormones.....                          | 23        |
| <b>5th BChO, 1997, Vilnius, Lithuania.....</b>                              | <b>24</b> |
| Problem 1 – INORG – Simple electrolysis.....                                | 24        |
| Problem 2 – INORG – Mercury from a gemstone.....                            | 24        |
| Problem 3 – EQUIL – Carbon monoxide conversion.....                         | 24        |
| Problem 4 – ELECTRO – A simple galvanic cell.....                           | 24        |
| Problem 5 – ABC – A funny ketone.....                                       | 25        |
| Problem 6 – ABC, BIO – Sweet toxins.....                                    | 25        |
| <b>6th BChO, 1998, Tartu, Estonia.....</b>                                  | <b>26</b> |
| Problem 1 – ABC, CALC – Another white powder in the lab.....                | 26        |
| Problem 2 – CALC – Analysis of gas mixture.....                             | 26        |
| Problem 3 – STEREO, SYNTH – Recreating a natural biosynthesis in a lab..... | 26        |
| Problem 4 – MECH – Lethally spicy.....                                      | 26        |
| Problem 5 – KINETICS – A rapid synthesis of ethane.....                     | 27        |
| Problem 6 – EQUIL – pH-dependent titration.....                             | 27        |
| <b>7th BChO, 1999, Kaunas, Lithuania.....</b>                               | <b>28</b> |
| Problem 1 – ABC – Haloalkane redox magic.....                               | 28        |
| Problem 2 – BIO, CALC – The ones that hide inside potatoes.....             | 28        |
| Problem 3 – ELECTRO, EQUIL – A way to dissolve silver.....                  | 28        |
| Problem 4 – EQUIL – Hydrazine.....                                          | 29        |
| Problem 5 – CALC – Carbon tet.....                                          | 29        |
| Problem 6 – STRUCT – A colorful manganese complex.....                      | 29        |
| Problem 7 – ABC – Four seasons.....                                         | 29        |
| <b>8th BChO, 2000, Riga, Latvia.....</b>                                    | <b>30</b> |
| Problem 1 – ABC – Volcanic combustion.....                                  | 30        |
| Problem 2 – ABC, EQUIL – A rainbow metal.....                               | 30        |
| Problem 3 – ABC – Same formula, different compounds.....                    | 30        |
| Problem 4 – SPECTRA, SYNTH – A breakthrough in surgery.....                 | 31        |
| Problem 5 – ELECTRO, EQUIL – A primitive pH meter.....                      | 31        |
| Problem 6 – RADIO – Nuclear waste with a red flame.....                     | 31        |
| <b>9th BChO 2001, Tartu, Estonia.....</b>                                   | <b>31</b> |
| Problem 1 – ELECTRO, EQUIL – Lead and oxalate.....                          | 32        |
| Problem 2 – KINETICS – NO <sub>x</sub> conversion of carbon monoxide.....   | 32        |
| Problem 3 – CALC – An unknown alloy.....                                    | 32        |
| Problem 4 – CALC – Unsafe moonshine.....                                    | 33        |
| Problem 5 – SYNTH – Urushi lacquer is expensive for a reason.....           | 33        |
| Problem 6 – BIO, MECH – Protein sequencing.....                             | 34        |
| <b>10th BChO, 2002, Palanga, Lithuania.....</b>                             | <b>34</b> |
| Problem 1 – ABC – A pink element.....                                       | 35        |
| Problem 2 – THERMO – The first step to fertilizers.....                     | 35        |
| Problem 3 – KINETICS – Logic and kinetics.....                              | 35        |
| Problem 4 – CALC – Professional burette applications.....                   | 36        |

|                                                                    |           |
|--------------------------------------------------------------------|-----------|
| Problem 5 – MECH, STEREO – Chemistry of essential oils.....        | 36        |
| Problem 6 – STEREO, SPECTRA, SYNTH – Spectroscopy on steroids..... | 37        |
| <b>11th BChO, 2003, Riga, Latvia.....</b>                          | <b>39</b> |
| Problem 1 – CRYSTAL – Packing of peas and lupine.....              | 39        |
| Problem 2 – STRUCT – Nitrogen hydrides.....                        | 39        |
| Problem 3 – RADIO – Polonium.....                                  | 39        |
| Problem 4 – EQUIL – Slow reaction.....                             | 40        |
| Problem 5 – EQUIL – Selenic acid.....                              | 40        |
| Problem 6 – ABC, BIO – Tropinic acid.....                          | 40        |
| <b>12th BChO, 2004, Tartu, Estonia.....</b>                        | <b>41</b> |
| Problem 1 – CALC, CRYSTAL, SPECTRA – European Union.....           | 41        |
| Problem 2 – ABC, SYNTH – After the fever is gone.....              | 41        |
| Problem 3 – KINETICS, MECH – Nucleophilic substitution.....        | 42        |
| Problem 4 – INORG, SPECTRA – Pharaoh's Compliment.....             | 42        |
| Problem 5 – EQUIL – Chemical equilibrium.....                      | 43        |
| Problem 6 – ELECTRO, EQUIL – Electrolysis.....                     | 43        |
| <b>13th BChO, 2005, Vilnius, Lithuania.....</b>                    | <b>44</b> |
| Problem 1 – INORG, STRUCT – Blue nitrogen.....                     | 44        |
| Problem 2 – STRUCT – Display of complex chemicals.....             | 44        |
| Problem 3 – MECH, STEREO – A cycle of additions.....               | 45        |
| Problem 4 – SPECTRA, STEREO – A greener soap for polymers.....     | 46        |
| Problem 5 – RADIO – An easy way to make a nuke.....                | 47        |
| Problem 6 – THERMO – A water cycle.....                            | 48        |
| <b>14th BChO, 2006, Riga, Latvia.....</b>                          | <b>49</b> |
| Problem 1 – ABC, EQUIL – Versatile purple.....                     | 49        |
| Problem 2 – CRYSTAL – Grand Theft Balls.....                       | 49        |
| Problem 3 – SPECTRA, SYNTH – One peak, two downhill pathways.....  | 50        |
| Problem 4 – CALC, STRUCT – How to set water on fire.....           | 50        |
| Problem 5 – MECH, SYNTH – Organic juggling.....                    | 51        |
| Problem 6 – EQUIL, THERMO – Killer lake.....                       | 52        |
| <b>15th BChO, 2007, Tartu, Estonia.....</b>                        | <b>53</b> |
| Problem 1 – THERMO – Polar winter in Antarctic.....                | 53        |
| Problem 2 – SYNTH – Synthesis of bicyclic compound.....            | 53        |
| Problem 3 – KINETICS – Isoleucine dating.....                      | 54        |
| Problem 4 – CRYSTAL – Goblin's element.....                        | 54        |
| Problem 5 – MECH – Sigmatropic rearrangement.....                  | 55        |
| Problem 6 – ABC, CRYSTAL, THERMO – Dolomite.....                   | 56        |
| <b>16th BChO, 2008, Vilnius, Lithuania.....</b>                    | <b>57</b> |
| Problem 1 – ABC, CRYSTAL – A mysterious substance.....             | 57        |
| Problem 2 – ELECTRO, STRUCT – Cobalt-Chameleon.....                | 57        |
| Problem 3 – KINETICS – Negative activation energy!.....            | 58        |
| Problem 4 – SYNTH – An elegant compound of the last century.....   | 59        |

|                                                                                                        |           |
|--------------------------------------------------------------------------------------------------------|-----------|
| Problem 5 – APPLIED, ELECTRO, THERMO – Li-ion battery.....                                             | 60        |
| Problem 6 – CALC, MECH, STEREO – Supramolecular basket.....                                            | 61        |
| <b>17th BChO, 2009, Riga, Latvia.....</b>                                                              | <b>63</b> |
| Problem 1 – KINETICS – Hydrolysis of pyrophosphate.....                                                | 63        |
| Problem 2 – ABC, CALC – Iodine and polyiodides.....                                                    | 63        |
| Problem 3 – MECH, SYNTH – Small rings fighting diabetes.....                                           | 64        |
| Problem 4 – ABC, INORG – Uses and misuses of nitrogen compounds.....                                   | 64        |
| Problem 5 – EQUILIB, KINETICS – Kinetics and equilibrium.....                                          | 65        |
| Problem 6 – SYNTH – Chanel №5.....                                                                     | 65        |
| <b>18th BChO, 2010, Tartu, Estonia.....</b>                                                            | <b>67</b> |
| Problem 1 – APPLIED, THERMO – Ethanol as a source of energy.....                                       | 67        |
| Problem 2 – CALC, KINETICS, STRUCT – Synthesis and aqation of<br>fluoropentaaquachromium(III) ion..... | 68        |
| Problem 3 – STEREO – Asymmetry without asymmetric center.....                                          | 69        |
| Problem 4 – ABC, CRYSTAL, EQUIL – Environmental hazards.....                                           | 70        |
| Problem 5 – CALC, CRYSTAL, ELECTRO – Half solid half melted.....                                       | 71        |
| Problem 6 – SPECTRA, SYNTH – Modafinil – work without sleep?.....                                      | 72        |
| <b>19th BChO, 2011, Vilnius, Lithuania.....</b>                                                        | <b>73</b> |
| Problem 1 – EQUIL, STRUCT – Aluminum.....                                                              | 73        |
| Problem 2 – ABC, KINETICS – Beware of light!.....                                                      | 73        |
| Problem 3 – EQUILIB – Ordinary Physical Chemistry.....                                                 | 74        |
| Problem 4 – ABC, INORG – Smart robot.....                                                              | 75        |
| Problem 5 – BIO, STEREO – Chiral polyhydroxylated cyclohexanoids.....                                  | 75        |
| Problem 6 – SYNTH – The hunt for the flat carbon.....                                                  | 76        |
| <b>20th BChO, 2012, Riga, Latvia.....</b>                                                              | <b>78</b> |
| Problem 1 – RADIO – Seasonal radioactivity.....                                                        | 78        |
| Problem 2 – EQUIL, THERMO – Ammonia.....                                                               | 78        |
| Problem 3 – MECH, SYNTH – The synthesis of proline.....                                                | 79        |
| Problem 4 – ABC, INORG, STRUCT – Antitumor agent.....                                                  | 79        |
| Problem 5 – EQUIL – Aspirin absorption.....                                                            | 80        |
| Problem 6 – SPECTRA, SYNTH – Algae against cancer.....                                                 | 81        |
| <b>21st BChO, 2013, Tartu, Estonia.....</b>                                                            | <b>83</b> |
| Problem 1 – BIO, ELECTRO – Photosynthesis.....                                                         | 83        |
| Problem 2 – CALC, EQUIL – Phenolsulfonphthalein.....                                                   | 84        |
| Problem 3 – STRUCT – Hydrides.....                                                                     | 85        |
| Problem 4 – BIO, SYNTH – Physostigmine.....                                                            | 85        |
| Problem 5 – THERMO – A national drink.....                                                             | 86        |
| Problem 6 – MECH, SYNTH – Benzyne.....                                                                 | 88        |
| <b>22nd BChO, 2014, Vilnius, Lithuania.....</b>                                                        | <b>90</b> |
| Problem 1 – EQUIL – Silver compounds.....                                                              | 90        |
| Problem 2 – STEREO, SYNTH – Fortamine.....                                                             | 90        |
| Problem 3 – APPLIED, ELECTRO – Redox flow battery.....                                                 | 91        |

|                                                                                              |            |
|----------------------------------------------------------------------------------------------|------------|
| Problem 4 – BIO, KINETICS – Kinetics of neuromuscular enzyme.....                            | 92         |
| Problem 5 – SPECTRA, STEREO – Cocaine.....                                                   | 94         |
| Problem 6 – ABC, CALC, THERMO – Chemistry of superacids.....                                 | 95         |
| <b>23rd BChO, 2015, Daugavpils, Latvia.....</b>                                              | <b>97</b>  |
| Problem 1 – ELECTRO – Copper Man.....                                                        | 97         |
| Problem 2 – CALC, SPECTRA – Determination of water content.....                              | 98         |
| Problem 3 – ELECTRO, EQUIL, KINETICS – Some simple physical chemistry.....                   | 99         |
| Problem 4 – CALC, KINETICS – Harpoons and collisions.....                                    | 99         |
| Problem 5 – BIO, SYNTH – Lucy in the Sky with Diamonds.....                                  | 101        |
| Problem 6 – SYNTH – Easy grow, easy bloom.....                                               | 103        |
| <b>24th BChO, 2016, Tartu, Estonia.....</b>                                                  | <b>105</b> |
| Problem 1 – APPLIED, ELECTRO – Lead-acid battery.....                                        | 105        |
| Problem 2 – CRYSTAL, THERMO – Fullerenes.....                                                | 107        |
| Problem 3 – SYNTH – The Great Drug of China.....                                             | 108        |
| Problem 4 – CRYSTAL, THERMO – The biggest coins in the world.....                            | 109        |
| Problem 5 – CALC, SPECTRA – “My precious”.....                                               | 111        |
| Problem 6 – BIO, SPECTRA, SYNTH – Ayahuasca.....                                             | 113        |
| <b>25th BChO 2017, Vilnius, Lithuania.....</b>                                               | <b>115</b> |
| Problem 1 – CRYSTAL – Crystal packing.....                                                   | 115        |
| Problem 2 – CRYSTAL, EQUIL, THERMO – Solubility.....                                         | 115        |
| Problem 3 – SYNTH – Analeptics.....                                                          | 116        |
| Problem 4 – CALC, SPECTRA, STRUCT – Nickel knickknackery.....                                | 117        |
| Problem 5 – INORG, KINETICS, THERMO – Cleaning oil pipes.....                                | 119        |
| Problem 6 – SYNTH – The synthesis of Stagonolide D.....                                      | 122        |
| <b>26th BChO 2018, Riga, Latvia.....</b>                                                     | <b>124</b> |
| Problem 1 – ABC, INORG – Nobel medals.....                                                   | 124        |
| Problem 2 – ELECTRO, STRUCT – Chemistry of metals in oxidation number of +3.....             | 125        |
| Problem 3 – EQUIL, THERMO – Don’t cry.....                                                   | 126        |
| Problem 4 – CALC, ELECTRO – Titrimetric determination of methoxyl groups.....                | 127        |
| Problem 5 – STEREO, SYNTH – Better do not eat.....                                           | 128        |
| Problem 6 – STEREO, SYNTH – Synthesis of Erythronolide B.....                                | 129        |
| <b>27th BChO 2019, Tartu, Estonia.....</b>                                                   | <b>131</b> |
| Problem 1 – STRUCT – Iron complexes.....                                                     | 131        |
| Problem 2 – EQUIL, THERMO – CaCO <sub>3</sub> in nature and laboratory.....                  | 132        |
| Problem 3 – ELECTRO, KINETICS – Colorful kinetics.....                                       | 133        |
| Problem 4 – EQUIL – Some penguin chemistry.....                                              | 134        |
| Problem 5 – MECH, SYNTH – Lithiation gone wrong.....                                         | 134        |
| Problem 6 – SPECTRA, SYNTH – Deformed polymers.....                                          | 136        |
| <b>28th BChO, 2022, Vilnius, Lithuania.....</b>                                              | <b>138</b> |
| Problem 1 – ABC, SPECTRA, STRUCT – Some chemistry of element X.....                          | 138        |
| Problem 2 – ELECTRO, THERMO – Thermodynamics of electrochemical CO <sub>2</sub> capture..... | 139        |
| Problem 3 – CRYSTAL – Solution ≠ liquid.....                                                 | 141        |

|                                                                                        |            |
|----------------------------------------------------------------------------------------|------------|
| Problem 4 – KINETICS – Kinetics ABC.....                                               | 144        |
| Problem 5 – MECH, SPECTRA, SYNTH – Total synthesis of (–)-Colombiasin A.....           | 145        |
| Problem 6 – SYNTH – Chiral pool.....                                                   | 147        |
| <b>29th BChO, 2023, Dobeles, Latvia.....</b>                                           | <b>150</b> |
| Problem 1 – CALC, EQUIL – Determination of protein content by the Kjeldahl method..... | 150        |
| Problem 2 – APPLIED, ELECTRO, STRUCT – Applications of the 7th group elements.....     | 151        |
| Problem 3 – KINETICS – Simple Surface Chemistry.....                                   | 154        |
| Problem 4 – INORG, STRUCT – Bromine goes hyper mode.....                               | 155        |
| Problem 5 – SYNTH – Synthetic alkaloids.....                                           | 157        |
| Problem 6 – MECH, STEREO, SYNTH – Lubiminol.....                                       | 160        |
| <b>30th BChO 2024, Tartu, Estonia.....</b>                                             | <b>163</b> |
| Problem 1 – EQUIL, STRUCT, THERMO – Polygonal chemistry.....                           | 163        |
| Problem 2 – ABC, EQUIL – Unknown amino acid.....                                       | 163        |
| Problem 3 – KINETICS – Reverse engineering.....                                        | 164        |
| Problem 4 – CRYSTAL, RADIO – Have you heard about cerium?.....                         | 164        |
| Problem 5 – SPECTRA, STRUCT, SYNTH – Poisonous chemicals.....                          | 167        |
| Problem 6 – SPECTRA, SYNTH – Simple organic chemistry.....                             | 169        |

## Forewords

The Baltic Chemistry Olympiad (BChO) is an annual event, where the brightest Chemistry minds of the three Baltic countries (Estonia, Latvia, Lithuania) meet and share the joy of solving challenging problems. The main values of the competition are Openness, Fairness, and Unity. This is a reason why the Baltic Chemistry Olympiad problems, although hosted in a different country each year, are being collectively written by professionals from all three countries. The value of openness is strongly upheld, and BChO is one of the two international-level Chemistry competitions (the other one being IChO) where the problems are publicly available in English.

Every school student from the Baltic countries has the possibility to participate in the competition through a carefully designed system of selection competitions, where school teachers, university lecturers and BChO alumni collaborate to create a motivating environment. BChO is a very important chemistry tradition in the Baltics. It plays an important role in selecting national teams for the International Chemistry Olympiad. Each year, the problem authors uphold the highest rigour standards for the Olympiad problems providing a challenge for the current generation of Chemistry students as well as education material for the future.

This book aims to be an anniversary compilation with some minor revisions for the previous year's problems. I have added a convenient tag system, so that the reader could find problems that relate specifically to their topics of interest, as well as added some insightful comments. Besides, I have provided all the problems with titles.

### ***Daniil Kargin, BChO participant in 2022 and 2023***

The book presents all the problems from the first 30 BChOs. It is the result of the cooperation of chemists from Latvia, Lithuania and Estonia, so it focuses on aspects of chemistry typical for the leading universities of the Baltic countries. In particular, this collection overviews the principles of chemical devices, such as different types of batteries, internal combustion engines, and fuel cells studied at the University of Tartu. Similarly, scientists from the Latvian Institute of Organic Synthesis prepared problems on the synthesis of organic compounds. Throughout years, the following mentors have edited the problems: Agris Bērziņš, Algirdas Neniškis, Anneli Kruve, Edvinas Orentas, Eduards Baķis, Eugenijus Butkus, Gintautas Bagdžiūnas, Gustavs Mežciems, Ida Rahu, Igors Kļimenkovs, Ināra Akmene, Jānis Briška, Jānis Āibietis, Juris Fotins, Jörgen Metsik, Kaspars Veldre, Kristi Koitla, Laurynas Riauba, Liis Siigur, Lona-Liisa Pruks, Lukas Šteinys, Marius Jurgelėnas, Natalia Nekrassova, Nauris Narvaišs, Olavs Rāciņš, Olga Tšubrik, Ott Kekišev, Raimondas Galvelis, Rein Pullerits, Ritums Cepītis, Rimantas Raudonis, Simonas Balkaitis, Siim Kaukver, Skaidrīte Pakule, Toms Rēķis, Uno Mäeorg, Vaidotas Navickas, Vidmantas Bieliūnas, Vladislav Ivaništšev, Vytautas Kavaliauskas, Vytautas Pečiukėnas and others. This olympiad is possible thanks to sponsors. On behalf of all participants and organizers, I thank: Alexela, Atbalsts izcilībai, Baltika, Bapeks, Bauskas alus, Biosan, Dobeles novads, Enamine, Estiko, Grindex, JSC OlainFarm, Linesa, Lithuanian agency of non-formal education, Ministries of Education and Research of Estonia, Latvia, and Lithuania, Ontic Minerals, Orange, Riga Technical University, Sangar, TBD pharmatech, The association of Lithuanian science Olympiads, The J. Molner Company, Universities of Daugavpils, Kaunas, Latvia, Tartu, and Vilnius, Tartu City, Xema, Yoga, Youth Academy and others. The editors are also grateful to Azamat Bukharbayev, Ivan Vnukov, Karlis Suvi, and Nikita Lastovka for the valuable comments regarding the texts. Solutions to the problems can be found at the website <http://eko.ut.ee/bcho>.

### ***Vladislav Ivaništšev, BChO participant in 2001–2003***

The idea to organize a joint Estonian, Latvian and Lithuanian Chemistry Olympiad was given by the chairman of the Latvian Chemistry Olympiad – Gunārs Rumba. According to the agreement, the first BChO took place in Riga from 3<sup>rd</sup> to 5<sup>th</sup> May 1993. Since then, participating countries have hosted the Olympiad in turns. The BChO's aim remains to allow students to compare their knowledge and skills in a competitive environment. Six students from each country attend BChO, and the host country can allow two more students to participate. Students solve theoretical and practical problems in two rounds, where theory gives 60–70% of scores and experiment 30–40%. These results are used to select the national teams for the International Chemistry Olympiad.

BChO will be held for the thirtieth time this year, proving its maturity, quality and necessity.

***Rein Pullerits, head mentor of the Estonian team in 1993–2006***



Joint photograph of participants and organizers of the 3rd Baltic Olympiad in Tartu (1996, Estonia). Monitors are standing in the second row (from right to left): Rimantas Raudonis, Natalia Nekrassova (behind), Rimantas Vaitkus, Gunārs Rumba, Rein Pullerits, Ināra Akmene, Vello Past, Peeter Purk. Photo from the personal archive of Rein Pullerits.

## Constants and equations

|                                                              |                                                                                                          |
|--------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|
| Atmospheric pressure                                         | $P_{\text{atm}} = 1.01325 \cdot 10^5 \text{ Pa} = 760 \text{ mmHg} = 760 \text{ Torr}$                   |
| Avogadro constant                                            | $N_A = 6.02214076 \cdot 10^{23} \text{ mol}^{-1}$                                                        |
| Boltzmann constant                                           | $k_B = 1.380649 \cdot 10^{-23} \text{ J K}^{-1}$                                                         |
| Elementary charge                                            | $e = 1.602176634 \cdot 10^{-19} \text{ C}$                                                               |
| Faraday constant                                             | $F = 96485 \text{ C mol}^{-1}$                                                                           |
| Mass of electron                                             | $m_e = 9.10938370 \cdot 10^{-31} \text{ kg}$                                                             |
| Planck constant                                              | $h = 6.62607015 \cdot 10^{-34} \text{ J s}$                                                              |
| Speed of light                                               | $c = 2.99792458 \cdot 10^8 \text{ m s}^{-1}$                                                             |
| Standard pressure                                            | $P = 1 \text{ bar} = 10^5 \text{ Pa}$                                                                    |
| Universal gas constant                                       | $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08205 \text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ |
| Absolute zero $0 \text{ K} = -273.15 \text{ }^\circ\text{C}$ | $1 \text{ \AA} = 10^{-10} \text{ m}$                                                                     |
| $1 \text{ Da} = 1.66053904 \cdot 10^{-27} \text{ kg}$        | $1 \text{ nm} = 10^{-9} \text{ m}$                                                                       |
| $1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J}$              | $1 \text{ pm} = 10^{-12} \text{ m}$                                                                      |

The dalton (Da) or unified atomic mass unit is a non-SI unit of mass defined as 1/12 of the mass of an unbound neutral atom of  $^{12}\text{C}$  in its nuclear and electronic ground state and at rest.

|                             |                                                                                                                                                                                       |
|-----------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Adiabatic expansion         | $\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$                                                                                                                         |
| Arrhenius law               | $k = A e^{\frac{-E_A}{RT}}$                                                                                                                                                           |
| Clausius-Clapeyron equation | $\ln \frac{P_1}{P_2} = \frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$                                                                                               |
| Electric current            | $I = \frac{Q}{t}$                                                                                                                                                                     |
| Energy of a photon          | $E = h\nu = \frac{hc}{\lambda}$                                                                                                                                                       |
| Entropy change              | $\Delta S = \frac{q_{\text{rev}}}{T}$ $q_{\text{rev}} - \text{heat for the reversible process}$ $\Delta S = nR \ln \frac{V_2}{V_1}$ <p>(for isothermal expansion of an ideal gas)</p> |
| Expansion-compression work  | $w = \frac{nR(T_2 - T_1)}{\gamma - 1}, w = -p(V_2 - V_1), w = -nRT \ln \frac{V_2}{V_1}$                                                                                               |

Faraday equation

$$It = nzF$$

Gibbs free energy

$$\Delta G = \Delta H - T\Delta S$$

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

$$\Delta G = \Delta_r G^\circ + RT\ln Q$$

Heat change

$$\Delta q = nc_m \Delta T$$

$c_m$  – molar heat capacity

Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]}\right)$$

Ideal gas law

$$pV = nRT = Nk_B T$$

Integrated rate laws for ...

1. 0<sup>th</sup> order

$$[\text{A}] = [\text{A}]_0 - kt$$

2. 1<sup>st</sup> order

$$\ln[\text{A}] = \ln[\text{A}]_0 - kt$$

3. 2<sup>nd</sup> order

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

Lambert-Beer equation

$$A = \log \left( \frac{I_0}{I} \right) = \epsilon lc$$

Nernst equation

$$E = E^\circ + \frac{RT}{nF} \ln \frac{c_{ox}}{c_{red}}$$

Van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \Rightarrow \ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

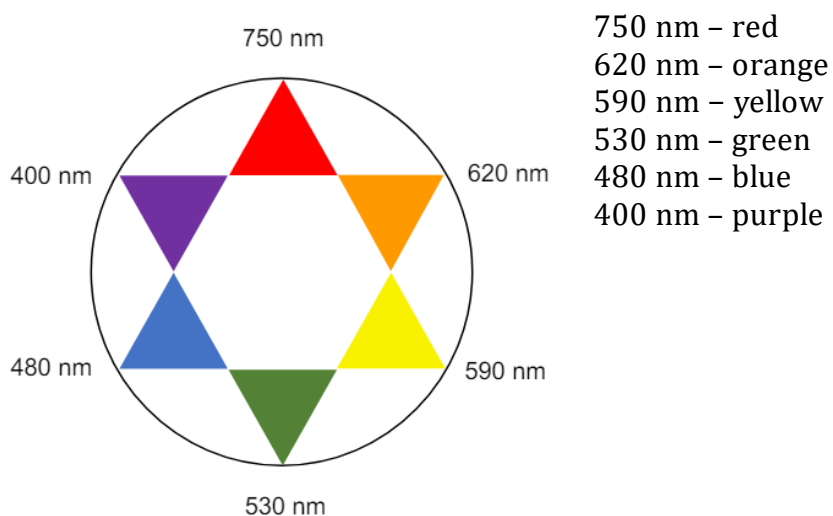
Surface area of a sphere with radius  $R$

$$A = 4\pi R^2$$

Volume of a sphere with radius  $R$

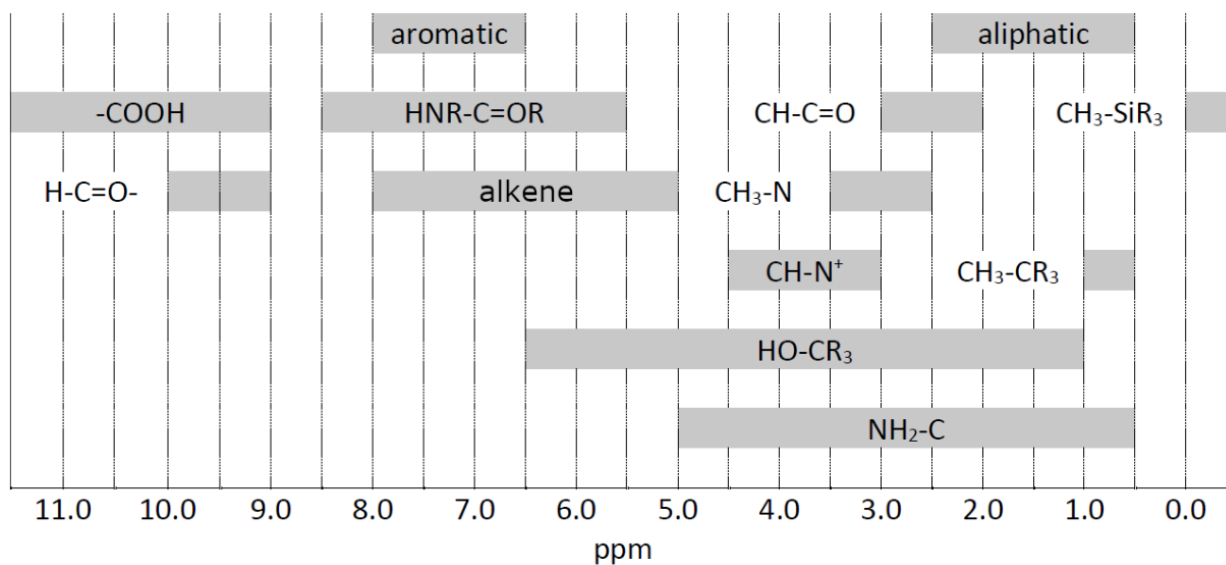
$$V = \frac{4}{3}\pi R^3$$

## Complementary colors of the visible light

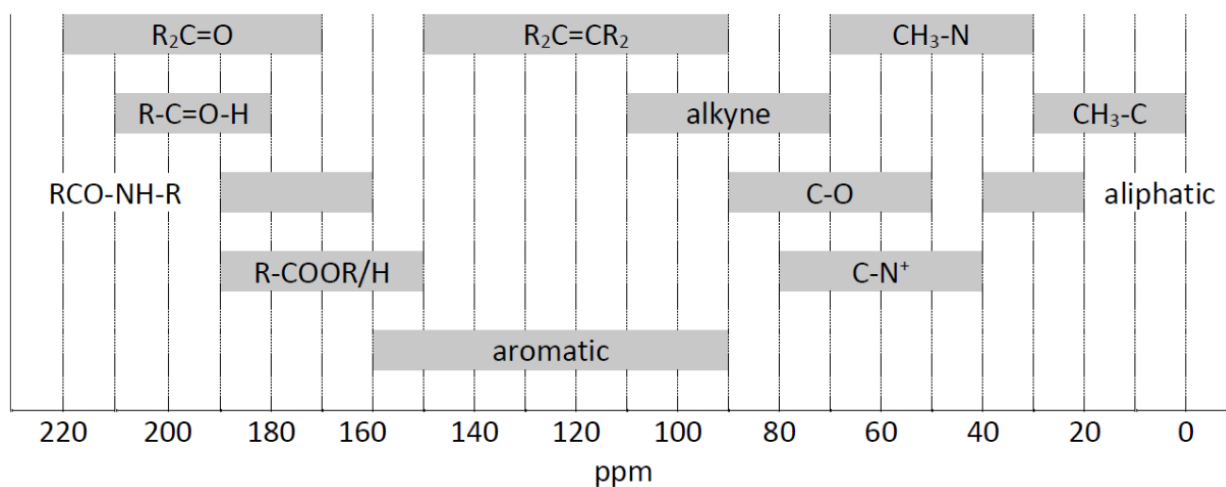


## NMR chemical shifts

### $^1\text{H}$ NMR chemical shifts



### $^{13}\text{C}$ NMR chemical shifts

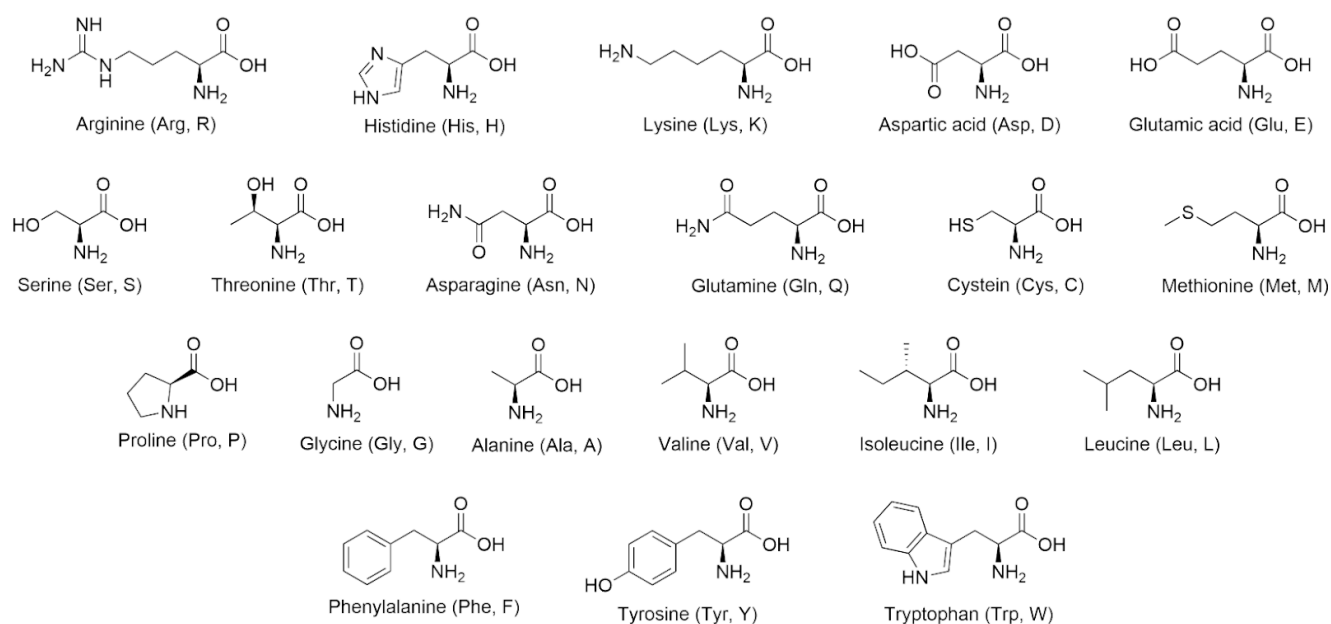


## <sup>1</sup>H NMR coupling constants

| Type of hydrogen                                                                | [J <sub>ab</sub> ], Hz                            |
|---------------------------------------------------------------------------------|---------------------------------------------------|
| R <sub>2</sub> CH <sub>a</sub> H <sub>b</sub>                                   | 4–20                                              |
| R <sub>2</sub> CH <sub>a</sub> –CR <sub>2</sub> H <sub>b</sub>                  | 2–12                                              |
| R <sub>2</sub> CH <sub>a</sub> –CR <sub>2</sub> –CR <sub>2</sub> H <sub>b</sub> | If rotation free: < 0.1<br>Otherwise (fixed): 1–8 |
| RH <sub>a</sub> C=CRH <sub>b</sub>                                              | <i>cis</i> : 7–12<br><i>trans</i> : 12–18         |
| R <sub>2</sub> C=CH <sub>a</sub> H <sub>b</sub>                                 | 0.5–3                                             |
| RH <sub>a</sub> C=CR–CR <sub>2</sub> H <sub>b</sub>                             | 0.5–2.5                                           |

## List of amino acids

Structures of amino acids and their three- and one-letter codes.



### Abbreviations for topics

For your convenience, abbreviations for topics are added to each problem, along with their name, so that you can easily find problems corresponding to your topics of interest:

**[ABC]** – “Riddle problem” where you have to identify compounds.

**[APPLIED]** – Applications of chemistry in real life – batteries, industrial processes, etc.

**[BIO]** – Anything related to biochemistry – peptides, proteins, enzymes, etc.

**[CALC]** – Calculations, such as titrations, potentiometry, etc.

**[CRYSTAL]** – Calculations related to crystallography, X-ray, crystal field theory, etc.

**[ELECTRO]** – Calculations related to electrochemistry.

**[EQUIL]** – Calculations including equilibrium constants.

**[INORG]** – All the miscellaneous inorganic problems that do not fit other categories.

**[KINETICS]** – Kinetics, involving both calculations and proofs of mechanisms.

**[MECH]** – Mechanisms of organic and inorganic reactions concerning arrow pushing.

**[RADIO]** – Radioactivity, decay chains, half-life and related concepts.

**[SPECTRA]** – Anything related to spectroscopy – AAS/AES, IR, NMR, UV-Vis, etc.

**[STEREO]** – Problems include stereochemistry.

**[STRUCT]** – Inorganic structures like complexes, Lewis dot structures and VSEPR.

**[SYNTH]** – Organic synthesis scheme and/or retrosynthesis.

**[THERMO]** – Thermodynamics calculation, including crystal-related calculations.

## 1st BChO, 1993, Riga, Latvia

### Problem 1 – ABC – A wet crystal

The hydrate of a stable salt **X** contains 2.79% H, 9.97% C, and 38.48% of element **A**. When **X** is heated at 800 °C, an oxide **Y** ( $w_0 = 14.73\%$ ) is formed. When **X** is heated at a lower temperature, compound **Z** containing 5.80% C, 27.07% O, and 67.13% of element **A** is formed.

- Write the chemical formulas of compounds **X–Z**.
- Write equations of the described reactions.

### Problem 2 – ABC, CALC – So similar but not the same

A solution contains sulfates of four metals. The metals are located in the same period (of the periodic table), next to each other, and in sulfates, their oxidation number is equal to +2. The quantities of the salts are 0.0100, 0.0100, 0.0200, and 0.0200 mole.  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  were added to the solution in excess. The resulting precipitate **A** was filtered and calcined to a constant mass of 2.47 g. After the filtrate was boiled, 2.36 g of precipitate **B** was obtained. The remaining solution contained no metal ions. Precipitate **A** was dissolved in an HCl solution, releasing 224 cm<sup>3</sup> of chlorine (STP). When precipitate **B** was dissolved in an HCl solution, 150 cm<sup>3</sup> of chlorine (STP) was released.

- Write the chemical formulas of metal sulfates.
- Calculate the mole amounts of these sulfates.
- Write equations of the described reactions.

### Problem 3 – ABC – Do not drink it

5.000 g of the characteristic odorless liquid **A** was burned in oxygen. The resulting products were absorbed in excess NaOH. The mass of the alkali solution increased by 16.41 g.  $\text{Ba}(\text{OH})_2$  was added to the solution, resulting in 59.74 g of precipitate. The precipitate was dissolved by heating in hydrochloric acid, and 6.660 dm<sup>3</sup> of gas (STP) was released.

- Write the empirical formula of compound **A**.
- Write all the possible structures of substance **A**.

### Problem 4 – STRUCT – Organic siblings

Write the structures of all such neutral, stable organic compounds whose molecules consist of C, H, and O (with empirical formulas  $\text{C}_m\text{H}_n$  and  $\text{C}_m\text{H}_n\text{O}_x$ ) in which the number of carbon atoms is between 2 and 6, and all are in  $sp^2$  hybridization and structurally equivalent to each other.

### Problem 5 – ABC, SPECTRA – Organic riddle

Substance **A** consists of 69.77% carbon and 11.63% hydrogen. Two peaks are recorded in the mass spectrum of substance **A**:  $m/z = 86$  (molecular ion) and  $m/z = 57$ . In the infrared spectrum, the line is around 1740-1720 cm<sup>-1</sup>. In <sup>1</sup>H NMR spectrum, two singlet  $\delta_1 = 1\text{--}1.5$  ppm and  $\delta_2 = 9.5\text{--}10$  ppm. The ratio of peak intensities is 9 : 1.

- Write the structural formula of substance **A**.
- Write reaction equations in which substance **A** reacts with i) formaldehyde, ii) acetaldehyde in an alkaline medium, and iii) aluminum isopropanolate in the presence of isopropanol.

**Problem 6 – BIO, STRUCT – Hemerythrin**

The protein hemoglobin is widely known as an oxygen transporter. Less well-known are other natural proteins capable of transporting oxygen. One of these, hemerythrin, has been found in some vertebrates. The oxygen-binding center of hemerythrin contains two iron atoms that form a complex by interacting with the side chains of amino acid residues. X-ray structural analysis showed that the distance between iron atoms in hemerythrin is 3.57 Å (in the crystal of metallic iron, the interatomic distance is 2.48 Å). One of the atoms is linked by coordination bonds with three, the other with two amino acid side chains (each chain contains a five-membered cycle). In addition, the iron atoms are linked to two other different amino acid residues by FeO coordination bonds.

- a) What amino acid residues are included in the complex?
- b) Draw the spatial structure of the oxygen-binding center.
- c) How and where can oxygen be bound in this center?
- d) What features of oxygen binding by hemoglobin do you know?

**Problem 7 – INORG – Toxic gold**

During the electrolysis of a gold cyano complex in an alkaline solution, 0.460 g of gold is precipitated at the cathode, and 13.06 cm<sup>3</sup> of oxygen (STP) is released at the anode. Write the electrode reactions and determine the degree of oxidation of gold in the complex, assuming that all reactions occur in 100% yield.

**Problem 8 – EQUIL – Basic acid reactions**

1 dm<sup>3</sup> of solution contained 0.365 g HCl and 6.00 g CH<sub>3</sub>COOH ( $K_a = 1.75 \cdot 10^{-5}$ ). 2.00 g of solid sodium hydroxide was added to the solution. Calculate the pH of the solution before and after adding NaOH.

## 2nd BChO, 1994, Vilnius, Lithuania

### Problem 1 – INORG – Famous for not just the wine

The Burgundy mixture is prepared from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$  (soda) and is used to protect plants from fungal diseases. In agriculture, 1% of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (by mass) is prepared and dissolved in an equivalent soda solution to produce 1% Burgundy mixture. To prepare the Burgundy mixture, a gardener took soda with 50% excess. Then, he added  $\text{CuSO}_4$  solution to the soda solution. The mixing was carried out in a zinc-coated vessel. Due to carelessness, instead of soda ash ( $\text{Na}_2\text{CO}_3$ ), the gardener took crystalline soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), assuming it is an anhydrous salt.

- Write equations of the described reactions.
- Estimate the mass percentage of soluble substances in the resulting solution.

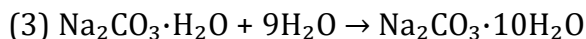
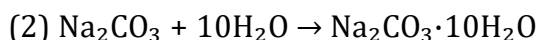
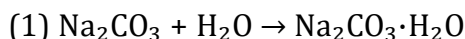
### Problem 2 – KINETICS – Unstable chemical

Substance **A** decomposes spontaneously. The half-life of substance **A** at 30 °C is 318 seconds, and at 24.7 °C – 460 seconds. How much time is needed for substance **A** to decay 99% at 35 °C.

### Problem 3 – EQUIL, THERMO – All the kinds of soda

The enthalpies of dissolution of  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  are  $-24.6 \text{ kJ mol}^{-1}$ ,  $-10.5 \text{ kJ mol}^{-1}$ , and  $66.6 \text{ kJ mol}^{-1}$ , respectively.

- Calculate the enthalpies of hydration of the following reactions.



10.0 grams of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  was dissolved in 10.0 grams of water.

- Calculate the molar fraction of  $\text{Na}_2\text{CO}_3$  in the solution.
- Calculate the pH of the solution ( $K_{a1} = 4.45 \cdot 10^{-7}$ ,  $K_{a2} = 4.69 \cdot 10^{-11}$ ;  $\rho = 1.2 \text{ g cm}^{-3}$ ).

### Problem 4 – INORG – Copper nitrate

19.1 grams of copper was dissolved in  $189 \text{ cm}^3$  of 40.0% nitric acid ( $\rho = 1.25 \text{ g cm}^{-3}$ ) which gave off  $6.72 \text{ dm}^3$  of gases (STP) with a density of 1.93 relative to air.

- Which gases were released and in what ratio?
- Write equations of the described reactions.
- How much unreacted nitric acid remained in the solution?

### Problem 5 – ELECTRO, EQUIL – A simple lead battery

Hydrogen and  $\text{Pb/Pb(OH)}_2$  electrodes were used to make a galvanic cell with KOH electrolyte.

- Write the reactions occurring at the electrodes (the hydrogen electrode, in this element, is the negative electrode).
- Write an equation to calculate the EMF and show that the EMF does not depend on the concentration of the solution.
- Calculate the solubility product value of  $\text{Pb(OH)}_2$  at 25 °C, knowing that  $\text{EMF} = 0.261 \text{ V}$ , the standard potential of lead with respect to  $[\text{Pb}^{2+}]$  is  $E^\circ(\text{Pb}^{2+}/\text{Pb}) = -0.126 \text{ V}$ , and  $K_w = 10^{-14}$ .

### Problem 6 – MECH, STEREO – Three children of cyclohexane

Three cyclohexane derivatives, **A**, **B**, and **C**, contain the same percentage of chlorine – 73.20%. In a  $4.70 \cdot 10^{-3}$  molar sodium hydroxide solution in ethanol, the reaction rates of **A**, **B**, and **C** were measured at the same concentration ( $8 \cdot 10^{-4}$  M). Substance **B** did not react. The reaction rate constants for compounds **A** and **C** were 0.167 and  $0.0435 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively. In both reactions, only one product (a diene) was formed.

- Explain why the reaction rate constants are different.
- Draw structural formulas of **A–C**. Label the absolute configurations for **A–C**.
- Write the reaction equations.

### Problem 7 – ABC, BIO – The smell of Baltics

Terpenoids consist of isoprene (2-methyl-1,3-butadiene) fragments and contain different functional groups (hydroxyl, etc.). These compounds have a pleasant odor and are found in the essential oils of plants. Terpene **A** is a cyclohexane derivative, which is oxidized to ketone **B** with chromic acid. Dehydration of **A** produces compound **C**, which contains 86.96% carbon and 13.04% hydrogen. When **C** is hydrogenated, compound **D** is formed. Ozonolysis of product **C** with water yields substance **E**. Oxidation of substance **E** under severe conditions yields a mixture of various acids and  $\text{CO}_2$ . It is possible to isolate 3-methylpropane-1,3-dicarboxylic acid ( $\beta$ -methyl- glutaric acid) from the mixture.

- Draw the structures of **A–E**.
- Write all the described reaction equations.
- Which plant essential oils contain substances **A–C**.

### Problem 8 – ABC, SPECTRA – Another fossil fuel

0.10 grams of a hydrocarbon was burned, and the gaseous products were passed through  $300 \text{ cm}^3$  of 0.0200 molar  $\text{Ba}(\text{OH})_2$  solution, resulting in 0.850 g of precipitate. The  $^1\text{H}$  NMR spectrum of this carbohydrate consists of one quartet. X-ray structural analysis showed that the lengths of C–C bonds between all carbon atoms in the hydrocarbon are the same. Write the structural formulas of three hydrocarbons that meet the conditions.

### 3rd BChO, 1995, Tartu, Estonia

#### Problem 1 – ABC, MECH, SPECTRA – Shapeshifting organics

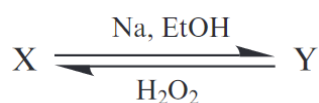
Compound **X** turns into hydrocarbon **Y** via reduction and rearrangement in the presence of  $\text{HBF}_4$ . The reverse intermolecular rearrangement occurs by heating the potassium salt of the oxidation product of the compound **Y** in  $\text{CO}_2$  atmosphere. After treatment with  $\text{D}_2\text{O}$ , the NMR spectrum of compound **X** presents a singlet at  $\delta = 8.1$  (DMSO). 1.4 times less oxygen is needed for the complete burning of 1 mole of compound **X** compared to the same amount of **Y**.

- Write the chemical equations for all the reactions.
- Write the mechanisms of the rearrangements.

#### Problem 2 – CALC, INORG – Oxidation of rhenium

Compound **X** [ $w(\text{Re}) = 68.16\%$ ] turns into compound **Y** according to the following scheme:

| $c_x [\text{M}]$ | $A(346 \text{ nm})$ | $A(330 \text{ nm})$ |
|------------------|---------------------|---------------------|
| 8.4422           | 0.1815              | 0.291               |
| 8.5924           | 0.1847              | 0.295               |
| 8.7989           | 0.1883              | 0.302               |



The results of absorption spectroscopic measurements of standard solutions of **X** are in the Table. Two more measurements were made as follows. 1.0360 g of compound **Y** was treated with hydrogen peroxide. The excess of the reagent was removed by boiling.

- The solution was quantitatively transferred into a  $500.34 \text{ cm}^3$  volumetric flask,  $2.50 \text{ cm}^3$  of concentrated  $\text{H}_2\text{SO}_4$  was added, and the flask was filled to the line. Result: at  $A(346 \text{ nm}) = 0.1844$ .
- $50.0 \text{ cm}^3$  of the solution a was pipetted into a  $100 \text{ cm}^3$  volumetric flask,  $0.250 \text{ cm}^3$  of concentrated  $\text{H}_2\text{SO}_4$  was added, and the flask filled to the line. Result: at  $A(330 \text{ nm}) = 0.294$ .

Write the chemical formulas of **X** and **Y**. Show your calculations.

#### Problem 3 – ELECTRO – Silver energy

The EMF of a silver-zinc cell  $\text{Zn} | \text{ZnSO}_4(\text{l}) || \text{AgNO}_3(\text{l}) | \text{Ag}$  is 1.562 V if the concentrations of the solutions are 1 M at  $T = 25^\circ\text{C}$ .

- Write the equations of the reactions in the whole cell and at single electrodes if current is taken from the cell.
- Calculate the EMF of the cell after 20 days of running at 0.050 A.

#### Problem 4 – KINETICS – The kinetics of March test

The kinetics of the decomposition of  $\text{AsH}_3$  was studied by measuring pressure in a closed glass tube. The initial pressure of gaseous  $\text{AsH}_3$  in the tube was 86.1 kPa. After 2 hours, the pressure in the tube was 112.6 kPa. The formed As condensed on the walls of the glass tube.

- Write the chemical equation of the decomposition reaction.
- Calculate the pressure in the glass tube after the reaction is completed.
- Calculate the rate constant and the rate of the reaction.
- Calculate the time necessary to decompose 99.9% of  $\text{AsH}_3$ .

### Problem 5 – ABC – A lot of heating

5.5541 g of a crystalline hydrate was heated at 100 °C. Its mass decreased to 4.1128 grams. The remnant was heated at 150 °C to obtain 2.0818 g of a gas with a volume of 7.044 dm<sup>3</sup> at 150 °C and 100000 Pa. The remnant of the other heating (2.0310 g) was treated with overheated steam to obtain 1.5910 g of a solid oxide containing 20.11% oxygen. All the mentioned heatings were carried out to constant weight.

- Write the chemical formula of the crystalline hydrate. Show your calculations.
- Write the chemical equations of all the reactions.

### Problem 6 – BIO – Don't starve

The oxidation of glucose is the human organism's primary energy source. However, while starving, the reserve of hydrocarbons is diminishing, and the oxidation of two monocarbonic acids, **A** and **B**, becomes the main energy source. The acids **A** and **B** turn easily into one another due to an enzymatic redox reaction. Acid **A** contains 47.06% C and 5.88% H; **B** contains 46.15% C and 7.70% H. Acid **A** decomposes slowly and spontaneously in blood, giving a volatile compound **C** that can be smelled in the air exhaled by a starving person. The density of the vapors of the compound **C** is 2.00 with respect to the air, and there is only one peak in its <sup>1</sup>H NMR spectrum. Write the structural formulas of **A**, **B**, and **C**.

### Problem 7 – ABC – Organic riddle

Compound **A** (C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>) dissolves only in concentrated sulfuric acid and reacts with hydrazine to form a precipitate. Compound **A** was hydrolyzed in an alkaline solution. Compound **B** was separated from the solution by extracting it with ether. The remnant was acidified to separate a solid compound **C** with a molar mass of 164 g mol<sup>-1</sup>. Compounds **A** and **C** react with an alkaline solution of iodine to give a precipitate **D**. The other product that formed in the reaction from compound **C** was turned into acid **E** by the agency of an acid. One mole of NaOH reacts with 83 g of the acid **E**. Heating the acid **E** results in compound **F**, which does not react with sodium hydrogen carbonate. Boiling compound **F** in water for a long time returns it to compound **E**.

Compound **B** has an unpleasant smell, and it dissolves in a 5% solution of HCl. It reacts with an acidified solution of sodium nitrite to liberate a gas and form compound **G**, which is insoluble in water but reacts with sodium. Compound **G** is oxidized with chromosulfuric acid to give compound **H**. Melting **H** with NaOH gives benzene.

- Write the structural formulas of compounds **A**–**H**.

### Problem 8 – EQUIL – Removal of iron from water

At what pH of the solution does FeS begin to precipitate if the initial concentration of the cation is 0.01 M, the total concentration of all the forms of sulfide ions in the solution is also 0.01 M, the dissociation constants for dihydrogen sulfide are  $K_1 = 1 \cdot 10^{-7}$  and  $K_2 = 1 \cdot 10^{-13}$  and the solubility product for FeS is  $K_{sp} = 1 \cdot 10^{-18}$ ? At what pH of the solution could the precipitation of FeS be considered complete (i.e. 99.9% of the initial amount of the cation has precipitated)?

## 4th BChO, 1996, Riga, Latvia

### Problem 1 – ABC – An unknown alloy

1.0000 g of powder of a mixture of two metals was heated at 300 °C in a stream of NO<sub>2</sub>. As a result, 0.6683 g of light yellow substance **A** ( $w_0 = 25.18\%$ ) was distilled off, and 0.7149 g of red powder remained in the reaction vessel. The reaction of **A** with concentrated hydrochloric acid produced 129.9 cm<sup>3</sup> of gas at 25 °C and 100.2 kPa. The density of this gas under these conditions is 2.8689 g dm<sup>-3</sup>. After the excess hydrochloric acid was neutralized with KOH, a compound with a chlorine content of 44.21% was isolated. This compound was dissolved in hydrochloric acid, and upon the addition of zinc, one of the parent metals was obtained.

- Identify two metals in the original mixture.
- Write equations for all reactions.

### Problem 2 – APPLIED, THERMO – Old-school hydrogen

One industrial method of hydrogen production is the Mark-1 thermodynamic cycle:

- |                                                                                    |                                                                                                    |
|------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| i) $\text{CaBr}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{HBr}$ | iii) $\text{HgBr}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaBr}_2 + \text{HgO} + \text{H}_2\text{O}$ |
| ii) $2\text{HBr} + \text{Hg} \rightarrow \text{HgBr}_2 + \text{H}_2$               | iv) $2\text{HgO} \rightarrow 2\text{Hg} + \text{O}_2$                                              |

A second purely thermodynamic hydrogen production cycle, Mark-8, was developed by the author of Mark-1 two years later. The Mark-8 cycle, like the Mark-1 cycle, utilizes water and thermal energy. The Mark-8 cycle involves the manganese compounds MnCl<sub>2</sub>, Mn<sub>3</sub>O<sub>4</sub>, and MnO<sub>2</sub>, as well as HCl, H<sub>2</sub>O, H<sub>2</sub>, and O<sub>2</sub>. Oxygen is released at 1170 K from manganese dioxide; the other two reactions occur at 970 K and 370 K.

- Write the reaction equations occurring in the Mark-8 cycle.
- Explain the advantages of each of the cycles.

### Problem 3 – ELECTRO – On cobalt and ammonia

For the determination of the ligand molecule number in complex cation  $\text{Co(NH}_3)_n^{2+}$ , the EMF of the following electrochemical cell  $\text{Co} \mid 0.05 \text{ M CoCl}_2 + x \text{ M NH}_3 \cdot \text{H}_2\text{O} \mid 1.00 \text{ M NaOH} \mid \text{HgO} \mid \text{Hg}$  at 25 °C was determined at various concentration of dissolved ammonia. The gas phase was, in all cases, in equilibrium with the solution. Calculate the  $n$  value using data given in the table assuming that in all solutions  $[\text{Co}^{2+}] \ll [\text{Co(NH}_3)_n^{2+}]$ , thus  $[\text{Co(NH}_3)_n^{2+}] \approx \text{const.}$

|                       |       |       |       |       |
|-----------------------|-------|-------|-------|-------|
| EMF [V]               | 0.619 | 0.659 | 0.683 | 0.715 |
| $p(\text{NH}_3)$ mmHg | 27.8  | 44.7  | 63.4  | 107.7 |

### Problem 4 – EQUIL, THERMO – Combustion of acid vapors

At 1000 K and pressure 10<sup>5</sup> Pa, the degrees of dissociation of water vapor and hydrogen chloride are  $2.48 \cdot 10^{-7}$  and  $1.10 \cdot 10^{-3}$ , correspondingly. Calculate the value of equilibrium constant and Gibbs free energy change for the reaction  $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{Cl}_2 + 2\text{H}_2\text{O}$ .

### Problem 5 – ABC, SPECTRA – Determining molecular mass without a mass spectrometer

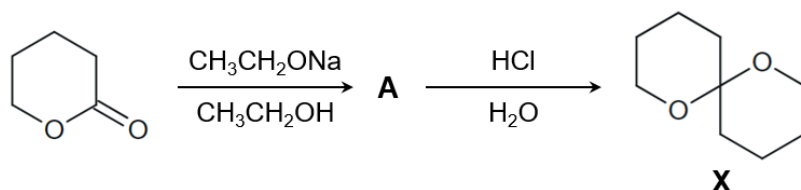
Organic compound **A** (melting point 167 °C) consists of two elements. The mass fraction of element **X** is 88.8%. In the <sup>1</sup>H-NMR spectrum of compound **A**, there is only one signal (singlet,  $\delta = 2.34$  m.d.). To determine the molecular weight by cryoscopy, 0.040 g of compound **A** was fused with 0.50 g of camphor – the melting point of the mixture was 159 °C (melting point of

pure camphor is 178 °C, cryoscopic constant  $K = 39.7 \text{ K kg mol}^{-1}$ ). Heating substance **A** in potassium permanganate solution, substance **B** ( $w_x = 42.1\%$ ). Heating **B** in excess of acetic anhydride yielded substance **C**, which also consists of two elements and the mass fraction of element **X** in the substance is 50.0%.

- Write the chemical formulas of **A–C**.
- Write the equations for all reactions.

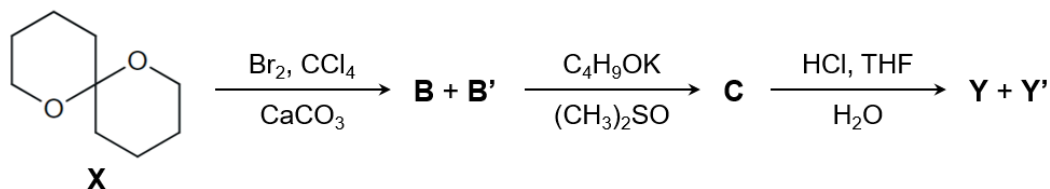
### Problem 6 – STEREO, SYNTH – Chemical hormones

The widespread use of insecticides causes a disturbance of the ecological balance, which makes it relevant to use pheromones to monitor this insect and to keep it under control. The main active substance of pheromone is 1,7-dioxaspiro(5,5)undecane – compound **X**. It is synthesized from  $\delta$ -valerolactone.



- Identify the intermediate compound **A**.
- Compound **X** exists in a single configuration. Draw the structure of this configuration and note the stereoelectronic effects that make it stable.
- Identify peaks in the  $^1\text{H}$  NMR spectrum of compound **X** at 3.52 (2H) and 3.65 (2H).

Feramon also contains compound **Y**. The scheme of its production is as follows:



- The halogenation of a carbonyl compound occurs via an enolic intermediate **X** (acetal). Write the mechanism of bromination of **X**.

Upon treatment of brominated **X** with potassium *tert*-butoxide in dimethyl sulfoxide at 110 °C, compound **B'** reacted completely. On further heating for 6 hours, compound **B** reacts completely as well. In both cases, compound **C** is formed.

- Write the structural formulas of **B** and **B'**. Explain the reactivity of compounds **B** and **B'** in terms of the reaction mechanism.

Compound **C** is converted into diastereoisomers **Y** and **Y'** ( $M = 172 \text{ g mol}^{-1}$ ) by stereospecific hydration in THF (tetrahydrofuran). The ratio of the stereoisomers **Y** : **Y'** = 18 : 1.

- Write their structural formulas and write reaction equations for each stage. Identify the structural effects that cause the preferential formation of compound **Y**.
- Write the absolute configurations of all chiral atoms in compounds **Y** and **Y'**.

## 5th BChO, 1997, Vilnius, Lithuania

### Problem 1 – INORG – Simple electrolysis

The  $\text{CuSO}_4$  solution was subjected to electrolysis for 30.0 hours with very intense stirring. During electrolysis, the current density was 1.00 A, and all the copper (31.75 g) from the solution precipitated.

- Which newly formed compound remains in solution?
- What amount (in moles) of this substance was formed?
- What volume of gas (under normal conditions) is released at the anode and cathode?
- Write reaction equations for all the processes.

### Problem 2 – INORG – Mercury from a gemstone

One of the methods for obtaining mercury is the calcination of mercury(II) sulfide cinnabar with calcium oxide at 600-700 °C. 500.00 g of cinnabar containing iron(II) sulfide was heated with 170.00 g of calcium oxide. 393.16 g of mercury was distilled off, the reducing agent was oxidized to the maximum. The gray residue was extracted in a Soxhlet extractor for a long time. From the original gray residue, 43.98 g of black powder **A** remained. The solution in the distillation flask and the precipitate formed therein were saturated by boiling with carbon dioxide. The resulting precipitate was filtered and dried; the resulting mass of the precipitate was 443.68 g. An excess of hydrochloric acid was added to the precipitate. After the reaction, precipitate **B** remained, the mass of which, after calcination at 400 °C, was 58.88 g.

- Write equations of all the reactions taking place.
- What mass of CaO is needed to react completely with this ore?
- Write the reaction equations if the reaction mixture was heated with calcium oxide in a current of air.
- What is the % of both FeS and HgS in the ore?
- Why was the solution boiled while being saturated with carbon dioxide?

### Problem 3 – EQUIL – Carbon monoxide conversion

Carbon dioxide formed during the combustion of solid fuel takes part in the equilibrium reaction (1)  $\text{C(s)} + \text{CO}_2\text{(g)} \rightleftharpoons 2\text{CO(g)}$ . The logarithms of the equilibrium constants at 1000 K of the following reactions are given: (2)  $\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightleftharpoons \text{CO(g)}$   $\log K_2 = 10.477$  and (3)  $\text{C(s)} + \text{O}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(g)}$   $\log K_3 = 20.675$ .

- Calculate the equilibrium constant of reaction (1) at 1000 K and 1 atm pressure.
- Find the content of gases ( $\text{CO}_2$ , CO,  $\text{N}_2$ ) in vol. % if the temperature in the furnace is 1000 K. The fuel burns in the air, the composition of which is assumed to be 80%  $\text{N}_2$  and 20%  $\text{O}_2$ .

### Problem 4 – ELECTRO – A simple galvanic cell

At 20 °C, the standard EMF of the cell  $\text{Pt, H}_2 \mid \text{HCl, HgCl}_2 \mid \text{Hg}$  is 0.2692 V; at 30 °C, it is equal to 0.2660 V. The calomel electrode is the positive pole.

- Write the total reaction equation of the cell.
- Determine  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and the equilibrium constant of the reaction at 25 °C.

### Problem 5 – ABC – A funny ketone

Compound **A** ( $C_{13}H_{15}NO$ ) can react with iodine in an alkaline aqueous solution. As a result of the reaction, yellow precipitate **B** ( $w_1 = 96.70\%$ ) and acid **C** ( $C_{12}H_{13}NO_2$ ) are formed. Compound **C** undergoes hydrolysis giving products **D** and **E** ( $C_7H_7NO_2$ ). The original compound **A** undergoes hydrolysis giving products **D** and **F**. When substance **F** reacts with iodine and sodium hydroxide, compounds **E** and **B** are formed after acidification of the reaction mixture with hydrochloric acid.

Compound **E** decomposes if heated with NaOH. In this case, it is possible to isolate the basic compound **G** ( $C_6H_7N$ ). This compound reacts with an aqueous solution of  $Br_2$  to form a precipitate. Compound **D** ( $C_5H_8O$ ) does not decolorize the solution of  $KMnO_4$ . It does not react with metallic sodium or silver oxide in ammonia. It can be oxidized under harsh conditions to acid  $C_5H_8O_4$ .

Draw the structural formulas of compounds **A–G**.

### Problem 6 – ABC, BIO – Sweet toxins

Many marine mollusks contain the toxic substance holothurin, which has the structure **R–O–TS**, in which **R** is a polycyclic alcohol residue, and **TS** is a tetrasaccharide composed of four different monosaccharides **A**, **B**, **C**, and **D**.

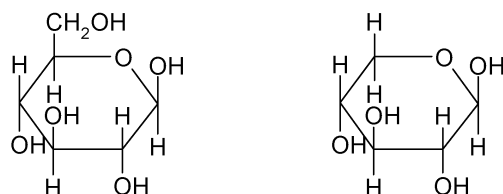
After complete acid hydrolysis, two monosaccharides are readily identifiable by paper chromatography. These monosaccharides are glucose (**A**) and xylose (**B**). The molecular mass of saccharide **C** is  $164 \text{ g mol}^{-1}$  and monosaccharide **D** is  $194 \text{ g mol}^{-1}$ . According to the NMR spectrum, monosaccharides **C** and **D** contain one methyl group. Both monosaccharides can be obtained from glucose: monosaccharide **C** is obtained by selective reduction; monosaccharide **D** is obtained by methylation at the third position.

By partial enzyme hydrolysis of the tetrasaccharide, the oligosaccharides **DA–OH**, **CD–OH**, and **DAB–OH** can be isolated (–OH represents the oligosaccharide's free reducing group).

a) Draw the structural formulas of **C** and **D**.

b) Draw the structural formula of a tetrasaccharide, assuming that all monosaccharides are in pyranose form and that all monosaccharides are joined by a  $\beta(1 \rightarrow 4)$  glycosidic bond.

The structures of glucose and xylose are as follows:



## 6th BChO, 1998, Tartu, Estonia

### Problem 1 – ABC, CALC – Another white powder in the lab

The analysis laboratory received a white crystalline material for analysis. The analyst weighed out two samples of the material. Sample 1, with a mass of 1.084 g, was dissolved in water. As the material dissolved, 26.17 cm<sup>3</sup> of gas, having a mass of 37.39 mg, was released. The resulting solution was found to be very acidic. Addition of hydrochloric acid caused a precipitate to form. After the addition of 47.5 cm<sup>3</sup> 0.0983 molar HCl, no more precipitate was formed. The precipitate was recovered, dried, and weighed. The mass of the precipitate was 0.6693 g.

Sample 2, with a mass of 1.120 g, was heated to above 300 °C. During heating, 324.6 cm<sup>3</sup> of gas was collected with a mass of 599.0 mg. After heating, a light-colored metal with a mass of 0.521 g remained. The gas was dissolved in 100 cm<sup>3</sup> of water. Not all the gas dissolved, 54.10 cm<sup>3</sup>, with a mass of 77.2 mg, remained. The pH of the solution was found to be 1.015.

- Determine the compound in the sample with calculations.
- What reactions took place during the analysis?

### Problem 2 – CALC – Analysis of gas mixture

A sample of a compound was heated at 600 °C. A solid with a mass of 4.51 g remained after heating and 21.48 dm<sup>3</sup> of gas was liberated at 600 °C. The solid contains 21.25% oxygen. After cooling to room temperature, the gas occupies 2.69 dm<sup>3</sup> and has a density of 1.61 g dm<sup>-3</sup>. After passing the gas through an alkaline solution, there remained 1.34 dm<sup>3</sup> of a combustible gas having a density of 1.25 g dm<sup>-3</sup>.

- Determine the compound in the sample.
- Write all appropriate equations.

### Problem 3 – STEREO, SYNTH – Recreating a natural biosynthesis in a lab

*R*-(+)-glycerol aldehyde can be transformed to (-)-malic acid (2-hydroxybutanedioic acid) according to the following scheme. *R*-(+)-glycerol aldehyde was treated with hydrogen cyanide and two isomeric compounds were formed, namely **A** and **B**. Those compounds were separated by fractional crystallization. Only isomer **B** was used for further transformations. This compound was converted to **C** (C<sub>4</sub>H<sub>8</sub>O<sub>5</sub>) upon hydrolysis and then oxidized by conc. nitric acid to produce compound **D** (C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>). Further, compound **D** was treated with phosphorus tribromide, thus, compound **E** (C<sub>4</sub>H<sub>5</sub>BrO<sub>5</sub>) was formed. Finally, compound **E** was converted to (-)-malic acid after the reaction of zinc with an acid.

- Write the equations of all reactions using stereochemical (Fisher projections) formulas.
- Explain why only one isomer **E** was formed from **D**.
- How many isomers of **E** can be formed starting the synthesis from an isomer **A**?

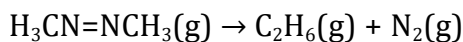
### Problem 4 – MECH – Lethally spicy

Mustard gas (2,2'-dichloro sulfide) can be used as a chemical weapon via releasing HCl in hydrolysis reaction. In comparison, 1,5-dichloropentane is hydrolyzed much more slowly.

- Write the mechanism of the above-described reaction for both compounds.
- Which well-known compound might be used to destroy this gas?
- Write a synthetic pathway to produce the mustard gas.

### Problem 5 – KINETICS – A rapid synthesis of ethane

The thermal decomposition of azomethane (compound **A**) follows the equation:



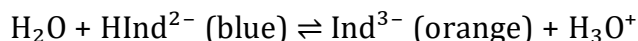
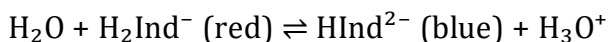
The half-life of compound **A** at 320.6 °C is 9.5 min. The total pressure of the mixture of gases at the temperature of 298.0 °C was measured at different time periods:

|            |       |       |       |          |
|------------|-------|-------|-------|----------|
| $t$ [min]  | 10.0  | 21.0  | 35.0  | $\infty$ |
| $p$ [Torr] | 491.9 | 548.0 | 609.7 | 861.6    |

- Prove that the process is a first-order reaction.
- Calculate the average value of the rate constant at 298.0 °C.
- Determine the activation energy of the reaction.

### Problem 6 – EQUIL – pH-dependent titration

Eriochrome Black T ( $\text{H}_3\text{Ind}$ ) is a typical metal ion indicator used in complex-formation titrations with EDTA ( $\text{Na}_2\text{H}_2\text{Y}$ ). This compound contains a sulfonic acid group, which is completely dissociated in water, and two phenolic groups that dissociate only partially ( $K_{a1} = 5.0 \cdot 10^{-7}$  and  $K_{a2} = 2.8 \cdot 10^{-12}$ ).



- The metal complexes of Eriochrome Black T are generally red. Calculate the minimum pH at which Eriochrome Black T can be used as an indicator in complex-formation titrations (assume that the detectable color change requires a tenfold excess of one or other colored species).
- Determine the transition range for Eriochrome Black T in titrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  at pH 10.0, given that the (thermodynamic) formation constant for  $\text{MgInd}^-$  is  $1.0 \cdot 10^7$  and for  $\text{CaInd}^-$  is  $2.58 \cdot 10^5$ .

50.00 cm<sup>3</sup> of 0.00500 M  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  solutions were both titrated with 0.0100 M EDTA solution at pH 10. Conditional formation constants (Instead of the equilibrium concentration of  $\text{Y}^{4-}$  the total concentration of all forms of EDTA is used) at that pH are  $1.72 \cdot 10^8$  for  $\text{MgY}^{2-}$  and  $1.75 \cdot 10^{10}$  for  $\text{CaY}^{2-}$ .

- Calculate the equilibrium concentrations of the metal cations at the equivalence point.
- Determine the sign of the relative error, connected with assuming that the stoichiometric point is judged to be approached at the first change of color of the solution.

## 7th BChO, 1999, Kaunas, Lithuania

### Problem 1 – ABC – Haloalkane redox magic

Compound **A** ( $C_8H_{15}Cl$ ) is a racemate. It does not discolor bromine in carbon tetrachloride or potassium permanganate solution. If **A** is treated with zinc and acetic acid and the resulting mixture is separated by chromatography, two fractions, **B** and **C**, with identical molecular formulas, are obtained. Fraction **B** is a racemate.

The reaction of **A** with sodium methoxide ( $CH_3ONa$ ) in ethanol yields compound **D**. Hydrogenation of **D** over a platinum catalyst gives the product **C**. Ozonolysis of **D** followed by the addition of zinc and water produces the dione **E**. From compound **E**, iodoform is formed by reaction with iodine in NaOH solution. After isolation of iodoform and acidification, adipic acid (1,4-butanedicarboxylic acid) is obtained.

- Write the structural formulas of **A**, **B**, **C**, **D**, and **E**.
- Show the stereoisomerism of the compounds.
- Write the reaction equations.
- Write the reaction mechanism for the preparation of compound **D** from compound **A**.

### Problem 2 – BIO, CALC – The ones that hide inside potatoes

Hydrolysis of starch in dilute aqueous acid solution yields only "sweet" products – saccharides: glucose, maltose, etc. Hydrolysis of 30-40% starch suspension in dilute HCl solution at 130-140 °C gives bittersweet saccharide **X**. Substance **X** was separated and purified for analysis. A series of experiments were carried out to identify it.

(1) Hydrolysis of starch in acidic solution. One of the products is glucose.

(2) Reducing properties.

25 mg of substance **X** was diluted in 25.0 cm<sup>3</sup> of 0.0100 M  $K_3[Fe(CN)_6]$  solution, 5 cm<sup>3</sup> of 0.1 M KOH solution was added and the mixture was heated at 100 °C for 15 minutes. The concentration of  $K_3[Fe(CN)_6]$  was determined using the iodometry method. KI and  $CH_3COOH$  were added; 10.5 cm<sup>3</sup> of 0.0100 M  $Na_2S_2O_3$  solution was required to titrate  $I_2$ .

(3) Methylation and oxidation.

Substance **X** was methylated with excess  $CH_3I$  in the presence of  $Ag_2O$ . The product was heated in a 30% nitric acid solution. Two acids were detected in the reaction mixture: 2,3,4-trimethoxy-5-hydroxyadipic acid,  $HOOC-CH(OH)-[CH(OCH_3)]_3-COOH$  and 2,3,4,6-tetramethoxy-5-hydroxycaproic acid  $H_3COCH_2CH(OH)-[CH(OCH_3)]_3COOH$ .

- Draw the structure of substance **X**.
- Write the reaction equations for the identification of substance **X**.

### Problem 3 – ELECTRO, EQUIL – A way to dissolve silver

The potential  $E_1$  of the silver electrode was determined in a solution of  $AgNO_3$  with a concentration of 0.0100 M. After that, 0.0170 g of  $NH_3$  was added to 10.0 cm<sup>3</sup> of the solution. In the resulting solution, the potential of the Ag electrode was different from  $E_1$  by 0.285 V. The temperature of the solution was 25 °C.

$NH_3$  forms a complex in  $AgNO_3$  solution according to the reaction  $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$ . Calculate the equilibrium constant of the above reaction.

#### Problem 4 – EQUIL – Hydrazine

25 cm<sup>3</sup> of 0.0160 M Zn(NO<sub>3</sub>)<sub>2</sub> solution and 75 cm<sup>3</sup> of 0.133 M hydrazine solution were mixed.  $K_{sp}[\text{Zn}(\text{OH})_2] = 1.20 \cdot 10^{-17}$ ,  $K_b(\text{H}_4\text{N}_2) = 1.3 \cdot 10^{-6}$  (proton addition).

- Write all the reaction equations and give expressions for the equilibrium constants.
- Calculate the equilibrium concentration for each component of the solution.
- Calculate the pH of the solution.

#### Problem 5 – CALC – Carbon tet

2.000 g of unknown metal oxide with an oxygen content of 31.58% was heated at 750 °C in a quartz tube. Gaseous CCl<sub>4</sub> was passed through the tube. The gases exiting the tube were passed through lime water. 1.974 g of a white substance precipitated, which dissolved in a hydrochloric acid solution. A red-purple powder remained in the tube. At a reduced temperature, chlorine was passed through the tube. At a reduced temperature, the solid turned into a gas which, in reaction with solid CO<sub>2</sub>, turned into a brown solid with a chlorine content of 73.1%. The reaction of this compound with water produced an acidic solution and a mixture of gases that changed the color of the KI solution to brown when passed through it.

- Write all the reaction equations and support them with calculations.
- What are the processes involved in the reaction of brown solid with water?

#### Problem 6 – STRUCT – A colorful manganese complex

KSCN solution was added to Mn(NO<sub>3</sub>)<sub>2</sub> solution and a crystalline substance with a molar mass of 445.8 g mol<sup>-1</sup> was obtained. The experimentally determined magnetic moment of this compound was equal to  $\mu = 6.1$  Bohr magneton.  $\mu = \sqrt{n(n + 2)}$ . Write the formula of the obtained substance, draw its structure, and explain what information the value of the magnetic moment provides.

#### Problem 7 – ABC – Four seasons

At 500 °C, 8.000 g of substance **B** and 2.469 dm<sup>3</sup> of gaseous substance **C** (20 °C and 740 mm Hg) are formed from salt **A** in water vapor. The gas **C** reacts completely with the original amount of substance **A** in an aqueous solution to form 16.800 g of substance **D**. When the resulting solution is boiled and then dried, the original amount of substance **A** is released.

Determine the compounds **A**, **B**, **C**, and **D** (all are water-soluble) and write and prove the reaction of **A** with water vapor.

## 8th BChO, 2000, Riga, Latvia

### Problem 1 – ABC – Volcanic combustion

Compound **X** is colored and burning. Burning 2.12 g of it produces 0.752 g of green solid compound with a very high melting temperature. Gases arising in this process were passed through the excess of lime water. There was 6.838 g of white precipitate, which dissolved in hydrochloric acid. When  $\text{H}_2\text{O}_2$  is added to lime water, the mass of the precipitate is 7.551 g, and only 19.7% (by mass) of the precipitate dissolves in hydrochloric acid. The relative density of the evolved gas against the air is 1.52.

- Determine compound **X**.
- Write equations of the described reactions
- What is the color of compound **X**?

### Problem 2 – ABC, EQUIL – A rainbow metal

To 10.00 mg of metal **A** was added 10 cm<sup>3</sup> of water. A stream of chlorine was passed through the water until **A** had dissolved completely and an equilibrium had been established. The obtained solution was evaporated in a vacuum to leave 20.91 mg of yellow crystals of a strong acid **B**. Acid **B** obtained in the first reaction was dissolved in water and neutralized exactly with 22.53 cm<sup>3</sup> of alkali with a concentration of 2.253 mM. The essentially colorless solution was diluted to 100 cm<sup>3</sup>, and a reducing agent was added. The solution turned bright red. The addition of any salts causes the solution to gradually turn blue. On standing, the blue solution very slowly deposits 10.00 mg of metal **A** and becomes colorless once again.

- Draw and explain the spatial structure of the anion of acid **B**.
- Write all the equations of the mentioned reactions.
- What kind of compounds are best suited to reduce **B** and obtain the red solution?
- What would be observed if the neutralized solution of **B** was not diluted prior to the reduction?
- Explain the role of salts in the color change of the solution.

Solutions of alkali metal salts of **B** are slightly acidic. Acidity decreases considerably if excess chloride is present. Explain this finding and calculate the relevant equilibrium constant.

| $n(\text{B})$ [mmol] | $n(\text{NaCl})$ [mmol] | $V_{\text{sol.}}$ [cm <sup>3</sup> ] | pH   |
|----------------------|-------------------------|--------------------------------------|------|
| 1.00                 |                         | 1000                                 | 3.17 |
| 1.00                 | 10.0                    | 1000                                 | 3.57 |

### Problem 3 – ABC – Same formula, different compounds

Three compounds, **A**, **B**, and **C**, have the formula  $\text{C}_6\text{H}_{10}$ . All three compounds rapidly decolorize bromine in  $\text{CCl}_4$ . Compound **A** gives a precipitate when treated with silver nitrate in ammonia, but compounds **B** and **C** do not. Compounds **A** and **B** both yield compound  $\text{C}_6\text{H}_{14}$  when treated with excess hydrogen in the presence of a platinum catalyst. Under these conditions, **C** absorbs only 1 mol of hydrogen per 1 mol of **C** and gives the product with the formula  $\text{C}_6\text{H}_{12}$ . When **A** is oxidized with hot potassium permanganate, and the resulting solution is acidified, the only organic compound that can be isolated is *n*-pentanoic acid. Similar oxidation of **B** gives only propanoic acid, and similar treatment of **C** gives only 1,6-hexanedicarboxylic acid.

- Draw the structural formulas of compounds **A**, **B**, and **C**.
- Write equations of the described reactions.
- Draw the stereochemical formula of the compound produced in the reaction of **C** with  $\text{Br}_2$ .

#### Problem 4 – SPECTRA, SYNTH – A breakthrough in surgery

(*N,N*-diethylamino)ethyl 4-aminobenzoate hydrochloride (novocaine) is used as a local anesthetic. It is commonly obtained from the toluene:



$\text{C}_7\text{H}_7\text{NO}_2$  and  $\text{C}_7\text{H}_5\text{NO}_4$  both have 1 singlet and 2 doublets in the  $^1\text{H}$ -NMR spectrum.  $\text{C}_9\text{H}_9\text{NO}_4$  has 2 doublets, 1 triplet, and 1 quartet and  $\text{C}_9\text{H}_{11}\text{NO}_4$  has 1 singlet, 2 doublets, 1 triplet and 1 quartet.

- Write all reaction equations.
- Write a mechanism for the last reaction in the presence of a catalytic amount of an alkoxide.
- Outline the  $^1\text{H}$ -NMR spectrum of Novocaine.
- Name the principal bands in its IR spectrum.

A test reaction for Novocaine includes successive treatment of the sample with an acidified solution of sodium nitrite and 2-naphthol. The reaction is positive when precipitate is formed.

- Write the reaction equation.

#### Problem 5 – ELECTRO, EQUIL – A primitive pH meter

A Voltaic cell is made up of two half-cells consisting of hydrogen electrodes (with  $\text{H}_2$  gas at  $10^5$  Pa and  $20^\circ\text{C}$ ). One of them is immersed in  $100\text{ cm}^3$  of  $0.10\text{ M}$   $\text{HCl}$  aqueous solution, the second one in  $100\text{ cm}^3$  of  $0.10\text{ M}$   $\text{CH}_3\text{COOH}$  ( $K_a = 1.75 \cdot 10^{-5}$ ) aqueous solution.

- Calculate the EMF of the Voltaic cell under given conditions.
- Calculate the EMF of the Voltaic cell when  $60\text{ cm}^3$  of  $0.10\text{ M}$   $\text{NaOH}$  solution was added to both initial solutions.
- Calculate the EMF of the Voltaic cell when both initial solutions were diluted 10 times.
- Calculate the volume (in  $\text{cm}^3$ ) of  $0.10\text{ M}$   $\text{NaOH}$  solution that should be added to the initial  $\text{CH}_3\text{COOH}$  solution to obtain an EMF of  $0.150\text{ V}$ .

#### Problem 6 – RADIO – Nuclear waste with a red flame

$^{90}\text{Sr}$  is one of the most common nuclear wastes from nuclear reactors. The spontaneous radioactive decay of this isotope can be described with the following equations:  $^{90}\text{Sr} = ^{90}\text{Y} + e^-$  and  $^{90}\text{Y} = ^{90}\text{Zr} + e^-$  ( $T_{1/2} = 64$  hours). For a sample of  $^{90}\text{Sr}$  containing  $2.64 \cdot 10^{10}$  atoms, the absolute disintegration rate was measured as 1238 decays per minute. The final Zr isotope is stable.

- Calculate the amount of energy (in kJ) that is released during one year if we start with one mole of  $^{90}\text{Sr}$ .
- Calculate the ratio of masses of charcoal and  $^{90}\text{Sr}$  that can give this amount of energy. The heat of combustion for charcoal is  $23\text{ MJ kg}^{-1}$ .  $m(^{90}\text{Sr}) = 89.907738\text{ Da}$ ,  $m(^{90}\text{Y}) = 89.907152\text{ Da}$ ,  $m(^{90}\text{Zr}) = 89.904703\text{ Da}$ ,  $m(e^-) = 5.4857 \cdot 10^{-4}$

## 9th BChO 2001, Tartu, Estonia

### Problem 1 – ELECTRO, EQUIL – Lead and oxalate

The solubility product value ( $K_{sp}$ ) for  $PbC_2O_4$  at 25 °C is  $8.50 \cdot 10^{-10}$ , and the standard reduction potential of the  $Pb^{2+}/Pb$  couple is  $E_1^\circ = -0.126$  V.

- Calculate the standard potential of the half-reaction:  $PbC_2O_4(s) + 2e^- \rightarrow Pb(s) + C_2O_4^{2-}(aq)$ .
- Calculate the concentration of  $Pb^{2+}$  ions in 0.0250 M solution of  $Na_2C_2O_4$  solution saturated with  $PbC_2O_4$ .
- Calculate the voltage of the  $PbC_2O_4/Pb$  electrode in 0.0250 M solution of  $Na_2C_2O_4$ .

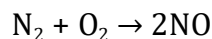
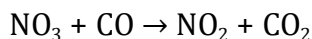
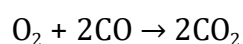
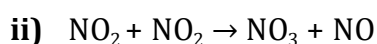
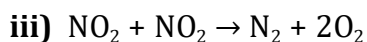
### Problem 2 – KINETICS – $NO_x$ conversion of carbon monoxide

One of the gaseous reactions taking place in car engines and exhaust systems is  $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ . Experimental data for this reaction are the following:

| Experiments | Initial $[NO_2]$ , M | Initial $[CO]$ , M | Initial rate<br>$\text{mol dm}^{-3} \text{s}^{-1}$ |
|-------------|----------------------|--------------------|----------------------------------------------------|
| 1           | 0.10                 | 0.10               | 0.0050                                             |
| 2           | 0.40                 | 0.10               | 0.080                                              |
| 3           | 0.10                 | 0.20               | 0.0050                                             |

- Determine the rate law.

Three possible mechanisms have been proposed for the given reaction:



- Which mechanism is the most reasonable? What is the rate-determining step?
- Draw the reaction energy diagram (energy-reaction coordinate) for the actual mechanism.

### Problem 3 – CALC – An unknown alloy

1.50 g of metal alloy was pulverized and treated with excess NaOH solution. The undissolved residue was filtered, washed with water, and dried. The weight of the obtained product was 0.903 g. 20% solution of  $NH_4Cl$  was added to the filtrate until no more precipitation occurred. The formed precipitate was filtered, washed, dried, and heated. 0.510 g of the white compound was obtained. The oxygen content in this compound is 47.1% (by mass). The Undissolved residue was treated with a hydrochloric acid solution. 112 cm<sup>3</sup> of hydrogen gas was formed. The Undissolved residue was separated as previously. Its weight was 0.624 g. This residue was treated with a nitric acid solution. The blue solution was obtained. When the ammonia solution is added to the blue solution, a blue precipitate is formed, which dissolves in excess ammonia. 0.179 g of metallic residue was obtained. The volume of the residue is 9.27 mm<sup>3</sup>.

- Determine the composition of metal alloy.
- Calculate the amount (in moles) of all metals in the alloy.
- Write the equations of all the described reactions.

#### Problem 4 – CALC – Unsafe moonshine

Colorless liquid (**A**) is found in the vessel. Apparently, it is a solution of unknown compounds in the water. The solution is slightly acidic. 100.0 cm<sup>3</sup> of this solution was measured and transferred in the distillation flask. Afterwards, 50 cm<sup>3</sup> of 20% NaOH solution was added. The distilled solution was collected in the flask that contained 100.0 g 3.00% HCl solution. Distillation was carried out until the volume of the solution in the collection flask was 150 cm<sup>3</sup>. 20.0 cm<sup>3</sup> of the obtained solution was measured and titrated with 0.100 M KOH solution in the presence of methyl orange. 6.96 cm<sup>3</sup> of titrant was used.

To the 100 cm<sup>3</sup> of solution (**A**), 15 g zinc was added and the procedures mentioned above were repeated. Distillation was interrupted when the volume of distillate was 150 cm<sup>3</sup>. In this case, 5.62 cm<sup>3</sup> 0.100 M NaOH solution was used for titration.

To the 20.0 cm<sup>3</sup> of the solution (**A**), an excess of BaCl<sub>2</sub> solution was added. 0.467 g of white precipitate was formed. This precipitate did not dissolve in hydrochloric acid. This reaction was repeated, but instead of BaCl<sub>2</sub>, a solution of Ba(NO<sub>3</sub>)<sub>2</sub> was taken. The weight of the obtained precipitate was the same (0.467 g).

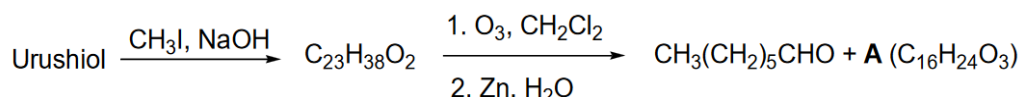
To the small volume of solution (**A**), sulfuric acid and FeSO<sub>4</sub> solution were added. By adding KSCN, the solution became red. The presence of the other ions was not detected.

- Determine the qualitative and quantitative composition of solution (**A**).
- Write equations of the described reactions.

#### Problem 5 – SYNTH – Urushi lacquer is expensive for a reason

Urushiols are the irritants in poison ivy and poison oak that give you rashes and make you itch upon exposure. Use the following information to determine the structure of urushiol C<sub>21</sub>H<sub>34</sub>O<sub>2</sub>, one of the members of a family of unpleasant compounds.

Urushiol was methylated and, after ozonolysis, gave two compounds as shown in the scheme:

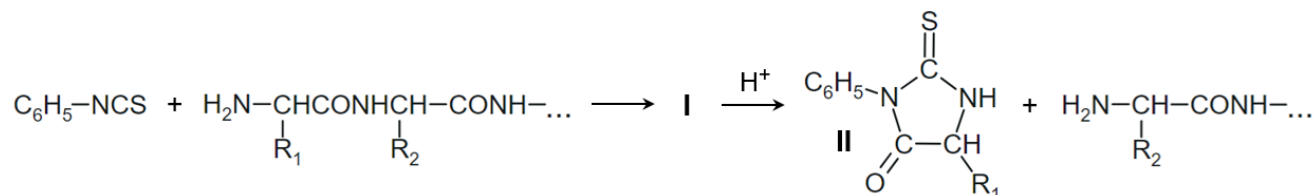


Synthesis of aldehyde **A** is achieved via the following scheme: treatment of methoxybenzene with fuming sulfuric acid and subsequent nitration with concentrated nitric acid in the presence of concentrated sulfuric acid afforded compound **B** (C<sub>7</sub>H<sub>7</sub>NSO<sub>6</sub>). Heating of **B** in dilute aqueous acid gave compound **C** (C<sub>7</sub>H<sub>7</sub>NO<sub>3</sub>). Treatment of **C** with Zn in HCl and subsequent addition of NaNO<sub>2</sub> in acidic media and heating gave compound **D** (C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>). The reaction of **D** with CO<sub>2</sub> and KHCO<sub>3</sub> at high pressure (The Kolbe reaction) led to compound **E** (C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>), which with CH<sub>3</sub>I and NaOH gave compound **F** (C<sub>9</sub>H<sub>10</sub>O<sub>4</sub>). Reduction of **F** with LiAlH<sub>4</sub> and subsequent oxidation with MnO<sub>2</sub> gave compound **G** (C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>). Wittig reaction of **G** with C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O(CH<sub>2</sub>)<sub>6</sub>CH=P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> gives unsaturated compound **H** (C<sub>23</sub>H<sub>30</sub>O<sub>3</sub>). Hydrogenation of **H** with hydrogen on Pd gave compound **I** (C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>) which upon oxidation with pyridinium chlorochromate afforded aldehyde **A**.

Draw the structural formula of urushiol and compounds **A–I**.

### Problem 6 – BIO, MECH – Protein sequencing

Edman degradation is the most important method for the identification of N-terminal amino acids of peptides and proteins. This method is based on the reaction of an uncharged N-terminal amino group with phenyl isothiocyanate. The addition product **I** is formed which, under mildly acidic conditions, decomposes into cyclic compound **II** and peptide or protein molecule shortened by one amino acid. The overall reaction equation is presented below:



- Draw the structural formula of the intermediate product **I**.
- Write the structural formula of cyclic compound **II** derived from terminal glycine.
- Propose a possible mechanism for the transformation of **I** into the final product.
- Write other methods for the identification of terminal amino acids.

Bradykinin is a nonapeptide released by blood plasma globulins. It is a very potent pain-causing agent. Complete acidic hydrolysis of 1 mol of bradykinin gives 3 moles of Pro, 2 moles of Arg, 2 moles of Phe, and also Gly and Ser (1 mole each). Both N- and C-terminals of bradykinin are residues of arginine (Arg). Partial hydrolysis of this nonapeptide gives a mixture of di- and tripeptides:

Phe-Ser, Pro-Gly-Phe, Pro-Pro, Ser-Pro-Phe, Phe-Arg, Arg-Pro

- Write the amino acid sequence of bradykinin.

## 10th BChO, 2002, Palanga, Lithuania

### Problem 1 – ABC – A pink element

A stream of heated  $\text{Cl}_2$  was passed through 0.300 g of element **A**. On cooling with ice, 1.06 g of pink solid **B** was collected in a receiver flask. Compound **B** was heated in a stream of  $\text{N}_2$ , and then the resulting gases were passed through a KI solution, which darkened in the process. The solution was then triturated with 0.120 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The white compound **C**, obtained by heating compound **B**, was dissolved in a small amount of water. The solution was distilled to dryness, and solid **D** was obtained. The distillate was diluted with water to 150.0  $\text{cm}^3$  (solution of **E**). 20.00  $\text{cm}^3$  of solution of **E** was titrated with 0.100 M NaOH solution. Compound **D** was heated above 400  $^\circ\text{C}$ , and 0.403 g of white solid **F** was obtained. Substance **F** was heated in a stream of  $\text{H}_2$ , and 0.300 g of the initial compound **A** was obtained.

- Write chemical formulas of the compounds **A–F**.
- Write all the equations of the reactions.
- Calculate the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution used for the titration.
- Calculate the volume of NaOH solution used to titrate 20.00  $\text{cm}^3$  of solution **E**.
- Why should compound **B** be heated in a stream of  $\text{N}_2$ ? What can be used instead of nitrogen?

### Problem 2 – THERMO – The first step to fertilizers

The following reaction is of great practical value:  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

- Determine thermodynamic characteristics for this reaction:  $\Delta H_r^\circ$ ,  $\Delta G_r^\circ$ ,  $\Delta S_r^\circ$  if standard values of enthalpy and Gibbs energy for the reaction of NO formation are  $\Delta H_f^\circ = 91.25 \text{ kJ mol}^{-1}$  and  $\Delta G_f^\circ = 87.58 \text{ kJ mol}^{-1}$ .
- Write the equation for the dependence of  $\Delta G_r^\circ$  on temperature  $T$  assuming that  $\Delta H_r^\circ$  and  $\Delta S_r^\circ$  do not depend on temperature.
- Estimate the temperature at which air (78%  $\text{N}_2$  and 21%  $\text{O}_2$ ) in a closed vessel will contain 0.1% of NO by volume at equilibrium.

NO is a chemically active compound that is readily oxidized by oxygen and halogens. Assume that the reaction of NO with bromine proceeds in 2 steps: **i)**  $\text{NO} + \text{Br}_2 \rightleftharpoons \text{NOBr}_2$  and **ii)**  $\text{NOBr}_2 + \text{NO} \rightarrow 2\text{NOBr}$ , where the final one is the rate-limiting step.

- Write the kinetic equation for the overall reaction of NOBr formation.

### Problem 3 – KINETICS – Logic and kinetics

The enzyme catalyzes the following reaction:  $\text{S} \rightarrow \text{P}$ , where S is the substrate and P is the corresponding product. The reaction rate at different substrate concentrations was measured:

| #                              | 1                   | 2                   | 3                   | 4                   | 5                    |
|--------------------------------|---------------------|---------------------|---------------------|---------------------|----------------------|
| [S], M                         | $1.0 \cdot 10^{-2}$ | $1.0 \cdot 10^{-3}$ | $1.0 \cdot 10^{-4}$ | $7.5 \cdot 10^{-5}$ | $6.25 \cdot 10^{-6}$ |
| $v_0$ , $\mu\text{M min}^{-1}$ | 75.0                | 74.9                | 60.0                | 25.25               | 15.0                 |

- Calculate  $v_{\text{max}}$  and  $K_m$  using only logic and the Michaelis–Menten equation.
- Calculate the  $v_0$  value at substrate concentrations of  $2.5 \cdot 10^{-5}$  and  $5 \cdot 10^{-5}$  M.
- Calculate the  $v_0$  value at a substrate concentration of 0.02 M.

The concentration of the enzyme was increased by a factor of 2.

- d) Determine the value of  $v_0$  if the substrate concentration is  $1 \cdot 10^{-4}$  M.
- e) Calculate the concentration of the product after 3 minutes in the initial concentration of substrate is 0.04 M.

#### Problem 4 – CALC – Professional burette applications

An analytical lab received a sample of some crystalline compound **X** of constant composition for analysis. The laboratory assistant was very experienced in titration, but first of all, he dissolved some part of the sample in water and performed some qualitative trials. He found that the solution of potassium thiocyanate turned red after the addition of some drops of yellow solution **X**. Also, when the solution of sample **X** was mixed with ferrous sulfate and concentrated sulfuric acid was allowed to run slowly down the inside wall of the test tube, a characteristic brown ring appeared at the interface between the two liquids. After that, the lab assistant turned to titration techniques.

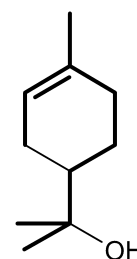
1.00 g of sample **X** was dissolved in 20.00 cm<sup>3</sup> of water and a small excess of TiCl<sub>3</sub> solution was added. Titration of that mixture required 23.00 cm<sup>3</sup> of titrant **A**. Titrant **A** was prepared by dissolving ceric(IV) sulfate in water. During standardization, 28.00 cm<sup>3</sup> of titrant **A** was required to titrate a standard solution prepared by dissolving 0.189 g of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O in water.

As the obtained information was insufficient, the laboratory assistant prepared a solution of titrant **B** (Fischer reagent). He dissolved crystalline iodine in pyridine, then passed SO<sub>2</sub> gas through this solution until the desired mass increase occurred. After that, he diluted the solution with methanol till the desired volume (assume that the solution was prepared using equimolar amounts of iodine and sulfur dioxide). 0.150 g of sample **X** was suspended in 5 cm<sup>3</sup> of methanol and this mixture was rapidly titrated with 8.50 cm<sup>3</sup> of titrant **B** (assume that titrant reacts with analyte in ratio 1 : 1 and cation does not interfere in reaction). During standardization, 3.40 cm<sup>3</sup> of titrant **B** was required to titrate a standard solution prepared by dissolving 0.1 g of KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O in methanol.

- a) What ions does the aqueous solution of sample **X** contain?
- b) Write the equations of standardizations of i) titrant **A** and ii) titrant **B**.
- c) Write the equations for the analysis of sample **X** using two different titrations.
- d) Determine the composition of sample **X**.
- e) What can be the main application of Fischer titration?
- f) Is it possible to titrate aldehydes or ketones using Fischer titration in this way?

#### Problem 5 – MECH, STEREO – Chemistry of essential oils

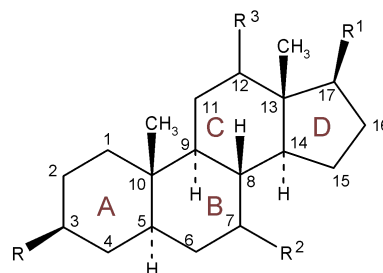
Terpenes are compounds with a carbon skeleton consisting of isoprene (2-methylbuta-1,3-diene) units that are linked in a head-to-tail fashion. They are often found in nature and give a characteristic aroma to many essential oils. Geraniol and nerol are also classified as steroids. These compounds are stereoisomers of a primary alcohol with two double bonds in the molecule. Geraniol is found in geranium oil, and nerol is found in nerol oil and bergamot oil. In the presence of acid, geraniol cyclizes to form α-terpineol, but nerol cyclizes much more rapidly. In the Figure, the carbon skeleton of the precursor alcohols is shown in bold.



- Draw the structural formulas of geraniol and nerol.
- What feature of the structure accounts for the rapid cyclization of nerol?  
 $\alpha$ -Terpineol, when dehydrated, forms terpinolene, which is found in the oil of Monteiro cypress.
- Depict the most probable structure of terpinolene.  
 In the presence of acid, terpinolene isomerizes to form three isomeric monocyclic dienes called terpinenes. Of these,  $\alpha$ -terpinene is the primary product. It is found naturally in marjoram, cardamom, and coriander oil. Only  $\alpha$ -terpinene is capable of a good Diels-Alder reaction. However, when treated with excess hydrogen chloride at low temperatures, all three terpinenes form the same addition product.
- Draw the structural formula of  $\alpha$ -terpinene.
- Draw the structural formula of the Diels-Alder product with maleic anhydride.
- Draw the structural formulas of the two remaining terpinenes.
- Draw the structural formulas of the reaction products of terpinenes with excess hydrogen chloride. Draw all possible stereoisomers of this compound.

### Problem 6 – STEREO, SPECTRA, SYNTH – Spectroscopy on steroids

Steroids are biological regulators in the human body. For example, they control sexual development and fertility. Among the most common steroids, cholesterol is present in almost all human and animal tissues. In steroids, the four cycles are condensed into the tetracyclic structure below. The junctions of the cycles are usually in transposition. The four cycles are labeled A, B, C, and D, and the carbon atoms are numbered according to a steroid-specific scheme. Many steroids have methyl groups at C10 and C13 and oxygen at NW. Bonds to groups above the plane of the steroid molecule are indicated in bold and those below the plane are indicated by dashed lines.



- Alternative wording: Draw the structural formula of the steroid above, indicating the conformations of six-membered cycles.
- Label the chiral atoms in this structure.
- Calculate the number of diastereomers of this molecule.  
 Cholesterol is a steroid in which  $R = OH$ ,  $R^1 = CH(CH_3)CH_2CH_2CH_2CH(CH_3)_2$ ,  $R^2 = R^3 = H$ , and there is a double bond between the 5 and 6 carbon atoms. This steroid is responsible for many circulatory diseases due to the fact that it precipitates in the arteries, causing arteriosclerosis and heart disease.
- Draw the structural formula of cholesterol and identify the configuration of the chiral atoms using (*R,S*)-designations.

Under the action of bacteria in the human digestive tract, cholesterol is converted to coprostanol. Use the following information to determine the structure of coprostanol. When treated with a Cr(VI) reagent, coprostanol forms compound **A** (IR:  $1710\text{ cm}^{-1}$ ; UV:  $\lambda_{\text{max}}(\epsilon) = 281$ ). Reaction of cholesterol with  $H_2$  over Pt gives compound **B**, the stereoisomer of coprostanol. Treatment of **B** with a Cr(VI) reagent gives compound **C**, which has a UV signal very similar to that of compound **A** (UV:  $\lambda_{\text{max}}(\epsilon) = 258$ ) and is, therefore, the stereoisomer of **A**.

Careful addition of Cr(VI) reagent to cholesterol gives **D** (UV:  $\lambda_{\max}(\epsilon) = 286$ ). Catalytic hydrogenation of **D** over Pt also gives **C**.

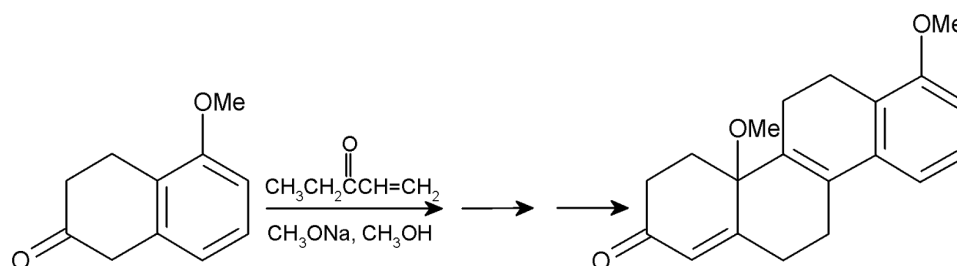
- e)** Draw structural formulas of compounds **A–D**. Label the stereochemistry of the atoms involved in the transformations using suitable steroid skeleton designations.

Cholesterol is the precursor to bile acids in the human body. Bile acids are formed in the liver as part of the fluid going into the duodenum to facilitate emulsification, digestion, and absorption of fats. An example is cholic acid ( $R = OH$ ,  $R^1 = CH(CH_3)CH_2CH_2COOH$ ,  $R^2 = R^3 = OH$ ), in which the articulation of cycles A and B is *cis*. This acid has surface-active properties.

- f)** Draw its conformational formula and a diagram showing the formation of micelles of cholic acid in aqueous solution.

Steroid synthesis in the laboratory is carried out using the Robinson annulation method. This reaction between enolates ketones and  $\alpha,\beta$ -unsaturated compounds is followed by intramolecular aldol condensation.

- g)** Suggest a scheme for the synthesis of the steroid indicated herein from a bicyclic ketone using one or more Robinson annulations and suitable components:



- h)** Write the mechanism of the first step of the synthesis.

## 11th BChO, 2003, Riga, Latvia

### Problem 1 – CRYSTAL – Packing of peas and lupine

- a) Calculate the layer's thickness of 1 mol of peas (6 mm in diameter), covering the entire surface of the Earth ( $5.10 \cdot 10^8 \text{ km}^2$ ) in the FCC arrangement. Assume that the surface is flat.
- b) Choose the correct answer that describes what would happen if these peas were mixed with 1 mol of lupine (2 mm in diameter). Fill in the gaps in your answer.
- ☐ With the particle size ratio smaller than 0.414, the FCC arrangement would transform into the ... arrangement and the layer's thickness would be ... m.
  - ☐ Lupine would fit into the ... holes of the FCC arrangement of peas, which can accommodate spherical particles with a diameter up to ... mm. The layer's thickness would not change.
  - ☐ Lupine would occupy the ... holes of the FCC arrangement, and it would expand slightly to increase the layer's thickness to ... m.
  - ☐ Lupine cannot fit into any holes of the FCC arrangement. It would form an independent layer on top of peas. The total thickness of both layers would be ... m.
  - ☐ Lupine would fit easily and indiscriminately into both ... and ... holes of the FCC arrangement. The layer's thickness would not change.

### Problem 2 – STRUCT – Nitrogen hydrides

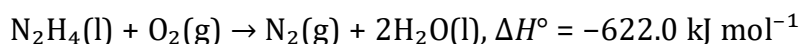
Nitrogen forms more than 20 binary compounds with hydrogen. The most important and well-known are ammonia  $\text{NH}_3$ , hydrazine  $\text{N}_2\text{H}_4$ , hydrogen azide (hydrazoic acid)  $\text{HN}_3$  (a non-cyclic molecule), and cyclotriazene  $\text{HN}_3$ .

- a) Draw possible Lewis dot structures for hydrogen azide  $\text{HN}_3$  and cyclotriazene  $\text{HN}_3$ .
- b) Show which two  $\text{HN}_3$  structures have the largest contribution to the resonance structure.
- c) Predict the bond angles in a hydrogen azide molecule using VSEPR.
- d) Predict the hybridization of each nitrogen atom in a hydrogen azide molecule of the two structures giving the largest contribution to the hybrid resonance structure.

$\text{NH}_3$  is extremely explosive and even dilute solutions should be treated as potentially hazardous. When dissolved in water, it is a weak acid with  $K_a = 1.80 \cdot 10^{-5}$ .

- e) Calculate the pH of  $5.00 \cdot 10^{-5} \text{ M}$   $\text{HN}_3$  solution.

Hydrazine  $\text{N}_2\text{H}_4$  is used as a rocket fuel. The oxidation of hydrazine is strongly exothermic:



- f) Calculate the standard enthalpy of formation of  $\text{N}_2\text{H}_4$  (l).  $\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] = -285.8 \text{ kJ mol}^{-1}$ .

### Problem 3 – RADIO – Polonium

In 1898, Pierre and Marie Curie discovered a new chemical element, polonium, in uranium tar ore (Bohemia, Joachimsthal). One ton of this ore contains 0.14 grams of  $^{226}\text{Ra}$  ( $T_{1/2} = 1580$  years). The discovered polonium isotope  $^{210}\text{Po}$  ( $T_{1/2} = 138.4$  days) is formed from  $^{226}\text{Ra}$  under  $\alpha$  and  $\beta$  decay.  $^{210}\text{Po}$  is extremely dangerous. When decaying to the stable  $^{206}\text{Pb}$  isotope, it emits  $\alpha$  particles, which are readily absorbed in tissues.

- a) Calculate the number of  $\alpha$  and  $\beta$  disintegrations in the transformation  $^{226}\text{Ra} \rightarrow ^{206}\text{Pb}$ .
- b) Derive the relation between the ratio of half-lives and the ratio of equilibrium concen-

trations assuming that the decay rate of both isotopes is the same.

c) Calculate the amount of ore (in tons, which contains exactly 1 mg of  $^{210}\text{Po}$ ).

d) Calculate the mass defect (in Da) of the  $^{226}\text{Ra} \rightarrow ^{210}\text{Po}$  transformation.

e) Calculate the energy released during the formation of exactly 1 mg of  $^{210}\text{Po}$ .

$m(^4\text{He}) = 4.00273 \text{ Da}$ ,  $m(\beta) = 0.00055 \text{ Da}$ ,  $m(^{226}\text{Ra}) = 226.02540 \text{ Da}$ ,  $m(^{210}\text{Po}) = 209.98286 \text{ Da}$

#### Problem 4 – EQUIL – Slow reaction

An equilibrium is established in a solution of hydrogen iodide at the silver electrode, which can be expressed by the equations: (i)  $\text{Ag(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{e}^-$  ( $E^\circ = 0.799 \text{ V}$ ) and  $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{AgI(s)}$  or using the total equation (ii)  $\text{Ag(s)} + \text{I}^-(\text{aq}) \rightleftharpoons \text{AgI(s)} + \text{e}^-$  ( $E^\circ = -0.152 \text{ V}$ ).

a) Write expressions for electrode potentials corresponding to equations (i) and (ii), and calculate the solubility product of AgI at 25 °C.

b) Show with calculations that hydrogen evaluation is theoretically possible at a silver electrode immersed into a 1 M solution of HI at 25 °C.

c) Explain why hydrogen evaluation occurs so slowly that it is unnoticeable.

#### Problem 5 – EQUIL – Selenic acid

1.29 g of crystalline selenic acid  $\text{H}_2\text{SeO}_3$  ( $\text{p}K_{\text{a}1} = 2.62$ ,  $\text{p}K_{\text{a}2} = 8.32$ ) was transferred into a measuring flask and distilled water was added up to 100  $\text{cm}^3$  mark. The solution was poured into a chemical beaker in which a glass electrode connected to a pH meter was placed.

a) Estimate the number that appeared on the pH meter screen.

To the selenic acid solution, 5.00  $\text{cm}^3$  of sodium hydroxide solution ( $c = 1.00 \text{ M}$ ) was added, it was stirred, and the pH was measured again. This procedure was repeated four more times, each time adding 5.00  $\text{cm}^3$  of sodium hydroxide and measuring the pH.

b) Calculate the pH values of all six solutions. Neglect any changes in volume.

#### Problem 6 – ABC, BIO – Tropic acid

Tropic acid,  $\text{C}_8\text{H}_{13}\text{O}_4\text{N}$ , is a degradation product of atropine, an alkaloid of the deadly cherry *Atropa belladonna*. Tropic acid does not react with cold dilute  $\text{KMnO}_4$  solution,  $\text{Br}_2/\text{CCl}_4$  solution, and benzenesulfonyl chloride. Complete methylation gives the following results:

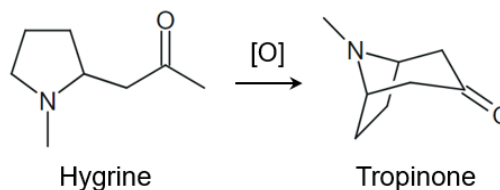
i) Tropic acid +  $\text{CH}_3\text{I} \rightarrow \text{A}$  ( $\text{C}_9\text{H}_{16}\text{O}_4\text{NI}$ )

ii)  $\text{A} + \text{Ag}_2\text{O} \rightarrow \text{B}$  ( $\text{C}_9\text{H}_{15}\text{O}_9\text{N}$ )

iii)  $\text{B} + \text{CH}_3\text{I} \rightarrow \text{C}$  ( $\text{C}_{10}\text{H}_{18}\text{O}_4\text{NI}$ )

iv)  $\text{C} + \text{Ag}_2\text{O} \rightarrow \text{D}$  ( $\text{C}_7\text{H}_8\text{O}_4$ ) +  $(\text{CH}_3)_3\text{N}$  +  $\text{H}_2\text{O}$

v)  $\text{D} + \text{H}_2/\text{Ni} \rightarrow \text{Heptanedioic acid}$



Tropic acid is formed by oxidation of tropinone with  $\text{CrO}_3$ . Reduction of tropinone gives tropine and pseudotropine (both  $\text{C}_8\text{H}_{15}\text{ON}$ ). When heated with base, tropine is converted to pseudotropine.

a) Draw the structural formulas of tropic acid and compounds A–D.

b) Draw the structural formulas of tropine and pseudotropine.

Tropinone is produced by enzymatic oxidation of hygrine with  $\text{NAD}^+$  or by chemical oxidation.

c) Draw the mechanism for this cyclization.

## 12th BChO, 2004, Tartu, Estonia

### Problem 1 – CALC, CRYSTAL, SPECTRA – European Union

Two chemists received for analysis two samples of a metal ( $\rho = 5.245 \text{ g}\cdot\text{cm}^{-3}$ ) with equal mass. Both chemists used X-ray analysis to determine that the metal crystallized in the BCC arrangement with the elementary cell edge length of  $4.582 \text{ \AA}$ .

The more careless chemist left the sample in the air, where its surface quickly lost metallic shine. When he crushed the sample and put it into a beaker with water, a vigorous reaction gave a white precipitate. The obtained solution was strongly basic. The solution containing the precipitate was acidified with hydrochloric acid and carefully evaporated to obtain  $363.7 \text{ mg}$  of colorless crystals. Sulfur(IV) oxychloride was added to the crystals and refluxed until the evolution of gases had ceased to give  $340.0 \text{ mg}$  of white deliquescent crystals. Their IR spectrum was obtained at low temperatures, in high dilution, in the matrix of an inert gas, and displayed four bands. The compound was put into a beaker and dissolved in water. Dilute sulfuric acid was added to the solution until no more precipitate formed.  $166.9 \text{ mg}$  of colorless crystals were obtained. On heating, the mass of the crystals reduced to  $134.2 \text{ mg}$  and did not change anymore.

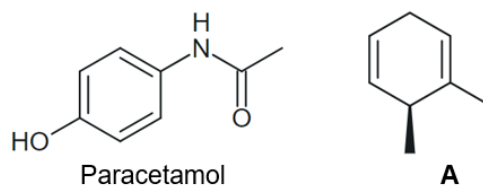
The other chemist never liked to go to the beaten path. So, he dissolved his sample in liquid ammonia to obtain, under an inert atmosphere, a blue solution. As he added ammonium chloride to the solution, the solution became colorless, a gas evolved, and some precipitate formed. The precipitate was gently heated *in vacuo* to yield  $293.3 \text{ mg}$  of a white crystalline solid. Its IR spectrum displayed three bands. The compound was put into a beaker and dissolved in water. Dilute sulfuric acid was added to the solution until no more precipitate formed. Some excess acid was added, and the solution was set aside to ensure complete precipitation. Yet, contrary to expectations, the mass of the colorless, crystalline precipitate significantly decreased on standing. By pure coincidence, the second chemist also obtained  $166.9 \text{ mg}$  of precipitate. On heating, the mass of the precipitate reduced further to  $134.2 \text{ mg}$  and did not change anymore.

- Using the X-ray data, determine the analyzed metal.
- Draw structural formulas for both compounds analyzed by IR spectroscopy. Identify vibrations corresponding to the observed bands.
- Write equations for all the mentioned reactions.

### Problem 2 – ABC, SYNTH – After the fever is gone

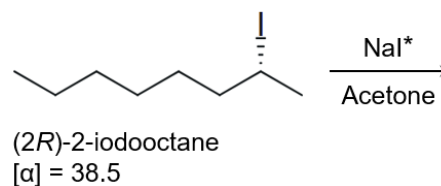
When **A** reacts with  $\text{O}_3$  in water, compounds **B** and **C** are formed. Both compounds react with  $\text{PCl}_5$  yielding **D** and **E**. Compound **D** can react with paracetamol to yield **F** and **G**. Compound **E** reacts with paracetamol yielding compound **H**. Vapor of **F** over anhydrous  $\text{AlCl}_3$  leads to compound **I**. In the presence of  $\text{HF} + \text{SbF}_5$  mixture, compound **H** isomerizes to **J** and **K**. When **I** is heated in attenuated sulfuric acid, compound **L** is formed. Under the same conditions, both **J** and **K** yield to **M**.

- Draw the structures for compounds **A–M**.
- Describe the function of anhydrous  $\text{AlCl}_3$ .
- Describe the function of  $\text{HF} + \text{SbF}_5$  for **H** isomerization.



### Problem 3 – KINETICS, MECH – Nucleophilic substitution

Nucleophilic substitution plays a prominent role in functional group transformations. We distinguish between two limiting mechanisms for nucleophilic substitution:  $S_N1$  (unimolecular) and  $S_N2$  (bimolecular). For some reactions, it is possible to determine the mechanism using chiral reagents. The reaction of (2*R*)-2-iodooctane with radioactive iodide ions was investigated.



Assuming that only nucleophilic substitution reactions take place and radioactive iodine isotope has the same chemical and physical properties as non-radioactive isotope, explain the experimental data:

|              |      |      |      |      |      |      |      |      |      |       |
|--------------|------|------|------|------|------|------|------|------|------|-------|
| $t$ [s]      | 0    | 633  | 1523 | 1945 | 2718 | 4214 | 5378 | 7163 | 9231 | 13332 |
| $\alpha$ [°] | 2.36 | 2.29 | 2.19 | 2.14 | 2.05 | 1.92 | 1.80 | 1.65 | 1.51 | 1.18  |

- Specific rotation of reaction mixture changes during the reaction. Which mechanism can be used to explain such results?
- The rate of non-radioactive iodine substitution with radioactive isotope is two times less than the racemization rate. How could you explain this phenomenon?
- What will the specific rotation of the reaction be after the reaction has ended?  
i)  $+38.5^\circ$ ; ii)  $-38.5^\circ$ ; iii)  $0^\circ$ ; iv)  $+77^\circ$ ; v)  $-77^\circ$ .
- To determine the radioactive isotope substitution rate, the reaction is stopped with the addition of cold water and extraction with  $\text{CCl}_4$ . What substance(s) are found in the water phase? Why is it better to use cold water?
- When the reaction is performed in methanol, the relation between the racemization rate and radioactivity of organic extract is not observed. How can this phenomenon be explained?
- Calculate the racemization if  $[2\text{-iodooctane}]_0 = 0.118 \text{ M}$  and  $[\text{NaI}^*]_0 = 0.0163 \text{ M}$ .

### Problem 4 – INORG, SPECTRA – Pharaoh's Compliment

To the cobalt(II) chloride solution, a white solid **A** (18.1% C, 7.52% H, and 53.3% Cl), NaOH and 30%  $\text{H}_2\text{O}_2$  were added separately. Orange compound **B** (19.8% C, 7.16% H, and 29.3% Cl) was obtained. In small amounts, concentrated ammonia and excess aqueous formaldehyde were added to the solution of **B** at pH 10, and a yellow solid **C** (31.9% C, 6.65% H, and 23.6% Cl) was isolated.  $^{13}\text{C}$  NMR spectra show one signal for **A** (43 ppm) and **B** (45 ppm) and two signals of equal intensity for **C** (54 and 67 ppm).  $^1\text{H}$  NMR spectra in  $\text{D}_2\text{O}$  show a singlet for **A** (2.65 ppm) and a broad singlet for **B** (2.85 ppm).

- Identify compounds **A**, **B**, and **C**.
- B** is an equimolar mixture of two enantiomers: **B1** and **B2**. Draw structural formulas for **B1** and **B2**. Propose how they can be isolated separately.
- Compound **C** was given the trivial name sepulchrates ("sepulchrum" means "grave or sarcophagus" in Latin). Write a structural formula for **C** and propose the reaction  $\text{B} \rightarrow \text{C}$  mechanism.

### Problem 5 – EQUIL – Chemical equilibrium

The vessel with a volume of  $1200\text{ cm}^3$  was vacuumed and filled with nitrogen monoxide up to pressure  $180.0\text{ mm Hg}$  at  $297\text{ K}$ . Then the gas was frozen, and  $720.0\text{ mg}$  bromine was added to the vessel. The temperature was raised to  $335\text{ K}$ . After the equilibrium was reached, the pressure in the vessel was  $230.0\text{ mm Hg}$ .

- Write the equation for the chemical reaction.
- Calculate the equilibrium constant  $K_p$  for the nitrosyl bromide decomposition (the vessel volume does not change with the temperature).
- How does the pressure influence the equilibrium state?
- Calculate the amount of nitrogen oxide moles in the equilibrium mixture.

### Problem 6 – ELECTRO, EQUIL – Electrolysis

The aqueous solution containing ethanoic acid and sodium ethanoate was electrolyzed. The gases deliberated on Pt-electrodes were collected and purged through a concentrated KOH solution. It was established that during the electrolysis at STP, the mass of the KOH solution was increased by  $5.213\text{ g}$ .

- Write the equations for electrode reactions.
- Calculate the amounts ( $\text{mol dm}^{-3}$ ) of gases evolved at the anode and reacting and not reacting with KOH solution. The relative density of non-reacting gas against hydrogen is  $15.0$ .
- Calculate the consumed electrical energy (A h) if the yield of anodic reaction products by current was  $100\%$ .
- What was the electrolysis duration if the current was  $706\text{ mA}$ ? Calculate the mass of Cu deposited in a copper coulometer serially connected with an electrolyzer.
- Calculate the equilibrium potential when the ratio of ethanate concentrations is  $1 : 3$  and the hydrogen partial solution is  $1.0 \cdot 10^5\text{ Pa}$ .  $K_a(\text{CH}_3\text{COOH}) = 1.85 \cdot 10^{-5}$ .

## 13th BChO, 2005, Vilnius, Lithuania

### Problem 1 – INORG, STRUCT – Blue nitrogen

Dinitrogen trioxide  $\text{N}_2\text{O}_3$  is an unstable compound that exists in both molecular and ionic forms. On heating, it breaks down into more stable compounds.

a) Write the empirical formulas for the ions that can exist in solid  $\text{N}_2\text{O}_3$ .

b) Write the chemical equation for the decomposition of  $\text{N}_2\text{O}_3$ .

Dinitrogen trioxide gives an acidic solution when dissolved in water. After careful investigation, it was found that two isomeric compounds were present in the solution.

c) Draw the Lewis structures of the two compounds formed in the reaction of  $\text{N}_2\text{O}_3$  with water. Show the distribution of all valence electrons. Write the formal charges of the atoms if they are not equal to zero. Write the assumed valence angles in Lewis structures.

A solution of compound **A** was prepared by dissolving an unknown amount of  $\text{N}_2\text{O}_3$  in water. When the solution of compound **A** was treated with a solution of  $\text{FeSO}_4$  of equal volume (acidified with sulfuric acid),  $n_1$  moles of gas **B** were formed. Then, an excess acidified KI solution was added to the same solution. This produced  $n_2$  moles of gas **B** and a certain amount of a dark-colored substance **C** (assume that **C** is completely insoluble).

d) Write the equation of the reaction between  $\text{N}_2\text{O}_3$  and water and the equations of all the reactions that occur when substance **A** reacts with  $\text{FeSO}_4$  and excess acidified KI solution.

e) At room temperature, gas **B** is paramagnetic. At very low temperatures, it is diamagnetic. Show schematically what happens to gas **B** at low temperatures.

When  $n_2$  moles of compound **B** react with hot graphite, a mixture of non-flammable gases is formed. If this mixture reacts with a saturated  $\text{Ca}(\text{OH})_2$  solution, an insoluble compound **D** is formed. Compound **D** has a mass 3.00 times smaller than that of compound **C**.

f) Calculate the ratio of the molar concentrations of  $\text{FeSO}_4$  and **A** in the starting solution.

g)  $0.10 \text{ dm}^3$  of gas **B** ( $100.0^\circ\text{C}$ ,  $1.00 \text{ atm}$ ) was reacted with chlorine  $\text{Cl}_2$ . The product of this reaction was dissolved in water to give a  $1.00 \text{ dm}^3$  solution. What is the degree of dissociation of the oxygen-containing acid in this solution? ( $K_a = 7.1 \cdot 10^{-4}$ )

### Problem 2 – STRUCT – Display of complex chemicals

Complex **X** has been studied a lot recently because of its unusual physical properties which are generally only characteristic of organic compounds. Compounds with such properties are produced to the tune of several billion dollars per year. Even now, you can see such a substance in front of you. Compound **X** is usually obtained from complex compound **Y** by a ligand exchange reaction.

Compound **Y** is synthesized directly from metal **Z** in a reaction with a ligand. Compound **Y** contains 36.34% of metal **Z**.

a) Identify the metal **Z**.

b) Write the molecular formula of compound **Y**. Draw its structure and show the metal hybridization.

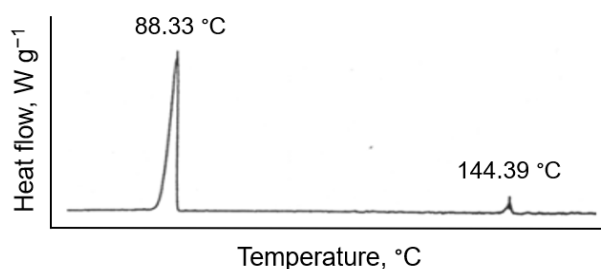
In order to carry out the ligand exchange reaction, compound **Y** is treated with hexanoic acid. This produces a gas and yields compound **X**, which contains 29.41% of metal **Z**. If  $2.00 \text{ g}$  of compound **X** is dissolved in  $100 \text{ g}$  of benzene, the melting point of benzene is reduced by

0.157 °C (the cryoscopic constant of benzene is 5.12 K kg mol<sup>-1</sup>). Compound **X** is diamagnetic and has no geometric isomers. If racemic 2-deuterohexanoic acid is used to prepare compound **X**, four compounds are obtained, two of which can be resolved to enantiomers.

- c) Write the molecular formula of compound **X**.
- d) Choose the correct answer explaining diamagnetism of compound **X**.
- ☐ **X** has an even number of electrons.
  - ☐ The ligands cause the *d*-orbitals of the metal to undergo energy splitting, resulting in a low spin complex.
  - ☐ A covalent bond is formed between the metal atoms.
  - ☐ **X** is unstable due to the repulsion of non-bonding *d* electron pairs of metal atoms.
- e) Based on the given data, write realistic structures for compound **X** and its analogues obtained in the reaction with deuterated hexanoic acid. Explain which orbitals are involved in which bond formation.

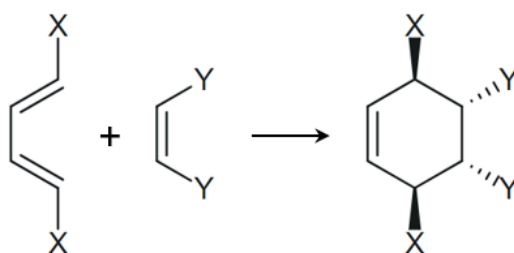
The unusual properties of compound **X** are determined by the interaction of its molecules, resulting in a ladder-like structure. The strongest evidence for these properties comes from differential scanning calorimetry (DSC) data, shown in the graph below. This graph shows the dependence between the heat absorbed by the sample and the temperature.

- f) Write the processes corresponding to the maxima in the DSC graph.  
What are the compounds with such properties called?

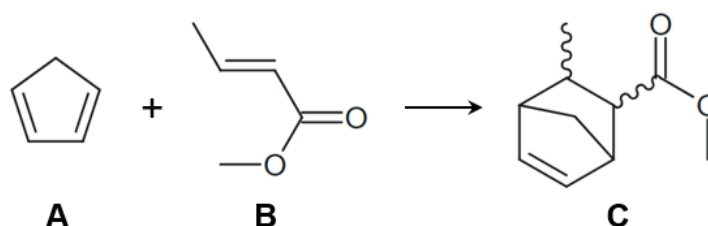


### Problem 3 – MECH, STEREO – A cycle of additions

Cycloadditions are very common in organic synthesis. The most important of these is the Diels–Alder reaction:

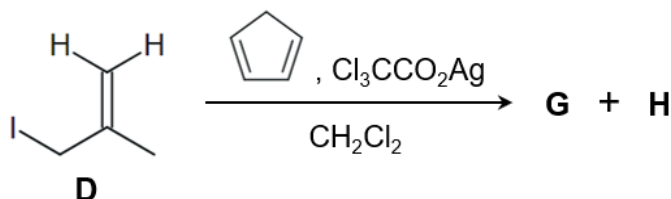


The reaction between cyclopentadiene **A** and methyl methacrylate **B** gives a mixture of isomers of compound **C**.

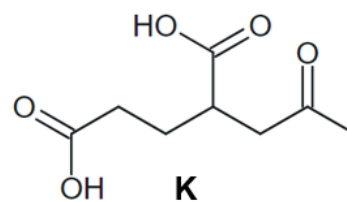


- Draw all the isomers (including stereoisomers) of compound **C** that are formed in this reaction.
- Mark all chiral centers with an asterisk and label each center according to the *R/S* nomenclature.
- Indicate which isomers of compound **C** are enantiomers and which are diastereomers.

Cyclopentadiene is involved in the following reaction:



Treatment of compound **G** with ozone and subsequent hydrolysis yields compound **I**. Ozonolysis of compound **H** yields compound **J**. Heating compound **I** in an acidic medium yields compound **K**. Analysis of compound **I** showed that it is a mixture of two enantiomers.



- Draw the structures of compounds **G**, **H**, **I**, and **J**.
- How many chiral centers are there in compounds **I** and **J**?
- How many stereoisomers are there for compound **J**?
- Write the mechanism of the reaction **D** → **G** + **H**

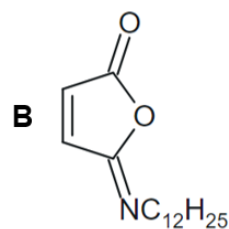
#### Problem 4 – SPECTRA, STEREO – A greener soap for polymers

As environmental requirements become more stringent, a new type of surfactant is used in emulsion polymerization to replace the well-known sodium alkyl sulfate. These new surfactants have a double bond that allows them to participate in the polymerization reaction and bind irreversibly to polymer particles. As a result, only a small amount of surfactant is consumed and does not end up in wastewater. Surfactant derivatives of (*Z*)-but-2-enoic acid (maleic acid) belong to such a class of compounds.

Surfactant **A** ( $C_{16}H_{28}NO_3$ ) is synthesized by the reaction of maleic anhydride with dodecylamine. Compound **A** has very low solubility in water, but its solubility increases with the addition of alkali, resulting in a good surfactant.

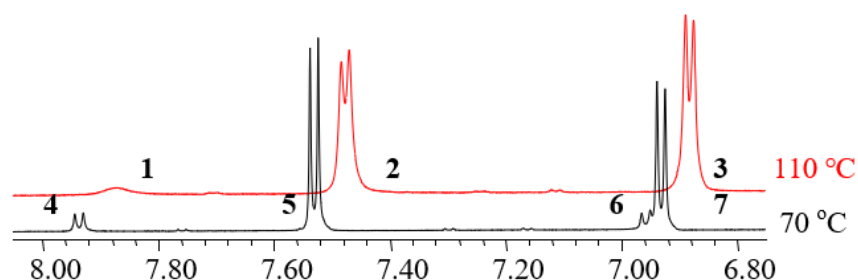
- Write the equations of the reactions involved.

Compound **A** can subsequently be used in the synthesis of various surfactants. The synthesis starts with the cyclization of compound **A**, resulting in compound **B**, which has two stereoisomers.



- Draw the structural formulae of these isomers and write the corresponding stereochemical descriptors.
- Which isomer (if any) would be dominant under equilibrium conditions? Indicate the reason for your choice.

The equilibrium between the isomers in the solution is achieved rapidly. Below is a fragment of the  $^1H$  NMR spectrum of compound **B** with signals corresponding to the double bond protons, and the table shows the relative intensities of the signals.



| T, °C     | 110 °C |       |       | 70 °C |       |       |
|-----------|--------|-------|-------|-------|-------|-------|
| Signal    | 1      | 2     | 3     | 4     | 5     | 6+7   |
| Rel. int. | 0.103  | 1.000 | 1.103 | 0.134 | 1.000 | 1.134 |

- d) Show the signals corresponding to each isomer (you do not need to determine the signal corresponding to a specific proton).
- e) Calculate the equilibrium constant between the two isomers at 70 °C and 110 °C. Also, calculate the reaction enthalpy of the transition between the isomers.

Compound **B** reacts readily with amines. Commonly, hydrophilic amines are used to produce surfactants, although the reaction also occurs with dodecylamine to give compound **C** ( $\text{C}_{28}\text{H}_{54}\text{N}_2\text{O}_2$ ). In the  $^1\text{H}$  NMR spectrum, there is only one sharp singlet corresponding to both double-bond protons.

- f) Write the reaction equation.

Compound **B** isomerizes to compound **D**, which has the same molecular formula but a significantly lower reactivity than **B**. It also has only one sharp singlet corresponding to both double-bond protons in the  $^1\text{H}$  NMR spectrum. Compound **B** has absorption maxima at  $1800\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$  in the IR spectrum, while compound **D** does not absorb at a lower wavenumber.

- g) Write the structural formula of compound **D**.

## Problem 5 - RADIO - An easy way to make a nuke

### Part I.

Irradiation of  $^{63}\text{Cu}$  with neutrons produces the radioactive isotope  $^{64}\text{Cu}$ , which has a spontaneous half-life of 12,700 hours. 61.0% of  $^{64}\text{Cu}$  atoms decay to  $^{64}\text{Zn}$  and 39.0% of  $^{64}\text{Cu}$  atoms decay to  $^{64}\text{Ni}$ .

- a) Write the reaction equations by filling in the gaps ( $^0\tilde{\nu}$  – neutrino;  $^0\nu$  – antineutrino):
- $^{63}\text{Cu} + ^1_0\text{n} \rightarrow ^{64}\text{Cu} + \dots$
  - $^{64}\text{Cu} \rightarrow ^{64}\text{Zn} + \dots + ^0\tilde{\nu}$
  - $^{64}\text{Cu} \rightarrow ^{64}\text{Ni} + \dots + ^0\nu$
- b) Calculate the percentage of the initial number of  $^{64}\text{Cu}$  atoms that make up the  $^{64}\text{Cu}$ ,  $^{64}\text{Ni}$ , and  $^{64}\text{Zn}$  atoms 25.4 hours after the start of the spontaneous decomposition of  $^{64}\text{Cu}$ .

## Part II.

Irradiation of  $^{238}\text{U}$  with neutrons produces the radioactive isotope  $^{239}\text{U}$ , which spontaneously decays in sequence to produce plutonium-239. The intermediate product of the decay of uranium-239 is  $^{239}\text{Np}$ .  $^{239}\text{U}$  has a half-life of 23.5 minutes and  $^{239}\text{Np}$  a half-life of 2.355 days. Plutonium-239 atoms can be considered stable.

- c) Finish the equations by filling in the gaps: i)  $^{238}\text{U} + {}^1_0\text{n} \rightarrow \dots + \gamma$ ; ii)  $^{239}\text{U} \rightarrow \dots + {}^0_{-1}\text{e}^- + {}^0_0\tilde{\nu}$ ;  
iii)  $^{239}\text{Np} \rightarrow ^{239}\text{Pu} + {}^0_{-1}\text{e}^- + \dots$

A radiochemically pure  $^{239}\text{U}$  sample was prepared to obtain  $^{239}\text{Pu}$ .

- d) Calculate the time  $t_{\text{max}}$  at which the amount of neptunium in the sample is maximal.  
e) Calculate the percentage of  $^{239}\text{U}$ ,  $^{239}\text{Np}$ , and  $^{239}\text{Pu}$  atoms relative to the initial number of  $^{239}\text{U}$  atoms after 170 min.

$$N(^{239}\text{Np}) = N(^{239}\text{U})_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad \frac{dN(^{239}\text{Np})}{dt} = N(^{239}\text{U})_0 \frac{k_1}{k_2 - k_1} (-k_1 e^{-k_1 t} + k_2 e^{-k_2 t})$$

## Problem 6 – THERMO – A water cycle

$V_1 = 10.00 \text{ dm}^3$  of water was placed in a container with perfectly elastic walls at a  $T_0 = 273.16 \text{ K}$  and an external pressure of  $1.000 \cdot 10^5 \text{ Pa}$ .

Stage 1. The water was converted to ice at 273.16 K, resulting in an increase in the volume of the container.

Stage 2. The ice was melted and the resulting water was heated to boiling point at  $0.900 \cdot 10^5 \text{ Pa}$  until it evaporated. Under these conditions, the volume of the vapor is  $V_2$ .

Stage 3. The vapor was compressed adiabatically to a volume  $V_3 = 10.00 \text{ m}^3$ .

Stage 4. The vapor was reversibly isothermally compressed to a volume  $V_4 = 5.00 \text{ m}^3$ .

Fill in the gaps in the table and make the necessary calculations.

|         | Temperature $T$<br>[K] | Volume $V$ [ $\text{m}^3$ ] | Thermodynamic<br>expansion-compression work $w$ [J] |
|---------|------------------------|-----------------------------|-----------------------------------------------------|
| Stage 1 | 273.16                 | 0.01000                     |                                                     |
| Stage 2 |                        |                             |                                                     |
| Stage 3 |                        | 10.00                       |                                                     |
| Stage 4 | 456.21                 | 5.00                        |                                                     |

The densities of water and ice at 0 °C are  $0.9987 \text{ g cm}^{-3}$  and  $0.917 \text{ g cm}^{-3}$  respectively. The boiling point of water is 100.00 °C (101325 Pa). The enthalpy of water evaporation is  $40.665 \text{ kJ mol}^{-1}$ , for water vapor  $\chi = 1.329$  ( $\chi = C_p/C_v$ ). By convention, the expansion work is considered negative.

## 14th BChO, 2006, Riga, Latvia

### Problem 1 – ABC, EQUIL – Versatile purple

Element **A** can be isolated from its compound **B** that occurs naturally in a mixture with Chile saltpeter. Firstly, compound **B** is treated with aqueous NaSH solution. Then, elemental **A** is extracted from the aqueous solution using xylene, which obtains a violet color. Element **A** also forms a blue-colored compound with a starch solution.

- a) Identify compounds **A** and **B**.
- b) Write the chemical formula of Chile saltpeter.
- c) Write the equation for the treatment of **B** with aqueous NaSH solution.

Element **A** is widely used in medicine. In 1986, after the Chernobyl nuclear power plant disaster, people living near the city of Pripjat were administered medicine containing **A**.

- d) Explain why it is necessary to take medicine containing element **A** during the radioactive nuclear fallout.

Element **A** is also used in electrical engineering. Many vehicles have some electric details containing small quantities of **A** and its tungsten salt.

- e) Write the equation of the reversible reaction taking place in the electric detail during its working cycle.

Upon the reaction of element **A** with wet red phosphorus, a colorless and toxic gas **C** is released. Gaseous compound **C** is a strong acid that protolyzes (dissociates into ions) completely in an aqueous medium.

- f) Write the equation depicting a reaction between element **A** and wet red phosphorus.
- g) 12.79 grams of **C** was dissolved in 1.00 dm<sup>3</sup> of water. Calculate the pH value of the aqueous solution of compound **C**.
- h) 1.00 cm<sup>3</sup> of the solution described in **g**) was diluted with 10.0 m<sup>3</sup> of pure distilled water. Calculate the pH value of the newly obtained solution.

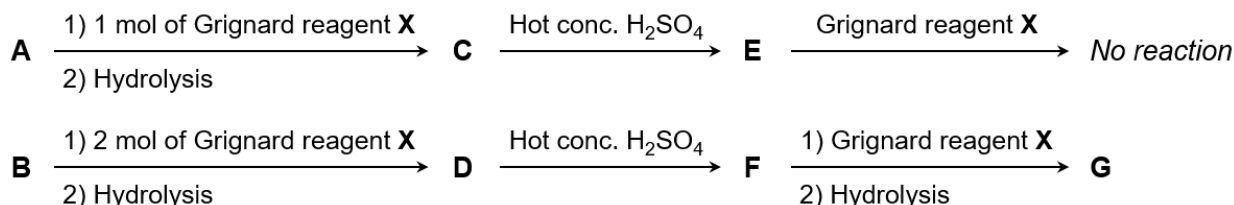
### Problem 2 – CRYSTAL – Grand Theft Balls

To keep the gold ration inviolable, the Schah ordered all the gold to be cast into the shape of spheres, 1 cm in diameter. Being very curious and having found out the richness of the master, the first Vizier decided to appropriate the part of treasures. To put his plan into action, he presented a metal box (75×75×75 cm) and Schah put 578813 gold balls into it in the only possible arrangement (arrangement **I**). Every day, Schah shook the box and checked whether it made any noise or not, meaning had anyone taken his treasures or not. The first Vizier replaced the balls (arrangement **II**) and put them in the right arrangement to keep them from thundering so Schah did not find out. So the first Vizier stole a large amount of gold, but it was not enough for him and he replaced the balls once more in such a way that they did not make any sound (arrangement **III**), having made a fool of his master.

- a) Calculate the packing arrangement efficiency of 578813 gold balls in the box. Make a conclusion about the type of arrangement **I**.
- b) Determine the position of atoms in arrangements **I–III**.
- c) Calculate the number of gold balls stolen by the first Vizier at the first and second time.

### Problem 3 – SPECTRA, SYNTH – One peak, two downhill pathways

Consider the following schemes:



The  $^1\text{H}$  NMR spectra of compounds **A–D** consist of just one singlet (after the addition of a drop of  $\text{D}_2\text{O}$ ), the  $^{13}\text{C}$  NMR spectra consist of just two lines. The  $^1\text{H}$  NMR spectra of compounds **E–G** consist of two singlets (after the addition of a drop of  $\text{D}_2\text{O}$ ). Combustion of compounds **A–G** yields only carbon dioxide and water.

- Determine compounds that fit this scheme and write all the reaction equations.
- Arrange compounds **A–D** and **X** in order of decreasing chemical shift of their only signal in the  $^1\text{H}$  NMR spectrum.

If the restriction of using 1 mol or 2 mol of the Grignard reagent in the first step of the reaction sequences is removed, one more starting compound fits the first scheme and another starting compound fits the second scheme. Using these compounds leads to the same reaction products **C** and **D**, respectively.

- Determine reaction products **C** and **D**.

### Problem 4 – CALC, STRUCT – How to set water on fire

The halogens combine with each other to form interhalogen compounds of four stoichiometries:  $\text{XY}$ ,  $\text{XY}_3$ ,  $\text{XY}_5$ , and  $\text{HY}_7$ , where **X** is the heavier halogen. In 1813–1814, J. L. Guy Lussac and H. Davy independently synthesized the first interhalogen compound  $\text{ICl}$ .

From the rotational spectrum of a gaseous substance, a rotational constant can be determined. This constant can be expressed in hertz Hz (notation  $B$ ) or in wave numbers (notation  $\bar{B}$ ). The rotational energy of a molecule can be described with the following formula:  $E_J = h \cdot B \cdot J(J+1)$ .

Rotational constant  $B = h/(8\pi I)$ , where  $I$  represents the moment of inertia  $I = \mu R^2$  and  $\mu$  is reduced mass. For diatomic molecules  $\mu = m_1 m_2 / (m_1 + m_2)$ , in which case  $R$  is the distance between two bonded atoms. The rotational constant of  $^{127}\text{I}^{37}\text{Cl}$  is  $3.28 \cdot 10^9$  Hz.

- Calculate bond length (in pm) in  $^{127}\text{I}^{37}\text{Cl}$  molecule.

Volatile molecular liquid  $\text{ClF}_3$  is one of the most reactive chemical compounds known. It spontaneously ignites asbestos, wood, and other building materials. This substance was used in incendiary bomb attacks in World War II.  $\text{ClF}_3$  reacts explosively with water and with most organic substances. Big amounts of this substance are used in nuclear fuel processing to produce  $\text{UF}_6$  (g):  $\text{U(s)} + 3\text{ClF}_3(\text{g}) \rightleftharpoons \text{UF}_6(\text{g}) + 3\text{ClF}(\text{g})$ .

- Write the Lewis structure for  $\text{ClF}_3$ .
- Sketch drawing that shows  $\text{ClF}_3$  molecular structure. Approximately predict bond angles and show them in your drawing.

In a closed evacuated container with excess solid uranium, some amount of  $\text{ClF}_3$  was injected. The initial concentration of this gaseous substance in the container was 0.0453 M.

When equilibrium in the container at 87 °C was established, the total pressure in the container was 1.69 atm.

**d)** Calculate the partial pressure of each gaseous substance in equilibrium.

Another interhalogen ClF reacts with AsF<sub>5</sub>:  $\text{AsF}_5 + 2\text{ClF} \rightarrow [\text{Cl}_2\text{F}]^+[\text{AsF}_6]^-$ .

**e)** Suggest the best Lewis structure for cation  $[\text{Cl}_2\text{F}]^+$ .

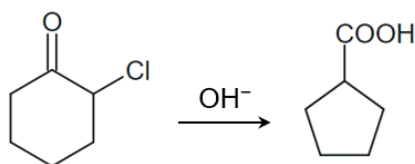
**f)** Choose the role of AsF<sub>5</sub> in this reaction: **i)** Lewis base or **ii)** Lewis acid.

Four interhalogen compounds between iodine and fluorine are known.

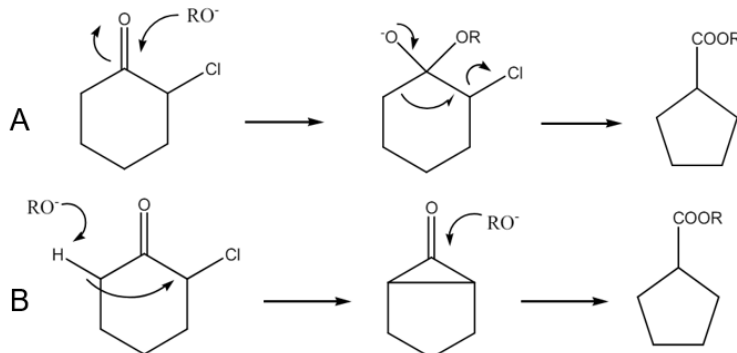
**g)** Which of these molecules is/are nonpolar: **i)** IF, **ii)** IF<sub>3</sub>, **iii)** IF<sub>5</sub>, **iv)** IF<sub>7</sub>.

### Problem 5 – MECH, SYNTH – Organic juggling

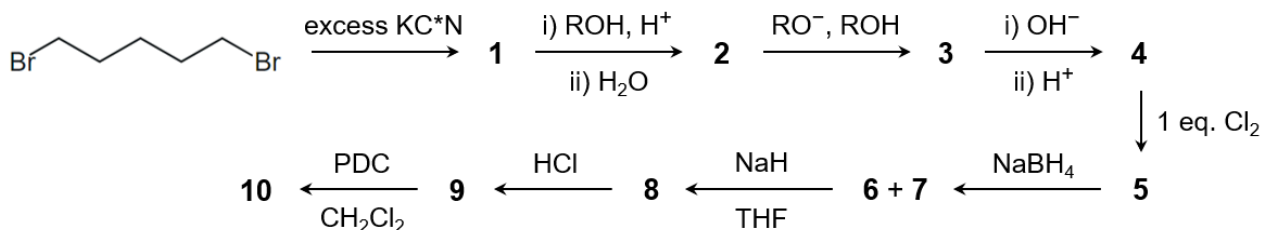
Molecular rearrangements are very important in organic chemistry not only as a versatile synthetic method but also being mechanistically very interesting. In the course of such reactions, functional groups usually undergo changes and atoms' connectivity order is altered. One of the most famous reactions of this kind is a Favorskii rearrangement, discovered more than a hundred years ago. A typical example of this reaction is shown below:



Favorskii rearrangement could also work with other nucleophiles such as alkoxide or cyanide ions. Two alternative mechanisms, A and B, have been proposed for this reaction:



In order to establish the real mechanism, a substrate with a radioactive carbon <sup>14</sup>C label was synthesized according to the scheme:



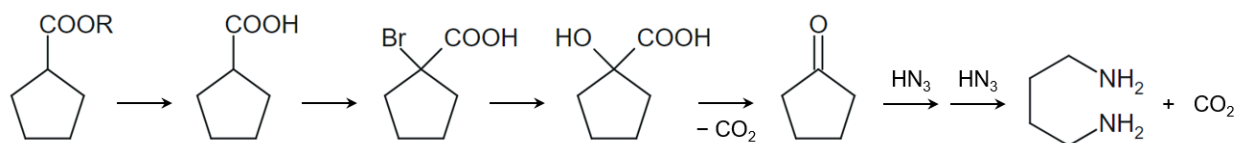
**a)** Draw the structural formulas of compounds **1–10** and denote <sup>14</sup>C atom with “\*.”

**b)** After the reduction of **5**, two isomeric compounds, **6** and **7**, were obtained. Only one of them, compound **7**, reacts further to give a compound **8**. Show stereochemical formulas of **6** and **7** and write the reaction mechanism with NaH.

The reaction of **10** with NaOMe affords Favorskii rearrangement product **11**.

- c) Show the place of the radioactive label and its relative intensity (radioactivity) in compound **11** according to mechanisms **A** and **B**.

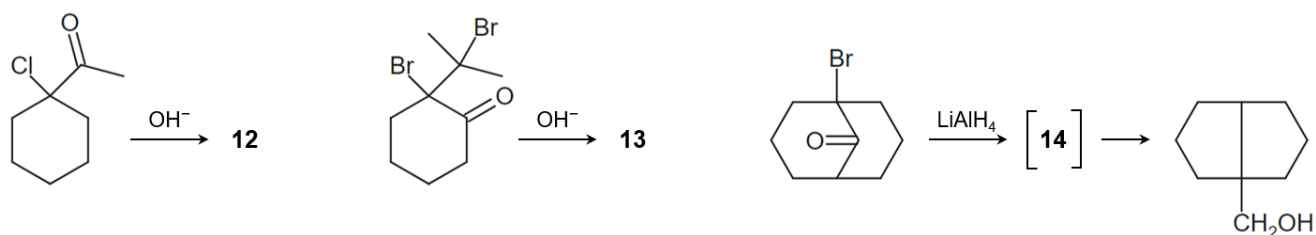
The product **11** was further degraded as shown below:



- d) It was shown that the total radioactivity of all degradation's gaseous products is 25% less than that of a starting ester. Which mechanism explains this fact?

There are a number of reactions that proceed via the Favorskii-type mechanism.

- e) Draw the structure of compounds **12–14** and the reasonable mechanisms of its formation. The compound **13** has a strong vibrational band at  $1670\text{ cm}^{-1}$ .



- f) What are the possible by-products when  $\alpha$ -haloketones react under Favorskii reaction conditions?

### Problem 6 – EQUIL, THERMO – Killer lake

Nyos is a low-activity volcanic lake. It is grievously known as a killer lake after a disaster happened in 1896 when the release of  $\text{CO}_2$  gas from the lake's depths caused the death of 1746 people. According to one of the hypotheses, cold tropical rain cooled the "surface layer" (50 meters), which fell 130 meters down, displaced "deep water" and disturbed the equilibrium. As a result, the lake "has exploded" like a bottle of champagne.

|                    | $\text{CO}_2$ (g) | $\text{H}_2\text{CO}_3$ (aq) | $\text{H}_2\text{O}$ (l) |
|--------------------|-------------------|------------------------------|--------------------------|
| $\Delta H_f^\circ$ | -393.5            | -699.0                       | -285.8                   |
| $\Delta S_f^\circ$ | 213.8             | 190.0                        | 70.1                     |

Assume that the lake looks like a cylinder with a bottom surface area of  $1.20\text{ km}^2$  and a height (depth) of 120 meters. The bottom of the lake is composed of  $\text{FeCO}_3$ , which is in equilibrium with  $\text{CO}_2$  via dissolution. It is also known that the "surface-layer" water (50 meters) does not mix with the deeper layers; temperature at 50–180 meters depth approximately equals  $23^\circ\text{C}$ .  $K_{a1}(\text{H}_2\text{CO}_3) = 3.57 \cdot 10^{-7}$ ,  $K_{a2}(\text{H}_2\text{CO}_3) = 4.40 \cdot 10^{-11}$ ,  $K_{sp}(\text{FeCO}_3) = 5.91 \cdot 10^{-11}$ .

- Calculate the constants  $K_H = [\text{H}_2\text{CO}_3(\text{aq})]/p(\text{CO}_2(\text{g}))$  value at  $23^\circ\text{C}$ .
- Calculate the pH at **i)** 50 and **ii)** 180 meters depth.
- Determine the maximum solubility of  $\text{CO}_2$  at **i)** 50 and **ii)** 180 meters depth.
- Assuming the linear dependence of concentration on depth (50-180 meters), evaluate the maximum quantity, mass, and volume at  $30^\circ\text{C}$  of  $\text{CO}_2$  that could be emitted from the lake.

## 15th BChO, 2007, Tartu, Estonia

### Problem 1 – THERMO – Polar winter in Antarctic

Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions that cause the Antarctic ozone hole. Worsnop et al. have measured thermodynamic parameters for the sublimation of nitric acid mono-, di- and trihydrates at 220 K:

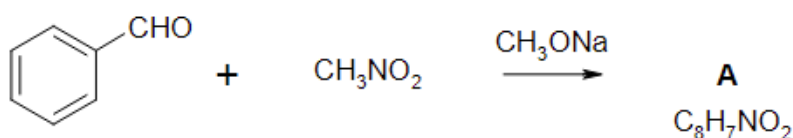
|                                                                                                                       | $\Delta G_r^\circ$ [kJ mol <sup>-1</sup> ] | $\Delta H_r^\circ$ [kJ mol <sup>-1</sup> ] |
|-----------------------------------------------------------------------------------------------------------------------|--------------------------------------------|--------------------------------------------|
| $\text{HNO}_3 \cdot \text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + \text{H}_2\text{O}(\text{g})$   | 46.2                                       | 127                                        |
| $\text{HNO}_3 \cdot 2\text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ | 69.4                                       | 188                                        |
| $\text{HNO}_3 \cdot 3\text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + 3\text{H}_2\text{O}(\text{g})$ | 93.2                                       | 237                                        |

- Calculate  $\Delta G_r^\circ$  at 190 K (the conditions of the polar winter stratosphere). Assume that  $\Delta H_r^\circ$  and  $\Delta S_r^\circ$  do not depend on temperature.
- Explain which hydrate is thermodynamically most stable at 190 K if  $p(\text{H}_2\text{O}) = 1.3 \cdot 10^{-2}$  Pa and  $p(\text{HNO}_3) = 4.1 \cdot 10^{-5}$  Pa?

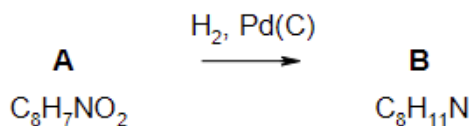
### Problem 2 – SYNTH – Synthesis of bicyclic compound

The bicyclic skeleton of compound **X** appears in many naturally occurring alkaloids. At the heart of the synthesis of **X** is the nitro-aldol reaction between benzaldehyde and nitromethane.

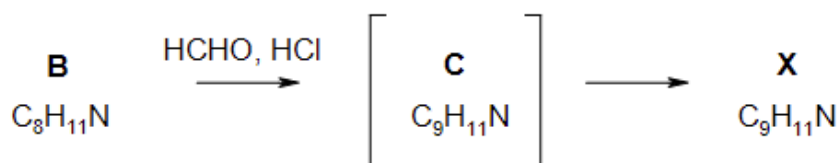
- Explain why nitromethane is acidic enough for an aldol reaction to occur.
- Under basic reaction conditions, benzaldehyde and nitromethane in nitro-aldol reaction give compound **A** ( $\text{C}_8\text{H}_7\text{NO}_2$ ). Based on the knowledge of the classical aldol reaction, suggest the structure of **A**.



- A** is fully reduced with hydrogen using palladium on charcoal as a catalyst to give **B** ( $\text{C}_8\text{H}_{11}\text{N}$ ). **B** is fairly basic and readily forms salts with acids. Draw the structure of compound **B**.

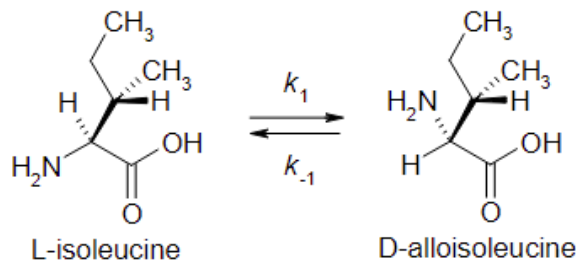


- B**, under acidic reaction conditions, reacts with formaldehyde to give final compound **X**. This transformation proceeds through the formation of **C** ( $\text{C}_9\text{H}_{11}\text{N}$ ), which under these reaction conditions undergoes cyclization to form bicyclic **X** ( $\text{C}_9\text{H}_{11}\text{N}$ ). **X** is fairly basic and is usually isolated in the form of a salt. Using your knowledge of the reactivity of carbonyl compounds, suggest structures of **C** and **X**.



### Problem 3 – KINETICS – Isoleucine dating

The isomerization rate of isoleucine in fossilized bone can be used as an indication of the average temperature of the sample storage.



At 20 °C, this reaction has a half-life of 125000 years, and its activation energy is 139.7 kJ mol<sup>-1</sup>. After a very long time, the ratio *allo/iso* reaches an equilibrium value of 1.38. You may assume that this equilibrium constant does not depend on temperature.

The time dependence of concentration for a reversible reaction is given by the equation:

$$\ln \left( \frac{[A] - [A]_{\text{eq}}}{[A]_0 - [A]_{\text{eq}}} \right) = -(k_1 + k_{-1})t$$

For a hippopotamus *mandible* that lived near a warm spring in South Africa, the present *allo/iso* ratio in bones is 0.42. Radiocarbon dating, which is temperature independent, determined the age of the hippo tooth, which was 38600 years.

- Assuming that no *allo* was present initially, determine constants for forward and reverse reactions and overall isomerization constant ( $k_1 + k_{-1}$ ).
- Calculate the average conservation temperature of the hippopotamus remains in the soil.

### Problem 4 – CRYSTAL – Goblin's element

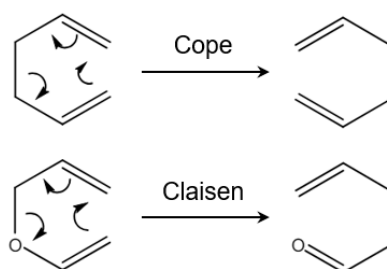
Metal **X** was discovered in 1735. Its name is derived from a German word meaning “goblin” or “evil spirit”. A sample of metal **X** immersed in H<sub>2</sub>O weighs 13.031 g. Meanwhile, the weight of the same sample in CCl<sub>4</sub> is 12.046 g. The density of CCl<sub>4</sub> is 1.5940 g cm<sup>-3</sup>. Neutron diffraction is used to identify the metal **X**. The diffraction pattern is specific to the FCC structure, and the angle of reflection (2θ) from the (222) plane is 76.956°. The velocity of neutrons in the diffractometer is 3115.0 m s<sup>-1</sup>. The same sample is heated in the O<sub>2</sub> atmosphere until metal **X** has reacted completely. The product of the reaction is compound **A** containing 26.577% oxygen (by mass). All of compound **A** reacts with dilute HCl releasing 1.0298 dm<sup>3</sup> of O<sub>2</sub> at 25.00 °C temperature and 100.0 kPa pressure, giving salt **B** and water only. Compound **B** is dissolved in an aqueous solution containing Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> ions. Complex ion **C** forms as one of the products. The formula of ion **C** is [XCl<sub>2</sub>Br<sub>2</sub>I<sub>2</sub>]<sup>n-</sup> and it is paramagnetic. Complex carbonyl compound **D** is prepared by heating metal **X** under high pressure of carbon monoxide. The formula of compound **D** is [X<sub>2</sub>(CO)<sub>8</sub>] and it is diamagnetic. Both atoms of metal **X** are equivalent in the structure of compound **D**. A CO molecule donates a pair of electrons to form a single bond only, but not all the CO molecules are equivalent in the structure of compound **D**.

- Calculate the density of metal **X** in g cm<sup>-3</sup>.
- Calculate the unit cell parameter (*a*) of metal **X** in pm.
- Calculate the molar mass of metal **X** in g mol<sup>-1</sup>. What element is metal **X**?
- Write a chemical formula of compound **A**.

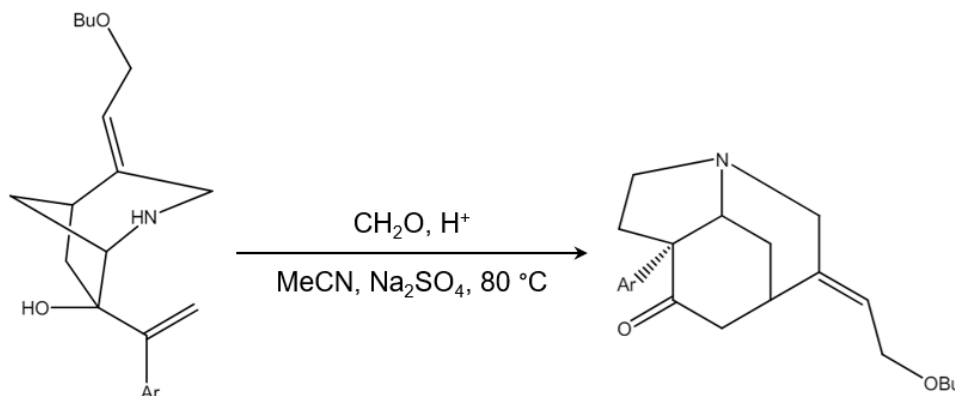
- e) Write the equation of the reaction of compound **A** with diluted HCl.
- f) Sketch the spatial structures of all possible isomers (including structural, geometrical and optical) of ion **C**.
- g) Count the number of unpaired electrons in ion **C**. Consider halogenides as weak field ligands.
- h) Sketch the spatial structure of compound **D**.

### Problem 5 – MECH – Sigmatropic rearrangement

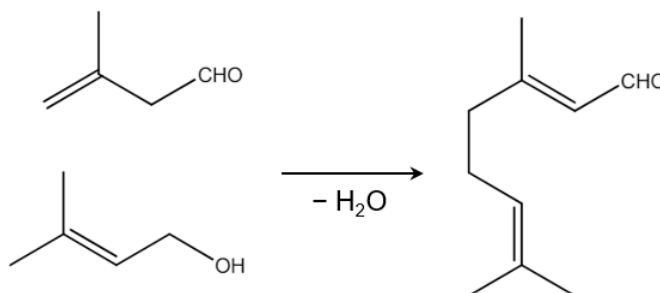
Pericyclic reactions are concerted processes that occur through a cyclic transition state in which more than one bond is formed or broken within the cycle. The so-called sigmatropic rearrangements constitute a large group of pericyclic reactions. Of all the sigmatropic rearrangements, the [3,3]-sigmatropic rearrangement has been used most in organic synthesis. The reaction involves the transformation of 1,5-dienes and in an all-carbon system, it is known as the Cope rearrangement, whereas with an allyl vinyl ether, the reaction is termed a Claisen rearrangement. Examples of these reactions are given below:



The sigmatropic rearrangement has been used in many syntheses of complex molecules and has industrial applications as well. The key step in the synthesis of the alkaloid strychnine was made by use of this chemistry:



The chemical company BASF manufactures citral (intermediate in the synthesis of vitamin A) by the remarkable synthesis shown below:



Write the reaction mechanism (except for the loss of water in example 2) and possible intermediates for both reactions. *Hint: by treating acetaldehyde with ethanol under the same reaction conditions as in example 2, vinyl ethyl ether could be obtained.*

### Problem 6 – ABC, CRYSTAL, THERMO – Dolomite

One of the most widespread minerals is dolomite, which in huge amounts can also be found in the Baltic States. Dolomite contains two metallic elements, **A** and **B**. Metal **A** crystallizes in a hexagonal close-packed atomic structure (unit cell parameters:  $a = 3.2094 \text{ \AA}$ ,  $b = 3.2094 \text{ \AA}$ ,  $c = 5.2108 \text{ \AA}$  and  $\gamma = 120^\circ$ ), while metal **B** crystallizes in a cubic close-packed atomic structure (unit cell parameter:  $a = 5.5884 \text{ \AA}$ ).

- Determine metallic elements **A** and **B**.
- Calculate the atomic radii for atoms of **A** and **B**.
- Calculate by how many percent the initial atomic radius of both metals decreases when they are ionized into their corresponding ions. It is known that the oxides of both elements have sodium chloride crystal structure and the radius of anion is  $1.28 \text{ \AA}$ . The unit cell parameters for both oxides are  $4.213 \text{ \AA}$  and  $4.811 \text{ \AA}$ , respectively.

Industrially, metal **A** can be produced from seawater. To purify chloride of metal **A** from other salts, hydroxide of metal **B** is added to seawater. The obtained white precipitate is dissolved in hydrochloric acid and evaporated till metal **A** salt hydrate forms. Then, the hydrate is heated and salt is melted and electrolyzed.

- Write equations of all the chemical reactions described above and calculate the time for electrolysis which has to be performed to isolate 1.0 tons of metal **A**. The current intensity is 9.0 kA. Faraday constant  $F = 96485 \text{ C mol}^{-1}$ .

One of the students' favorite reactions is burning metal **A** in the air. The reaction produces a huge amount of UV light and two binary compounds, one of which is an oxide of metal **A**.

- Write equations of the described reactions.

Metal **A** is also used in the army to prepare food in field conditions. To heat food wrapped in aluminum foil, a special heater, which contains  $30 \text{ cm}^3$  water, is used. The heating material is a composite, where powder of metal **A** and iron are associated in a matrix of high-density polyethylene. In the presence of chloride ions, metal **A** reacts with water, forming hydroxide and hydrogen, which is available for burning to obtain extra heat.

- Using thermodynamic constants shown below, calculate the minimum mass of element **A**, which is needed to heat  $1.0 \text{ dm}^3$  of water from  $20^\circ \text{C}$  to  $100^\circ \text{C}$ . Assume that all chemical reactions proceed under standard conditions.

| Compounds                       | $\Delta H_{f,298} [\text{kJ mol}^{-1}]$ | $\Delta S^\circ [\text{J mol}^{-1} \text{K}^{-1}]$ | $C_p [\text{J mol}^{-1} \text{K}^{-1}]$ |
|---------------------------------|-----------------------------------------|----------------------------------------------------|-----------------------------------------|
| $\text{H}_2 (\text{g})$         | 0                                       | 130.52                                             | 28.83                                   |
| $\text{H}_2\text{O} (\text{g})$ | -241.81                                 | 188.72                                             | 33.61                                   |
| $\text{H}_2\text{O} (\text{l})$ | -285.83                                 | 69.85                                              | 75.30                                   |
| Metal <b>A</b> (s)              | 0                                       | 32.68                                              | 24.89                                   |
| Hydroxide of metal <b>A</b> (s) | -924.66                                 | 63.18                                              | 76.99                                   |

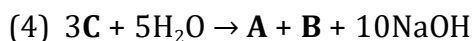
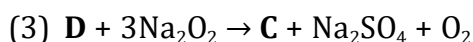
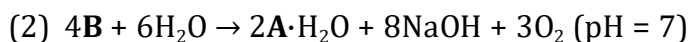
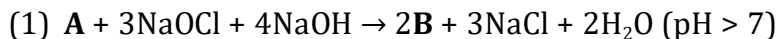
- Metal **A** hydroxide, which forms in the reaction, is slightly soluble. Calculate the solubility ( $\text{mg dm}^{-3}$ ) of the mentioned hydroxide in distilled water.  $pK_{sp} = 11.25$ .

## 16th BChO, 2008, Vilnius, Lithuania

### Problem 1 – ABC, CRYSTAL – A mysterious substance

#### Part I.

Compound **A** is an oxide and compound **D** is a salt (sulfate). Using chemical equations and data given below, identify compounds **A–D**. Support your answers with calculations.



The color of the solution, containing compound **B**, is deep red-purple. If 0.10 g of compound **C** is dissolved in 100 cm<sup>3</sup> distilled water, the pH of the solution becomes 12.2 (**B** fully dissociates).

a) Write chemical formulas for compounds **A–D**.

#### Part II.

Wustite is a mineral form of iron(II) oxide. It is a non-stoichiometric compound as it is always Fe-deficient and is formulated as Fe<sub>1-x</sub>O (0.04 < x < 0.11). To counter the charge imbalance caused by Fe<sup>2+</sup> vacancies, some Fe<sup>3+</sup> ions are present in the lattice.

b) How many Fe<sup>3+</sup> ions are needed to counter one Fe<sup>2+</sup> ion vacancy?

c) Express the ratio  $n(\text{Fe}^{3+})/n(\text{Fe}^{2+})$  as a function of x.

Iron atoms in wustite form a face-centered-cubic lattice. The oxygen atoms occupy octahedral gaps between iron atoms.

d) Calculate the lattice constant and the distance between the two closest iron atoms (in Å) in wustite (Fe<sub>0.925</sub>O, density 6.02 g cm<sup>-3</sup>).

e) Calculate the distance between the two closest oxygen atoms in wustite.

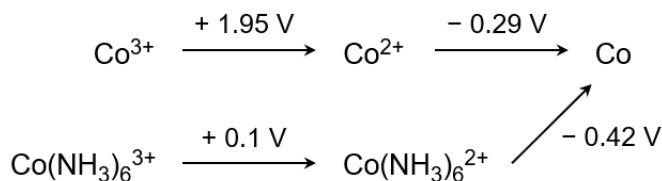
f) Express density as a function of x, assuming that the lattice parameter does not change in the given interval of x.

### Problem 2 – ELECTRO, STRUCT – Cobalt-Chameleon

Cobalt is one of the most well-known metals. Since ancient times, cobalt salts have been used to color glass and make enamels. Various cobalt compounds were found in sculptures of ancient Egypt, Persian jewelry, and among the remains of the city of Pompey.

For more than 100 years, scientists have been interested in complex cobalt salts, in which the oxidation state of the metal is +3 rather than the more common +2.

a) Using the given Latimer diagram of cobalt, prove mathematically whether it is possible for cobalt(II) to undergo disproportionation in acidic media. Explain why the more stable oxidation state for complex cobalt ions is +3, whereas for classical cobalt ions it is +2.



At the end of the 19<sup>th</sup> century, investigations of cobalt complexes with amines gained high popularity, for example, compounds with a general formula  $[\text{Co}(\text{NH}_3)_{6-x}\text{Cl}_x]\text{Cl}_{3-x}$ , where  $x$  is a small natural number.

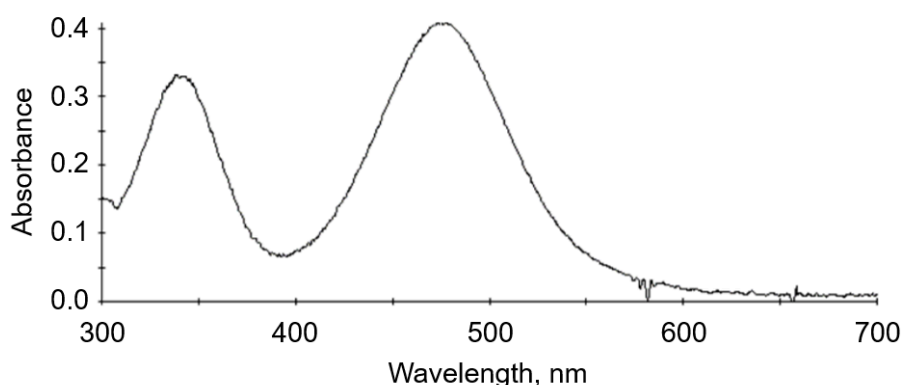
- b) Write all possible isomers for compounds with this general formula, assuming that the coordination number of cobalt is 6 and the oxidation state is +3.
- c) The stability of complex ions can be evaluated based on electrochemical measurements. Using the given data, calculate the stability constants for cobalt(II) and cobalt(III) complexes with amines.

At the beginning of the 20<sup>th</sup> century, complexes of cobalt with organic molecules were widely investigated, for example, the well-known cobalt complex with ethylenediamine (en).

- d) Write the formula of this compound, provide the structures of all possible isomers and explain the difference in physical properties of these isomers. What type of ligands does ethylene diamine belong to? In this regard, what is its difference from ammonia and chloride anion?

It is well-known that  $d$ -orbitals can be split into numerous sublevels by the ligand field.

- e) Provide a diagram of split  $d$ -orbitals of the cobalt in  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  complex. For every energy level, give the index of the  $d$ -orbital from which the new orbital was formed. Explain your choice.
- f) Based on the spectrum provided below, calculate the energy difference between  $d$ -orbitals.



### Problem 3 – KINETICS – Negative activation energy!?

According to the results of the investigation, the direct reaction  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  has a negative apparent activation energy.

|   | $[\text{NO}], [\text{M}]$ | $[\text{O}_2], [\text{M}]$ | $r = d[\text{NO}]/dt, [\text{M s}^{-1}]$ |
|---|---------------------------|----------------------------|------------------------------------------|
| 1 | 0.010                     | 0.010                      | $2.5 \cdot 10^{-5}$                      |
| 2 | 0.020                     | 0.010                      | $1.0 \cdot 10^{-4}$                      |
| 3 | 0.010                     | 0.020                      | $5.0 \cdot 10^{-5}$                      |

- a) Determine the partial reaction orders based on the data given in the table.
- b) Calculate the rate constant  $k$ .

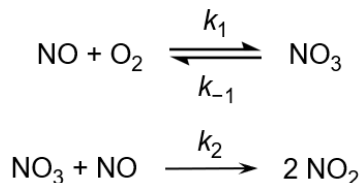
The rate constant ( $k'$ ) of the reverse reaction at 327 °C and 372 °C is 83.9 and 407  $\text{M}^{-1} \text{s}^{-1}$ .

- c) Calculate the activation energy of the reverse reaction ( $E_a'$ ).
- d) Calculate the reaction enthalpy  $\Delta H_r$  according to the data given in the table.

|                                                      | NO    | NO <sub>2</sub> |
|------------------------------------------------------|-------|-----------------|
| $\Delta H_f$ [kJ mol <sup>-1</sup> K <sup>-1</sup> ] | 90.29 | 33.10           |

- e) Sketch the reaction energy diagram in the coordinates energy vs reaction coordinate, and mark  $E_a$ ,  $E_a'$ ,  $\Delta H_r$  on it.

Based on experimental data, the following reaction mechanism was suggested:



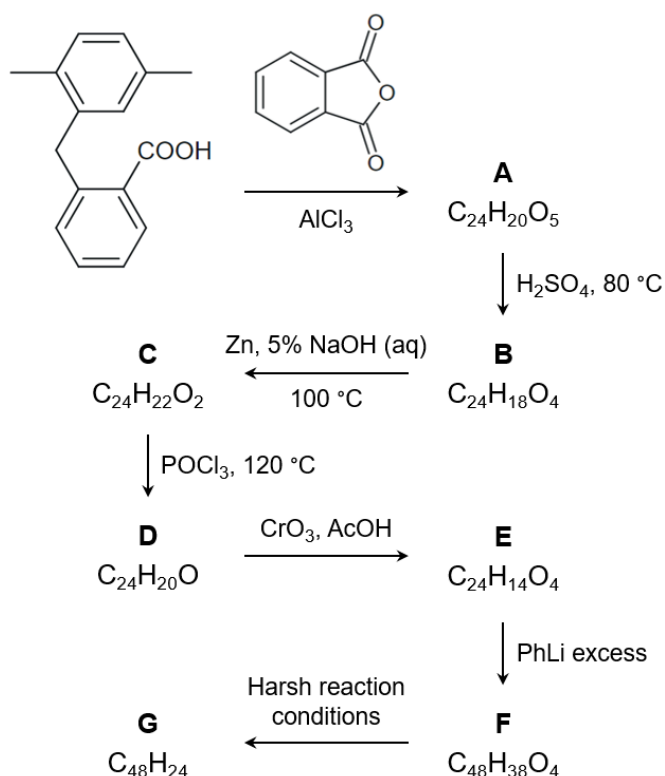
- f) Derive the rate equation.
- g) Decide whether the suggested mechanism supports kinetic and thermodynamic data. Explain why the value of the apparent activation energy is less than zero and the dependence of the rate constant of a direct reaction on temperature

#### Problem 4 – SYNTH – An elegant compound of the last century

The target compound **G** in this problem is a polycyclic aromatic hydrocarbon. It was first synthesized in 1964 by Professor Erich Clar at the University of Glasgow. At the time of the synthesis, this type of compound was associated with the investigation of theoretical problems of aromaticity. In modern times, with the rapid developments in the field of nanoscience, these compounds find their use as novel materials used as liquid crystals and synthetic “metals”.

Draw the structural formulas of compounds **A–G** in the scheme provided below. Pay particular attention to the following notes:

- (1) Dicarboxylic acid **A** is the major isomer of all the possible products in this acylation reaction.
- (2) In compound **B**, there is only one new ring formed.
- (3) Compound **D** is pentacyclic.
- (4) The <sup>1</sup>H NMR spectrum of compound **E** has three sets of signals with relative intensities of 1 : 1 : 3.
- (5) The last chemical transformation is lousy in terms of chemical yield but it does provide an elegant structure **G**.



### Problem 5 – APPLIED, ELECTRO, THERMO – Li-ion battery

Video cameras, smartphones, laptops, etc, require a portable power source – batteries. The ideal battery is reliable, lightweight, long-lasting, stable, and environmentally safe. A battery consists of anode, cathode, and electrolyte.

| Metal                        | Li    | Ca    | Al    | Cd    |
|------------------------------|-------|-------|-------|-------|
| $\rho$ [g cm <sup>-3</sup> ] | 0.53  | 1.54  | 2.70  | 8.64  |
| $E^\circ$ [V]                | -3.04 | -2.87 | -1.66 | -0.40 |

The table provides density and standard potential for metals that are usually used as anodes.

- Write the half-reactions of these metals.
- Calculate the electrochemical capacity of these metals. The electrochemical capacity is defined as the maximal quantity of electric charge produced per 1 g of metal (A h g<sup>-1</sup>).
- Which metal is most suitable for the battery anode? Provide two reasons.

The standard reduction potential of water is -0.83 V.

- Write the reduction reaction of water.
- Which of the listed metals react with water at room temperature? Write the reaction equations and explain the answer.
- Calculate the equilibrium constant for the reaction between water and lithium. Is the process spontaneous? Provide an explanation.

The ions solvate in the electrolyte during the oxidation of the metal. The formed solution must be a good electrolyte. Lithium hexafluorophosphate(V) is added to the solvent to increase its electrical conductivity.

- Which of the solvents: (a) water, (b) ethanol, (c) dimethyl sulfoxide, (d) hexane is the most suitable for a lithium battery? Provide an explanation.

| Compounds          | Bi <sub>2</sub> O <sub>3</sub> | FeS <sub>2</sub> | LiCl | Li <sub>2</sub> O | Li <sub>2</sub> S | CuCl <sub>2</sub> |
|--------------------|--------------------------------|------------------|------|-------------------|-------------------|-------------------|
| $\Delta G_f^\circ$ | -493                           | -160             | -384 | -562              | -439              | -382              |

- Draw the spatial structures of dimethyl sulfoxide and lithium hexafluorophosphate(V) using the VSEPR model. Write the hybridization and partial charge of S and P atoms.

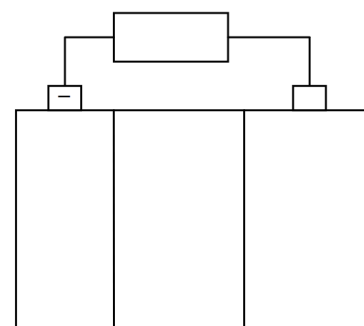
Sulfides, oxides and halogenides are used as materials for cathodes.

- Write the equation of the total reaction in the lithium battery if the cathode is (a) Bi<sub>2</sub>O<sub>3</sub>, (b) FeS<sub>2</sub>, (c) CuCl<sub>2</sub> and the metal will be released as an element. For which battery (a-c) is the maximum non-expansion work of the reaction largest?

FeS<sub>2</sub> was used as the cathode of the lithium battery and the electrolyte was LiPF<sub>6</sub> solvated in dimethyl sulfoxide.

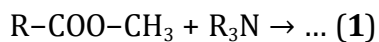
- Write the shorthand notation of the lithium battery. Write the cathodic half-reaction and calculate its standard potential.
- Rewrite on the block diagram of the lithium battery: Li, FeS<sub>2</sub>, lithium hexafluorophosphate(V), „+“, dimethyl sulfoxide, anode (A), cathode (K), electrolyte and engine. Mark the direction of the movement of electrons in the outer circuit.

- Which material should be in excess in the lithium battery? Why?



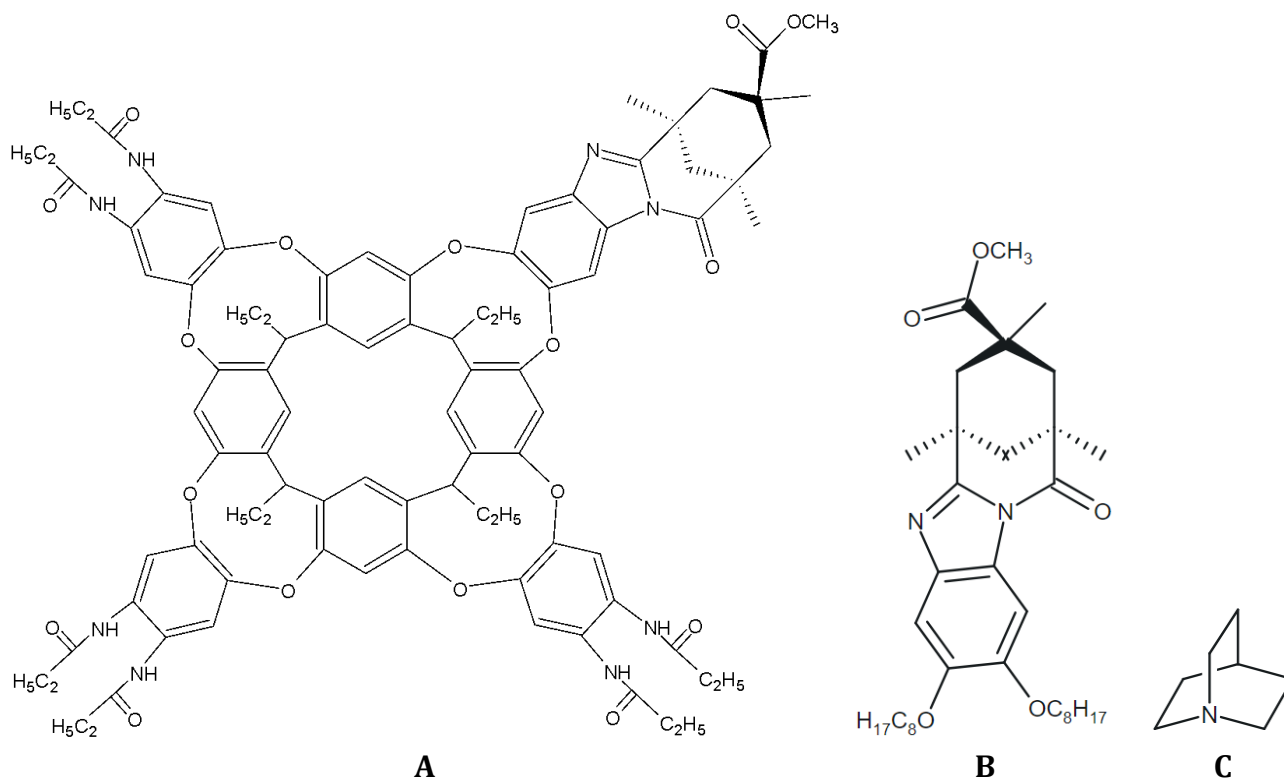
### Problem 6 – CALC, MECH, STEREO – Supramolecular basket

It is well known that carboxylic acid methyl esters react with tertiary amines:

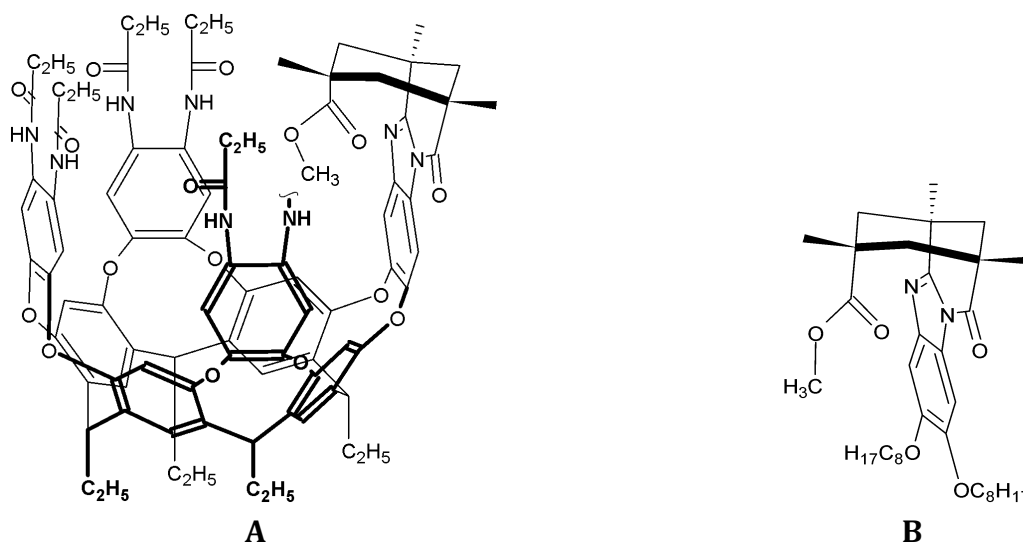


- a) Write the reaction products and the mechanism.
- b) The reaction is generally slow, taking hours to days. Why does **reaction 1** proceed faster in polar solvents like dimethylformamide than in non-polar ones like heptane?

Compounds **A** and **B** are esters, which react with quinuclidine **C** in the same manner as is shown in **reaction 1**. Despite the fact that atoms near ester groups in compounds **A** and **B** are exactly the same, the quinuclidine reaction with ester **A** in mesitylene (1,3,5-trimethylbenzene) completes in 3 minutes, however, the reaction of compound **B** and quinuclidine at the same conditions is so slow that it is practically not observed.

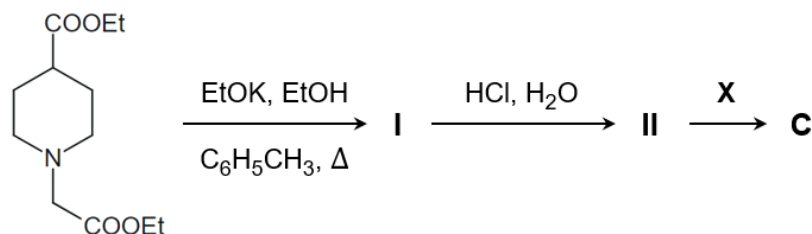


The three-dimensional structures of compounds **A** and **B** are as follows:



- c) Explain why ester **A** in mesitylene does not have a plain structure but has a cavitated shape.

- d) Complete the synthesis of quinuclidine identifying intermediate products **I** and **II**, write the mechanism of the formation of compound **I**, and give the reagent **X** in the last step. Draw the three-dimensional shape of quinuclidine **C**. Identify chiral atoms in structures **II** and **C**.



- e) Draw the three-dimensional structure of the transition complex of the reaction between ester **A** and quinuclidine and write a reaction product. (Draw schematically, don't waste your time keeping exact proportions and drawing every bond and atom. Show only the general shape of molecules, their location and the position of ester methyl and carboxyl atoms with respect to the quinuclidine nitrogen atom).
- f) It is calculated that the volume of the ester's **A** cavity is  $160 \text{ \AA}^3$ . Consider the shape of the cavity as a sphere, all the bonds in a quinuclidine molecule are  $1.2 \text{ \AA}$  and the radius of a hydrogen atom is  $1.2 \text{ \AA}$ . Estimate approximately the size of the quinuclidine molecule and calculate how many quinuclidine molecules can fit into the cavity of one "basket" of ester **A**.
- g) Calculate the quinuclidine concentration (M) in a cavity.
- h) When quinuclidine is mixed with ester **A** in chloroform (trichloromethane), the reaction is as slow as the reaction of quinuclidine with ester **B**. Explain this result.

**Problem 1 – KINETICS – Hydrolysis of pyrophosphate**

Let us take a look at the hydrolysis of pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ) by the enzyme. It is assumed that the concentration of pyrophosphate is much lower than the Michaelis constant; thus, the reaction is formally supposed to be first-order. At pH = 7 at 25 °C, the apparent first-order rate constant (relative to pyrophosphate total concentration) is  $k_7^* = 0.0010 \text{ s}^{-1}$ . The mechanism of the hydrolysis is as follows:  $\text{H}_2\text{P}_2\text{O}_7^{2-} \rightleftharpoons \text{HP}_2\text{O}_7^{3-} \rightleftharpoons \text{P}_2\text{O}_7^{4-} \rightarrow 2\text{HPO}_4^{2-}$  where  $\text{p}K_{\text{a}1} = 6.12$  and  $\text{p}K_{\text{a}2} = 8.95$  (1<sup>st</sup> and 2<sup>nd</sup> stages), and  $k$  is the true rate constant that does not depend on pH (3<sup>rd</sup> stage). It is assumed that acid dissociations are faster compared to hydrolysis.

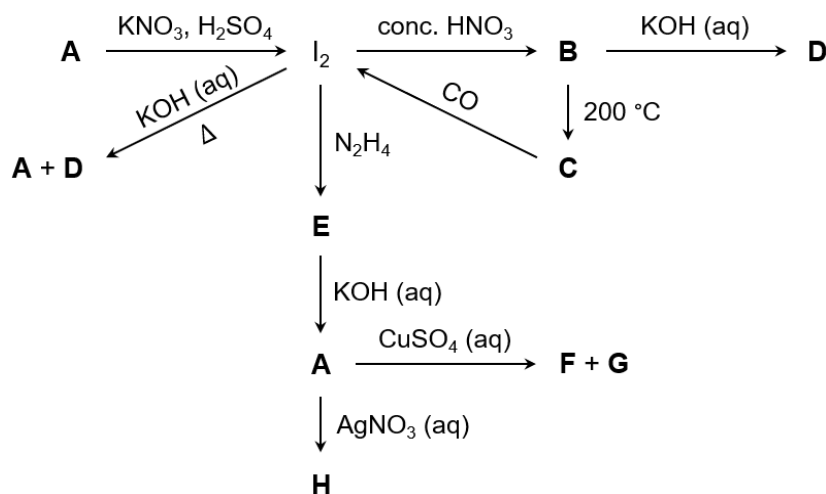
- Calculate the value of true rate constant  $k$  relative to  $[\text{P}_2\text{O}_7^{4-}]$ .
- Calculate the values of apparent rate constants  $k_6^*$  and  $k_8^*$  at pH = 6 and 8.

**Problem 2 – ABC, CALC – Iodine and polyiodides**

Iodine was discovered in 1811 by the French chemist Courtois during the process of manufacturing potassium nitrate, with which he supplied Napoleon's armies. While washing seaweed ashes with sulfuric acid, he noticed violet fumes that condensed on his copper equipment and caused corrosion. Below, you see a diagram that represents some iodine chemistry. Only iodine-containing substances **A** to **H** are indicated in this diagram. In some cases, it might be more reaction products.

- Write chemical formulas of compounds **A–H**.

- Write chemical equations from the scheme:



One of the remarkable features of iodine is the possibility of forming so-called polyiodide ions. One of the simplest polyiodide ions is present in the tincture of iodine. This tincture is prepared by dissolving iodine in a KI solution. In this mixture, triiodide ions  $\text{I}_3^-$  are present. Until now, anions of the form  $\text{I}_2^-$  to  $\text{I}_{29}^{3-}$  have been established.

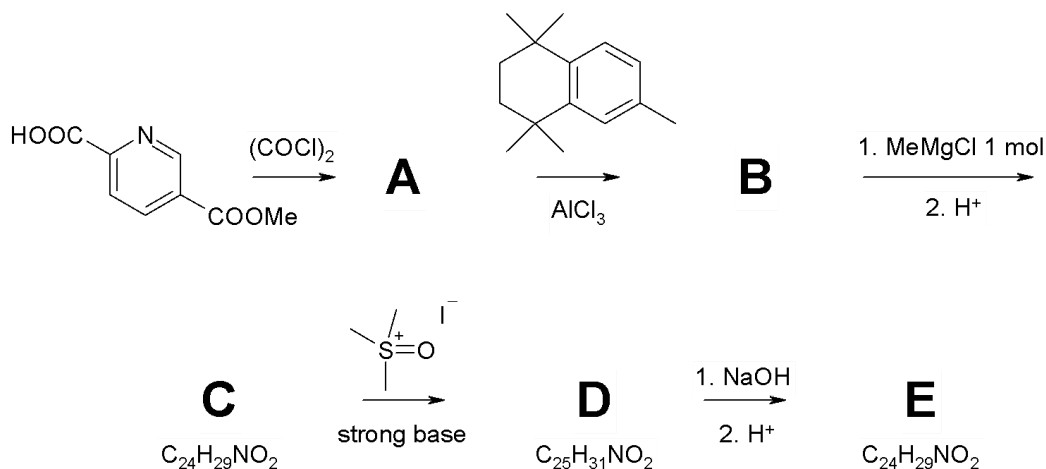
- Write Lewis structures of  $\text{I}_3^-$  and  $\text{I}_5^-$  ions with correct geometry.

Polyiodides are not very stable compounds, but large cations with high symmetry can be used to obtain thermally stable polyiodides. In the laboratory, polyiodide  $\text{R}_4\text{NI}_{2x+1}$  ( $x = 1, 2, 3, 4, \dots$ ) large cations were investigated. R is a radical of alkane. For titration of 0.219 g of  $\text{R}_4\text{NI}_{2x+1}$ ,  $10.23 \text{ cm}^3$  of 0.112 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution was consumed.

- Determine the molecular formula of  $\text{R}_4\text{NI}_{2x+1}$ . Show your calculations.

### Problem 3 – MECH, SYNTH – Small rings fighting diabetes

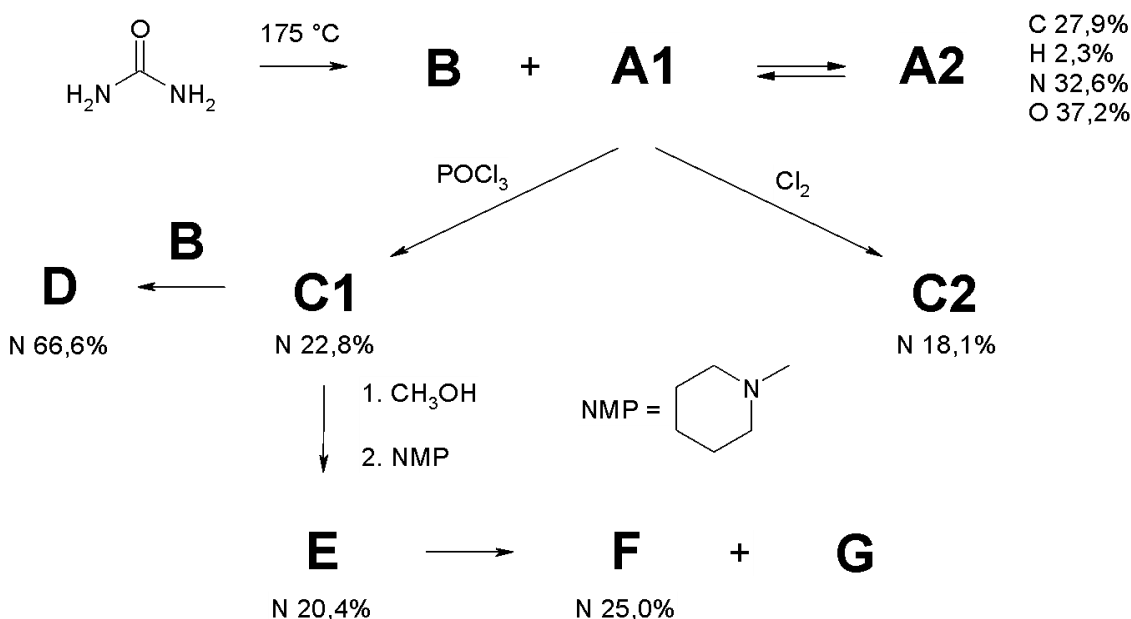
The scheme shown below represents the industrial synthesis of a new class of drugs for the treatment of type 2 diabetes. The synthesis, remarkable in its simplicity and especially in the effortless purification of products, is used to produce the target molecule in kilogram quantities for clinical development.



- Draw structural formulas of compounds A–E.
- Draw the mechanism for the formation of **D** from **C**. Consider this reaction as a three-step process. Formation of the active reagent from sulfur compound and strong base, its addition to **C** and elimination of side product to give **D**.

### Problem 4 – ABC, INORG – Uses and misuses of nitrogen compounds

The thermal decomposition of urea at 175 °C affords the highly symmetrical, acidic ( $\text{p}K_{\text{a}1} = 7$ ) compound **A** ( $\text{C}_n\text{H}_n\text{N}_n\text{O}_n$ ) along with colorless gas **B**. Compound **A** exists in solution as a mixture of isomers **A1** and **A2**, where aromatic isomer **A1** is the predominant form. **A** can be converted into two different chlorides, **C1** ( $w_{\text{N}} = 22,8\%$ ) and **C2** ( $w_{\text{N}} = 18,1\%$ ). **C1** is well suited for multiple functionalizations with nucleophiles and is commonly used as a precursor in the production of pesticides and fluorescent dyes, while **C2** found its widespread use as a water disinfectant and bleaching agent. Although it is not commercially viable, compound **D**, in principle, could be obtained from **C1** and gas **B**. **D** has a very high nitrogen content ( $w_{\text{N}} = 66,6\%$ ). The use of **D** in dairy products to artificially boost protein content was at the core of the scandal in China in 2008. **C1** is also widely utilized in organic synthesis. The wide range of reagents based on **C1** allows a simple one-step transformation of a carboxylic acid into amide, ester and even alcohol. Sequentially treating **C1** with methanol and then *N*-methylpiperidine (NMP) affords coupling agent **E** ( $w_{\text{N}} = 20,4\%$ ) in the form of chloride salt. Coupling reagent **E** is primarily used in the synthesis of various amides. Although **E** is cheap and easy to use, which allows the synthesis even on a multikilogram scale, it has one significant drawback. The reaction solvent choice is limited to tetrahydrofuran. In other solvents, like chloroform or acetonitrile, **E** undergoes rapid degradation with the formation of neutral compound **F** ( $w_{\text{N}} = 25,0\%$ ) and gas **G**.



- Draw structural formulas of compounds **A1**, **A2**, **B**, **C1**, **C2**, **D**, **E**, **F** and **G**.
- Suggest a solution to avoid degradation of activating agent **E**.
- Draw the mechanism for the conversion of  $\text{RCOOH}$  into  $\text{RCONHR}$  using activating agent **E**.

### Problem 5 – EQUILIB, KINETICS – Kinetics and equilibrium

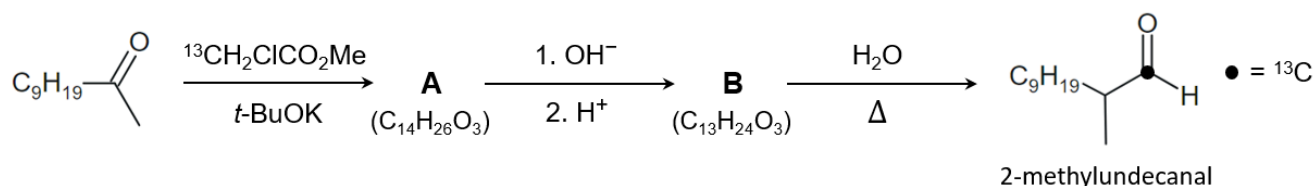
The rate constant for the reaction  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$  at 273 K is  $0.0375\text{ s}^{-1}$  and at 298 K –  $0.0021\text{ s}^{-1}$ . Under standard condition  $\Delta H_r^\circ = 4730\text{ J mol}^{-1}$ ,  $\Delta S_r^\circ = -33,5\text{ J mol}^{-1}\text{ K}^{-1}$ . Assume that  $\Delta H_r^\circ$  and  $\Delta S_r^\circ$  have the same values under normal conditions.

- Calculate the equilibrium constants of the reaction at 0 °C and 25 °C.
- Calculate the activation energy for the backward reaction.

### Problem 6 – SYNTH – Chanel №5

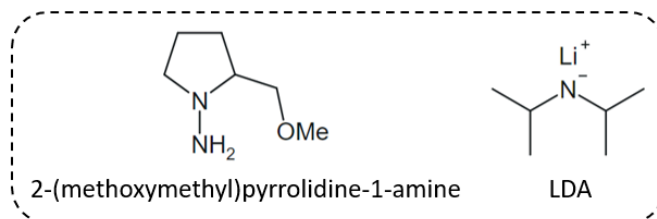
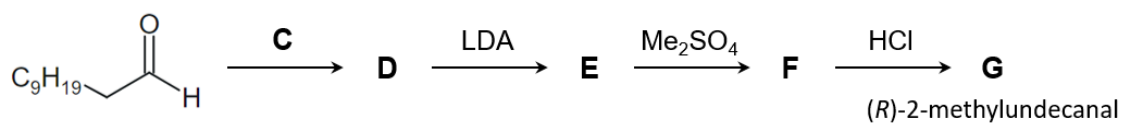
The legendary fragrance Chanel No. 5 was created in 1921 and retains its popularity nowadays. It was Marilyn Monroe's favorite perfume. She noted she only slept wearing a few drops of Chanel No. 5. One of the stories tells that this scent was accidentally made by the assistant adding too much 2-methylundecanal to the mixture. Like the majority of all the perfumes' components, 2-methylundecanal is a purely synthetic artificial substance, so a convenient synthesis was proposed.  $^{13}\text{C}$  carbon isotope was used to make the investigation of the reaction mechanism easier.

- Draw the structural formulas of compounds **A** and **B**.



- Draw the mechanisms of the first and the third reaction.

A stereoselective synthesis of (*R*)-2-methylundecanal **G** was also suggested to find out which of the two enantiomers has the required odor for the perfume. The asymmetric center was introduced using a chiral 2-(methoxymethyl)-pyrrolidin-1-amine **C**.



- c)** Draw the structural formula of *(R)*-2-methylundecanal **G**.
- d)** Which 2-(methoxymethyl)pyrrolidine-1-amine **C** enantiomer is used in the synthesis?
- e)** Draw the structural formula of compounds **D–F**.

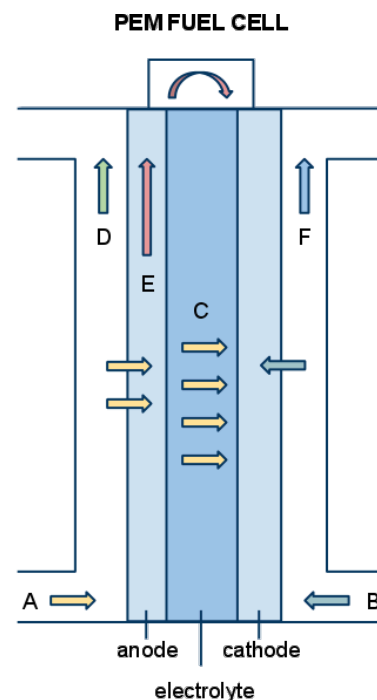
After completing the synthesis, it was discovered that both the isomers have very similar smells.

**Problem 1 – APPLIED, THERMO – Ethanol as a source of energy**

Since ancient times, ethanol has been used for lamp oil and cooking, along with plant and animal oils. Nowadays, the vast majority of ethanol is used as fuel and is produced on a large scale by fermentation, in which certain species of yeast metabolize sugar producing ethanol. It can be said that sunlight is used to run the engine of a vehicle, as a simple sugar is created in the plant by photosynthesis, and during ethanol combustion, carbon dioxide and water are produced with a release of energy.

- a) Write chemical equations for sugar synthesis, ethanol production and combustion.

Early in 1860, Nikolaus August Otto used ethyl alcohol as fuel for an internal combustion engine. Today, ethanol may be used as a fuel to power both direct-ethanol fuel cells (DEFC) and combustion engines. One of the first DEFC, for which a schematic diagram is given above, was introduced in the ShellEco-Marathon in 2007.



- b) Identify chemical species A–F in the figure.
- c) From thermodynamic data, calculate DEFC maximal energy conversion efficiency ratio:  $\eta = \Delta_r G^\circ / \Delta_r H^\circ$  (25 °C).

| Compounds                                       | O <sub>2</sub> | H <sub>2</sub> | CO <sub>2</sub> | H <sub>2</sub> O | C <sub>2</sub> H <sub>5</sub> OH | C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> |
|-------------------------------------------------|----------------|----------------|-----------------|------------------|----------------------------------|-----------------------------------------------|
| $\Delta H^\circ$ , kJ mol <sup>-1</sup>         | 0              | 0              | -394            | -286             | -278                             | -1273                                         |
| $S^\circ$ , J mol <sup>-1</sup> K <sup>-1</sup> | 205            | 131            | 214             | 70               | 161                              | 212                                           |

- d) For comparison, calculate the efficiency of the combustion engine running on Otto cycle using the equation for maximal efficiency:  $\eta = 1 - 1/r^{(\gamma-1)}$ , where  $\gamma = C_p/C_v \approx 1.4$ ,  $r$  is compression ratio which equals 9 and 12.5 for ethanol and gasoline, respectively. Assume that only half of the efficiency is achieved in practice.

There are several unsolved issues concerning DEFC, thus, in closer perspective, it is more promising to convert ethanol into hydrogen in order to use the latter in a typical hydrogen fuel cell.

- e) Using the given data, calculate the maximal energy conversion efficiency ratio ( $\eta = \Delta_r G^\circ / \Delta_r H^\circ$ ) of the hydrogen fuel cell.

To be more realistic, it should be considered that in order to move a vehicle, the electric energy must be converted into mechanical energy. Let's assume that the conversion efficiency of subsystems is: 90% for inverter, 90% for motor, and 90% for gas compressor. The overall conversion efficiency ratio may be compared to the energy conversion efficiency ratio of a combustion engine in which chemical energy is directly converted to mechanical energy.

- f) Estimate the overall efficiency of a hydrogen vehicle.
- g) Name one to two main advantages of using i) ethanol over gasoline fuel in internal combustion engine; ii) fuel cell over internal combustion engine.

## Problem 2 – CALC, KINETICS, STRUCT – Synthesis and aquation of fluoropentaaquachromium(III) ion

5.0 cm<sup>3</sup> 2.0 M chromium(III) perchlorate and 5.0 cm<sup>3</sup> 2.0 M potassium fluoride were brought together; the solution was boiled under reflux for 3 hours and cooled to 0 °C, and the precipitate **X** was removed. The density of all solutions is 1.1 g cm<sup>-3</sup>. In the water solution, the chromium(III) perchlorate is presented as aquachromium cation with a coordination number equal to six.

a) Write the formula for aquachromium cation and precipitate **X**.

During reflux, the water in the inner sphere of the complex is replaced by anion.

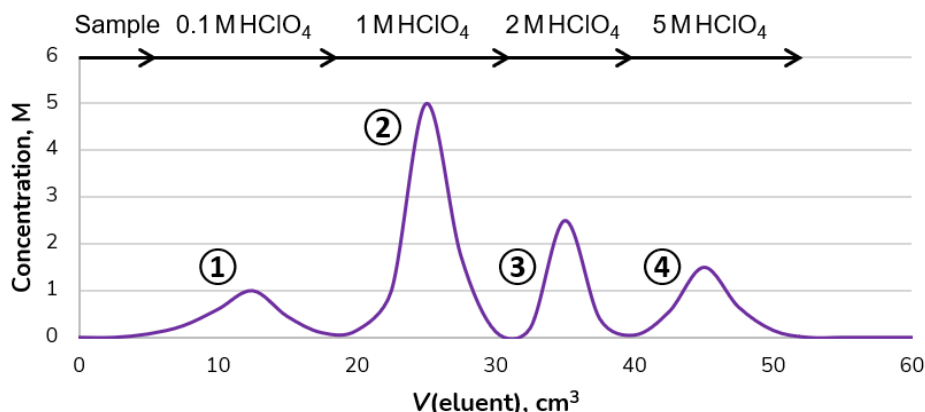
b) Write the equation of reaction.

The solubility product of the salt **X** is  $K_{sp} = 2.9 \cdot 10^{-3}$  at 0 °C, but it is possible to dissolve 10.9 g of the salt in 50 g water at 100 °C ( $\rho = 1.1 \text{ g cm}^{-3}$ ).

c) Calculate how many grams of salt **X** precipitated during the cooling process.

The reaction mixture contained various complexes of chromium. Cation-exchange (contains R-SO<sub>3</sub>H groups) separation allowed isolation of hexaaquachromium(III) ions, fluoropentaaquachromium(III) ions, difluorotetraaquachromium(III) ions and hydrolytic dimers of chromium. During the elution process, the sample was first taken into the column and afterwards the ions were eluted out using HClO<sub>4</sub> with varying concentrations.

d) Identify which species the peaks correspond to on the chromatogram. Which compound would come out of the column during the process of taking the sample into the column?



The contents of chromium and fluoride in purified fluoropentaaquachromium(III) ions were established. 10.0 cm<sup>3</sup> of the sample was first decomposed using the alkaline solution of hydrogen peroxide. The fluoride ion is liberated and the oxidation state of chromium changes from III to VI. After that, the sample was divided into two equal parts. The first part was acidified using concentrated HCl and then 3 g KI was added. After 5 min, the solution was titrated using 18.5 cm<sup>3</sup> 0.0975 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The endpoint was determined using the starch solution. The second part was analyzed using the fluoride ion selective electrode which was calibrated using solutions with known concentration of F<sup>-</sup>. The equation of the calibration curve was  $E = 183 \text{ mV} - 56 \text{ mV} \cdot \log[F^-]$ . The reading of the voltmeter was 252.6 mV and the final volume of the solution was 10 cm<sup>3</sup> after adjusting the pH of the solution to six.

e) Write all the equations of chemical reactions in the analysis process and calculate the ratio of  $n(F)/n(Cr)$  in the sample.

The pseudo first order rate coefficient of aquation of fluoropentaaquachromium(III) ion  $[\text{Cr}(\text{H}_2\text{O})_5\text{F}]^{2+} + \text{H}^+ + \text{H}_2\text{O} = [\text{Cr}(\text{H}_2\text{O})_6]^{3+} + \text{HF}$  ( $\Delta H_r = -5.41 \text{ kJ mol}^{-1}$ ) is

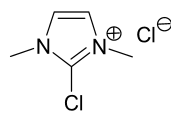
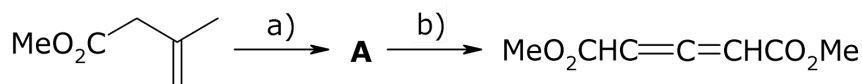
$$k = \frac{2.303 \left( [\text{CrF}^{2+}]_0 - [\text{CrF}^{2+}]_\infty \right)}{t \left( [\text{CrF}^{2+}]_0 + [\text{CrF}^{2+}]_\infty \right)} \log \frac{[\text{CrF}^{2+}]_0^2 - [\text{CrF}^{2+}] [\text{CrF}^{2+}]_\infty}{[\text{CrF}^{2+}]_0 \left( [\text{CrF}^{2+}] - [\text{CrF}^{2+}]_\infty \right)}$$

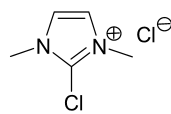
where  $[\text{CrF}^{2+}]_0 = 5.28 \cdot 10^{-3} \text{ M}$  is the starting concentration and  $[\text{CrF}^{2+}]_\infty$  is equilibrium concentration of the complex ion.

- f) Calculate the time  $t$  (h) needed to aquate 70% of the complex ion at  $77.2^\circ \text{C}$  if the concentration of hydrogen ions is  $0.414 \text{ M}$ , the rate constant is  $4.40 \cdot 10^{-6} \text{ s}^{-1}$  and the equilibrium constant of the reaction is  $0.048$ . The water is in excess and not included in the equilibrium constant.
- g) Calculate  $\text{p}K_a(\text{HF})$  at  $25^\circ \text{C}$  if the equilibrium constant of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + \text{F}^- \rightleftharpoons [\text{Cr}(\text{H}_2\text{O})_5\text{F}]^{2+} + \text{H}_2\text{O}$  reaction is  $K = 2.1 \cdot 10^4$ .

### Problem 3 – STEREO – Asymmetry without asymmetric center

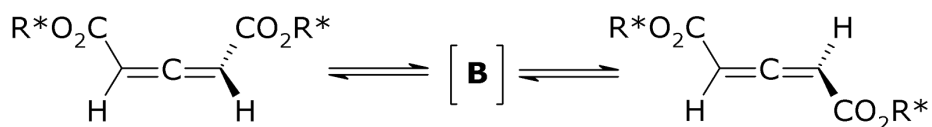
Allenes are not only versatile starting materials in organic synthesis but also present an interesting case of molecular chirality. Since it is quite difficult to synthesize allenes in a stereoselective manner, they are first obtained as a racemic mixture and then resolved into individual enantiomers. One of the ways of synthesizing allenes is depicted below.



(1)  $i\text{-Pr}_2\text{NLi}$ , THF; then the addition of  $(\text{CH}_3\text{O})_2\text{O}$ ; (2) ,  $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ .

- a) Identify symmetric structure **A**. Keep in mind that this reaction is not very efficient and **A** is only one of few possible products in this reaction.
- b) Provide the mechanism for the conversion of **A** into an allene.

One of the methods to produce allenes in pure enantiomeric form is dynamic resolution of racemic mixtures. The method takes advantage of quick epimerization and the low solubility of one of the stereoisomers. Epimerization means interconversion of one enantiomer into another proceeding through a common intermediate **B** (see the scheme below). Since all of the compounds are in equilibrium, the position of the equilibrium is shifted in the direction of the less soluble stereoisomer, which is then collected as a precipitate.



Reaction conditions: room temperature,  $\text{Et}_3\text{N}$  (0.05 eq), pentane;  $\text{R}^*$  is (–)-menthyl.

- c) Draw structural formula of **B**.

In order to establish the absolute configuration of the allene **X** obtained by dynamic resolution, one can follow a method developed by Agosta in 1964. To better understand the essence of the method let us consider all transformations performed on both enantiomers.

The allene ester is first hydrolyzed to dicarboxylic acid and then in Diels-Alder reaction with cyclopentadiene is transformed into a mixture of separable products.

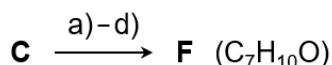
- d)** Provide structures for all possible adducts with cyclopentadiene that could be formed from each allene enantiomer ( $C_{1-4}$  from one allene enantiomer and  $C_{5-8}$  from the other).

Each of the individual compounds  $C_{1-8}$  is then subjected to 2 test reactions: a) iodolactonization ( $I_2$ ,  $NaHCO_3$ ) and b) cyclic anhydride formation (acetic anhydride).



- e)** In your list of adducts, identify which structures  $C_{1-8}$  are capable of giving desired products in both test reactions. Draw an equation for one iodolactonization reaction (**D**) and one cyclic anhydride formation (**E**).

The compound(s) **C** that gives positive results in both test reactions is (are) then degraded according to the following scheme: a)  $Pd/C$ ,  $H_2$ ; b)  $CH_2N_2$ ; c)  $O_3$ ; d)  $HCl$ , reflux.



In summary, the explicit assignment of the absolute configuration by the method of Agosta is based on the fact that one enantiomer of **F** can only be produced from (*R*)-allene, while the opposite enantiomer of **F** stems only from the (*S*)-allene.

- f)** In the aforementioned case of dynamic resolution of allenes, the degradation yields exclusively (1*S*,4*R*)-**F** stereoisomer. Draw the structure of **F**.
- g)** Based on the structure of compound (1*S*,4*R*)-**F** and the identification method by Agosta, suggest the structure of allene **X** which was obtained by dynamic resolution.

#### Problem 4 – ABC, CRYSTAL, EQUIL – Environmental hazards

Around World War II, the Jinzu River in Toyama prefecture, Japan, was contaminated with element  $X_1$  compounds and nowadays, Japan is still one of the top three producers of this element. Element  $X_1$  accumulates in rice and can cause Itai-Itai disease in humans; it also replaces calcium in bones. This element is produced from compound **A** which is its only mineral of practical importance. Compound **A** is also a direct band gap semiconductor and has many applications, for example, in light detectors and as thermally stable pigments.

Binary compound **A** also contains nonmetallic element  $Y_1$  and this compound forms minerals greenockite (first discovered in Scotland and named after the landowner Lord Greenock) and hawleyite. The first mineral has a hexagonal structure, while the second mineral has a cubic structure. The mass fraction of  $X_1$  in compound **A** is 77.6%.

Element  $X_1$  can be obtained from **A** by roasting it in air. Obtained oxide is treated with sulfur trioxide to form  $X_1$  sulfate which is dissolved in water and electrolyzed.

- a)** Determine element  $X_1$ .
- b)** Write equations for all mentioned reactions taking place in element production.
- c)** Calculate the mass of metal  $X_1$  which can be obtained by electrolysis of 0.15 M metal sulfate solution with a 0.50 A current that is one hour long.
- d)** Write an electron formula for element  $X_1$  ions in sulfate solution, knowing that there are no *f* electrons in this ion.

- e) The table with lattice parameters for greenockite and hawleyite is shown below. Calculate  $Z$  value (number of “molecules” in a unit cell) for hawleyite and the density for greenockite.

| Parameter  | Greenockite                                                              | Hawleyite                |
|------------|--------------------------------------------------------------------------|--------------------------|
| System     | hexagonal                                                                | cubic                    |
| Parameters | $a = b = 3.82 \text{ \AA}$<br>$c = 6.26 \text{ \AA}, \gamma = 120^\circ$ | $a = 5.818 \text{ \AA}$  |
| $Z$        | 2                                                                        | ?                        |
| Density    | ?                                                                        | $4.87 \text{ g cm}^{-3}$ |

Practically important is also compound **B** which is used for the production of solar energy panels and which contains nonmetallic element  $Y_2$ . The mass fraction of element  $X_1$  in compound **B** is less than 50% and it is known that element  $Y_2$  is in the same group as element  $Y_1$  but electronegativity for element  $Y_2$  is smaller than for  $Y_1$ .

- f) Determine element  $Y_2$ .

Usually, element  $X_1$  is found together with element  $X_2$  which is placed in the same group in the periodic table. Binary compound of element  $X_2$  with  $Y_1$  crystallizes in cubic face-centered crystals (FCC) with parameter  $a = 5.406 \text{ \AA}$ . The density of this compound is  $4.09 \text{ g cm}^{-3}$ .

- g) Determine element  $X_2$ , show your calculations.

- h) Order all possible binary compounds from elements  $X_1$ ,  $X_2$ ,  $Y_1$  and  $Y_2$  in order of increasing covalent bond content and decreasing ionic bond content.

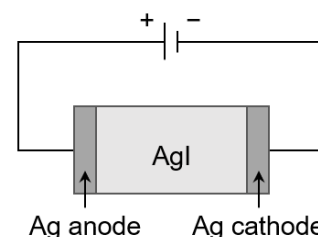
Elements  $X_1$  and  $X_2$  can also be separated due to different solubilities of their hydroxides. Hydroxides and carbonates are the forms of  $X_1$  compounds which are now found in the Jinzu River bed ( $X_1$  concentration approx. 2 ppm).

- i) Which element ( $X_1$  or  $X_2$ ) hydroxide has better solubility in alkaline solutions? Explain it using the atomic structure of elements.
- j) Calculate the solubility (M) of both compounds in water at pH = 10.0. Consider the formation of a complex ion. All necessary data are given in the following table:

|           | $pK_{sp}$ | $pK_1$ | $pK_{1,2}$ | $pK_{1,2,3}$ | $pK_{1,2,3,4}$ |
|-----------|-----------|--------|------------|--------------|----------------|
| <b>I</b>  | 14.14     | 4.17   | 8.33       | 9.02         | 8.62           |
| <b>II</b> | 16.5      | 4.40   | 11.30      | 14.14        | 17.66          |

### Problem 5 – CALC, CRYSTAL, ELECTRO – Half solid half melted

In 1914, Tubandt and Lorenz showed that solid silver iodide above  $147^\circ\text{C}$  transforms into  $\alpha\text{-AgI}$  modification that is a good electrical conductor. A temperature of  $147^\circ\text{C}$  may be considered as the melting point for silver ion sublattice. The remaining iodide ion sublattice is stable until  $557^\circ\text{C}$ . It was determined that iodide ions form body-centered cubic (BCC) sublattice with lattice constant (lattice parameter)  $5.04 \cdot 10^{-10} \text{ m}$ . Tubandt's electrochemical cell is shown in the following scheme.



In this cell, silver electrodes  $0.1000 \text{ g}$  each were placed in contact with both sides of solid AgI pellet. Then, electric current of  $35.2 \text{ mA}$  flowed for  $15.5 \text{ min}$ . After that, silver electrodes were taken off the pellet and placed into two labeled  $100.0 \text{ cm}^3$  volumetric flasks (label “Solution A” for anode and “Solution B” for cathode). Excess of dilute  $\text{HNO}_3 (\text{aq})$  was added into both flasks. After the dissolution of metallic electrodes both volumetric flasks were filled with distilled

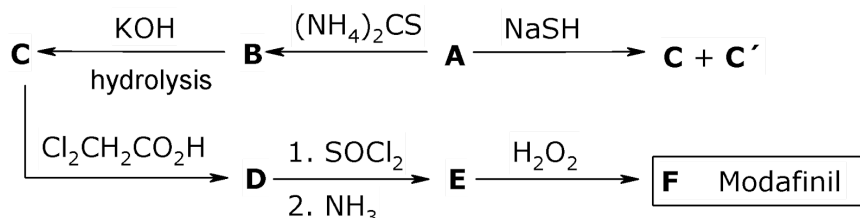
water till the calibration mark. Solution A and Solution B were used for titration of 10.00 cm<sup>3</sup> samples of 0.0113 mol dm<sup>-3</sup> NaCl solution that contains a small amount of K<sub>2</sub>CrO<sub>4</sub>. The endpoint for these titrations was the appearance of brick-red precipitate.

- Write half-reactions that represent what was happening at the anode and at the cathode during the electric current flow.
- Write the chemical equation describing the action of dilute HNO<sub>3</sub> onto electrodes.
- Write a formula for the brick-red compound that precipitates at the titration endpoint.
- Calculate the ratio  $V(\text{Solution A})/V(\text{Solution B})$  (ratio of volumes of respective solutions that were used up for the titration of samples of NaCl solution).
- Determine the radius of iodide ion in the BCC sublattice.
- Calculate the density of solid AgI conductor.
- AgI is a light-sensitive compound suitable for photography. After the development of a black and white photo, the image should be "fixed" by dissolving away all the remaining silver iodide (or other silver salts). Sodium thiosulfate Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is a suitable fixing agent. In reaction with silver iodide, it produces a compound that contains 26.9% of silver by mass. Write a chemical equation that shows what is happening during the "fixing" photo.

#### Problem 6 – SPECTRA, SYNTH – Modafinil – work without sleep?

Modafinil was originally created to treat narcolepsy (a condition when a person falls asleep at inappropriate times), but it spread widely among students and businessmen. Although a productive day after a sleepless night sounds unbelievable, it is not the only effect of modafinil; it also acts as an antidepressant and improves memory in some cases. Modafinil has a considerably smaller list of side effects than caffeine but due to its unknown long-term effects, it remains a prescription drug.

An industrial synthesis scheme of Modafinil is presented below. In the <sup>1</sup>H NMR spectrum of compound **A**, there is one singlet (6.0 ppm) and ten times more intensive multiplet (7.3 ppm). In its mass spectrum, two peaks of equal intensity for the molecular ion are observed at 246 and 248 *m/z*. After treating compound **A** with sodium hydrosulfide, a side product **C'** was detected, therefore, to avoid its formation, one additional step was introduced in the synthesis.



- Draw the structural formulas of all letter-named compounds.
- Sketch a mechanism for the reaction **D** → **E**.

Modafinil is actually a mixture of two enantiomers, where only the *R*-isomer shows the indicated biological activity.

- Draw the structural formula of Modafinil's active enantiomer.

## 19th BChO, 2011, Vilnius, Lithuania

### Problem 1 – EQUIL, STRUCT – Aluminum

Aluminum is the most abundant metal in the Earth's crust. Some compounds of aluminum, like alum (the double sulfate  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ), have been in use since ancient Greece time.

- a) The freezing point depression constant for water is  $K_f = 1.86 \text{ }^\circ\text{C kg mol}^{-1}$ . Calculate the freezing point of the solution prepared by dissolving 9.48 g of  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  in 100.0 g of water.
- b) The most important aluminum ore is bauxite, which contains  $\text{Al}_2\text{O}_3$  and impurities. Bauxite can be purified by dissolving in a concentrated  $\text{NaOH}$  solution. Write a molecular equation that shows what happens when  $\text{Al}_2\text{O}_3$  reacts with  $\text{NaOH}$  solution.
- c) After removing insoluble impurities, a weak acid is added to the solution obtained in part b), and  $\text{Al}(\text{OH})_3$  is precipitating. Solubility product  $K_{sp}$  for  $\text{Al}(\text{OH})_3$  is  $1.3 \cdot 10^{-33}$  (at  $25 \text{ }^\circ\text{C}$ ). Calculate the mass of pure  $\text{Al}(\text{OH})_3$  that can be dissolved in  $10.0 \text{ dm}^3$  of pure water at  $25 \text{ }^\circ\text{C}$ .

EDTA (ethylenediaminetetraacetic acid or its salts) is among the most important and widely used reagents in titrimetry. Unfortunately, this reagent is not good for the direct determination of aluminum ions because EDTA reacts with aluminum ions too slowly. The problem can be solved by applying the back titration method. In the beginning, EDTA and aluminum compound solution are allowed to react in the hot solution for several minutes, and then excess EDTA can be fast and easily titrated with  $\text{Zn}^{2+}(\text{aq})$ . The analysis is performed in the presence of a buffer solution. Reactions taking place in this method can be represented as  $\text{Al}^{3+} + \text{EDTA}^{4-} \rightarrow \text{AlEDTA}^-$  and  $\text{Zn}^{2+} + \text{EDTA}^{4-} \rightarrow \text{ZnEDTA}^{2-}$ .

- d)  $20.00 \text{ cm}^3$  of solution, that contains  $\text{Al}^{3+}$ , was transferred into a flask that contained  $50.00 \text{ cm}^3$   $0.0500 \text{ M}$  EDTA solution. The mixture was boiled for several minutes. For titration of the resulting mixture,  $23.25 \text{ cm}^3$  of  $0.0500 \text{ M}$   $\text{Zn}^{2+}$  solution was necessary. Calculate the molar concentration of  $\text{Al}^{3+}$  in the initial solution.

Trihalides of aluminum (like  $\text{AlCl}_3$ ) are very strong Lewis acids and find extensive use as catalysts. With some ligands (L), aluminum trichloride may form four-coordinated  $\text{AlCl}_3\text{L}$  or even five-coordinated  $\text{AlCl}_3\text{L}_2$ .

- e) Assuming that L is a monodentate ligand, draw all possible geometrical isomers of  $\text{AlCl}_3\text{L}_2$ .
- f) In the gas phase, aluminum trichloride is an  $\text{Al}_2\text{Cl}_6$  molecule with two bridging Cl atoms. Make a drawing that represents the spatial structure of the  $\text{Al}_2\text{Cl}_6$  molecule.

### Problem 2 – ABC, KINETICS – Beware of light!

Students found in a laboratory a bottle with a little bit of wet reagent **A**, which had the label "light-sensitive". Students have not paid attention to this label and left the bottle on the bench over the summer break. As a result, the bottle was in direct sunlight for several hours a day. After the summer break, students noticed that some changes had happened to the content of the bottle. There were three compounds formed: **B**, **C** and **D**. Compound **A** is also used to increase the solubility of **C** in aqueous solutions. In this process, anion **E** is formed, which is also a part of compound **D**. If concentrated solutions of **A** are mixed with concentrated solution **B** and then the obtained solution is allowed to react with some yellow-green gas **F**, two new compounds are formed. Of this mixture, compound **G** in acidic media reacts with **A**, which leads to **C** as one of the products. Oxygen content in compound **G** is 22.4% (by mass).

If compound **G** reacts with the acid derived from **F**, which consists of only two elements, the reaction leads to **C**, **F** and two other products.

- Write the chemical formulas of compounds **A–G**.
- Write reaction equations for all mentioned processes.
- Why is compound **A** sensitive to light but nothing happens if it is stored in the dark?
  - ☐ Light is a form of activation energy provided.
  - ☐ Light initiates electrolytic dissociation.
  - ☐ Light initiates the formation of radicals.
  - ☐ Light is an oxidizing agent.
  - ☐ Light is a reducing agent.
- Why does the solubility of **C** in water increase if compound **A** is added?
- Draw the Lewis structure of anion **E**.
- Calculate the maximum pH at which a reaction between **A** and **G** still proceeds at 25 °C, if  $[G] = 0.25 \text{ M}$  and  $[A] = 0.10 \text{ M}$ .  $E^\circ(A) = 0.536 \text{ V}$ ,  $E^\circ(G) = 1.195 \text{ V}$ .

Before the summer holidays started, students used compound **A** to investigate reaction kinetics. It is known that compound **A** reacts with persulfate ions ( $S_2O_8^{2-}$ ) forming compound **C** and sulfate ions. Investigating kinetics at 25 °C temperature, they obtained data of initial reaction rate  $v_0$  depending on reactant concentrations  $c_0$ . The data are shown in the table.

| $c_0(S_2O_8^{2-}), \text{ mM}$ | $c_0(A), \text{ mM}$ | $v_0 \times 10^8, \text{ mol dm}^{-3} \text{ s}^{-1}$ |
|--------------------------------|----------------------|-------------------------------------------------------|
| 0.10                           | 10                   | 1.1                                                   |
| 0.20                           | 10                   | 2.2                                                   |
| 0.20                           | 5.0                  | 1.1                                                   |

- Write the chemical equation for the reaction of persulfate ions with compound **A**.
- Determine reaction partial orders, write a kinetic expression and calculate reaction rate constant at 25 °C.
- They found in literature that activation energy for this reaction is  $42 \text{ kJ mol}^{-1}$ . Calculate the temperature (in °C) needed to increase the reaction rate 10 times if reactant concentrations remain the same.
- Calculate what time (in hours) is necessary to decrease reactant concentrations 10 times if initial concentrations for both reactants are equal to  $1.0 \text{ mmol dm}^{-3}$  at 25 °C.

### Problem 3 – EQUILIB – Ordinary Physical Chemistry

#### Part I.

Initial conditions of the reaction  $H_2 + N_2 \rightarrow NH_3$  is  $n_0(H_2) = n_0(N_2)$ ,  $n_0(NH_3) = 0$ . At 400 °C, the equilibrium constant  $K_p$  of the reaction is  $1.60 \cdot 10^{-14} \text{ Pa}^{-2}$ .

- Write the reaction equation.
- Express analytically the mole fraction  $x(NH_3)$  and  $K_p$  in terms of a ratio  $y$ , which is a fraction of the amount of produced ammonia to twice the initial amount of reagents,  $y = n_\infty(NH_3)/2n_0$  or  $n_\infty(NH_3) = 2yn_0$ .
- Calculate the pressure (Pa) under which the partial pressure of  $NH_3$  is 11.11% of the total.

## Part II.

A mixture of gases containing CO, H<sub>2</sub>, and CH<sub>3</sub>OH is blown over a catalyst at 500 K.

d) Would methanol form in the reaction  $\text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH}$  under the given conditions:

$$p_{\text{CO}} = 9p_{\text{H}_2} = 99p_{\text{CH}_3\text{OH}}, p_{\text{CH}_3\text{OH}} = 9900 \text{ Pa, and } \Delta G_r^\circ = 21.21 \text{ kJ mol}^{-1}.$$

e) Calculate the value of  $Q$  when  $\Delta G_r = 0 = \Delta G_r^\circ + RT \ln Q$ . Is it the minimal or maximal value above or below which the equilibrium is shifted towards methanol production?

### Problem 4 – ABC, INORG – Smart robot

The hero of the movie “Star Wars” – a very intelligent robot R2-D2 received 20.0 mg of radioactive sample **P** known to contain only element **A**. The robot divided this sample into two halves of equal masses. With the help of the gas diffusion method, it quickly separated the first half into two parts. It obtained two equal volumes of gases (under appropriate conditions) whose weights were 4.92 and 5.08 mg; activities equaled  $5.19 \cdot 10^{13}$  and  $2.94 \cdot 10^{13}$  decays per second, respectively. These two were isotopes of element **A**. R2-D2 chlorinated the second half of the sample yielding higher chloride **B**, which, after hydrolysis in water, gave a solution of triprotic acid **C** and strong acid **D**. This solution was titrated with 19.95 cm<sup>3</sup> of 0.1234 M NaOH solution.

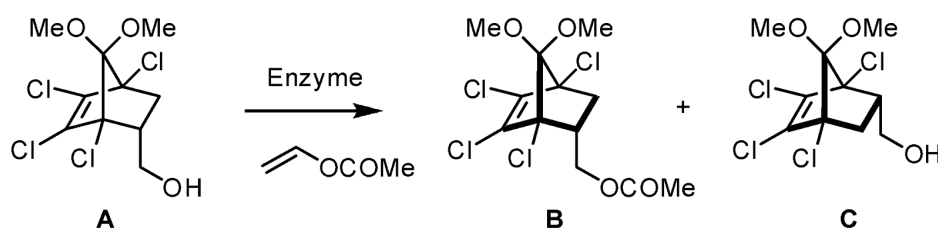
- Write the chemical symbols for element **A** and formulas for compounds **B–D**.
- Write four equations for the reactions mentioned above.
- Provide calculations to confirm the validity of your solution.
- By what time will all the samples have almost completely decayed, i.e. would the total remaining activity be less than 0.1% of the initial one?

R2-D2 found that after this time, the remaining 10.0 mg of sample **P** consisted of two isotopes of element **E**. Robot could not resist the delight of chlorinating them. As a result, it obtained yellow substance **F**. When hydrolyzed in water, substance **F** formed diprotic weak acid **G**, diprotic oxyacid **H**, and acid **D**. This solution was titrated with 2.136 cm<sup>3</sup> of 0.4321 M NaOH solution.

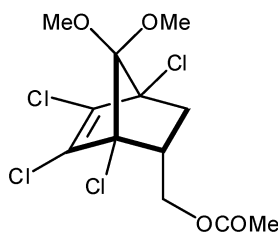
- Write the chemical symbols for element **E** and formulas for compounds **F–H**.
- Write five equations for chemical reactions and two reactions of radioactive decay of isotopes of element **A**.
- Provide calculations to confirm the validity of your solution. *Hint: Assume that the molar mass of an isotope is an integer number.*

### Problem 5 – BIO, STEREO – Chiral polyhydroxylated cyclohexanoids

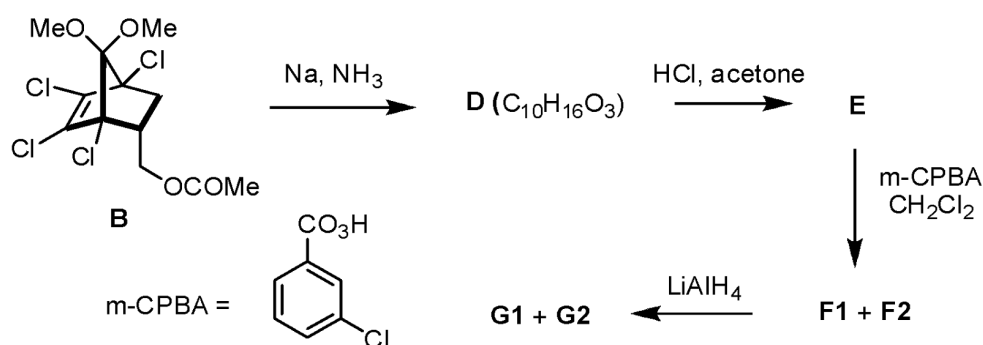
Enantiomerically pure polyhydroxylated cyclohexanoids could be useful for treating diabetes, viral infections, and cancers. The scheme shows the enzyme-catalyzed kinetic enantiomeric separation of compound **B**:



- a) Which class of enzymes will catalyze this reaction: **i)** oxidoreductase, **ii)** isomerase, **iii)** lipase, **iv)** ligase?
- b) What is the maximum yield of compound **B**: **i)** 100%, **ii)** 90%, **iii)** 75%, **iv)** 50%?
- c) Identify chiral centers of compound **B** and indicate their configurations.



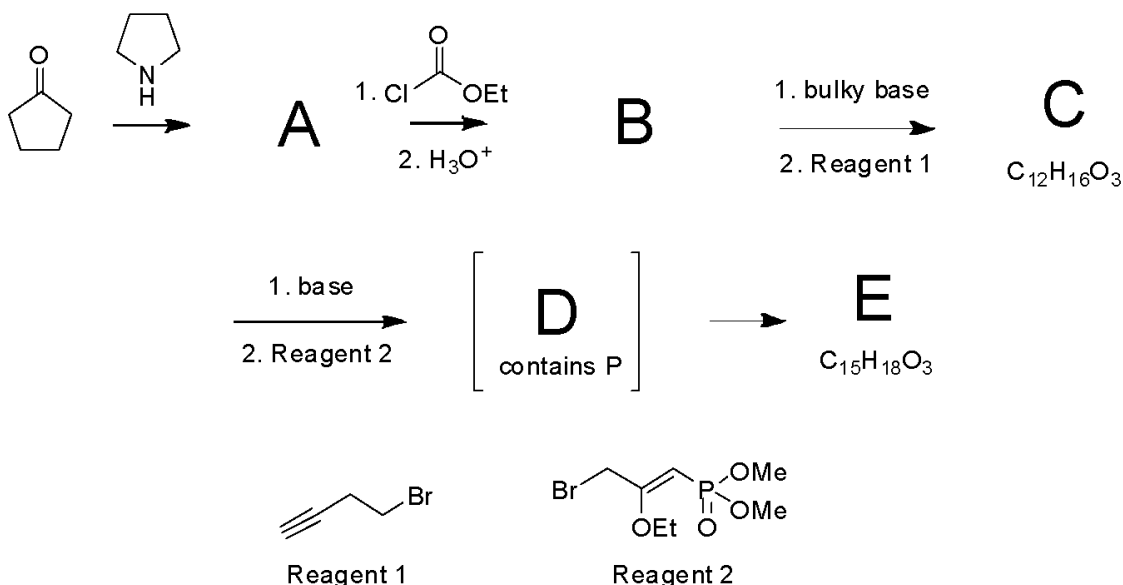
Compound **B** is a starting compound for the synthesis of enantiomerically pure polyhydroxylated compounds **G1** and **G2**:



- d) Draw the structural formulas of compounds **D–G**.
- e) With respect to each other, compounds **G1** and **G2** are: **i)** enantiomers, **ii)** structural isomers, **iii)** diastereomers, **iv)** conformers.

### Problem 6 – SYNTH – The hunt for the flat carbon

Incorporating a “flat” carbon atom in  $sp^3$  hybridization in a molecule would be a very exciting achievement from a theoretical point of view. Such geometry is associated with an enormous amount of strain, and it is a huge challenge to incorporate such an element in a “stable” molecule.

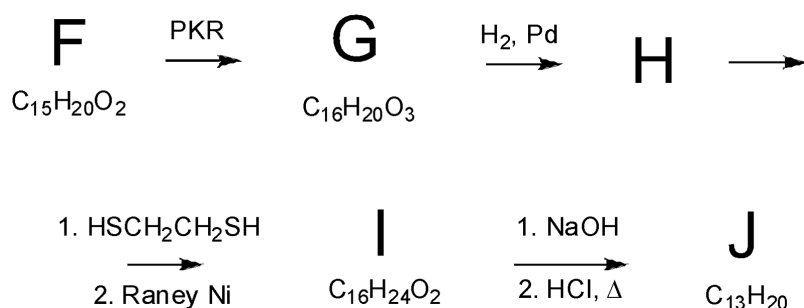


A special class of compounds – fenestranes, could as well be an answer to this scientific challenge. However, it must be noted that the most desirable symmetrical  $C_9$  fenestrane, which could have planar symmetry, has not yet been synthesized.

The problem outlined below shows the synthesis of  $C_{13}$  symmetrical fenestrane. Even though bond angles in this molecule are distorted to a large extent, the planar symmetry around the carbon atom is not achieved.

- Bulky base means 2 equivalents of sterically hindered (bulky) base like LDA.
- The theoretical amount of base needed to obtain **D** is one mole.
- The base used in the deprotonation of **C** does not react with terminal alkyne.
- **D** is formed in the initial  $S_N2$  reaction and contains phosphorus, under acidic workup conditions, this compound is unstable and converts into **E**.
- **E** is a  $C_8$  bicyclic compound.

Further carbon skeleton construction required the Pauson-Khand reaction (PKR). In general, PKR involves alkyne, alkene, and carbon monoxide. In the presence of a cobalt catalyst, PKR leads to the formation of a cyclopentenone ring. Note: In order to apply PKR in the present synthesis, the carbonyl group in **E** was removed to give **F**.



- **G** already possesses the carbon skeleton found in **J**.
- **J** is very symmetrical.

- Draw the structural formulas of compounds **A–J**.
- Suggest a mechanism for transformation **D**  $\rightarrow$  **E**.

**Problem 1 – RADIO – Seasonal radioactivity**

In some northern regions of Estonia, surface soil is enriched with uranium. Therefore, due to the high concentration of radioactive gas  $^{222}\text{Rn}$ , it is not recommended to build houses in these regions. In the basement of a private house, the floor area equals  $100\text{ m}^2$  and the height is 2 m. The house is built in a potentially hazardous region. Radon concentration in the basement is low in the summertime, while during winter, radioactivity holds at  $400\text{ Bq m}^{-3}$  level ( $\text{Bq}$  = decay per second).

- a) Why is the concentration of radon in the basement much greater during winter than in summertime?
  - i) The concentration of radon is higher at lower temperatures obeys  $pV = nRT$ .
  - ii) Soil under the basement does not freeze in winter, while the soil around the house does freeze. Consequently, radon gas leaks into the house through gaps and cracks inside the basement. In the summertime, gas escapes through the soil around the house.
  - iii) The rate of radon production from uranium is higher at lower temperatures. Therefore, a greater amount of radon enters the basement during winter.
- b) The half-life of  $^{222}\text{Rn}$  is 3.82 days. Calculate the time needed for radon to decay, decreasing activity from 400 to  $4\text{ Bq m}^{-3}$ . Assume that there is no entry of radon from the outside.
- c) Estimate the average radioactivity of radon in the basement during a year. Assume that the radon leaking rate is expressed as follows:  $v_{\max} \cdot \cos^2(\pi d/365)$ , where  $v_{\max}$  is the maximal leaking rate,  $d$  is the day number from the beginning of the year.
- d) For comparison, calculate the total radioactivity ( $\text{Bq m}^{-3}$ ) in an average banana (118 g,  $124\text{ cm}^3$ ). One banana contains 422 mg of potassium ions and 28 g of carbohydrates ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). Among potassium atoms, there are 0.0117% isotopes of radioactive  $^{40}\text{K}$  ( $T_{1/2} = 1.277 \cdot 10^9\text{ y}$ ). Among carbon atoms,  $1.2 \cdot 10^{-10}\%$  isotopes of radioactive  $^{14}\text{C}$  ( $T_{1/2} = 5730\text{ y}$ ).
- e) What is more hazardous:  $^{40}\text{K}$  and  $^{14}\text{C}$  in bananas or  $^{222}\text{Rn}$  in the air of the basement? Think of the total ionization energy released in a sequence of radioactive decay; the total rate of accumulation of radioactive isotopes and their daughter nuclei in a human body; and the calculated radioactivity per  $\text{m}^3$ .

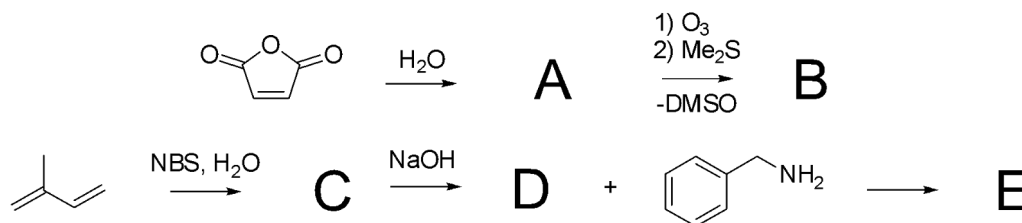
**Problem 2 – EQUIL, THERMO – Ammonia**

Nitrogen and hydrogen react to form ammonia:  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ .

- a) Calculate the equilibrium constant at i) 298 K and ii) 450 K. Assume that enthalpy and entropy change of the reaction is constant for the given interval of temperatures.  $\Delta G_f^\circ(\text{NH}_3) = -16.30\text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(\text{NH}_3) = -45.86\text{ kJ mol}^{-1}$ .
- b) Express equilibrium partial pressure of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  at pressure  $p$  assuming stoichiometric amounts of reactants.
- c) Stoichiometric amounts of reactants react at  $10.0 \cdot 10^5\text{ Pa}$  pressure at 450 K. Calculate the percent of nitrogen that, in the course of the reaction, transforms into ammonia.
- d) At what pressure at 450 K nitrogen conversion into ammonium would be 25% (at stoichiometric amount of reactants)?

### Problem 3 – MECH, SYNTH – The synthesis of proline

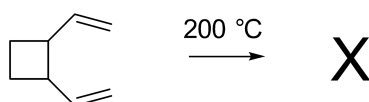
Proline is an  $\alpha$ -amino acid, one of the twenty DNA-encoded amino acids. Its derivatives have shown to exhibit interesting biological activities, so a number of synthetic strategies have been utilized throughout the years to synthesize substituted proline derivatives, including this clever pericyclic reaction of a cationic intermediate.



NBS – *N*-bromosuccinimide, DMSO – dimethyl sulfoxide

- a) Draw the structural formulas of compounds **A–E**. *Hints: 2 moles of B are obtained from 1 mol of A; structures D and E each contain one monosubstituted double bond!*

Before going next to the main step in the synthesis of proline, consider a much simpler example of this type of transformation. Properly substituted cyclobutane under thermal conditions provides structure **X** in a single reaction. All double bonds in **X** have *Z*-configuration.



- b) Draw the structural formula of **X** and the starting cyclobutane, clearly indicating the stereochemical information that guides the formation of all *Z*-configuration in **X**.

**X** is used in the synthesis of the very popular reducing reagent 9-BBN (9-borabicyclo[3.3.1]nonane) by reacting with borane-dimethyl sulfide complex.

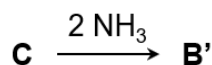
- c) Draw the structural formula structure of 9-BBN.

Completion of proline synthesis: **B** + **E**  $\rightarrow$  [**F**  $\rightarrow$  **G**]  $\rightarrow$  **H**. Combining **B** and **E** initiates the two reaction sequences, the so-called domino reaction or cascade reaction, where the first reaction is similar to the one described above. Both **F** and **G** are iminium ions.

- d) Draw the structural formulas of compounds **F**, **G**, and **H**.  
e) Provide the mechanisms of transformation **B** + **E**  $\rightarrow$  **H**.

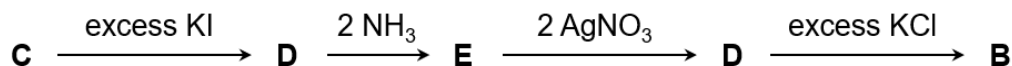
### Problem 4 – ABC, INORG, STRUCT – Antitumor agent

In 1989, L. S. Hollis et al. discovered a new antitumor agent – a coordination compound **A** which contains transition metal **X** with an oxidation number of +2. It is synthesized from neutral inorganic compound **B**. Although the preparation of **B** may seem straightforward, it is actually done in multiple steps, as described by S. C. Dhara. A straightforward method for synthesis of **B** would be from potassium salt **C** in reaction with two equivalents of ammonia (Scheme 1). However, in this reaction, compound **B'** forms and, as a byproduct, potassium chloride solution is obtained. It is known that **C** consists of three chemical elements and the molecular mass ratio of compounds **C** : **B** is 1.383.



- a) Find out element **X** and molecular formulas of compounds **B**, **B'** and **C**.  
b) Draw the structural formulas of **B** and **B'** with stereochemistry.

Synthesis of **B** is actually carried out as shown in scheme 2:



c) Draw the structural formulas of compounds **D–F** with stereochemistry.

**A** was prepared by heating an equimolar amount of **B** and pyridine (azabenzene, Py). In this reaction, no byproduct forms.

d) Draw the structural formula of compound **A** with stereochemistry.

e) Provide a method for how **A** can be isolated from the reaction mixture without **B**.

If metal **X** is replaced by nickel in compound **C** and nickel analogue of **B** is synthesized, by both straightforward (scheme 1) and provided method (scheme 2), the same product **G** is obtained.

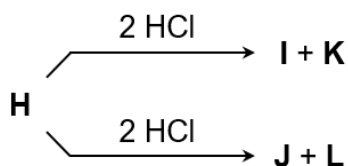
f) Explain this result and draw the structure of compound **G** with stereochemistry.

In 2008, USA scientists, using an analytical method, proved that compound **A** binds to DNA chains and found out the exact binding site and position of molecules in the formed product.

g) What type of binding is possible between compound **A** and a DNA chain?

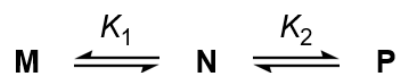
h) What analytical method is capable of identifying the exact binding site and position of molecules in a formed product?

If the reaction of **B'** is carried out with two equivalents of pyridine, compound **H** is obtained. If **H** reacts with two equivalents of hydrochloric acid, two compounds with the same stereochemistry, **I** and **J** may form giving byproducts **K** and **L**, respectively. The reaction scheme is as follows:



i) Write the structural formulas of compounds **H–L** with stereochemistry.

There are known reactions with coordination compounds where from arbitrary compound **N** only two isomers, **M** and **P**, are formed.



j) Calculate equilibrium concentrations of **N**, **M** and **P** if the initial concentration of **N** was  $\alpha$  and equilibrium constants are  $K_1$  and  $K_2$  as shown in the scheme above.

### Problem 5 – EQUIL – Aspirin absorption

When administered orally, a popular analgesic, Aspirin (2-acetoxybenzoic acid), passes through a membrane in the stomach to enter the bloodstream. To model this process two solutions representing the gastric acid and blood were prepared. To a flask containing some water, 10.00 cm<sup>3</sup> of 85.0% H<sub>3</sub>PO<sub>4</sub> and 50.00 cm<sup>3</sup> of 4.00% NaOH solution were added. The mixture was diluted to 1.00 dm<sup>3</sup> and is called the “Stomach” solution.

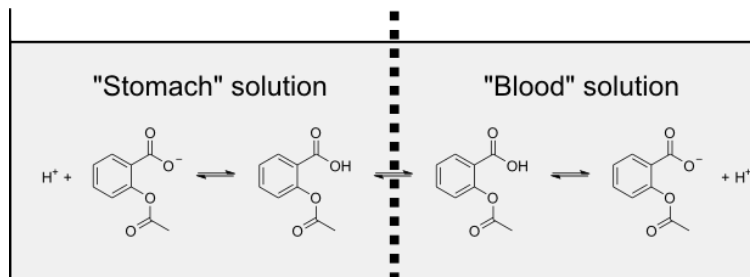
The data for 85.0% H<sub>3</sub>PO<sub>4</sub>:  $\rho = 1.685 \text{ g cm}^{-3}$ ;  $K_{a1} = 7.25 \cdot 10^{-3}$ ;  $K_{a2} = 6.31 \cdot 10^{-8}$ ;  $K_{a3} = 3.98 \cdot 10^{-13}$ .

a) Calculate the pH of the “Stomach” solution.

To prepare 1.00 dm<sup>3</sup> of the “Blood” solution, 10.00 cm<sup>3</sup> of 85.0% H<sub>3</sub>PO<sub>4</sub> was used.

- b) Calculate the volume of 4.00% NaOH solution one needs to add so the pH of the resulting "Blood" solution is 7.40.

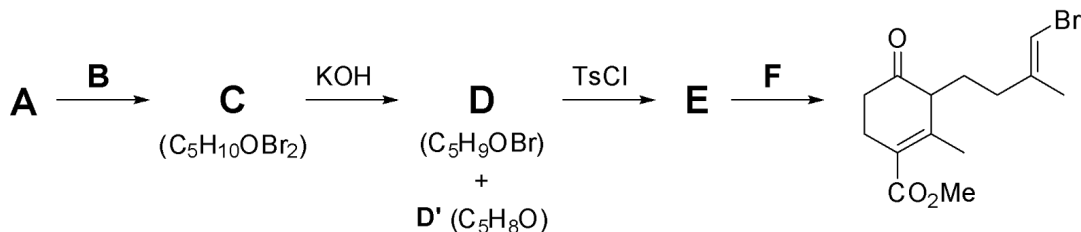
The "Stomach" and "Blood" solutions (1.00 dm<sup>3</sup> of each) are separated by a membrane, which can be passed only by Aspirin in its neutral form. 1.00 g of aspirin is added to the "Stomach" solution. An equilibrium is considered to be reached when the concentrations of neutral Aspirin are equal in both solutions ([HA]<sub>stomach</sub> = [HA]<sub>blood</sub>). Aspirin  $K_a = 3.02 \cdot 10^{-4}$ .



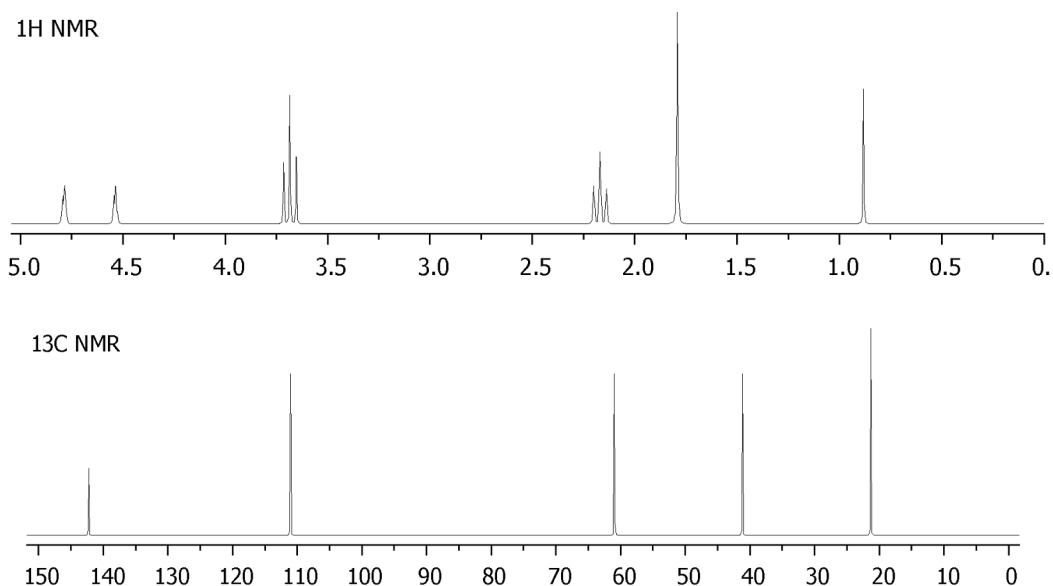
- c) Write the mass-balance equation for Aspirin.
- d) Calculate the concentrations for ionized and neutral Aspirin in both solutions ( $A^-$ <sub>stomach</sub>,  $HA$ <sub>stomach</sub>,  $HA$ <sub>blood</sub>,  $A^-$ <sub>blood</sub>) when equilibrium is reached.

### Problem 6 - SPECTRA, SYNTH - Algae against cancer

Red algae from the genus *Laurencia* are known to produce a variety of bioactive compounds. Screening an extract from *Laurencia cartilaginea* led to the discovery of two closely related chamigranes that showed selective and potent cytotoxicity in anti-tumor tests, being particularly effective against colon cancer. Here is an attempt at a total synthesis of a chamigrane class compound majusculone.

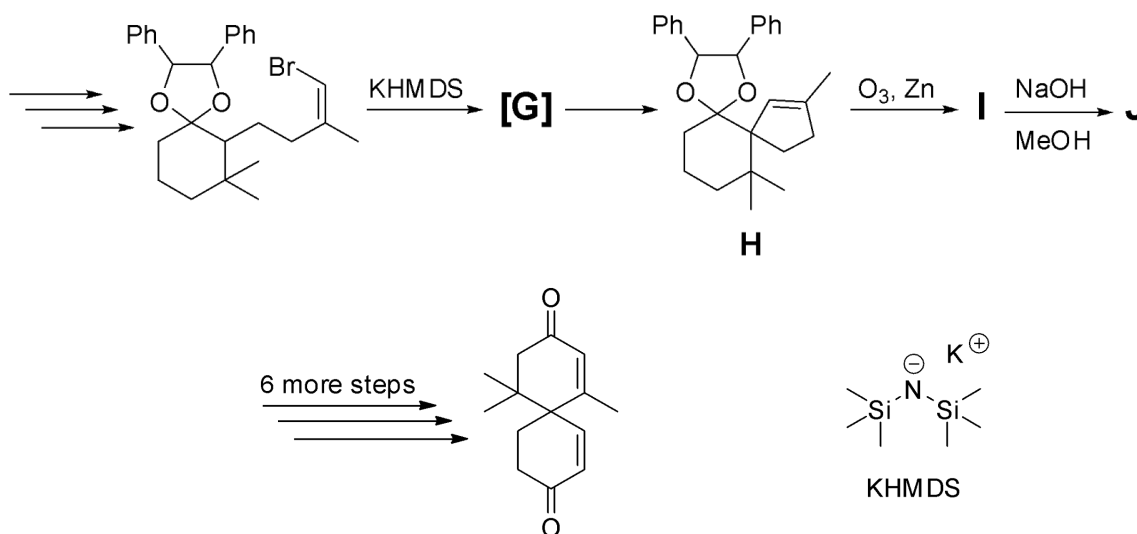


Compound A NMR spectra:



Notes: The  $^1\text{H}$  NMR signal at 0.9 ppm disappears after the addition of some  $\text{CD}_3\text{OD}$ . Ratios of the areas below the  $^1\text{H}$  NMR peaks are 1 : 1 : 2 : 2 : 3 : 1. The molecular mass of the compound **A** is  $86.07 \text{ g mol}^{-1}$ . **D'** is a side product of the reaction.

- Draw the structural formulas of compounds **A–E**.
- Provide reaction conditions and reagents needed for step **F**.



Notes: **G** is a reactive neutral intermediate formed during  $\alpha$ -elimination reaction. It contains a carbon atom with only six valence electrons.  $\text{KHMDS}$  is a strong, hindered base.

- Draw structural formulas of the intermediate **G** and compounds **I** and **J**.
- Determine whether the final product is chiral or achiral. If it is chiral, provide the structure of one of its stereoisomers and specify absolute configurations for all stereogenic centers.
- Write the number of possible stereoisomers of **H**.
- Draw the mechanisms for the formation of **G** and transformation **I**  $\rightarrow$  **J**.

### Problem 1 – BIO, ELECTRO – Photosynthesis

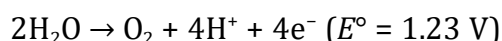
Photosynthesis consists of light and dark phase reactions. Light reactions produce NADPH and ATP, which is followed by dark reactions where the carbon dioxide is being fixed. Chlorophyll becomes excited when a light photon hits it.

- a) Which one is preferably absorbed by the active chlorophyll, green (532 nm) or red (680 nm) photon?

The standard reduction potential for chlorophyll equals 0.78 V.

- b) Calculate the standard reduction potential for chlorophyll for the photochemical process:  $\text{Chlorophyll}^+ + e^- \rightarrow \text{Chlorophyll}^*$ , where an asterisk denotes an excited state.

The splitting of water produces protons and dioxygen when the electrons are carried to the redox systems:

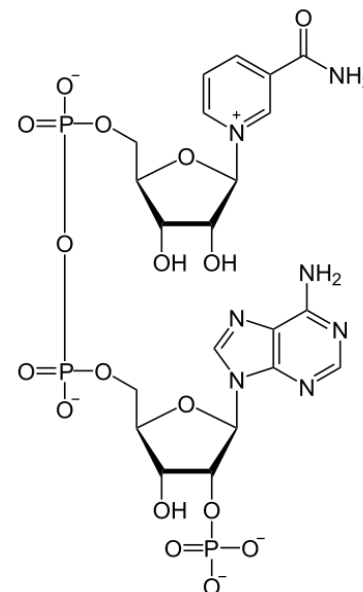


The electrons from the reaction are used to form NADPH:



Actually,  $\text{NADP}^+$  (shown in the figure) binds two protons.

- c) Mark the two new hydrogens in the NADPH structure.  
d) Calculate the potential for cell conditions (pH = 7).  
e) Calculate the  $\Delta G$  for the NADPH formation reaction.



The accumulation of protons inside the chloroplast thylakoid creates a concentration cell.

- f) Calculate the voltage of such a concentration cell if the pH outside the membrane is 7.8 but inside the membrane, the pH is 5.4.

However, nature has used a different approach – the protons are used for the preparation of ATP. The protons synthesized in the inner side of the membrane pass out through the spinning enzyme ATP synthase, producing ATP from phosphate and ADP:  $\text{ADP} + \text{P}_i \rightarrow \text{ATP} + \text{H}_2\text{O}$  ( $\Delta G^\circ = +30.5 \text{ kJ mol}^{-1}$ ).

- g) Draw the structure of ATP.  
h) Calculate  $\Delta G$  for ATP hydrolysis in real cell conditions if the ATP concentration is twice larger than ADP concentration and the phosphate concentration is 5 mM.  
i) Calculate the approximate number of protons needed for the preparation of one ATP molecule.

The following are the dark reactions, which do not need light to function, just a supply of energetic compounds and  $\text{CO}_2$ . Carbon dioxide is bound in a cascade of reactions called the Calvin cycle. Some of the intermediates in the Calvin cycle are used to make glucose as well as other bioorganic compounds.

The NADPH reducing properties are used in the third reaction of the cycle, where 1,3-bisphosphoglycerate is converted to glyceraldehyde-3-phosphate.

- j) Write the equation with correct chemical structures.

It also takes 18 ATP molecules to prepare one glucose molecule.

- k) Write the sum reaction for the dark phase of photosynthesis per one glucose molecule.

**l)** Calculate Gibbs energy for this reaction in cell conditions.

In summary, green plants utilize sunlight to convert  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to organic compounds (glucose  $\text{C}_6\text{H}_{12}\text{O}_6$ ) and  $\text{O}_2$ . The reaction  $\Delta G = 2880 \text{ kJ mol}^{-1}$  and  $\Delta S = -257 \text{ J mol}^{-1} \text{ K}^{-1}$ .

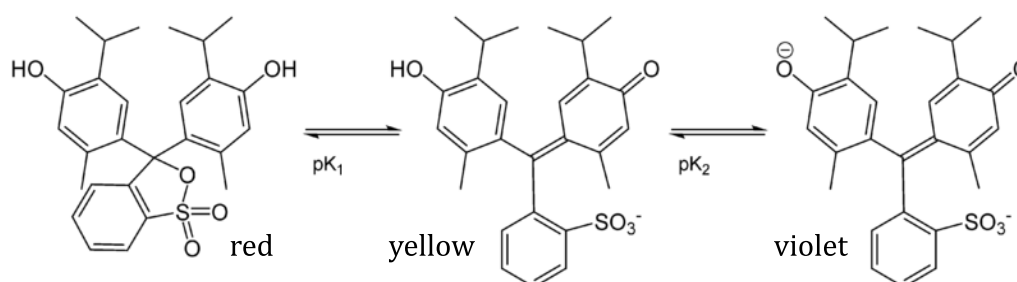
**m)** Calculate the minimum number of photons ( $\lambda = 680 \text{ nm}$ ) required to make one molecule of glucose from  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

**n)** Comment on the spontaneity of this reaction at  $25^\circ\text{C}$  and other temperatures.

### Problem 2 – CALC, EQUIL – Phenolsulfonphthalein

For determination of the endpoint in an acid-base titration, mainly two methods are used – either using an indicator or potentiometric titration. One possible indicator is phenolsulfonphthalein.

| pH    | A      |
|-------|--------|
| 5.02  | 0.0043 |
| 7.42  | 0.0350 |
| 8.32  | 0.2116 |
| 9.23  | 0.6828 |
| 10.26 | 0.9631 |
| 12.61 | 1.0076 |



Unfortunately, not all indicators are applicable for all acid-base titrations. A suitable indicator needs to have its transition range (the pH range where the indicator changes color) near the equivalent point of the titration curve. The transition range is mostly the pH range where the ratio of protonated and deprotonated form of the indicator changes from 1 : 10 to 10 : 1 or vice versa. To validate if phenolsulfonphthalein is a suitable indicator, its  $\text{pK}_{a2}$  value was determined using the spectrophotometric method. In order to do this, the absorbance of phenolsulfonphthalein was measured ( $\lambda = 590 \text{ nm}$ ) at different pH values (the concentration of phenolsulfonphthalein and optical length were kept constant). The obtained results are indicated in the table. It is known that at the lowest measured pH, only  $\text{HA}^-$  occurs in the solution and at the highest measured pH, only  $\text{A}^{2-}$  occurs. It is also known that Beer's law is additive:

$$A = A(\text{HA}^-) + A(\text{A}^{2-}) = \varepsilon(\text{HA}^-)l[\text{HA}^-] + \varepsilon(\text{A}^{2-})l[\text{A}^{2-}]$$

where  $\varepsilon$  is the molecular absorbance coefficient and  $l$  is the optical length in the cuvette.

**a)** Derive a formula to evaluate the  $\text{pK}_{a2}$  values according to the previously described information.

**b)** Calculate the estimated  $\text{pK}_{a2}$  values (4 values) and the average  $\text{pK}_{a2}$  value according to the data given in the table.

50.00  $\text{cm}^3$  of 0.01000 M ammonia ( $\text{pK}_b = 4.75$ ) is titrated with HCl (0.1000 M).

**c)** Calculate the pH of the titration solution if **i)** 4.90, **ii)** 5.00, and **iii)** 5.10  $\text{cm}^3$  of the titrant is added to the solution.

**d)** Can phenolsulfonphthalein be used as an indicator for this titration?

50.00  $\text{cm}^3$  of 0.01000 M acetic acid ( $\text{pK}_a = 4.76$ ) is titrated with NaOH (0.1000 M).

**e)** Calculate the pH of the titration solution if **i)** 4.90, **ii)** 5.00, and **iii)** 5.10  $\text{cm}^3$  of the titrant is added to the solution.

**f)** Can phenolsulfonphthalein be used as an indicator for this titration?

### Problem 3 – STRUCT – Hydrides

Hydrogen is a versatile element. It forms a wide range of binary compounds with metallic and nonmetallic elements. With transition metals, hydrogen forms so-called metallic or interstitial hydrides. When chromium is electrodeposited at low temperatures, a face-centered cubic chromium hydride  $\text{CrH}_x$  can be produced. The unit cell of this hydride may be described as consisting of chromium atoms in a face-centered cubic arrangement and hydrogen atoms located in tetrahedral holes of this cell.

- a) Write a theoretically possible chemical formula for chromium hydride assuming that all tetrahedral holes were filled with hydrogen atoms.

In reality, metallic hydrides are nonstoichiometric compounds, e.g., palladium forms hydride  $\text{PdH}_{0.7}$  instead of theoretically possible  $\text{PdH}$ . This hydride forms upon passing hydrogen gas over palladium. On the other hand, on heating, palladium hydride readily releases hydrogen gas. This fact has an important commercial application – palladium is used for the purification of hydrogen gas and could be used as a fuel tank for hydrogen-powered cars.

The hydrogen storage capacity of a palladium-based fuel tank may be characterized by the ratio  $V(\text{liquid H}_2)/V(\text{solid hydride})$  when both volumes contain the same amount of hydrogen atoms. Density of liquid  $\text{H}_2$  is  $0.0710 \text{ g cm}^{-3}$ . Density of  $\text{PdH}_{0.7}$  is  $12.1 \text{ g cm}^{-3}$ .

- b) Calculate  $V(\text{liquid H}_2)/V(\text{solid hydride})$  ratio for  $\text{PdH}_{0.7}$ .

Another type of hydride are ionic or salt-like hydrides. These compounds contain  $\text{H}^-$  ions. Unknown metal **M** forms hydride  $\text{MH}_x$ , where  $x$  is an integer number. When 1.000 g of  $\text{MH}_x$  reacted with excess water,  $3.216 \text{ dm}^3$  of gas was collected over water at  $25^\circ\text{C}$  and  $100.00 \text{ kPa}$  pressure. Vapor pressure of water at a given temperature is  $23.0 \text{ mm Hg}$ .

- c) Determine the unknown metal **M**.

Crystalline structure of  $\text{MH}_x$  could be described as follows:  $\text{H}^-$  ions arranged in a face-centered cubic lattice and metal ions occupy some holes in this lattice. The lattice constant is  $a$ . Let us assume that we have a sample of  $\text{MH}_x$  that consists of very small cubic crystals of exactly the same size. For a short time, this sample was exposed to open air. Due to the reaction with water vapor, all surface  $\text{H}^-$  ions were transformed into  $\text{OH}^-$  ions. However, ions inside of the crystals remained unchanged. After that, the sample was investigated using  $^1\text{H}$ -NMR-spectroscopy. There are two peaks (for  $\text{H}^-$  and  $\text{OH}^-$ ) in the ratio, accordingly  $150 : 1$  in the resulting spectrum.

- d) Determine the edge length (expressed as a multiple of  $a$ ) of the crystals in the sample.

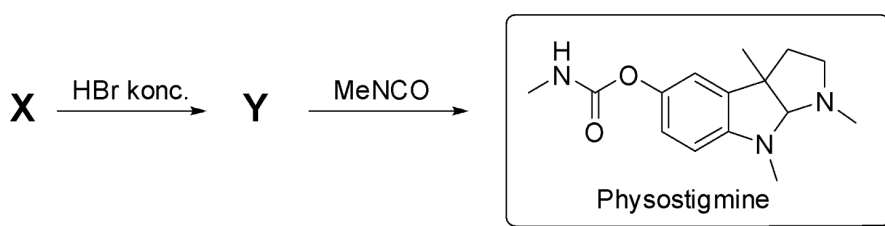
With non-metals, hydrogen forms covalent hydrides. Some of these compounds consist of small molecules, some are polymeric substances.

Boron forms a wide range of binary compounds with hydrogen. The simplest of these compounds is diborane  $\text{B}_2\text{H}_6$ .

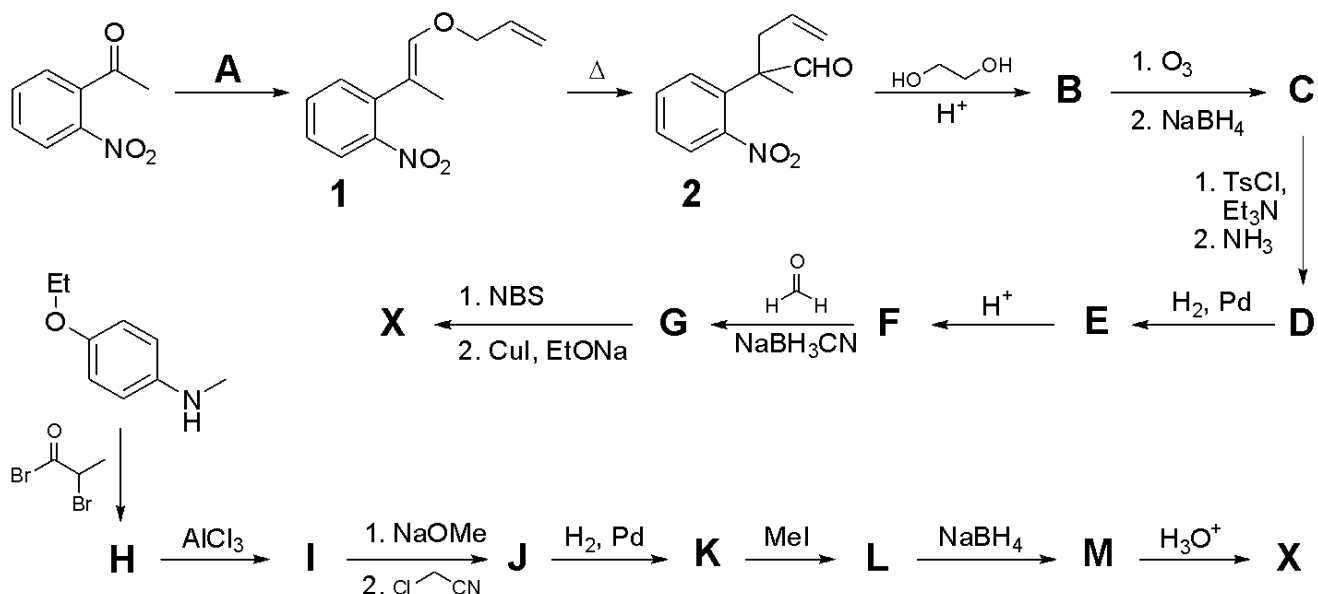
- e) Draw a spatial structure of a  $\text{B}_2\text{H}_6$  molecule.

### Problem 4 – BIO, SYNTH – Physostigmine

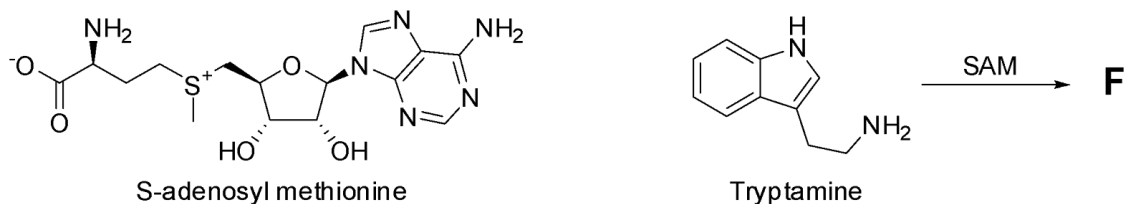
Physostigmine is a reversible acetylcholinesterase inhibitor that can be extracted from *Physostigma venenosum* beans. This compound can be used to treat myasthenia gravis, glaucoma and Alzheimer's disease. In addition, physostigmine enhances short-term memory. Physostigmine is easily obtained from compound **X**:



Compound **X** can be produced using two different methods:



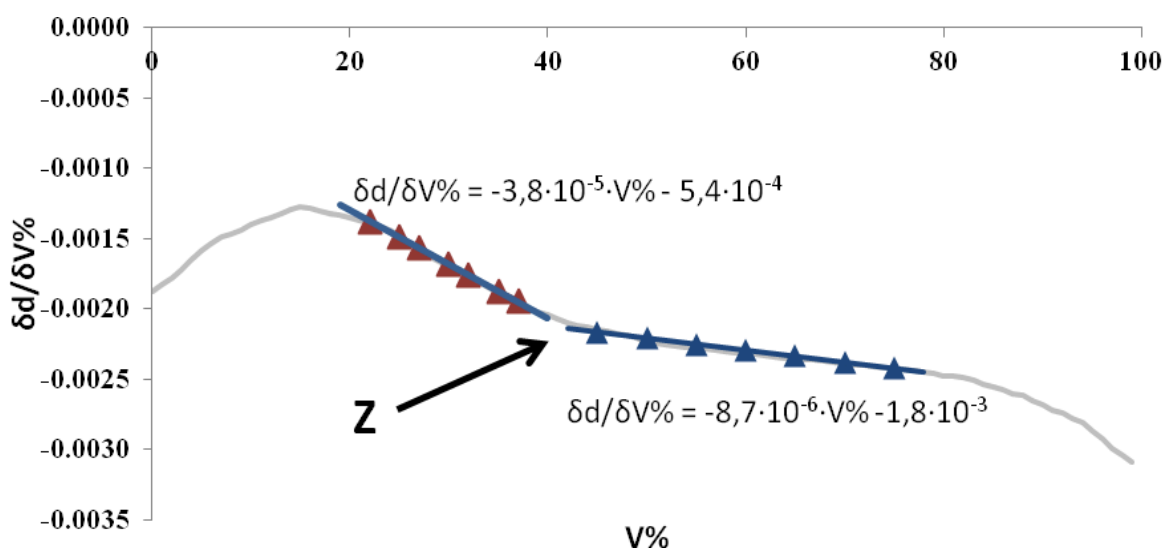
The tricyclic compound **F** is biosynthesized from tryptamine with the aid of methylating coenzyme S-adenosylmethionine (SAM):



- Provide skeletal formulas for the compounds **A–M**, **X** and **Y**.
- Provide mechanisms for the biosynthesis of compound **F** and the transformation of **1** to **2**.
- Write the number of possible physostigmine stereoisomers.

### Problem 5 – THERMO – A national drink

It may seem that famous Russian chemist Dmitri I. Mendeleev (1834–1907) dedicated his life to the periodic table of elements. However, Mendeleev wrote his doctoral thesis, “A Discourse on the Combination of Alcohol and Water”, where he investigated the relationship between density and composition of solutions. Mendeleev’s experiment was repeated using data available on the web and the graph shown below was obtained. It shows derivatives of the density against the volume fraction of the ethanol in solution plotted as a function of the volume fraction of the ethanol. In the graph, there are several extreme points and one of them is marked as **Z**. Such extreme points Mendeleev explained by the formation of ethanol-water hydrates. Density of ethanol is  $0.789 \text{ g cm}^{-3}$ .



- Calculate the composition of ethanol-water hydrate **Z**, where composition is expressed as volume fraction of ethanol in water. Does it fit the Russian vodka standard of 40%?
- Calculate the composition of hydrate **Z** expressed as mass fraction and molar fraction of ethanol in solution. If you were unable to solve question **a)**, you may assume that **Z** corresponds to 40% ethanol (volume fraction).
- Point out the main intermolecular forces acting between the ethanol and the water molecules in the hydrate.

Pure ethanol is a colorless liquid with a boiling point of 78.37 °C (pressure  $p = 101.33$  kPa), while at 20.00 °C its vapor pressure is 5.95 kPa. Assume that all enthalpy and entropy changes given and calculated in this problem are temperature-independent.

- Calculate the molar enthalpy and entropy of vaporization of ethanol.
- Compare the obtained value with molar enthalpy of vaporization of water, which is  $44.0 \text{ kJ mol}^{-1}$  at 80 °C. Explain why the obtained enthalpy value is greater/smaller than the enthalpy of vaporization of water.

Ethanol is widely used in homemade window cleaning solutions but it is not very effective as ethanol quickly evaporates. It also may be used as a window cleaner for cars during winter.

- Calculate the melting point for 35% (mass fraction) ethanol solution. The cryoscopic constant for water is  $1.85 \text{ K kg mol}^{-1}$ .

Ethanol is also used as an additive in biofuel. The leading country in the use of ethanol as a gasoline additive is Brazil, where fuel E25 contains 25% (volume fraction) ethanol while the rest is petrol. Let's assume that the petrol consists of pure octane ( $\rho_{\text{octane}} = 0.703 \text{ g cm}^{-3}$ ).

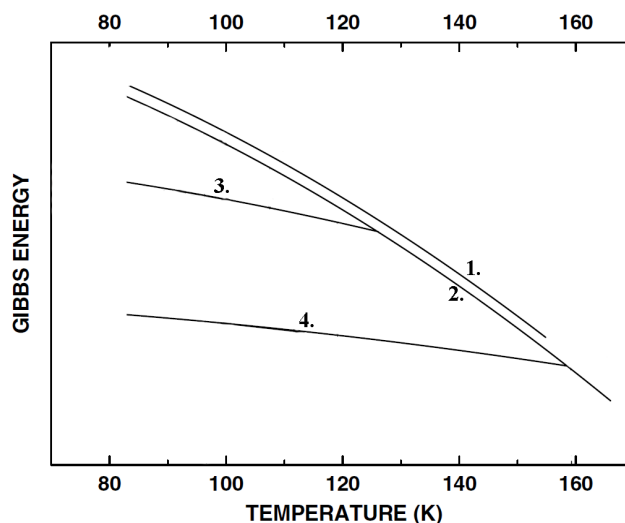
- Calculate the enthalpy of combustion for octane and ethanol (in kJ per mol) using average bond enthalpies given in Table. Calculate the heat ratio between combustion of 1.0 kg of ethanol and combustion of 1.0 kg octane.

| Chemical bond                                | C-H | C-C | C-O | O=O | H-O | C=O |
|----------------------------------------------|-----|-----|-----|-----|-----|-----|
| $\Delta H(\text{bond}), \text{ kJ mol}^{-1}$ | 413 | 348 | 358 | 498 | 463 | 804 |

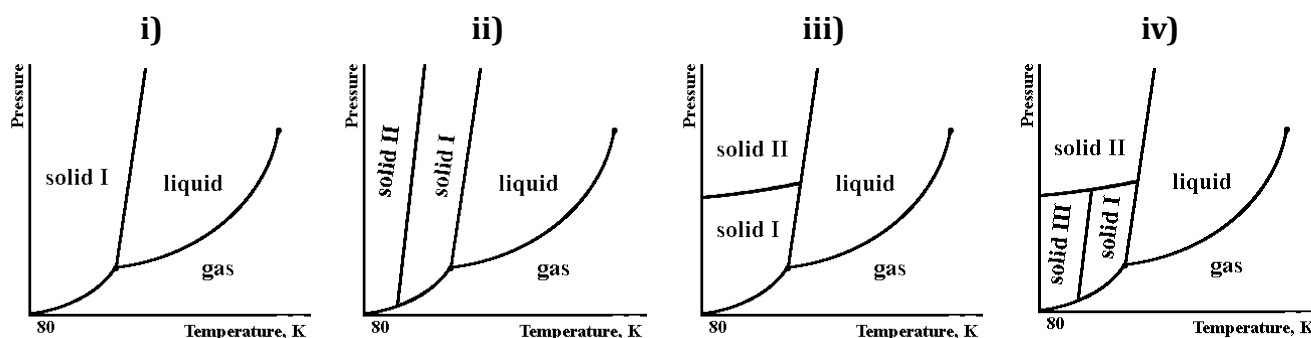
- Enthalpy of the chemical reactions can be calculated using the standard enthalpies of formation. Using the data from Table, calculate the enthalpy of combustion of ethanol and identify the main reason for differences between values calculated here and in question **g)**.

| Compound                                | Ethanol (l) | Carbon dioxide (g) | Water (l) |
|-----------------------------------------|-------------|--------------------|-----------|
| $\Delta H^\circ$ , kJ mol <sup>-1</sup> | -277.0      | -393.5             | -285.0    |

At low temperatures, ethanol exists in solid state and it has been detected that there are two different polymorphic modifications of ethanol. Gibbs energy curves for different phases of ethanol are shown below.



- Identify these curves as corresponding to **i)** liquid ethanol, **ii)** thermodynamically stable solid form, **iii)** metastable solid form, and **iv)** supercooled liquid and explain your choice.
- Determine the melting point of the thermodynamically stable and metastable forms.
- Which of the following phase diagrams can correspond to ethanol? What are the limitations for pressure for selected diagrams, if there are any? Show these limitations by marking the pressure that corresponds to the data given in Figure 2.



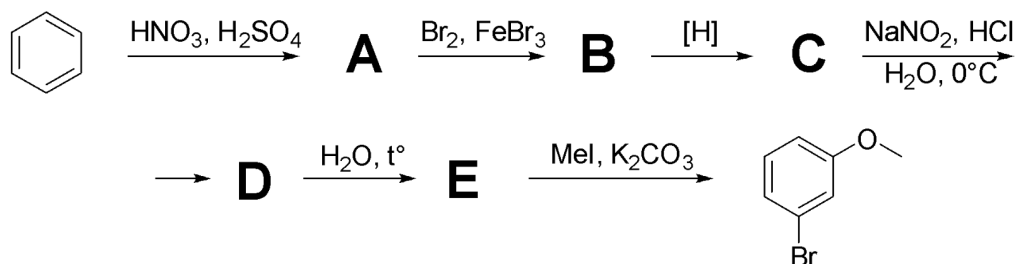
### Problem 6 - MECH, SYNTH - Benzyne

Some of the most fascinating types of reactions are those involving the intermediacy of benzyne. Benzyne is benzene minus two adjacent hydrogens, producing a formal triple bond – C<sub>6</sub>H<sub>4</sub>. The structure of benzyne has been examined both experimentally and theoretically, and the alkyne representation is most widely accepted, although two other structures are considered significant resonance contributors. Using IR spectroscopy, the vibrational frequency of the triple bond in benzyne was assigned to be 1846 cm<sup>-1</sup>; an unstrained alkyne has a vibrational frequency of approximately 2150 cm<sup>-1</sup>.

- What does this say about the relative strength of the benzyne triple bond compared to unstrained alkyne? Circle correct answer(s): **i)** stronger; **ii)** longer; **iii)** weaker; **iv)** shorter.

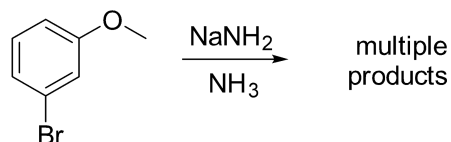
Due to the extreme reactivity of arynes, they must be generated in situ. In the early days of benzyne chemistry, harsh conditions were needed to generate benzyne from aryl halide and a strong base. Consider the following scheme for the synthesis of *m*-bromoanisole, which is then used as a substrate for an experiment involving a benzyne intermediate.

b) Suggest structures for **A**, **B**, **C**, **D**, and **E**.



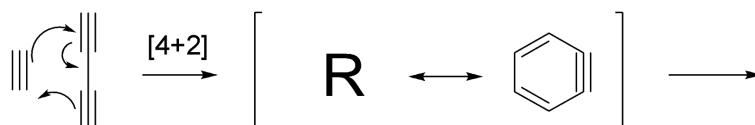
The reaction of *m*-bromoanisole with amide anion in liquid ammonia could potentially give multiple benzyne intermediates and multiple products.

c) Suggest structures for all possible intermediate benzyne(s) and all possible final products after the workup step!



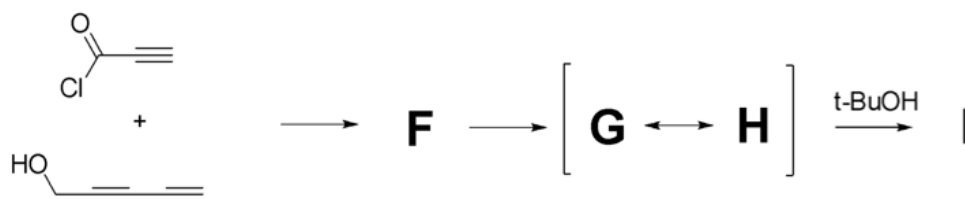
A hexadehydro-Diels-Alder (HDDA) reaction was developed to generate benzyne intermediates in a very sensitive manner. HDDA involves the cycloaddition of 1,3-diyne and alkyne.

d) Draw the structural formula of the resonance structure **R**.



Consider the following scheme, in which a novel benzyne generation approach was used.

d) Suggest the structures for **F**, **G**, **H** and **I**.

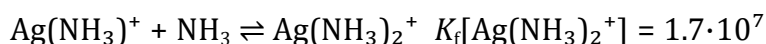


### Problem 1 – EQUIL – Silver compounds

Silver forms sparingly soluble salts with chloride, bromide, iodine, and cyanide. Their  $K_{sp}$  values are  $1.77 \cdot 10^{-10}$ ,  $5.2 \cdot 10^{-13}$ ,  $8.3 \cdot 10^{-17}$ , and  $5.97 \cdot 10^{-17}$ , respectively.

- Determine the order of precipitation of the anions in an equimolar solution. Assume that precipitation is the only reaction and that cyanide ions do not hydrolyze.
- To what extent (in percent) have bromide ions precipitated by the time chloride ions start to precipitate?
- Cyanide ions correspond to a weak acid hydrogen cyanide ( $pK_a = 9.21$ ) and are, therefore, hydrolyzed to a different extent depending on the pH of the solution. If the pH of the solution is 7.0, what extent of the cyanide ions has been hydrolyzed?
- Determine the order of precipitation of the chloride, bromide, iodine, and cyanide anions in the equimolar solution (pH = 7.0) while accounting for the hydrolyses of  $CN^-$  ions.
- Is it possible to selectively (left into the solution less than 0.1% of the starting concentration) precipitate iodine so that other ions do not coprecipitate at pH = 7?

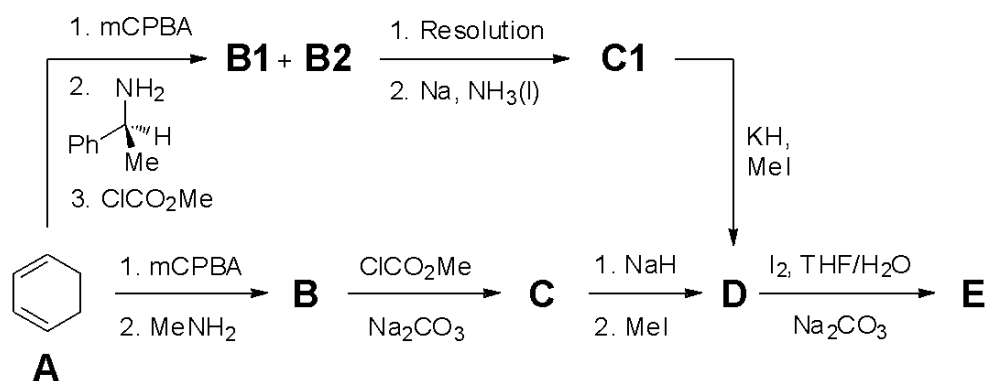
In the solutions with high halogen content, ammonia ( $pK_b = 4.75$ ) is often added to avoid precipitation. In the solution, two possible complexes are formed:

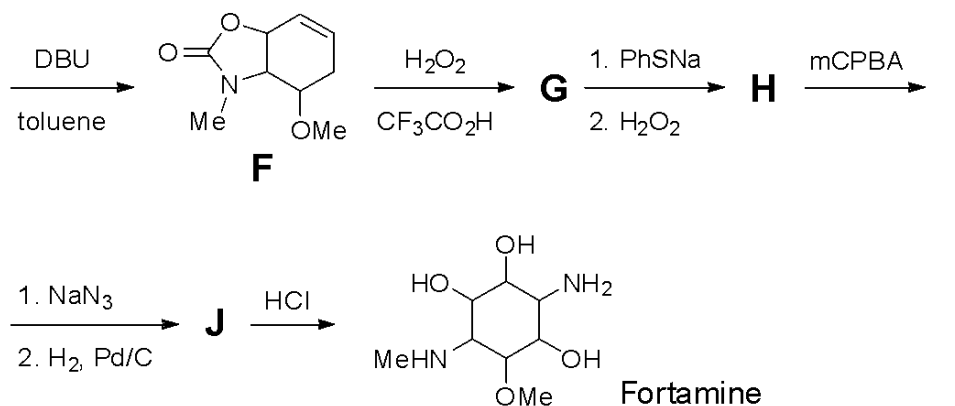


- Determine how much silver is not bound to the complexes if the solution contains 0.10 M  $Ag^+$ , 0.50 M ammonia, and the pH of the solution is 7.0.
- How much silver can be dissolved in 0.10 M chloride solution that also contains 0.50 M ammonia and the pH is 7.0?

### Problem 2 – STEREO, SYNTH – Fortamine

Antibiotic Fortamine has an interesting structure – all of its cyclohexane carbon atoms are chiral. You must deduce the absolute configuration for all of them (besides the other questions). The stereochemical information must be shown unambiguously for all the compounds.





The starting material **A** was treated with *m*-chloroperoxybenzoic acid, followed by methylamine to produce compound **B**. The reaction of **B** with methyl chloroformate and then NaH/Mel yields racemic product **D**. Since Fortamine must be enantiomerically pure, an alternative method to access single enantiomer of **D** was proposed via intermediates **B1** and **B2** (which are diastereomers to each other). During the resolution of **B1** and **B2**, the (*S,S,S*)-compound was isolated and treated with sodium in liquid ammonia to produce enantiomerically pure **C1**.

**a)** Draw the structures of compounds **B**, **B1**, **B2**, **C**, and **C1**.

The conversion of **D** to **E** is a modification of a classical reaction, where a carboxylic acid is used instead of an ester. However, both the ester and acid would yield the same product **E**. The latter was treated with a non-nucleophilic base DBU to give an elimination product **F**.

**b)** Draw the structures of compounds **D** and **E**.

**c)** Show the mechanism for the reaction **D** → **E**.

Unlike *m*-CPBA and other peroxyacids,  $\text{CF}_3\text{CO}_3\text{H}$  is able to coordinate not only with hydrogen-bond donors but also to protect alcohols. In this case, it leads to a stereoselective reaction. Treatment of **G** with PhSNa followed by elimination gives compound **H**, which, after a few subsequent reactions, is transformed into enantiomerically pure Fortamine.

**d)** Show the structure of the intermediate molecular complex of reaction **F** → **G**.

**e)** Draw the structural formulas for compounds **G–J**.

**f)** Indicate the configuration of all the chiral carbons of Fortamine using *R/S* nomenclature.

### Problem 3 – APPLIED, ELECTRO – Redox flow battery

A redox flow battery consists of two electrolyte tanks and two (usually carbon) electrodes, which are separated by a proton exchange membrane. One of the tanks contains an oxidizer aqueous solution and the other reducing agent aqueous solution. If the oxidation-reduction reactions are reversible, the system can be used as a rechargeable battery. Some high energy density flow battery systems are promising candidates as an energy source for an electric car.

In the case of the vanadium redox battery (VRB), both electrolytes contain vanadium redox species, which exist in oxidation states V, IV, III, and II. The cathode electrolyte with 1 M vanadium cation concentration was prepared by dissolving vanadium(V) oxide in 4 M sulfuric acid, yielding a hydrated cation with a molecular mass of  $155 \text{ g mol}^{-1}$ . The anode electrolyte was prepared by electrochemical reduction of the cathode electrolyte.

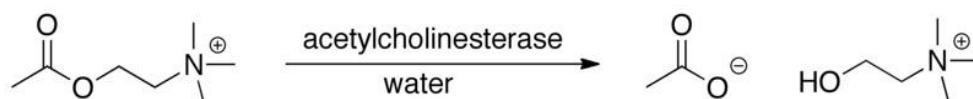
During VRB discharging, the cathode electrolyte changes from yellow to green and, finally, blue; the anode electrolyte turns from violet to green.

If ammonium vanadate(V) is reduced with zinc in a sulfuric acid solution, the following color changes can be seen: yellow → green → blue → green → violet.

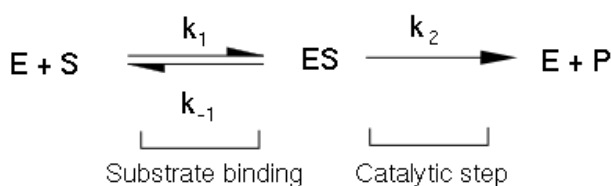
- Deduce the reactions taking place during ammonium vanadate(V) reduction with zinc.
- Identify redox compounds and write **i)** anode, **ii)** cathode, and **iii)** overall reaction during discharging of VRB.
- i)** Write a formula for calculating the EMF of the VRB cell as a function of vanadium redox potentials and concentration of cations. **ii)** How much does the voltage of VRB change when pH is one unit lower?
- The experimental voltage of VRB is 1.4 V. Calculate **i)** Gibbs energy and **ii)** equilibrium constant  $K$ .
- Calculate and compare the energy density of VRB with lead-acid battery ( $40 \text{ Wh kg}^{-1}$ ). For simplification, the volume of the VRB can be taken equal to the volume of electrolyte solutions with a density of  $1.3 \text{ g cm}^{-3}$ .

#### Problem 4 – BIO, KINETICS – Kinetics of neuromuscular enzyme

Acetylcholinesterase is the enzyme in the neuromuscular junction that catalyzes the degradation of acetylcholine – a neurotransmitter released by the parasympathetic nervous system. Inhibitors of this enzyme are used in medicine to treat glaucoma and postural tachycardia syndrome. In this problem, the kinetics of this enzyme is analyzed.



It is known that the first step of this enzymatic reaction is the reversible binding of the acetylcholine (substrate, S) to the acetylcholinesterase (enzyme, E), producing enzyme-substrate complex (ES). The second step is the reaction itself and the release of the products (P) and free enzyme (E), and it is known that this is the rate-determining step.



It is also known that this reaction obeys the Michaelis–Menten kinetics:  $v = \frac{v_{\max}[\text{S}]}{K_{\text{M}} + [\text{S}]}$ , where  $v_{\max}$  is the maximum rate of the reaction and  $K_{\text{M}}$  is Michaelis constant.

- By assuming that the enzyme-substrate complex is in a steady state, derive the Michaelis–Menten equation.

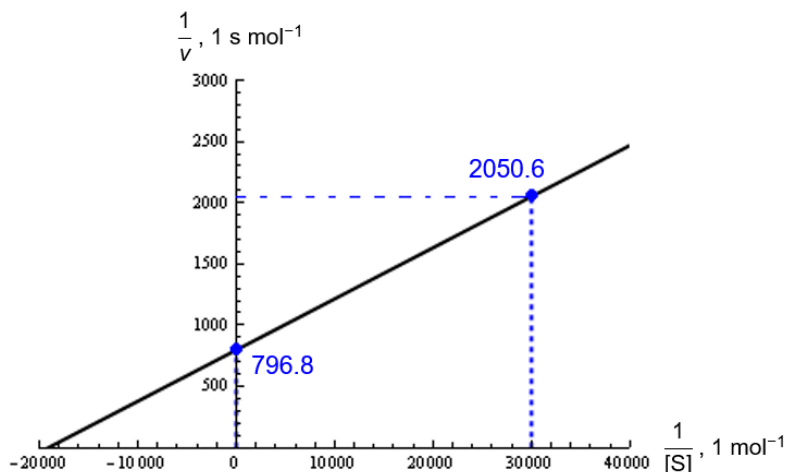
Using the Michaelis–Menten equation, determine reaction rate order with respect to the substrate in two cases: **i)** substrate concentration in solution is huge; **ii)** substrate concentration is very small.

- Sketch the graph showing reaction rate dependence on the enzyme concentration.

The reaction rate is temperature-dependent.

- Sketch two graphs showing reaction rate as a function of temperature in classical reaction (case **i)** and in enzymatic reaction (case **ii)**.

In the experiment, the rate of this enzymatic reaction was measured at various acetylcholine concentrations. The results are shown as a plot of the inverse of the rate against the inverse of substrate (acetylcholine) concentration. Two data points are marked in the graph.

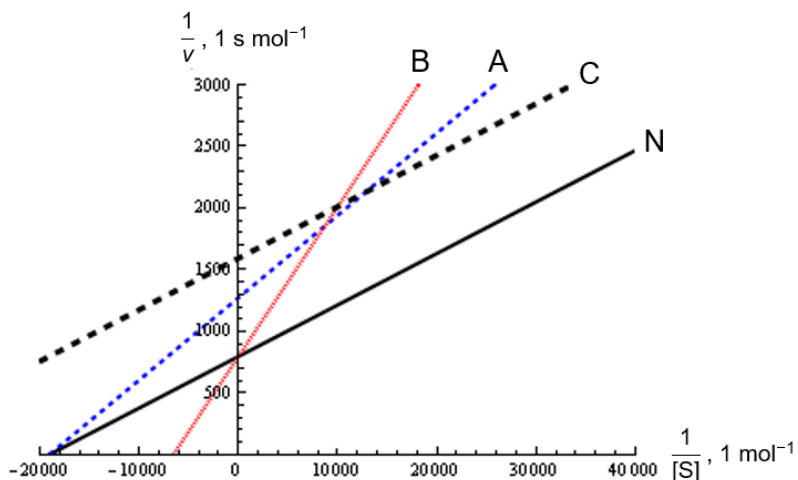


- d) Which method is more suitable for investigating acetylcholine hydrolysis reaction: **i) gasometry; ii) gravimetry; iii) conductometry; iv) titrimetry?**
- e) Linearize the Michaelis-Menten equation to obtain an equation consistent with the data presented in the Figure.
- f) Calculate  $v_{\max}$  and concentration of the substrate at which the reaction rate is half the maximum.
- g) Calculate the rate constant  $k_2$ , if the total concentration of acetylcholinesterase in the experiment was  $2.00 \cdot 10^{-5}$  M.

The activity of acetylcholinesterase was tested in the presence of 3 different inhibitors:

- Physostigmine – competitive inhibitor used in the treatment of glaucoma;
- Caffeine – non-competitive inhibitor, effects of coffee partly originate from this inhibition; Caffeine can bind with both free enzyme and enzyme-substrate complex, rate of both reactions is the same;
- A2435 – uncompetitive inhibitor which binds only to the enzyme-substrate complex.

The effects of these three inhibitors are shown in a plot of the inverse of rate against the inverse of substrate concentration with inhibitors (A, B, C) and without an inhibitor (N).



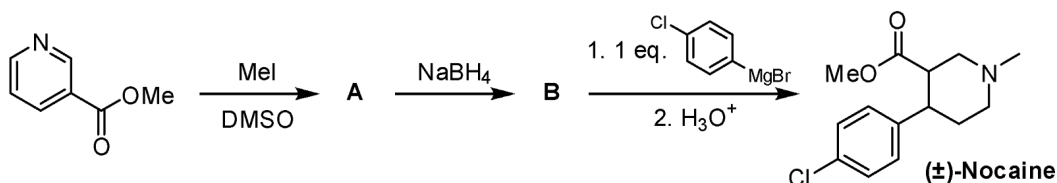
- h) Which of the lines A, B, or C correspond to each of the inhibitors mentioned above?

There is another way of linearizing the Michaelis–Menten equation to a different form. In this form, plotting  $[S]/v$  against  $X$  gives a straight line.

i) Determine the variable  $X$ .

### Problem 5 – SPECTRA, STEREO – Nocaine

Nocaine effects on CNS are similar to those of cocaine, but due to its less pronounced addictive effect, it has been used in cocaine addiction treatment. Some of its derivatives show enhanced activity, while others have an entirely different mode of action.



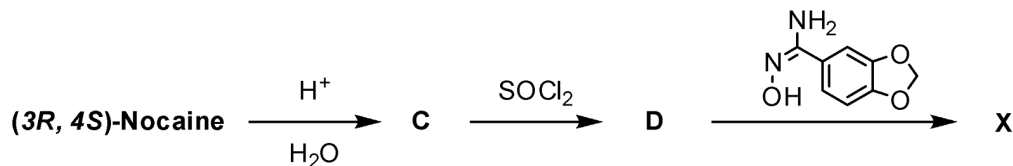
NMR spectra of compound **B**:  $^1\text{H}$  NMR (500 MHz)  $\delta$ : 2.37 (2H, dt,  $J = 6.0, 3.0$  Hz), 2.41 (3H, s), 2.50 (2H, t,  $J = 6.0$  Hz), 3.15 (2H, s), 3.74 (3H, s), 7.00 (1H, t,  $J = 4.0$  Hz).

$^{13}\text{C}$  NMR (125 MHz)  $\delta$ : 26.5, 45.6, 50.7, 51.4, 53.2, 128.9, 137.5, 166.9.

a) Draw structures for compounds **A** and **B**.

b) Assign NMR signals to their respective atoms. It will be considered that some of the  $^{13}\text{C}$  signals cannot be assigned unambiguously.

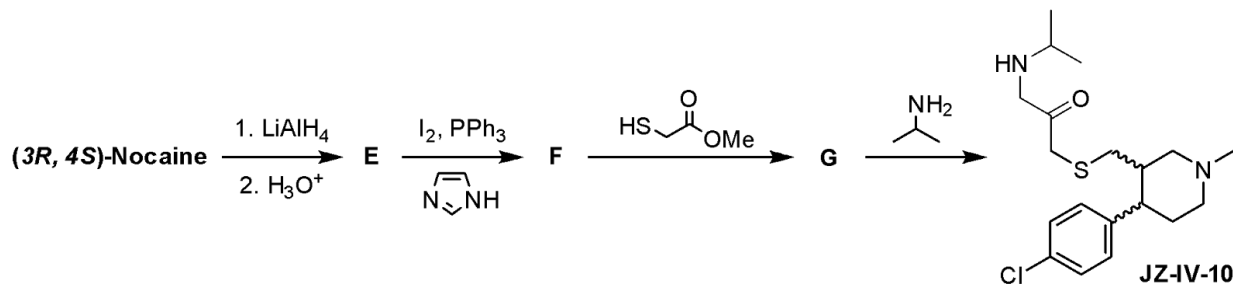
1,2,4-oxadiazoline derivative **X** is both more potent and more resistant to metabolism than nocaine, which means it can be used in lower doses.



c) Draw structural formulas of compounds **C**, **D**, and **X**.

d) Provide a mechanism for the formation of 1,2,4-oxadiazoline ring (**D**  $\rightarrow$  **X**).

Another nocaine derivative, JZ-IV-10, does not display cocaine-like euphoric and stimulant effects; however, it does increase wakefulness and reduces the need for sleep.



e) Draw structures for compounds **E**–**G**.

f) The 3*R*,4*S* stereoisomer of the nocaine derivatives is usually the most active. Draw the JZ-IV-10 structure, indicating the correct absolute configuration.

g) Provide the mechanism for the **E**  $\rightarrow$  **F** transformation. The reaction also produces triphenylphosphine oxide and imidazolium iodide.

h) Which method could theoretically be used to separate (3*R*,4*S*)-nocaine from (3*S*,4*R*)-nocaine?

### Problem 6 – ABC, CALC, THERMO – Chemistry of superacids

According to the classical definition, a superacid is an acid with an acidity greater than that of 100% sulfuric acid. According to the modern definition, a superacid is a medium in which the chemical potential of the proton is higher than in pure sulfuric acid.

The simplest class of superacids is the Brønsted superacids. The first acid named accordingly was chlorine-containing **A** because of its ability to protonate aldehydes and ketones. Due to its explosive hazard, its use is partially limited. By adding anhydrous **A** to concentrated nitric acid, salt **B** can be obtained.

- a) Draw the chemical formula for **A** and **B** and the Lewis structure formulas for ions in **B**. Draw all resonance structures of the cation in **B**.

A superacid **C** is considered to be the strongest among superacids known so far and is prepared in a simple reaction between a Lewis superacid **D** and Brønsted superacid **E**, both being binary compounds containing a common chemical element. The ratio of the weight fraction of this element in **D** and **E** is 2.1668. It is known that **C** is ionic and consists of two ions,  $C_+$  and  $C_-$ .

- b) Draw the chemical formulas and Lewis structures of **D** and **E**. What is the geometrical shape of **D**? Write equations of the described reactions.
- c) Draw the chemical formula of **C**. Draw the Lewis structures of  $C_+$  and  $C_-$ . What is the geometrical shape of these ions?

This extraordinarily strong acid is able to protonate nearly all organic compounds. It has been shown it removes  $H_2$  from isobutane (2-methylpropane) and methane from 2,2-dimethylpropane. Note that in this way, cation  $K_+$  is obtained.

- d) Write the equations of these chemical reactions by showing the carbon atom that will be protonated. What considerations will determine which carbon atom gets protonated?

Recently, a group of scientists from Freiburg, Germany, reported the superacidity of **F**, which is prepared in a simple reaction between a Brønsted acid **G** and a Lewis acid **H**, both containing a common chemical element. It is known that the weight fraction of element **X** (not present in **G**) in **H** is 0.10117, and also that **F** is ionic and its anion can exist in two chemically distinct forms for which molecular weight ratio  $F_{-B} : F_{-A}$  is 1.7695.

- e) Draw the chemical formula of **F**,  $F_{-A}$ ,  $F_{-B}$ , **G**, and **H**. Draw the Lewis structures and predict the geometry of  $F_{-A}$  and **H**. Draw the geometry of  $F_{-B}$ .

**F** can protonate benzene by producing an ionic compound **J** containing anion  $F_{-B}$ .

- f) Write the chemical structure of **J**. How many signals will there be in the  $^1H$ ,  $^{13}C$  and **X** NMR spectra of **J**?

Interestingly, the reaction between the Lewis acid **H** and 2-bromo-2-methylpropane produced an ionic compound **K** with the same anion  $F_{-B}$  and a cation  $K_+$ .

- g) Write the chemical structure of **K**. How many signals will there be in the  $^1H$ ,  $^{13}C$  and **X** NMR spectra of **K**?

It has been shown that thermodynamic characteristics of ionic compounds similar to **K** can be calculated by the use of empiric equations. As input data, experimentally determined compound properties or those obtained from quantum chemical calculations can be used. Equations for calculation of vaporization, solvation (enthalpy for the transition from ions in the gas phase to ions in the liquid state), and lattice enthalpies are given below:

$$\Delta H_{\text{vap}} = aV_{\text{m}}^{2/3} + bH_{\text{g}} + c; \Delta H_{\text{solv}} = -\Delta H_{\text{vap}} - \Delta H_{\text{diss}}; \Delta H_{\text{latt}} = d\Delta H_{\text{solv}} + e$$

$$a = -224 \text{ kJ mol}^{-1} \text{ nm}^{-2}, b = 0.0929, c = 194 \text{ kJ mol}^{-1}, d = -0.685, \text{ and } e = 172 \text{ kJ mol}^{-1}$$

- h)** Use the provided equations (consistent with the Born–Haber cycle) to calculate the lattice enthalpy of **K**, if  $V_{\text{m}}$  of **K** is  $0.4175 \text{ nm}^3$  (determined by single-crystal X-Ray diffraction),  $H_{\text{g}} = 394.9 \text{ kJ mol}^{-1}$ , and  $\Delta H_{\text{diss}} = 395.9 \text{ kJ mol}^{-1}$  (both found by quantum chemical calculations).

The reaction between  $0.100 \text{ mol}$  of **H** and  $0.100 \text{ mol}$  of 2-bromo-2-methylpropane was performed in a calorimeter filled with  $2.00 \cdot 10^2 \text{ g}$  of ethanol (specific heat capacity of  $2.44 \text{ J g}^{-1} \text{ K}^{-1}$ ). By performing the reaction at  $0^\circ \text{C}$  it was found that the temperature of ethanol increased by  $5.94^\circ \text{C}$ , while by performing the same reaction at  $20^\circ \text{C}$ , the temperature of ethanol increased by  $2.46^\circ \text{C}$  (assume the calorimeter constant to be 0 and enthalpy being temperature independent). It was determined that the melting point of **K** is  $2^\circ \text{C}$ .

- i)** Calculate the reaction enthalpy at  $0^\circ \text{C}$  and at  $20^\circ \text{C}$ . Calculate the enthalpy of fusion of **K**.
- j)** Use the Born–Haber cycle to calculate the enthalpy of fusion of **K** from the results in question **h)**. Identify the main cause of errors for each of the approaches used to determine the enthalpy of fusion.

The experimental enthalpy of vaporization of 2-bromo-2-methylpropane ( $+32 \text{ kJ mol}^{-1}$ ) and the sublimation enthalpy of **H** ( $+85 \text{ kJ mol}^{-1}$ ) are tabulated in handbooks of physical chemistry.

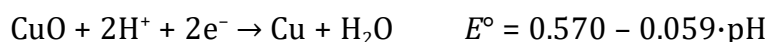
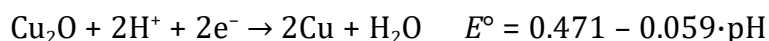
- k)** Use the Born-Haber cycle to calculate the reaction enthalpy for the reaction between **H** and 2-bromo-2-methylpropane in the gas phase (where separated ions **F<sub>-B</sub>** and **K<sub>+</sub>** in the gaseous state are obtained).

### Problem 1 – ELECTRO – Copper Man

“Copper Man” was a Chilean copper miner who was entrapped in a copper mine in 550 AD and subsequently copperized (coated in copper). The mummy has become a subject of interest in archeology, metallurgy, and, more recently, art. Under the right conditions, charcoal dust can promote a reaction leading to Copper Man’s coating. Assume that Copper Man is coated in  $\text{Cu}_2\text{O}$  and  $\text{Cu}^0$ , originating from  $\text{Cu}^{2+}$  salts in the copper mine.

- a)** State the role of charcoal in this reaction: **i)** reducing agent; **ii)** oxidizing agent; **iii)** catalyst; **iv)** insulator; **v)** none of the above.

Consider the following reactions and reduction potentials:

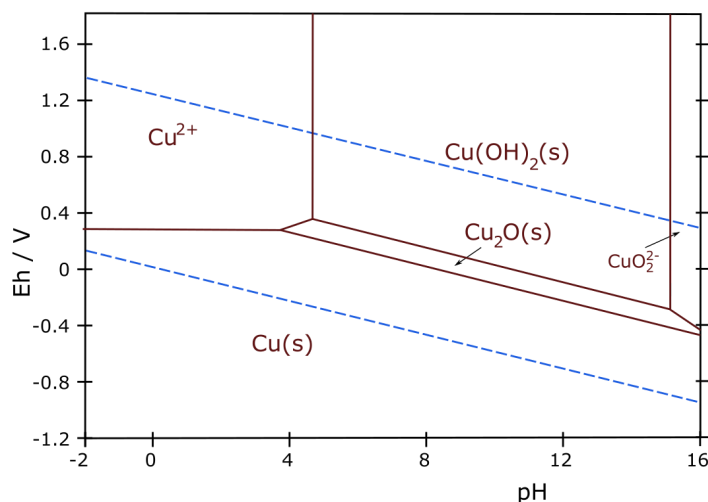


- b)** For a neutral ( $\text{pH} = 7.0$ ) environment, construct a Latimer diagram for the above couples and calculate the potential for the  $\text{CuO}/\text{Cu}_2\text{O}$ .

Chalcanthite, the pentahydrate of copper sulfate, was the mineral that Copper Man was harvesting from the mine. In order to extract copper from the chalcanthite, Copper Man heated the chalcanthite to  $>700^\circ\text{C}$  in the presence of  $\text{Na}_2\text{O}$ , at which point an explosion would occur due to the following reactions: (1)  $4\text{CuSO}_4 + 4\text{Na}_2\text{O} \rightarrow 4\text{Na}_2\text{SO}_4 + 2\text{Cu}_2\text{O} + \text{O}_2$  and (2)  $\text{Cu}_2\text{O} + \text{CO} \rightarrow 2\text{Cu}^0 + \text{CO}_2$ .

- c)** Calculate the Gibbs free change energy for these reactions using the half-reaction standard potentials. For  $\text{CO}_2 + 2\text{e}^- \rightarrow \text{CO} + \text{O}^{2-}$ , use  $E^\circ = 0.11\text{ V}$ , and for  $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$  use  $E^\circ = 1.23\text{ V}$ .

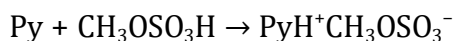
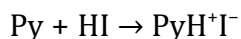
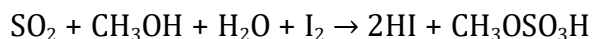
For an exhibition, you must recreate Copper Man using a galvanic cell. Consider the Pourbaix diagram of copper.



- d)** Draw a diagram of a two-compartment galvanic cell that incorporates Copper Man as an electrode in solution **X** coupled to a metal **Y** electrode in a solution of the same metal ions. Label all components, including the electrodes (cathode and anode), the electrolyte species, and the reactions occurring at the electrodes. Choose the main component of the solution **X**:  $\text{CuCl}_2$ ,  $\text{Na}_2\text{CuO}_2$ ,  $\text{Cu(OH)}_2$ ,  $\text{CuCl}$ . Choose metal **Y** suitable for copper plating in the galvanic cell: Zn, Ag, Na, Au.

## Problem 2 – CALC, SPECTRA – Determination of water content

Very small water quantities can be measured with different methods: Karl Fischer titration, nuclear magnetic resonance, infrared spectroscopy, gas chromatography, and UV-Vis spectroscopy. In Karl Fischer titration, a mixture of iodine, pyridine (Py), sulfur dioxide, and methanol is used. In the presence of water, the following reactions take place:



Usually, the limiting component of the reaction is iodine. As Karl Fischer's titrant is somewhat unstable, the practical titer (mass of analyte per volume of titrant) is often determined right before the analyses of a sample. An analyst weighed 260.3 mg of pure water and filled the 100 cm<sup>3</sup> volumetric flask with acetonitrile that did not contain any water. 10.00 cm<sup>3</sup> of the sample was taken for analyses, and 6.20 cm<sup>3</sup> of titrant was spent to reach the endpoint.

**a)** Calculate the titre (mg cm<sup>-3</sup>) of the Karl Fischer titrant.

The same titrant was used to determine the water content of commercial acetonitrile. 20.00 cm<sup>3</sup> of the commercial acetonitrile was titrated with 5.12 cm<sup>3</sup> of titrant. The density of acetonitrile is 0.786 g cm<sup>-3</sup>.

**b)** Determine the water content in commercial acetonitrile (% and ppm).

A coulometric Karl Fischer titration is used in a laboratory, where one of the reagents I<sub>2</sub> is generated electrochemically from I<sup>-</sup>. The bias of the coulometric titration was of interest. 4.113 g of acetonitrile (with an unknown amount of water) was analyzed with the coulometric Karl Fischer method, and 138.7 C was passed through a coulometer. 143.2 mg of water was weighed into a 100 cm<sup>3</sup> volumetric flask and filled with the same acetonitrile to mark. 2.714 g of the sample was taken for analysis and 145.3 C was used for complete titration of the sample.

**c)** Calculate the bias for this titration.

The same procedure was repeated with 1.356 g of water weighted into a 100 cm<sup>3</sup> volumetric flask. For titrating 1.194 g of this sample, 306.7 °C was used.

**d)** Calculate the bias for this titration.

**e)** Explain why two titrations can have a significantly different bias in this case.

Karl Fischer titration can also be used for water determination in solid samples if these can be dissolved in the appropriate solvent. However, some building materials such as cement, chalk, and ceramic materials can not be analyzed in this way due to occurring side reactions. Therefore, infrared spectroscopy was used. Two chalk-based reference materials containing 2.1 mg kg<sup>-1</sup> and 17.2 mg kg<sup>-1</sup> of H<sub>2</sub>O were measured with the attenuated total reflectance (ATR) method. At peak, maximum absorptions observed were 0.045 and 0.371 AU.

**f)** What side reaction occurs for these materials, and how does it influence the bias of Karl Fischer's method?

Lambert-Beer law states that  $A = \epsilon lc$ , where  $A$  is the absorption at wavelength  $\lambda$ ,  $\epsilon$  is the molar attenuation coefficient at wavelength  $\lambda$ ,  $l$  is the optical path length, and  $c$  is the analyte concentration. Assume that the optical path length is the same for all three measured materials.

- g) With the IR-ATR method, a chalk sample was also analyzed, and an absorbance of 0.276 AU was recorded at the peak maximum. Based on the Lambert-Beer law, calculate the water content in the chalk sample.

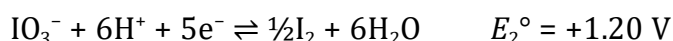
### Problem 3 – ELECTRO, EQUIL, KINETICS – Some simple physical chemistry

An equilibrium is reached in 0.10 M AgNO<sub>3</sub> and  $x$  M NH<sub>3</sub>·H<sub>2</sub>O solution:



- a) Calculate the value of  $x$  at the maximal concentration of  $[\text{Ag}(\text{NH}_3)]^+$ .

Equal amounts of KIO<sub>3</sub> and KI (0.10 M each) react in a solution of H<sub>2</sub>SO<sub>4</sub> at an initial pH value of 3.00.



- b) Calculate the pH value of the solution at equilibrium.

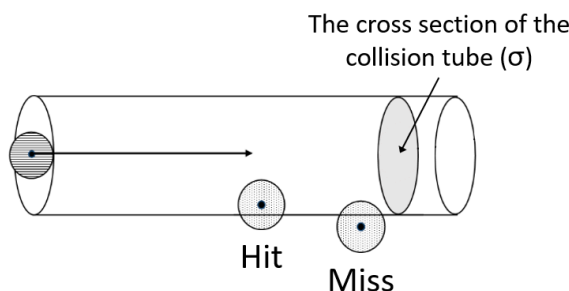
$\alpha$ -halogenation of aldehydes and ketones is an autocatalytic reaction, i.e. the byproduct H<sup>+</sup> is the catalyst for that reaction:  $\text{R}'\text{COR} + \text{X}_2 = \text{RCORX} + \text{H}^+ + \text{X}^-$ . The reaction rate is expressed as:

$$r = k[\text{R}'\text{COR}][\text{X}_2][\text{H}^+].$$

- c) Calculate the concentration  $[\text{X}_2]$  at which the rate is maximal if  $[\text{R}'\text{COR}]_0 = [\text{X}_2]_0$ .

### Problem 4 – CALC, KINETICS – Harpoons and collisions

When modeling the path of a single atom A, it is useful to use it as a point of reference and “freeze” all the other species in their own places. Therefore, we only have to consider any other particles when they collide with the atom whose path we are modeling. If a center of another species B is located in such a way that the atom A will hit it, it is said to be in the *collision tube* of the atom A.



- a) Given that a golf ball with a radius of 2.3 cm is touching a basketball with a radius of 12.5 cm, calculate the distance between their centers.
- b) Hence, calculate the radius ( $R$ , in meters) and area ( $\sigma$ , in square meters) of the cross-section of the collision tube created by a gaseous potassium atom moving through bromine gas. The radius of a potassium atom is 243 pm and the “radius” of a bromine molecule is 165 pm.

The collision tube as a model is used in the kinetic theory of gases. By applying this model, a useful equation for the rate constant of second-order reactions can be obtained:

$$k_2 = \sigma \bar{c} N_A \exp\left(\frac{-E_a}{RT}\right),$$

where  $\bar{c}$  is the average effective velocity of the gas molecules. The pre-exponential term describes the number of collisions occurring, while the exponential term describes the proportion of successful collisions

- c) Write the more common form of this equation.
- d) A second-order reaction has a rate constant of  $1000 \text{ M}^{-1} \text{ s}^{-1}$ , an effective cross-sectional area of the collision tube of  $1.0 \cdot 10^{-18} \text{ m}^2$ , and an average effective velocity of gas molecules of  $100 \text{ m s}^{-1}$  in standard conditions. What is the activation energy of the reaction in  $\text{kJ mol}^{-1}$ ?
- e) Consider a reaction whose activation energy is 0 J. Choose the correct statements:
- ☐ An appropriately selected catalyst would speed up this reaction;
  - ☐ Every reactant atom/molecule has sufficient energy for the reaction;
  - ☐ The reaction enthalpy change has to be zero or negative;
  - ☐ The reactants are likely to be charge free and only contain paired electrons.
- f) Referring back to the beginning of the problem, calculate the  $k$  ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) of the reaction between gaseous potassium and bromine at  $800^\circ \text{C}$ . Assume that the activation energy of the reaction is 0 J.  $\bar{c} = \sqrt{8k_B T / \pi \mu}$ , where  $\mu$  is the reduced mass of the particles involved  $\mu = m_1 m_2 / (m_1 + m_2)$ .

However, the measured  $k$  of the reaction is larger than the calculated value at  $1.0 \cdot 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ , which seemingly suggests that *more* species react than actually collide. This is because of the so-called harpoon mechanism – the potassium atom “shoots” an electron into the bromine molecule even before the collision takes place. This occurs due to the fact that the cross-sectional area ignores the effect of the geometry of collisions on the reaction, as it assumes that all collisions, in most cases, are equal.

- g) Assess how the transfer of the electron impacts the size of the particles and, thus, the cross-sectional area of the collision tube! (Note: each incorrect answer will incur negative marks, with the total for this question not less than 0)
- i) What is the effect of ionization of the K atom on its size?
- i) It increases as the loss of the charge of one electron weakens the attraction between the nucleus and the electron cloud.
  - ii) It increases as the loss of the 4s orbital weakens the shielding experienced by other orbitals, thus diffusing them.
  - iii) It decreases as the lost electron is the only one in the 4<sup>th</sup> energy level.
  - iv) It decreases as the volume of the orbital the electron occupies is lost.
- ii) What is the effect of electron transfer to the bromine molecule on its size?
- i) It increases as the new electron occupies a bonding molecular orbital.
  - ii) It increases as the new electron occupies a non-bonding molecular orbital.
  - iii) It decreases as the new electron occupies a bonding molecular orbital.
  - iv) It decreases as the new electron occupies a non-bonding molecular orbital.
- iii) What is the net effect of the electron transfer on the cross-sectional area of the collision tube: i) It increases; ii) It decreases; iii) Insignificant effect; iv) Not enough data given.

The modified reactive cross-section area  $\sigma^*$ , which should be used for reactions proceeding by a harpoon mechanism, can be calculated from radius  $R_h^*$  using the equation:  $\sigma^* = \pi(R_h^*)^2$ .

$R_h$  describes the separation of centers of reacting species. There are three contributions to the energy of interaction between the colliding species: ionization energy of potassium (abbreviated as  $I$ ), electron affinity of bromine gas ( $E_{EA}$ ) and Coulombic interaction (CI) energy between the ions when they have been formed given by the equation:  $CI = -e^2/(4\epsilon_0 R_h)$ .  $R_h$  is a distance when all these three contributions to the energy are in balance, thus,  $0 = I - E_{EA} + CI$ .

**h)** Calculate the radius  $R_h$  and reactive cross-section area  $\sigma$ , if it is given that  $I = 420 \text{ kJ mol}^{-1}$ ,  $E_{EA} = 250 \text{ kJ mol}^{-1}$ , vacuum permittivity constant  $\epsilon_0 = 8.854 \cdot 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ , and elementary charge  $e = 1.602 \cdot 10^{-19} \text{ C}$ .

Usually, to describe such a reaction, a steric factor  $P$  is introduced, which connects reactive cross-section area  $\sigma^*$  with collision cross-section area  $\sigma$  so that  $\sigma^* = P\sigma$ .

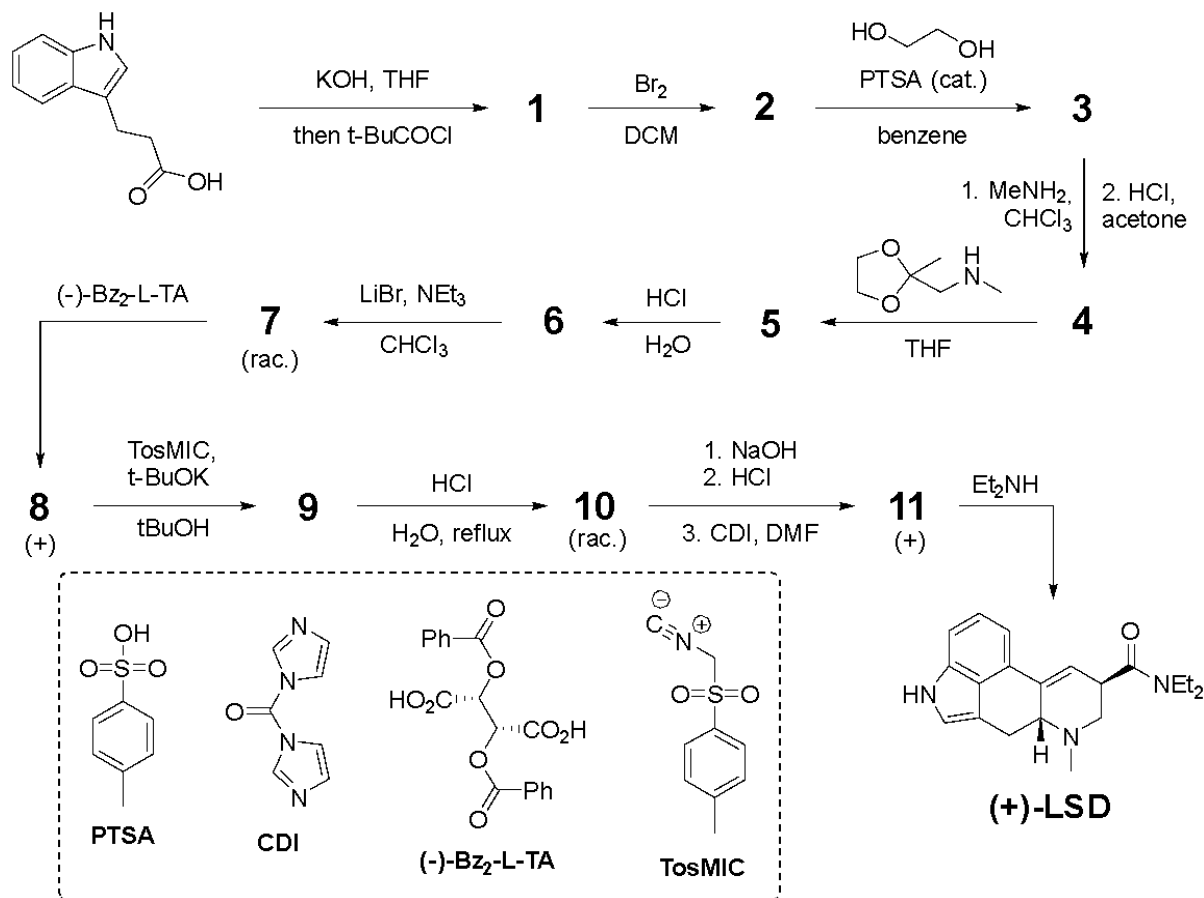
**i)** Calculate the steric factor  $P$ .

**j)** Now calculate the  $k$  ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) of the same reaction at  $800^\circ \text{C}$  using  $\sigma^*$  instead of  $\sigma$ .

### Problem 5 - BIO, SYNTH - Lucy in the Sky with Diamonds

Back in the days of 1967, this famous song by the Beatles was released. It did not take long for hippies to notice that an abbreviation would be LSD. This, one of the most widely known chemical substances, was first synthesized in 1938 by Swiss chemist Albert Hofmann. Up to around 1980, it was used as a psychiatric drug or for research purposes.

Today, you will have a chance to synthesize (on paper!) this highly biologically active compound that boasts a tetracyclic carboskeleton. Such an arrangement was and still is quite problematic if one tries to devise a synthesis route from very simple starting materials. Hence, you will begin your synthesis from already bicyclic indole-3-propionic acid.

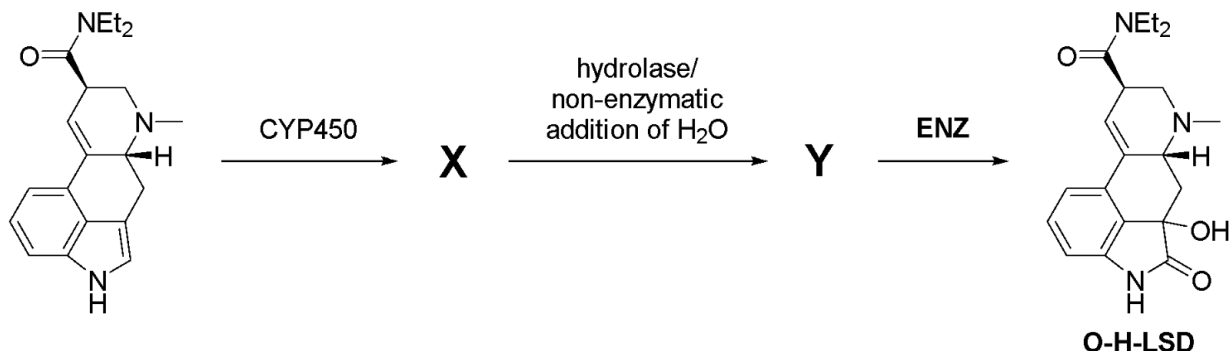


Compound **1** is known to be tricyclic; compound **7** is known to be tetracyclic; (rac.) denotes “racemate”; compound **9** has one stereocenter.

a) Draw structural formulas of compounds **1–11** with stereochemistry.

b) Draw reaction mechanism of **8** + TosCH<sub>2</sub>NC: → **9**.

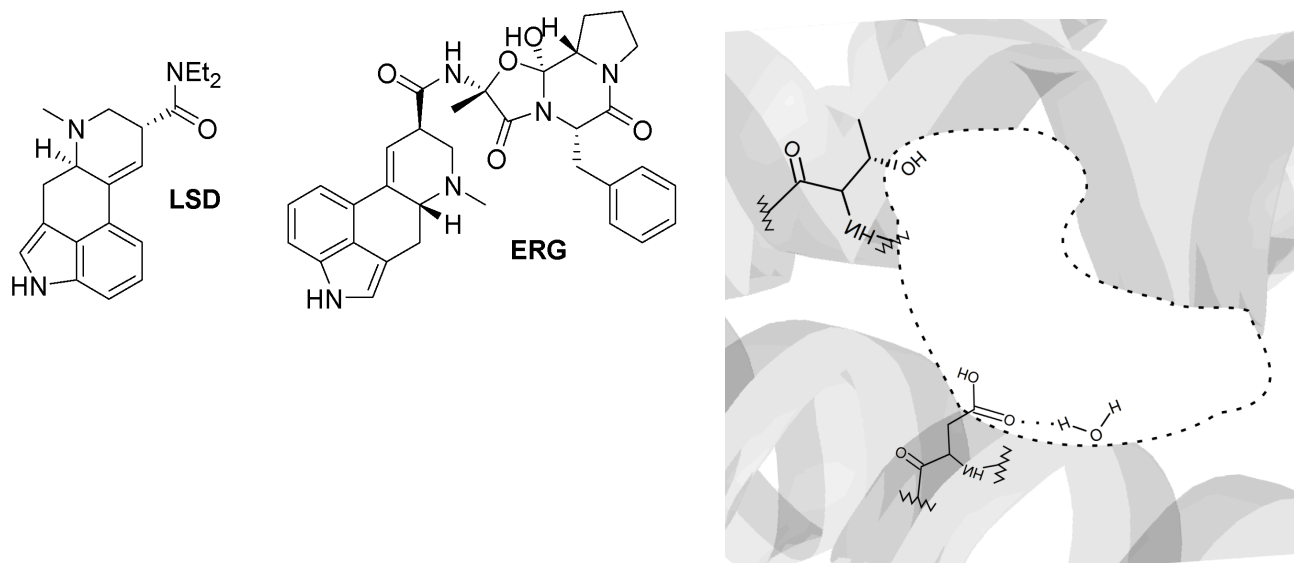
From a biochemical standpoint, lysergic acid diethylamide binds to the serotonin receptors in the body, but the hallucinogenic effect lasts for up to 6-8 hours, meaning that its metabolism is quite fast. Studies have shown that metabolism in human organisms proceeds through O-H-LSD intermediate. A mechanism of O-H-LSD formation was proposed, but it seems that some information is missing.



c) Decipher structures **X** and **Y** and suggest an enzyme (**ENZ**) for the final step. It is known that **ENZ** should belong to Oxidoreductases. Note: The substrate of the enzyme is not supposed to be specified, e.g., the answers deaminase or oxidase are specific enough.

Biochemists have shown that LSD and its precursor ergotamine ERG bind the same serotonin receptor to its active site.

d) Considering that LSD and ERG bind the same receptor site, outline the physiologically active part in each molecule.



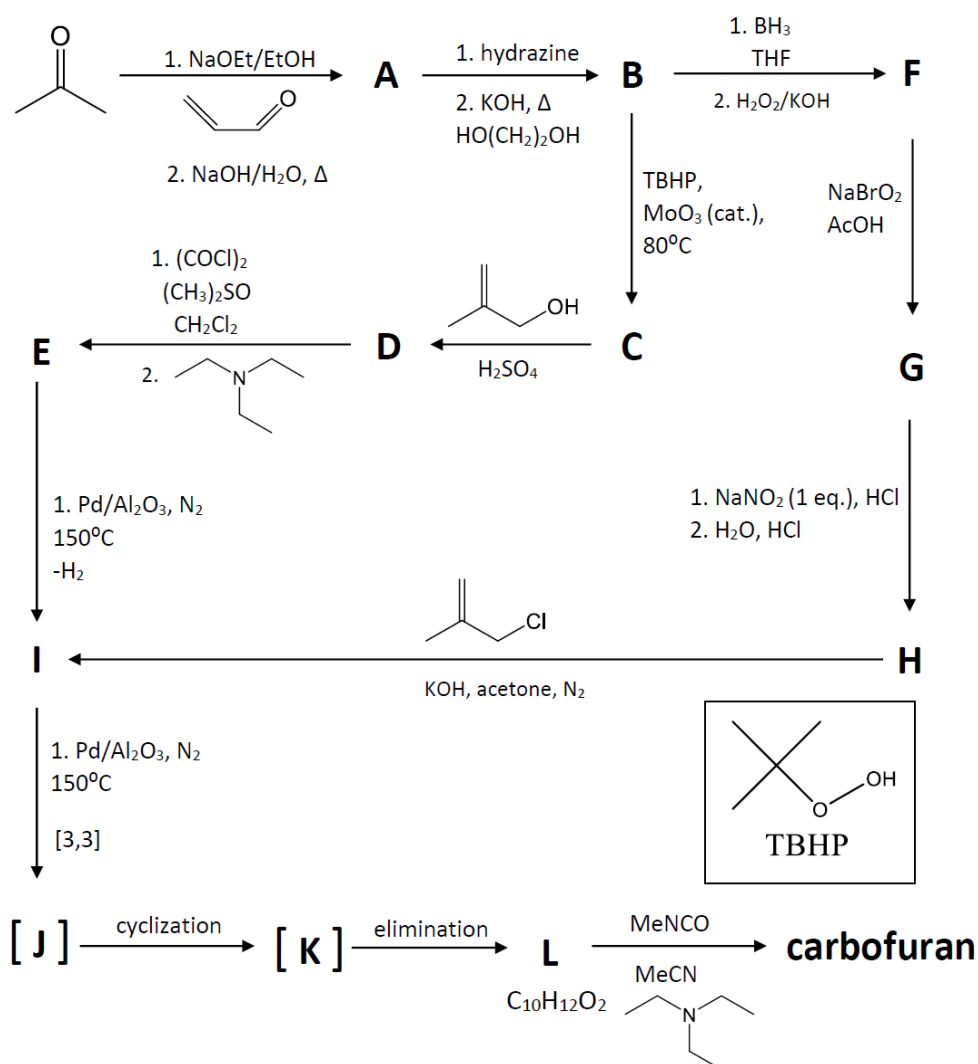
e) Fit the LSD molecule into the active site of the serotonin receptor and show molecular interactions.

## Problem 6 – SYNTH – Easy grow, easy bloom

Carbofuran is one of the most toxic insecticides and, therefore, is banned in Canada and the European Union. However, this pesticide is still widely used in other countries to control the amount of insects in potato, pumpkin, and sunflower fields.

Carbofuran can be produced quite easily from many simple chemical substances, but the main drawbacks of these processes are the expense of production and the toxicity of chemicals involved in the syntheses. However, in the 1980s, several alternative methods for carbofuran production were invented, which are relatively safe and require cheap starting materials (acetone in this case). The synthesis scheme of carbofuran, a bicyclic compound, is given below.

(*cat.*) – catalyst, (*eq.*) – equivalent



- Draw the mechanism of the reaction **A** → **B**.
- Draw the structural formulas of **C** and **D**. Also, write all possible compound **D** stereoisomers, which can be produced in the reaction **C** → **D**, mark all the stereocenters with "\*", and indicate their *R/S* configuration.
- Draw the structure of compound **E**. Taking into account that the reaction **D** → **E** was carried out using only enantiomerically pure compound **D'** (one of **D** stereoisomers) with all the stereocenters having only *R*-configuration, draw the stereoisomer(s) of compound **E** which would be synthesized in the reaction **D** → **E**.

**d)** Write the structural formulas of compounds **F**, **G**, **H** and **I**.

**e)** Show the mechanism of the reaction **G** → **H**.

Compound **E** heated with Pd/alumina catalyst in nitrogen atmosphere produces intermediate **I** which further heated under the same conditions gives more stable compound **J** and then, bicyclic compound **K**. These intermediates are not extracted in this synthesis but are further heated to produce compound **L**.

**f)** Draw the structures of compounds **J**, **K** and **L**.

**g)** In the reaction from **J** to **K**, a second ring is formed. How could the ring be named separately?

- ☐ Oxyfuran
- ☐ Dehydrofuran
- ☐ Benzofuran
- ☐ Dihydrofuran
- ☐ Ketofuran

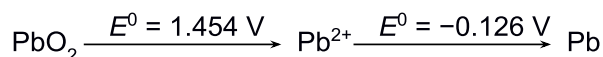
**h)** Finally, the last step gives us the final product, carbofuran. Draw the structure of carbofuran.

**Problem 1 – APPLIED, ELECTRO – Lead-acid battery**

The lead-acid rechargeable battery is still one of the most common car batteries at the beginning of the 21<sup>st</sup> century. It has some superior characteristics, and it could be almost completely recycled. During the discharge process, the lead of one electrode and lead(IV) oxide of the other electrode are converted into lead sulfate. The sulfuric acid is used as the electrolyte.

- a) Write the anode, cathode and total reactions of the lead-acid battery during the discharge process.

The solubility product of  $\text{PbSO}_4$  is  $K_{\text{sp}} = 1.6 \cdot 10^{-8}$ . The Latimer diagram of lead (in acid) is:



- b) Is the disproportionation reaction of lead(II) ions a spontaneous process? Justify the answer using calculations.
- c) Calculate the open circuit potential  $E_{\text{cell}}^{\circ}$  of one cell of the fully charged battery.
- d) Calculate the open circuit potential ( $E_{\text{cell}}$ ) of one cell of the fully charged lead-acid battery (at 25 °C) which contains sulfuric acid with density of  $1.275 \text{ g cm}^{-3}$ .

| %wt | $\rho \text{ (g cm}^{-3}\text{)}$ | %wt | $\rho \text{ (g cm}^{-3}\text{)}$ | %wt | $\rho \text{ (g cm}^{-3}\text{)}$ |
|-----|-----------------------------------|-----|-----------------------------------|-----|-----------------------------------|
| 2   | 1.0104                            | 34  | 1.2479                            | 66  | 1.5602                            |
| 4   | 1.0234                            | 36  | 1.2647                            | 68  | 1.5829                            |
| 6   | 1.0367                            | 38  | 1.2818                            | 70  | 1.6059                            |
| 8   | 1.0502                            | 40  | 1.2991                            | 72  | 1.6292                            |
| 10  | 1.0640                            | 42  | 1.3167                            | 74  | 1.6526                            |
| 12  | 1.0780                            | 44  | 1.3346                            | 76  | 1.6761                            |
| 14  | 1.0922                            | 46  | 1.3530                            | 78  | 1.6994                            |
| 16  | 1.1067                            | 48  | 1.3719                            | 80  | 1.7221                            |
| 18  | 1.1215                            | 50  | 1.3911                            | 82  | 1.7437                            |
| 20  | 1.1365                            | 52  | 1.4109                            | 84  | 1.7639                            |
| 22  | 1.1517                            | 54  | 1.4310                            | 86  | 1.7818                            |
| 24  | 1.1672                            | 56  | 1.4516                            | 88  | 1.7968                            |
| 26  | 1.1829                            | 58  | 1.4726                            | 90  | 1.8091                            |
| 28  | 1.1989                            | 60  | 1.4940                            | 92  | 1.8188                            |
| 30  | 1.2150                            | 62  | 1.5157                            | 94  | 1.8260                            |
| 32  | 1.2314                            | 64  | 1.5378                            | 96  | 1.8305                            |

The open circuit potential of one cell of a lead-acid battery is  $E_{\text{cell}}^{\circ} = 2.033 \text{ V}$  at 5 °C.

- e) Calculate the temperature coefficient ( $dE_{\text{cell}}^{\circ}/dT$ ) of one cell of the lead-acid battery in this temperature region.
- f) Calculate the reaction enthalpy of the discharging process in the battery.
- g) During the discharging of the battery:
- ☐ The temperature of the battery increases;
  - ☐ The temperature of the battery decreases;
  - ☐ The temperature of the battery does not change;
  - ☐ The water could evaporate from the battery because of the overheating;
  - ☐ The output voltage of the usual lead-acid battery is 12 V, and it consists of several cells.

- h)** How many cells should be used to get a 12 V battery?
- i)** Draw an electrical circuit demonstrating how the individual cells are connected in the 12 V lead-acid battery.
- j)** Calculate the theoretical output voltage of 12 V lead-acid battery, i.e. use the open circuit potential  $E_{\text{cell}}$  calculated in **d**).

The weight of the commercial lead acid battery is 4.05 kg (9.75×9.8×15.1 cm), the capacity is 12 A h, and the internal resistance of the battery is 100 mΩ.

- k)** Calculate the charge which could be withdrawn from the battery that is fully charged.

The battery was discharged, and the density of the electrolyte measured was 1.195 g cm<sup>-3</sup>. The fully charged battery contained 580 cm<sup>3</sup> of sulfuric acid.

- l)** Calculate how many hours it would take to fully charge the battery using average current 3 A. The efficiency of the charging process is 65%. Assume that the amount of water is constant.

- m)** During discharging, the internal resistance of the battery:

- ☐ Increases;
- ☐ Decreases;
- ☐ Decreases drastically;
- ☐ Does not change.

- n)** The open circuit potential of the battery:

- ☐ Does not change during charging;
- ☐ Does not change during discharging;
- ☐ Increases during discharging;
- ☐ Increases during charging;
- ☐ Decreases during charging.

The efficiency of the charging process is much lower than 100% because high overvoltage is applied to the electrodes and instead of charging, also side reactions could occur: hydrogen evolution and oxygen evolution.

- o)** Write the equations of side reactions on the anode and cathode during the charging process.

The performance of various energy-storing devices could be compared using maximum energy density  $W_{\text{max}} = qE/m$ , where  $q$  is the charge stored in the device,  $E$  – operation voltage window, and  $m$  – weight of the device. Maxwell ultracapacitor BCAP3000 has the following characteristics: capacitance – 3000 F, voltage window – 2.7 V and mass of the device – 510 g.

- p)** For which energy storage device the maximum energy density (Wh kg<sup>-1</sup>) is higher? During the discharge of the battery, the potential does not change but during the discharge of the capacitor, the potential decreases almost linearly, i.e. the average potential should be used.

- q)** The energy density of the lead-acid battery:

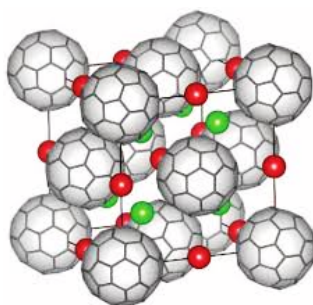
- ☐ Increases with the temperature;
- ☐ Decreases with the temperature;
- ☐ Does not change with the temperature;
- ☐ Increases during discharging;
- ☐ Increases during charging.

## Problem 2 – CRYSTAL, THERMO – Fullerenes

Some of the alkali metal-doped fullerenes have a superconducting state. In these compounds, the alkali metal atoms fill the holes in a face-centered cubic lattice formed by the molecules of fullerene. Molecules in the fullerene crystal are also arranged in the face-centered cubic lattice.

- Calculate the lattice parameter ( $a$ ) of the fullerene crystal with a density of  $1.67 \text{ g cm}^{-3}$ .
- Estimate the radius of the fullerene molecule, assuming that the distance between the neighboring molecular spheres is  $d = 1.42 \text{ Å}$ , i.e. one C–C bond length.
- Estimate the radii of spheres ( $r_{\text{oct}}$  and  $r_{\text{thd}}$ ) that can fit the octahedral and tetrahedral holes of the fullerene crystal. The radius of a tetrahedron circumsphere is given as  $r_{\text{thd}} = \sqrt{3/8} \cdot t$ , where  $t$  is the length of the tetrahedron edge.

The figure below shows the crystal structure of face-centered cubic  $A_nC_{60}$ , where  $A = \text{Li, Na, K, Rb, Cs}$ , and  $n$  is an integer number.



- Prove that  $n = 3$  for the illustrated crystal structure. Note that all tetrahedral and octahedral holes are occupied by the alkali metal atoms.

In the Table below are given atomic ( $r(A^0)$ ) and ionic ( $r(A^+)$ ) radii of Li, Na, K, Rb and Cs, metal vaporization enthalpies ( $\Delta H_{\text{vap}}(A)$ ) and ionization energies ( $\text{IP}(A)$ ), as well as lattice parameters of corresponding fullerides.

|    | $r(A^0), \text{Å}$ | $r(A^+), \text{Å}$ | $\Delta H_{\text{vap}}(A), \text{kJ mol}^{-1}$ | $\text{IP}(A), \text{kJ mol}^{-1}$ | $a(A_nC_{60}), \text{Å}$ |
|----|--------------------|--------------------|------------------------------------------------|------------------------------------|--------------------------|
| Li | 1.52               | 0.76               | 136                                            | 520                                | –                        |
| Na | 1.86               | 1.02               | 108                                            | 496                                | 14.191                   |
| K  | 2.27               | 1.38               | 90                                             | 419                                | 14.240                   |
| Rb | 2.48               | 1.52               | 69                                             | 403                                | 14.384                   |
| Cs | 2.65               | 1.67               | 66                                             | 376                                | 14.761                   |

- Calculate  $r_{\text{thd}}$  values for each of the alkali metal-doped fullerenes. Compare the calculated values with the  $r(A^0)$  and  $r(A^+)$  values from the table and prove that the alkali metal atoms are charged.
- Calculate the lattice energy for  $\text{Li}_3\text{C}_{60}$  using the Kapustinskii equation:  $\Delta U_{\text{lattice}} = -107000 \cdot v \cdot |z_+| \cdot |z_-| / (r_+ + r_-)$ , where  $v$  is the total number of ions in the empirical formula,  $z_+$  and  $z_-$  are the charges of the individual ions,  $r_+$  and  $r_-$  are the ionic radii in pm, and the result is given in  $\text{kJ mol}^{-1}$ . Assume,  $r_+ + r_- \approx r_{\text{thd}}(\text{Li}_3\text{C}_{60}) + 4.31 \text{ Å}$ .

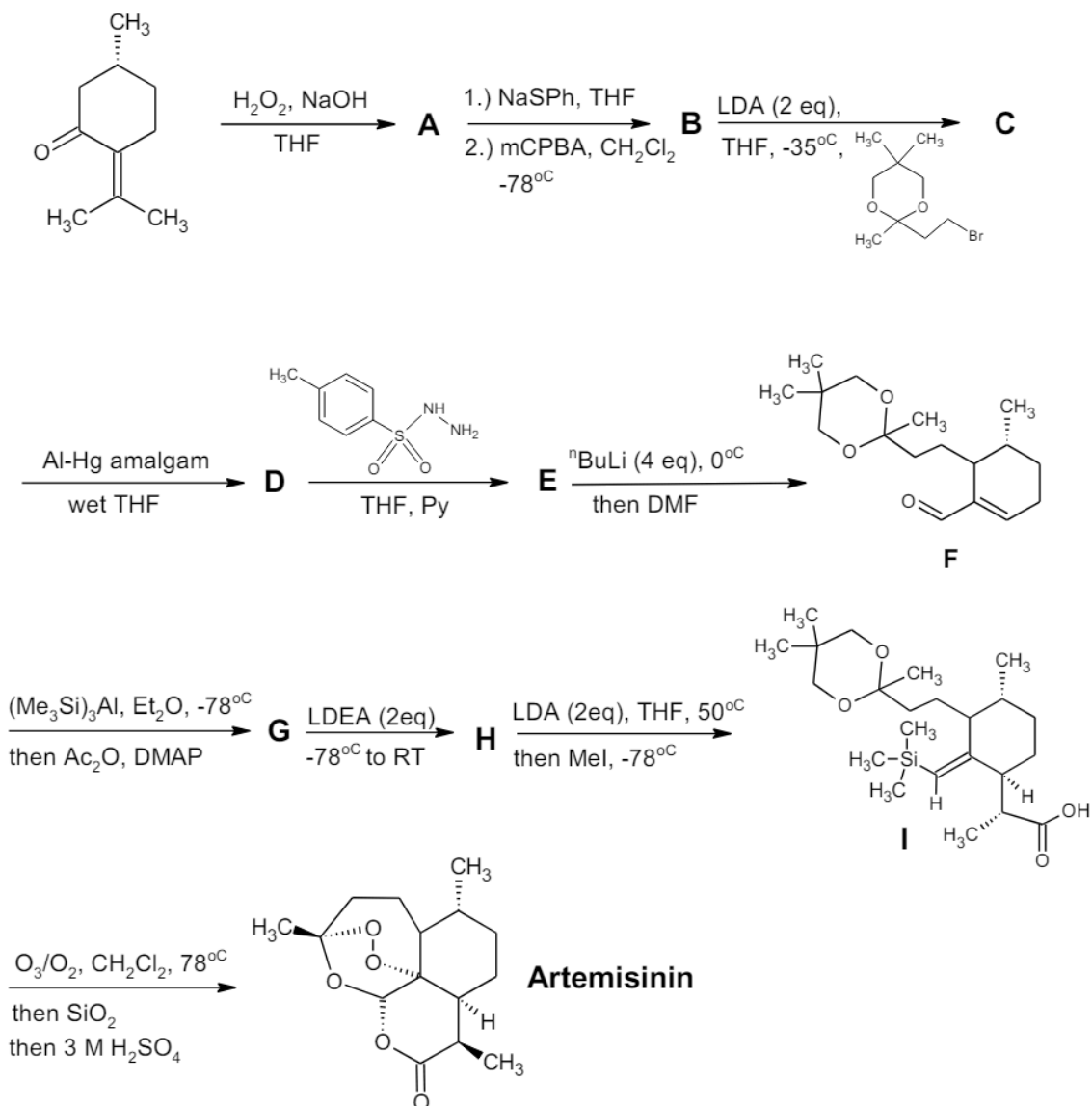
The first reported superconductor in the fulleride family was  $\text{K}_3\text{C}_{60}$ . In a year,  $\text{Rb}_3\text{C}_{60}$  and  $\text{Cs}_3\text{C}_{60}$  were synthesized. The preparation of  $\text{Na}_3\text{C}_{60}$  was more difficult and took longer. So far, it has

not been possible to produce  $\text{Li}_3\text{C}_{60}$ . There is a correlation between the formation enthalpy values and the sequence of the  $\text{A}_3\text{C}_{60}$  studies.

- g) Write the  $\text{A}_3\text{C}_{60}$  formula in ascending order of the corresponding formation enthalpy absolute values. You may estimate the relative values using the data from the table.

### Problem 3 – SYNTH – The Great Drug of China

Artemisinin is a drug that possesses the most rapid action of all of the drugs used to treat Malaria. It was discovered in the 1970s by Tu Youyou, a Chinese scientist, who was awarded a Nobel Prize in 2015. She was the first Chinese Nobel Prize laureate. Initially, artemisinin was obtained by isolation from the plant *Artemisia annua*. Unfortunately, no significant quantities of this plant are being grown, so in 1992, Avery et al. published a synthetic route to the Artemisinin shown below.



- The empirical formulas of compounds are: **B** –  $\text{C}_{13}\text{H}_{16}\text{O}_2\text{S}$ , **D** –  $\text{C}_{16}\text{H}_{28}\text{O}_3$ , **G** –  $\text{C}_{22}\text{H}_{40}\text{O}_4\text{Si}$
- All steps from **B** → **I** are stereoselective. Thus, you must draw the major enantiomers of all the intermediates from **C** to **I**.
- $\text{LDA}$  and  $\text{LDEA}$  are bulky bases.
- Conversion **G** to **H** is the Claisen rearrangement reaction.

- a) Draw the structural formulas of the compounds **A–E** with stereochemistry.
- b) Propose a reaction mechanism for the conversion **A** → **B**.
- c) Propose a mechanism for converting **E** to **F**. Note that DMF (dimethylformamide) is not the solvent of the reaction and that there is no racemization.
- d) What is the major driving force of the reaction **E** → **F**?
  - A. The product can form hydrogen bonds with the solvent.
  - B. Having three oxygen in the molecule is better than having two.
  - C. Nitrogen is produced and released during the reaction.
  - D. The product is more conjugated than the starting material.
  - E. Compound **E** is harmful, but compound **F** is not.
- e) Draw the structural formulas of the compounds **G** and **H**. Pay attention to the stereochemistry.
- f) Propose a reaction mechanism for the conversion **G** → **H**.
- g) Assign the configuration (*R* or *S*) for all of the stereocenters of compounds **G** and **I**.

#### Problem 4 – CRYSTAL, THERMO – The biggest coins in the world

The beginning of the 17<sup>th</sup> century was a turning point in Sweden's economics as it lost control over silver mines in Norway but added the Baltic region (including Tartu and Riga) to their territories. The Mine of Falun had rich stores of raw material, and the Swedish king decided to produce copper coins (plates) of value close to the value of silver coins. The first copper coins were issued in 1624, the weight of one coin was 19.7 kg and the volume of 2205 cm<sup>3</sup>. Copper has a face-centered cubic lattice (FCC) with a lattice parameter of 361.5 pm. In nature, copper is usually found as sulfide minerals, for example – chalcopyrite (contains 35% of copper by mass and iron) and chalcocite (contains 80% of copper by mass).

- a) Calculate the chemical formulas of chalcopyrite and chalcocite.  
Nowadays, copper is extracted from ores, where the copper content is as small as 0.60%.
- b) Write equations showing the extraction of copper from ore containing chalcocite when copper(I) oxide forms as an intermediate.
- c) Calculate the mass of the ore to be recycled to produce copper that is necessary to make one Swedish coin.

Copper(I) oxide is a reddish-brown substance used as a component of some antifouling paints. Copper(I) oxide is reduced when it is mixed with chalcocite, free copper and sulfur dioxide are formed.

| Substance and its state                          | Cu <sub>2</sub> O (s) | Chalcocite (s) | Cu (s) | SO <sub>2</sub> (g) |
|--------------------------------------------------|-----------------------|----------------|--------|---------------------|
| $\Delta H_f^\circ$ [kJ mol <sup>-1</sup> ]       | -168.6                | -79.5          |        | -296.8              |
| $S^\circ$ [J mol <sup>-1</sup> K <sup>-1</sup> ] | 93.1                  | 120.9          | 33.2   | 248.2               |
| Melting point [°C]                               | 1232                  | 1130           | 1084   |                     |
| $\Delta H_{fus}^\circ$ [kJ mol <sup>-1</sup> ]   |                       |                | 13     |                     |

- d) Calculate Gibbs energy of copper(I) oxide reduction reaction at **i)** 25 °C and **ii)** 1100 °C.

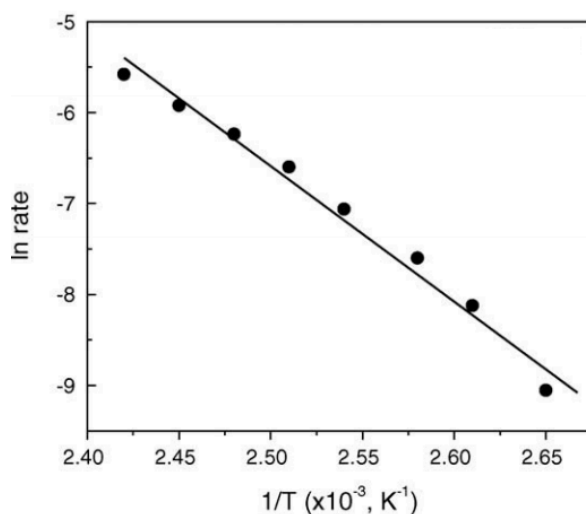
Young chemist Grzegorz decided to reuse copper coins; he made up the electrolytic cell, attached Swedish copper coin and almost pure copper wire as electrodes, and used copper(II) nitrate as the electrolyte.

- e) Which electrode (anode/cathode) was made from Swedish copper coin? Write the corresponding half-reaction.
- f) How long (in hours) does it take to recycle all Swedish coins if electrolysis is performed with 1.00 A current?
- g) Nowadays, copper is used to prepare internet cables. Calculate the length of copper fiber of diameter 0.1 mm which can be produced from Swedish copper coins.
- h) How many copper coins are needed to recycle to produce a copper fiber with a length of 600 km (distance from Tallinn to Vilnius via Riga)?

Most of the used copper is recycled. Another recycling process includes the dissolution of copper in nitric acid. Nitric acid reacts with copper in two ways giving NO and NO<sub>2</sub>.

- i) Complete and balance both oxidation-reduction reaction equations.

Scientific papers state that complete oxidation of carbon monoxide can be achieved at room temperature over unsupported copper(II) oxide catalyst by a careful and controlled generation of the oxide. The Figure below shows the natural logarithm of the oxidation reaction rate as a function of  $1/T$ , where  $T$  is the temperature in Kelvin (K).

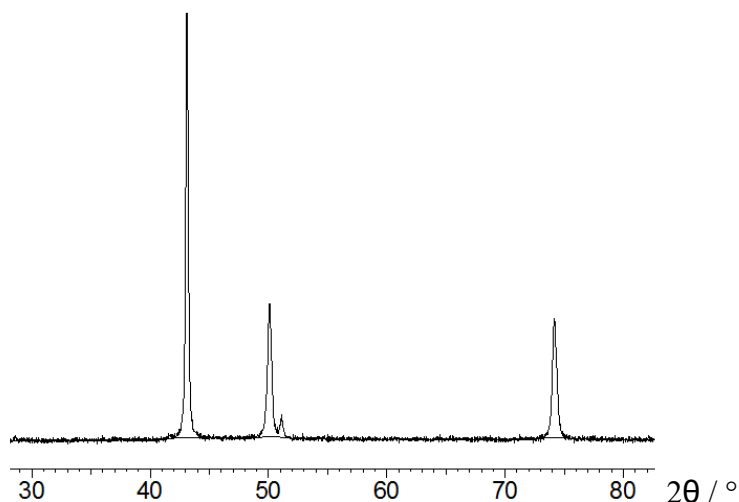


- j) Calculate the activation energy for the oxidation of carbon monoxide.

The enthalpy of the complete combustion of carbon (in the solid state as graphite) is  $-393 \text{ kJ mol}^{-1}$ , but the standard enthalpy of the formation of carbon monoxide is  $-111 \text{ kJ mol}^{-1}$ .

- k) Sketch the energy diagram of the carbon monoxide oxidation reaction and state exact energy difference values where possible.

Copper is still used in the production of coins. Young chemist Grzegorz decided to prove it and analyzed a 2 EUR coin by X-ray diffraction. The diffraction pattern for the analyzed coin is shown below.



Use Bragg's law:  $\lambda = 2d \cdot \sin(\theta)$ , where  $d$  is the distance between diffraction planes (nm,  $d = a/\sqrt{h^2 + k^2 + l^2}$ );  $\lambda$  is the wavelength of X-rays (0.15408 nm),  $\theta$  is the diffraction angle,  $a$  is the lattice parameter,  $h$ ,  $k$ , and  $l$  are Miller indices. For the face-centered cubic lattice (FCC), only diffraction peaks where all Miller indices are odd numbers or all Miller indices are even numbers are allowed.

- 1) Indicate in diffraction pattern which peak(s) correspond to copper and state, at least, one set of Miller indices for each copper peak.

### Problem 5 - CALC, SPECTRA - "My precious"

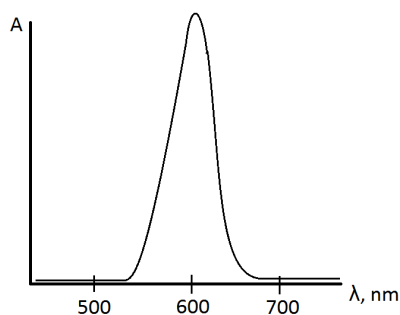
Silver jewelry is seldom made of absolutely pure silver. Different alloys are usually used instead of pure silver. Chemistry student Grzegorz decided to analyze his mom's silver ring and find out how much copper it contained because he knew that this ring had some copper impurity. So, Grzegorz dissolved 1.00 g of that ring in a small volume of concentrated nitric acid and diluted the solution to 25 ml. Let's call it solution **A**. It was colored, and because of that, the student decided to calculate the amount of copper in the solution using its feature to absorb visible light. He measured the absorbance of the solution using the photometer. Usually, molar extinction coefficients of metal salt solutions are less than  $1000 \text{ M}^{-1} \text{ cm}^{-1}$ . In this problem, use the Bouguer-Beer-Lambert law:  $A = \log(I_0/I) = \epsilon cl$ . In his measurements, Grzegorz used the photometer, which can measure the smallest value of absorption  $A = 0.001$ .

- a) Calculate the smallest concentration of hypothetical substance **X** that can be measured by this device when  $\lambda = 600 \text{ nm}$ ,  $\epsilon_{600} = 3.25 \text{ M}^{-1} \text{ cm}^{-1}$ , and  $l = 1.000 \text{ cm}$ .

Light filters are usually used in photometers to generate the monochromatic light beam.

- b) What is the color of the filter if it absorbs only violet (390 nm) light?

The absorbance spectrum of hypothetical substance **X** is given in the figure below.



- c) Draw the absorbance spectrum of the best suitable filter for the substance **X** analysis. “Best suitable” means that when that filter is used, Lambert-Beer law holds the smallest possible substance **X** concentrations can be measured, and the most accurate results are obtained.

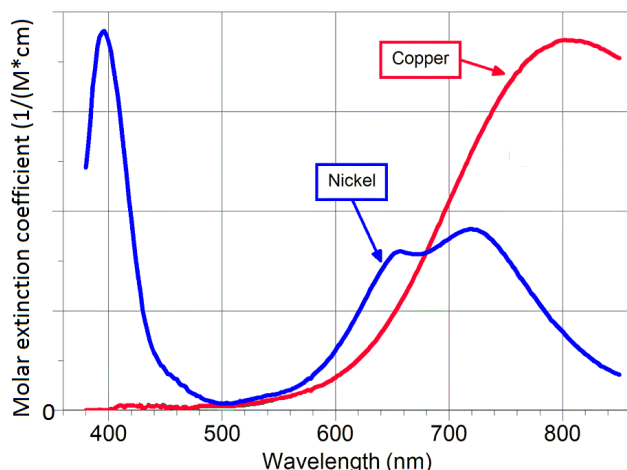
To find out the copper concentration in solution **A**, he used the “addition method”. In the beginning, Grzegorz measured the absorbance of solution **A** in a 3.00 cm cuvette at  $\lambda = 700$  nm wavelength. The photometer showed 0.240. Assume that silver ions do not absorb visible light.

- d) Calculate the fraction (in percent) of initial light intensity that is transmitted through the sample.

After that, Grzegorz weighed 5.12 g of copper sulfate pentahydrate, dissolved it in a 20 cm<sup>3</sup> volumetric flask, and diluted it to the mark (solution **B**). Then he mixed 15 cm<sup>3</sup> of solution **A** and 1 cm<sup>3</sup> of solution **B** and also measured the absorbance of this mixture in a 1.00 cm cuvette at  $\lambda = 700$  nm wavelength. The photometer showed the value  $A = 0.694$ .

- e) Calculate the mass fraction (in percent) of copper in the ring.

Grzegorz was so interested in his mom’s jewelry analysis that he measured the quantitative composition of his mom’s earring, which was made from Monel metal (copper-nickel alloy). So, the student dissolved a piece of that earring in concentrated nitric acid (let us call it solution **C**) and measured the absorbance of solution **C** in a 1.00 cm cuvette at  $\lambda_1 = 400$  nm wavelength and at  $\lambda_2 = 800$  nm wavelength. He also measured the absorbance of earlier prepared standard solution **D** in which  $[\text{Cu}^{2+}] = 0.025$  M and  $[\text{Ni}^{2+}] = 0.055$  M. The results he got are listed in the Table below. The Figure below shows the molar extinction coefficient dependence on wavelength for copper and nickel. The molar extinction coefficient for nickel at wavelength 800 nm  $\epsilon_{800} = 4.41 \text{ M}^{-1} \text{ cm}^{-1}$ .



| $\lambda$ [nm]<br>Solutions | 400   | 800   |
|-----------------------------|-------|-------|
| <b>C</b>                    | 0.765 | 0.548 |
| <b>D</b>                    | 0.894 | 0.638 |

Table. Absorbance dependence on solution and  $\lambda$ .

- f) Determine the composition (in mass percent) of the earring.

Grzegorz’s friend Piotr told Grzegorz about metal complexes. Piotr pointed out that it is better to evaluate metal concentrations in solutions using organic compounds that make complexes with metal ions. Due to recent changes in safety rules, Grzegorz’s school has been trying to eliminate carcinogenic cobalt(II) chloride. So Grzegorz waited for the right moment and deliberately took the salt as he devised an idea to analyze cobalt(II) complex formation reaction.

| Conc. <b>R</b> [M] · 10 <sup>-5</sup> | Absorbance ( <b>A</b> ) |
|---------------------------------------|-------------------------|
| 1.50                                  | 0.106                   |
| 3.25                                  | 0.232                   |
| 4.75                                  | 0.339                   |
| 6.25                                  | 0.441                   |
| 7.75                                  | 0.500                   |
| 9.50                                  | 0.523                   |
| 11.5                                  | 0.529                   |
| 12.5                                  | 0.531                   |
| 16.5                                  | 0.529                   |
| 20.0                                  | 0.530                   |

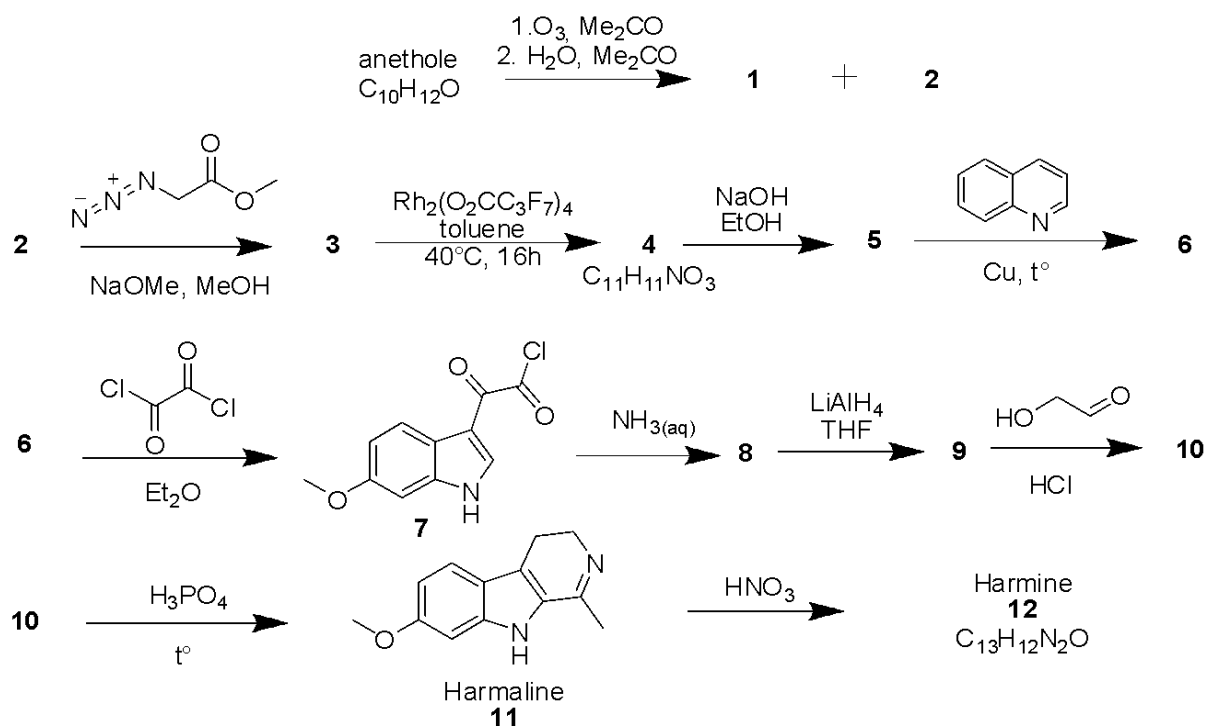
The complex between Co(II) and the ligand **R** was investigated photometrically. A green filter at 550 nm (the wavelength of absorbance maximum for the complex) was used for the measurements. Assume that only the complex absorbs the light. The initial cation concentration was  $2.5 \cdot 10^{-5}$  M in solutions with different concentrations of **R**. The absorbance data (1 cm cell) were obtained as follows:

- g) Draw a graph of absorbance versus **R** concentration and determine the ligand-to-cation ratio for the complex.
- h) Determine the value of molar extinction coefficient  $\epsilon_{550}$  for the complex from question g).
- i) Which one of the following statements best describes the advantage of using complexes in photometry?
  - i) To increase the molecular mass of the analyst;
  - ii) To enhance the solubility of the analyst;
  - iii) To increase the molar extinction coefficient of the analyst;
  - iv) All of the above.

### Problem 6 – BIO, SPECTRA, SYNTH – Ayahuasca

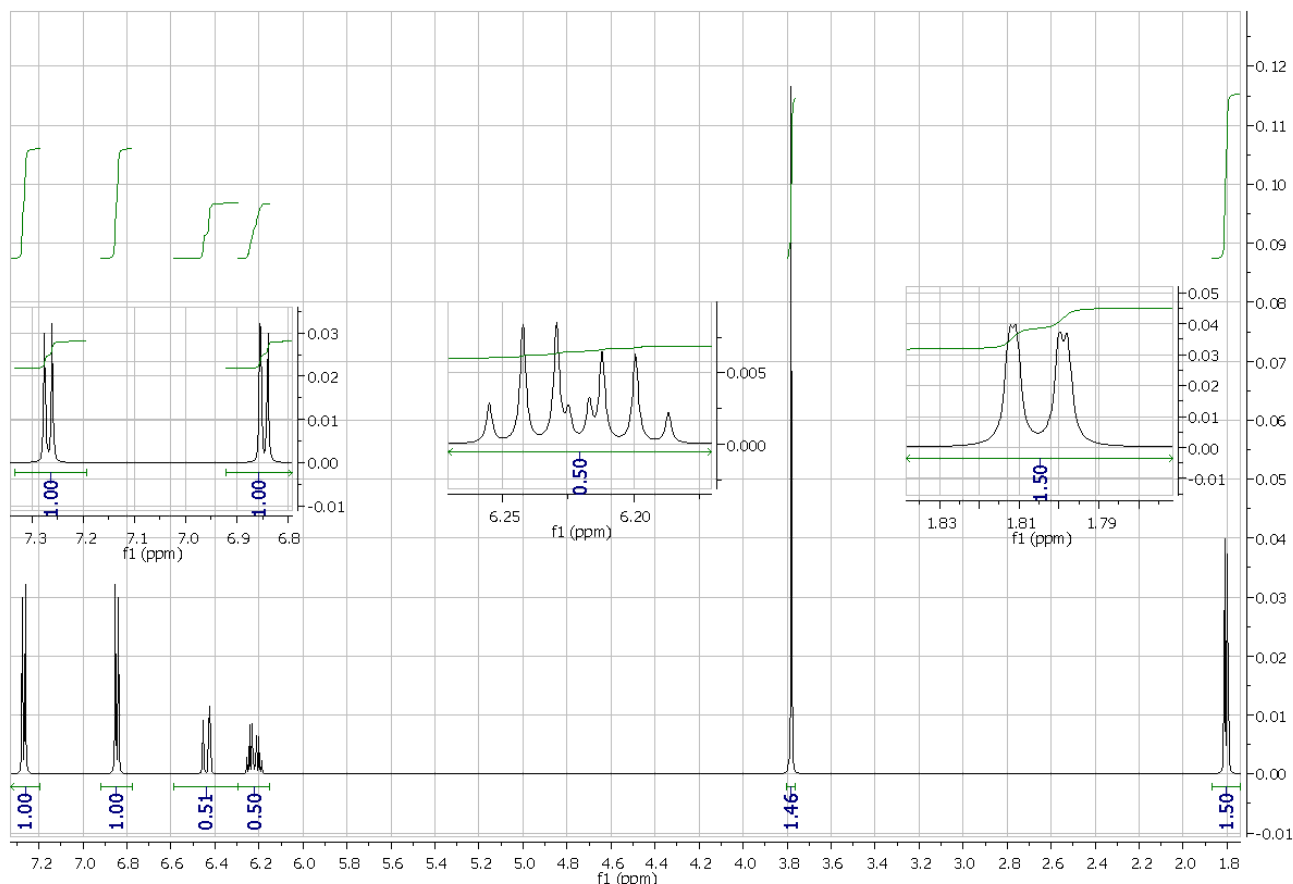
Ayahuasca is a brew made out of *B. caapi* vine. This brew is used orally as a traditional spiritual medicine in ceremonies in South America. It can be mixed with leaves containing DMT for a significantly different – psychedelic effect. *N,N*-dimethyltryptamine (DMT) is a psychedelic compound of the tryptamine family, and it is a structural analog of serotonin and melatonin. It is interesting to notice that DMT taken orally is broken down by the enzyme monoamine oxidase through a process called deamination and is quickly inactivated orally unless combined with a monoamine oxidase inhibitor.

Harmala alkaloids are monoamine oxidase-inhibiting *beta*-carbolines. Two of the three most studied harmala alkaloids in the *B. caapi* vine are harmine and harmaline. In this problem, you have to complete the synthesis of harmine and harmaline given below.



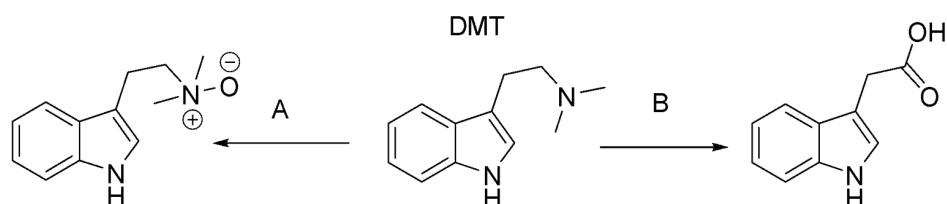
Hints: anethole exhibits cis/trans isomerism; products **1** and **2** are both aromatic compounds;  $Rh_2(O_2CC_3F_7)_4$  is used as an intramolecular reaction catalyst; compound **5** has broad signal in IR spectra ( $\sim 3000\text{ cm}^{-1}$ ) whereas compound **6** does not.

- a) Investigate a  $^1\text{H}$  NMR spectrum (which is given below) of the starting material – anethole. Draw the molecule, assign the peaks to the protons, and mark signal multiplicity (s for singlet, d for doublet, dd for doublet of doublets, etc.).

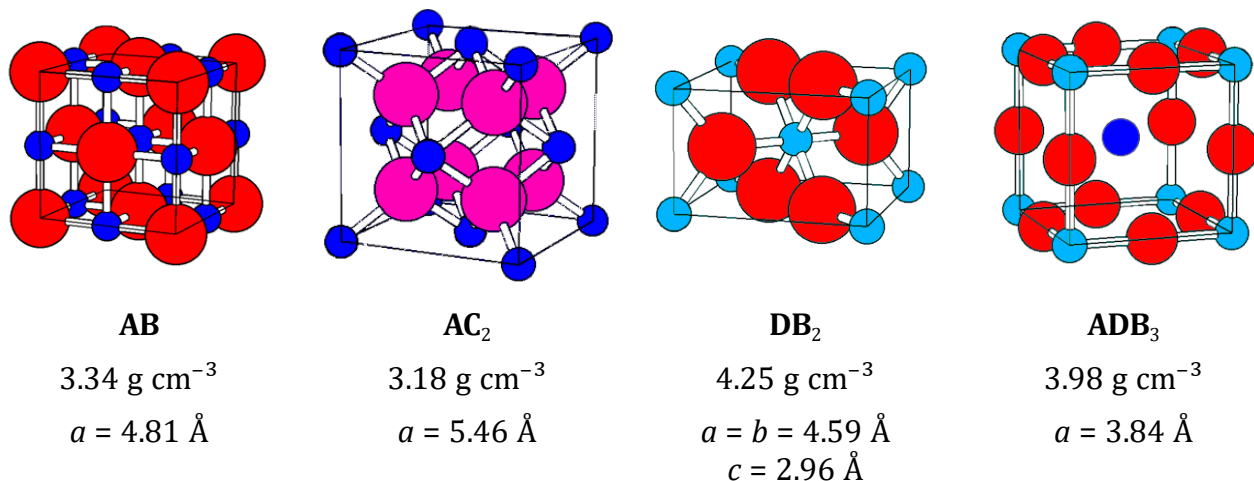


- b) Propose an alternative synthesis of *p*-anisaldehyde (compound **2**). Use *p*-cresol (4-methylphenol) as a starting material.
- c) Name a purification procedure that could be used to separate products **1** and **2**.
- d) Identify compounds **1–10** and **12** and draw their structures.

DMT can be metabolized in at least two different ways in one's mouth. One pathway is governed by a monoamine oxidase and aldehyde dehydrogenase enzyme activity (MAO-ADH). Other products are obtained through other modifications. Two products are given below.



- e) MAO-ADH enzyme is hidden under the letter: A; B; Both; None.

**Problem 1 – CRYSTAL – Crystal packing**


Unit cells, densities, and lattice parameters of four crystals are given in the Figure.

- Determine the number of each ion in each unit cell (**AB**, **AC<sub>2</sub>**, **DB<sub>2</sub>**, **ADB<sub>3</sub>**).
- Determine the coordination number of **A** and **D** in all crystals (**AB**, **AC<sub>2</sub>**, **DB<sub>2</sub>**, **ADB<sub>3</sub>**).
- Calculate the molar mass of each compound (**AB**, **AC<sub>2</sub>**, **DB<sub>2</sub>**, **ADB<sub>3</sub>**).
- Determine the elements **A–D**.

**Problem 2 – CRYSTAL, EQUIL, THERMO – Solubility**

In the table below are ionic radii and standard reduction potentials ( $\text{Me}^{n+}/\text{Me}$ ) for a set of metals:

|                                                | Fe <sup>3+</sup> | Fe <sup>2+</sup> | Cu <sup>2+</sup> | Cu <sup>+</sup> | Zn <sup>2+</sup> | Hg <sup>2+</sup> | Pb <sup>2+</sup> | Ag <sup>+</sup> | Hg <sup>+</sup> |
|------------------------------------------------|------------------|------------------|------------------|-----------------|------------------|------------------|------------------|-----------------|-----------------|
| $r_+ [\text{\AA}]$                             | 0.55             | 0.61             | 0.73             | 0.77            | 0.74             | 1.14             | 1.19             | 1.15            | 1.19            |
| $E^\circ(\text{Me}^{n+}/\text{Me}) [\text{V}]$ | -0.04            | -0.45            | +0.34            | +0.52           | -0.76            | +0.85            | -0.13            | +0.80           | +0.80           |

Enthalpy change of the metal-iodide solvation ( $\text{MeI}_n(\text{s}) \rightarrow \text{Me}^{n+}(\text{aq}) + n\text{I}^-(\text{aq})$ ) can be roughly estimated using Latimer and Kapustinskii equations:

$$\Delta H_{\text{solv}} = A \cdot \frac{|z_+|^2}{r_+ + r_0} + n\Delta H_{\text{hyd}}(\text{I}^-) - B \cdot \frac{v \cdot |z_+| \cdot |z_-|}{r_+ + r_-}$$

where  $A = -610 \text{ kJ \AA mol}^{-1}$ ,  $B = -1080 \text{ kJ \AA mol}^{-1}$ ,  $r_0 = 0.50 \text{ \AA}$ ,  $v$  is the number of ions in the empirical formula,  $z_+$  and  $z_-$  are the charges on the cation and anion, respectively, in elementary charges, and  $r_+$  and  $r_-$  are the radii of the cation and anion, respectively, in  $\text{\AA}$ ,  $\Delta H_{\text{hyd}}(\text{I}^-) = -308 \text{ kJ mol}^{-1}$ . The radius of the iodide is  $2.06 \text{ \AA}$ .

The entropy change of the metal-iodide solvation can be estimated using Sackur-Tedore and Powell-Latimer equations:

$$\Delta S_{\text{solv}} = C + n\Delta S_{\text{hyd}}(\text{I}^-) - D \cdot \frac{|z_+|}{(r_+ + r_{\text{dip}})^2} - E \cdot \ln M_+$$

where  $C = 88 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $D = 644 \text{ J \AA}^2 \text{ mol}^{-1} \text{ K}^{-1}$ ,  $r_{\text{dip}} = 1.30 \text{ \AA}$ ,  $E = 12.5 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $M$  is the molar mass of the cation,  $\Delta S_{\text{hyd}}(\text{I}^-) = -58.1 \text{ J mol}^{-1} \text{ K}^{-1}$ .

- a) Show with calculations that for  $\text{CuI}$   $\Delta G_{\text{solv}} > 0$ , while for  $\text{CuI}_2$   $\Delta G_{\text{solv}} < 0$ .
- b) Which of the following iodides are insoluble in water:  $\text{FeI}_2$ ,  $\text{CuI}$ ,  $\text{ZnI}_2$ ,  $\text{HgI}_2$ ,  $\text{PbI}_2$ ,  $\text{AgI}$ ,  $\text{HgI}$ .  
In aqueous solution,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  reduce  $\text{I}^-$  to  $\text{I}_2$ .  $E^\circ(\text{I}_2/\text{I}^-) = 0.535 \text{ V}$ .
- c) Calculate the standard reduction potential for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and show that the reduction of  $\text{I}^-$  to  $\text{I}_2$  by  $\text{Fe}^{3+}$  is spontaneous under standard conditions.
- d) Calculate the standard reduction potential for  $\text{Cu}^{2+}/\text{Cu}^+$  and show that the reduction of  $\text{I}^-$  to  $\text{I}_2$  by  $\text{Cu}^{2+}$  is spontaneous.  $K_{\text{sp}}(\text{CuI}) = 1.1 \cdot 10^{-12}$ .

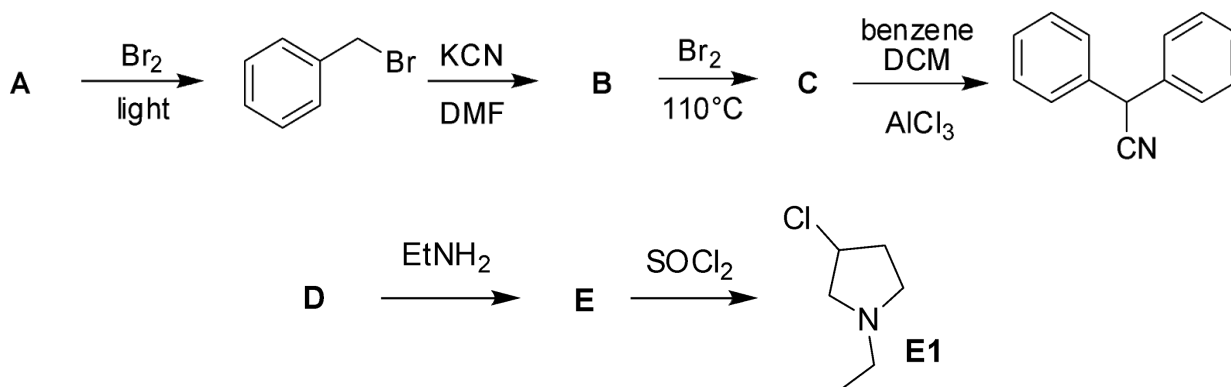
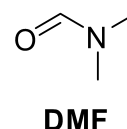
Five test tubes **A–E** contain 0,1 M aqueous solutions of one of the following substances:  $\text{AgNO}_3$ ,  $\text{CuSO}_4$ ,  $\text{FeCl}_3$ ,  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{KI}$ . The results of the identification of the particular test tubes by mutual reactions are shown in the following table:

|          | <b>A</b>          | <b>B</b> | <b>C</b> | <b>D</b> | <b>E</b> |
|----------|-------------------|----------|----------|----------|----------|
| <b>A</b> | –                 |          |          |          |          |
| <b>B</b> | Orange-red P      | –        |          |          |          |
| <b>C</b> | Yellow P, brown S | –        | –        |          |          |
| <b>D</b> | Brown S           | –        | –        | –        |          |
| <b>E</b> | Yellowish P       | –        | –        | White P  | –        |

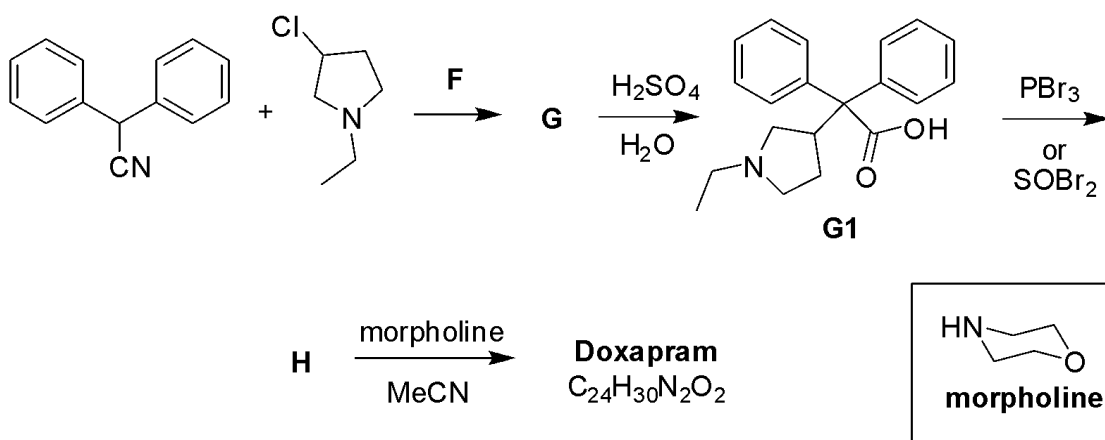
- e) Determine the content of tubes **A–E** and write chemical equations of the reactions marked in the table (P – precipitate, S – solution).

### Problem 3 – SYNTH – Analeptics

It is known that when people are highly intoxicated with depressants, they tend to stop breathing and could even die. It happens because of breathing center depression in the human brain. Analeptics (breathing stimulators) such as Doxapram could help in such critical situations when injected. Following, you will find two synthesis schemes of the main components used in Doxapram manufacture.



- a) Draw the structural formula of compounds **A–E**.
- b) Why is light so important in the first reaction?
- c) Would compound **E1** be racemic or not if we used enantiomerically pure **D**?



- Compound **H** is neither **acidic** nor **basic**.
- In Doxapram, all carbons attached to the N atom (from morpholine) are  $sp^3$ .

- d) Draw the structural formula of compounds **F–H** and Doxapram.
- e) What are the most suitable conditions **F**: **i)** HCl/MeOH; **ii)** *t*-BuOK/THF; **iii)** beeswax and naphtha; **iv)**  $\text{Et}_2\text{O} \cdot \text{BF}_3$ .
- f) Draw reaction mechanism **G1**  $\rightarrow$  **H**.

#### Problem 4 – CALC, SPECTRA, STRUCT – Nickel knickknackery

By exploring the deepest corners of his table drawers, a student Dominykas (respectfully called Cheminykas by his friends) found a bottle containing a green crystalline substance with a writing  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . It might be due to the never-coming spring, mesmerized by the greenery of this substance, Cheminykas decided to carry out a few experiments with this material.

After dissolving it in water, he treated the solution with concentrated ammonia solution, the odor of which might wake even the heaviest sleeper from the deepest winter hibernation. A colorful metal-ammine complex is formed when the reaction takes place.



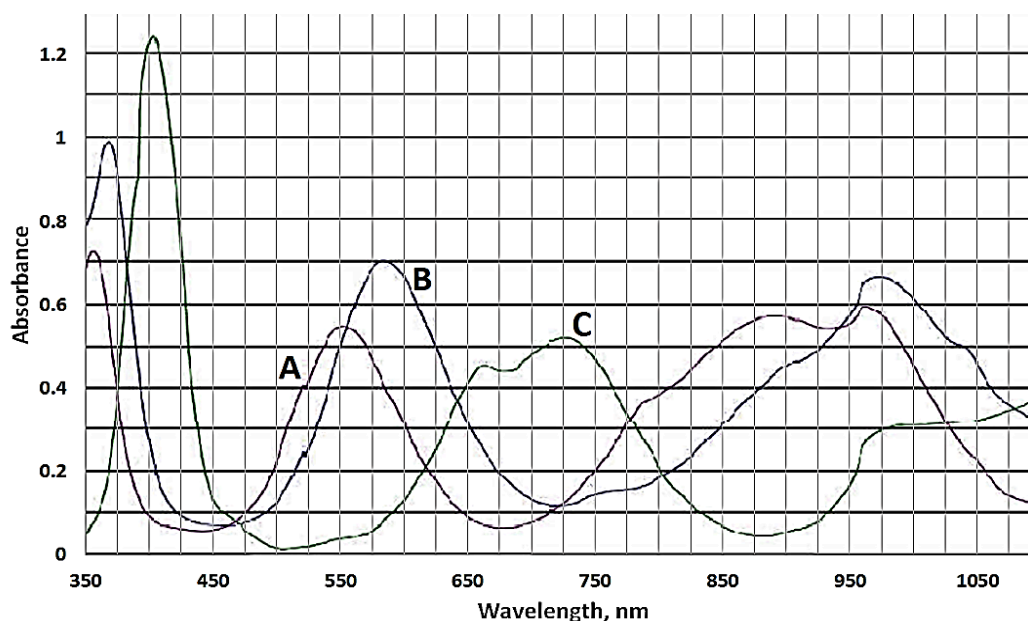
Several colorful crystals have formed, were filtered, dissolved in  $5 \text{ cm}^3$  of water, poured into the spectrophotometric cuvette and placed into the spectrophotometer. After registering the UV-Vis spectrum, Cheminykas observed that the most intense absorbance occurred at 394 nm wavelength. Wanting to explore this material more thoroughly, he decided to carry out a photometric analysis.

Consequently, he dissolved 0.2017 g of obtained colorful crystals in  $10.0 \text{ cm}^3$  water and poured this solution into a photometric cuvette with a 5.00 cm optical path length. The device showed that the solution transmitted only 0.7% of light. Knowing that the device is not very accurate at this part of the scale, he transferred the solution from the cuvette into a volumetric flask, diluted it to  $25.0 \text{ cm}^3$ , and again transferred  $10.0 \text{ cm}^3$  of this solution to the same photometric cuvette. This time, the device showed that 13.5% of light was transmitted.

- a) Calculate the molar absorption coefficient of this material.

The color wheel is a simplified but effective visual tool to predict the absorbance bands without having to use a spectrophotometer.

- b) Determine the colors of substances **A**, **B**, and **C**.



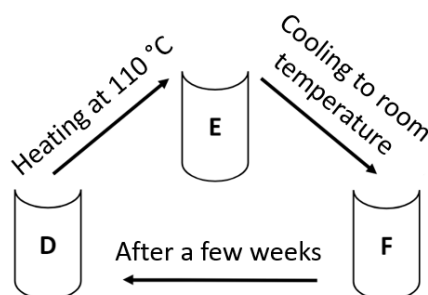
Three absorption bands in the UV-VIS spectrum are usually observed for the coordination compounds of octahedral geometry, given in the descending order of transition energy:  ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$ ,  ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$  and  $T_{2g} \leftarrow {}^3A_{2g}$ .

- c) Calculate the difference between  ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$  transition energies of  $[Ni(en)_3]^{2+}$  (en – ethylenediamine) (substance A) and  $[Ni(NH_3)_6]^{2+}$  (substance B), providing an answer in electronvolts (eV).

Later on, Cheminykas heated the  $NiCl_2 \cdot 6H_2O$  salt to remove water and treated it with dry dimethylammonium chloride to synthesize another compound  $((CH_3)_2-NH_2)_2[NiCl_4]$  bis(dimethylammonium) tetrachloronickelate(II), the coordination number of which is 6.

Having completed the synthesis, he took some of the material for characterization but carelessly left the remaining material on the heating plate. When the temperature rose to 110 °C, the color of the substance changed from red (substance D) to deep blue (substance E). Cheminykas quickly noticed that and turned off the heating plate. He further noticed that while the substance was cooling down to room temperature, the color of it changed again from blue to yellow (substance F). Even more so, in two weeks, it returned to its original red color while being stored at room temperature.

Genuinely interested in this phenomenon, Cheminykas carried out literature research and found out that materials that possess an ability to reversibly change their color according to their temperature are called thermochromic, and the phenomenon itself is called thermochromism. He raised a few hypotheses to explain the thermochromic behavior of  $((CH_3)_2-NH_2)_2[NiCl_4]$ .



- d) Which of the following statements best describes the color change of  $((\text{CH}_3)_2\text{-NH}_2)_2[\text{NiCl}_4]$  upon heating?
- With an increasing temperature, enough energy is passed to the material to surpass the activation energy of reforming crystal lattice and formation of a more thermodynamically stable  $((\text{CH}_3)_2\text{-NH}_2)_2[\text{NiCl}_4]$  stereoisomer.
  - A decomposition reaction of organic ligands is taking place, followed by a change in the chemical composition of the coordination compound.
  - Because of the increased temperature, hydrogen bonds are weakened, and an infinite two-dimensional structure is destroyed, accompanied by the shift from octahedral to tetrahedral coordination geometry.
  - The temperature excites the electrons in  $\text{Ni}^{2+}$   $d$ -orbitals, enabling the electronic transitions within the semiconductor bandgap.
- e) Draw all possible coordination stereoisomers of  $((\text{CH}_3)_2\text{-NH}_2)_2[\text{NiCl}_4]$ . If there are any optically active stereoisomers (enantiomers) – mark them.
- f) Schematically depict the absorbance spectra of thermochromic nickel coordination compound before heating (substance **D**), at thermochromic shift temperature (substance **E**) and after cooling back to room temperature (substance **F**). Only one absorption band per material is required to draw.
- g) Compared with the  $((\text{CH}_3)_2\text{-NH}_2)_2[\text{NiCl}_4]$  at thermochromic shift temperature, after cooling to room temperature, the required energy for  $d$ - $d$  electronic transitions is:
- Lower than at thermochromic shift temperature.
  - Higher than at thermochromic shift temperature.
  - Same as at thermochromic shift temperature.

Finally, Cheminykas decided to treat the thermochromic nickel complex with some bromine and ethylenediamine ( $\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_2$ , en) which is a common bidentate ligand in coordination chemistry. He obtained a compound  $[\text{NiBrCl}(\text{en})_2]$ , the coordination number of which is 6.

- h) Draw all possible coordination stereoisomers of  $[\text{NiBrCl}(\text{en})_2]$ . If there are any optically active stereoisomers (enantiomers) – mark their pairs.

### Problem 5 – INORG, KINETICS, THERMO – Cleaning oil pipes

As wells are drilled in deeper and deeper waters, the accumulation of paraffin, asphaltene and hydrates is increasing due to the extremely low temperatures on the ocean floor. Removing the wax from wells and pipelines will entail additional costs such as the use of deep-water divers and special equipment to cut and remove paraffin build-up from the pipelines.

One simpler solution is to melt paraffin. A reaction between ammonium chloride and sodium nitrite has been proposed to achieve this (**reaction 1**).

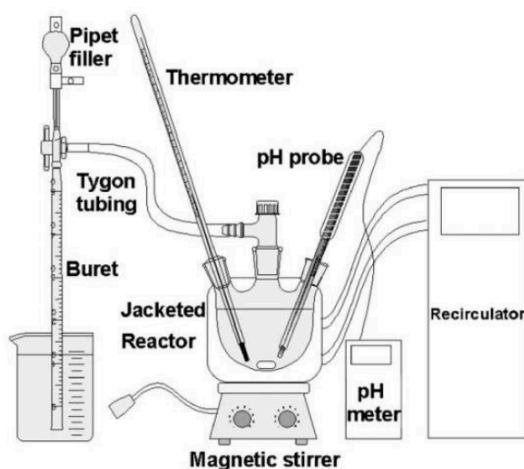
- a) Calculate the standard enthalpy of the reaction if the enthalpies of formation are:  
 $\Delta H_f(\text{NaNO}_2) = -359.4 \text{ kJ mol}^{-1}$ ;  $\Delta H_f(\text{NH}_4\text{Cl}) = -314.43 \text{ kJ mol}^{-1}$ ;  $\Delta H_f(\text{NaCl}) = -411.12 \text{ kJ mol}^{-1}$ ;  $\Delta H_f(\text{H}_2\text{O}) = -285.8 \text{ kJ mol}^{-1}$ .
- b) We know that the equilibrium constant of **reaction 1** is  $K \approx 10^{60}$ . What can we say about reaction 1 based on this information and the previous calculations? Choose which of the following statements is the most correct.
- The reaction is endothermic and reversible.

- ii) The reaction is exothermic and irreversible.
- iii) The reaction is endothermic and irreversible.
- iv) The reaction is exothermic and reversible.

To use **reaction 1** in the oil industry, it is necessary to know the reaction rate and mechanism. Research Group I thought that the reaction was of the second order and that the rate-limiting step was the reaction of nitrosyl ion ( $\text{NO}^+$ ) with molecular ammonia. Group II, on the other hand, was convinced that the reaction was of the third order and that the rate-limiting step was the reaction of  $\text{N}_2\text{O}_3$  (from  $\text{HNO}_2$ ) with  $\text{NH}_3$ .

- c) Draw the Lewis structures of the compounds and particles mentioned above and, where appropriate, also the resonance structure.

Research Group III replicated and adapted the experiments of the previous two groups. They mixed, at different temperatures and pH values, 150  $\text{cm}^3$  sodium nitrite solution and 150  $\text{cm}^3$  ammonium chloride solution. pH was adjusted by adding HCl or NaOH solution to the reaction mixture. Before the experiment, the reaction vessel was cleaned with nitrogen gas to minimize the occurrence of side reactions. The tools used to study the kinetics of reaction 1 are shown.



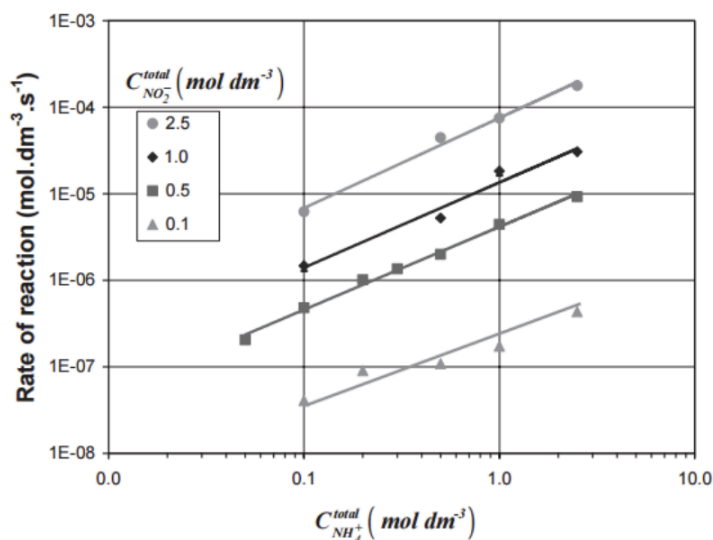
- d) What are the possible adverse reactions if the test was carried out at pH 3–7? Choose one or several answers.

- i)  $\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2$
- ii)  $2\text{HNO}_2 \rightleftharpoons \text{NO}_2 + \text{NO} + \text{H}_2\text{O}$
- iii)  $\text{NH}_4\text{Cl} + \text{NaOH} \rightarrow \text{NH}_3 + \text{H}_2\text{O} + \text{NaCl}$ ,  $\text{p}K_a(\text{NH}_4^+) = 9.25$
- iv)  $\text{NaNO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{NaNO}_3$

Once the side reactions have been eliminated, the rate of **reaction 1** can be differentiated from the volume of the gas produced.

- e) Differentiate the rate equation for **reaction 1** via the volume of the gas using the commonly used variables (symbols).

Reaction rates at different concentrations of nitrite and ammonium ions were calculated and plotted on the graph shown in Figure 2 ( $T = 25^\circ\text{C}$ ,  $\text{pH} = 5$ ). Determine the reaction order for both of the two reactants on the basis of the graph below.

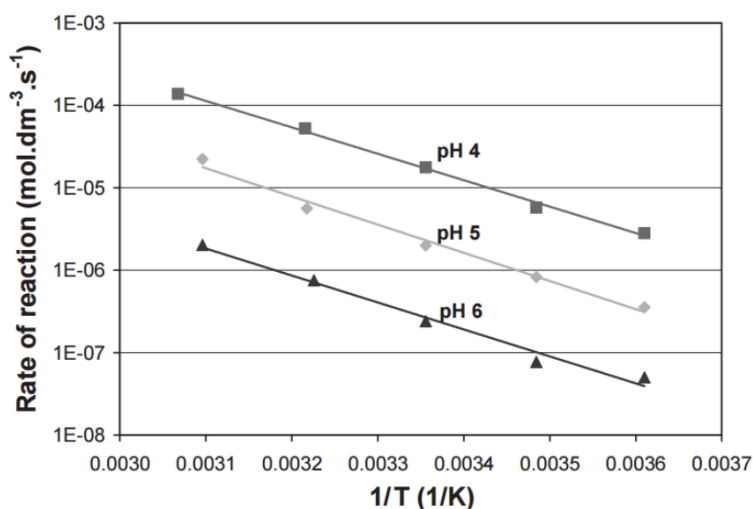


f) Determine the reaction order for ammonium ions (ammonium chloride).

g) Determine the reaction order for nitrite ions ( $\text{HNO}_2$ ).

h) Give the value and unit of the rate constant of the reaction ( $T = 25^\circ\text{C}$ ,  $\text{pH} = 5$ ).

The temperature dependence of the reaction between ammonium chloride ( $c_0 = 0.5\text{ M}$ ) and sodium nitrite ( $c_0 = 0.5\text{ M}$ ) was investigated in the temperature range  $4\text{--}50^\circ\text{C}$  at  $\text{pH } 4, 5$  and  $6$ . As expected, the reaction rate followed the Arrhenius equation.



i) Derive the activation energy from available data.

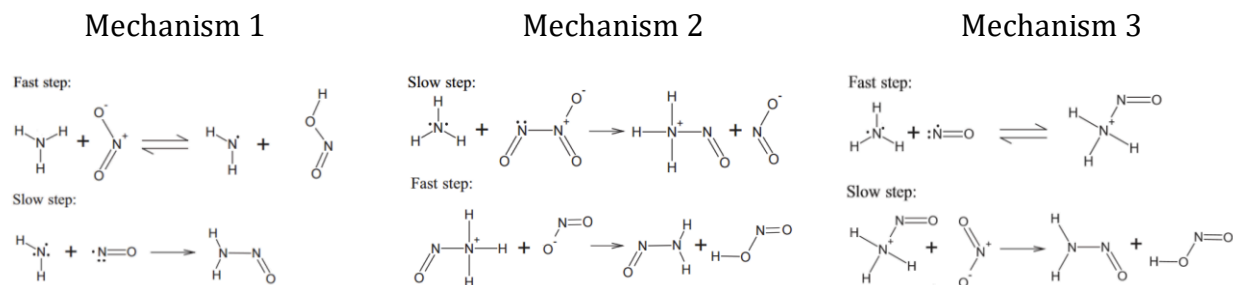
Research Group III continued its studies to determine the mechanism of the reaction. First, they assumed that there was an intermediate from which two end products ( $\text{N}_2$  and  $\text{H}_2\text{O}$ ) could be rapidly formed. They then proposed different reactions to obtain the intermediate from the two reactants originally used ( $\text{NH}_3$  and  $\text{HNO}_2$ ) or their derivatives. The most probable intermediate was thought to be nitrosamine ( $\text{H}_2\text{N}-\text{N}=\text{O}$ ), yielding two final products.

j) Draw the mechanism of nitrosamine degradation.

There are several ways to obtain nitrosamine from the initial compounds. To investigate the possibility of an initiation reaction, one can compare its internal Arrhenius activation energy ( $E^*$ ) with the Arrhenius activation energy ( $E$ ) determined in a kinetics experiment. The internal Arrhenius activation energy is described by the equation  $E^* = \Delta H^* + RT$ , where  $\Delta H^*$  is the enthalpy change of the slowest phase.

k)  $\text{HNO}_2$  (aq) has been shown to be in equilibrium with  $\text{N}_2\text{O}_3$ , NO and  $\text{NO}_2$ . Write the equilibrium reaction equations for the reactions describing the equilibrium state.

Scientists proposed three following mechanisms for nitrosamine production:



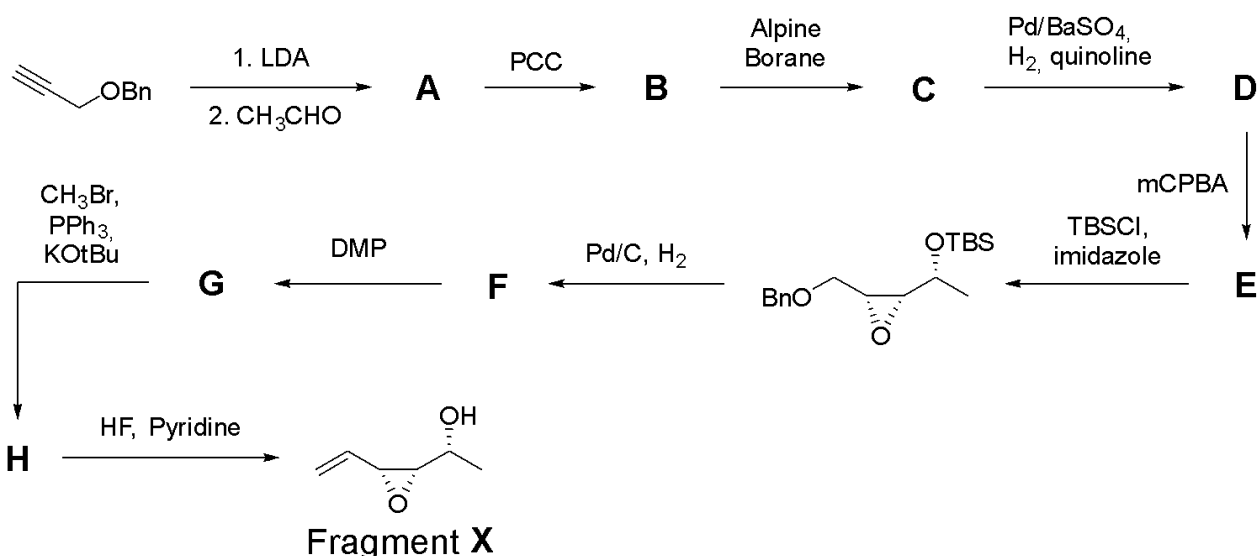
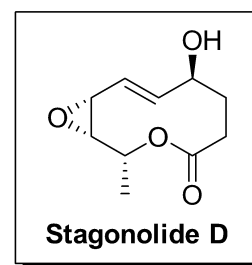
l) Write the expression for the reaction rate for all three mechanisms (using  $\text{HNO}_2$  and  $\text{NH}_3$  concentrations) and a derivation.

m) Compare the internal Arrhenius activation energies at standard conditions ( $T = 25^\circ\text{C}$ ) and decide which of these mechanisms could be correct. Bond dissociation energies:

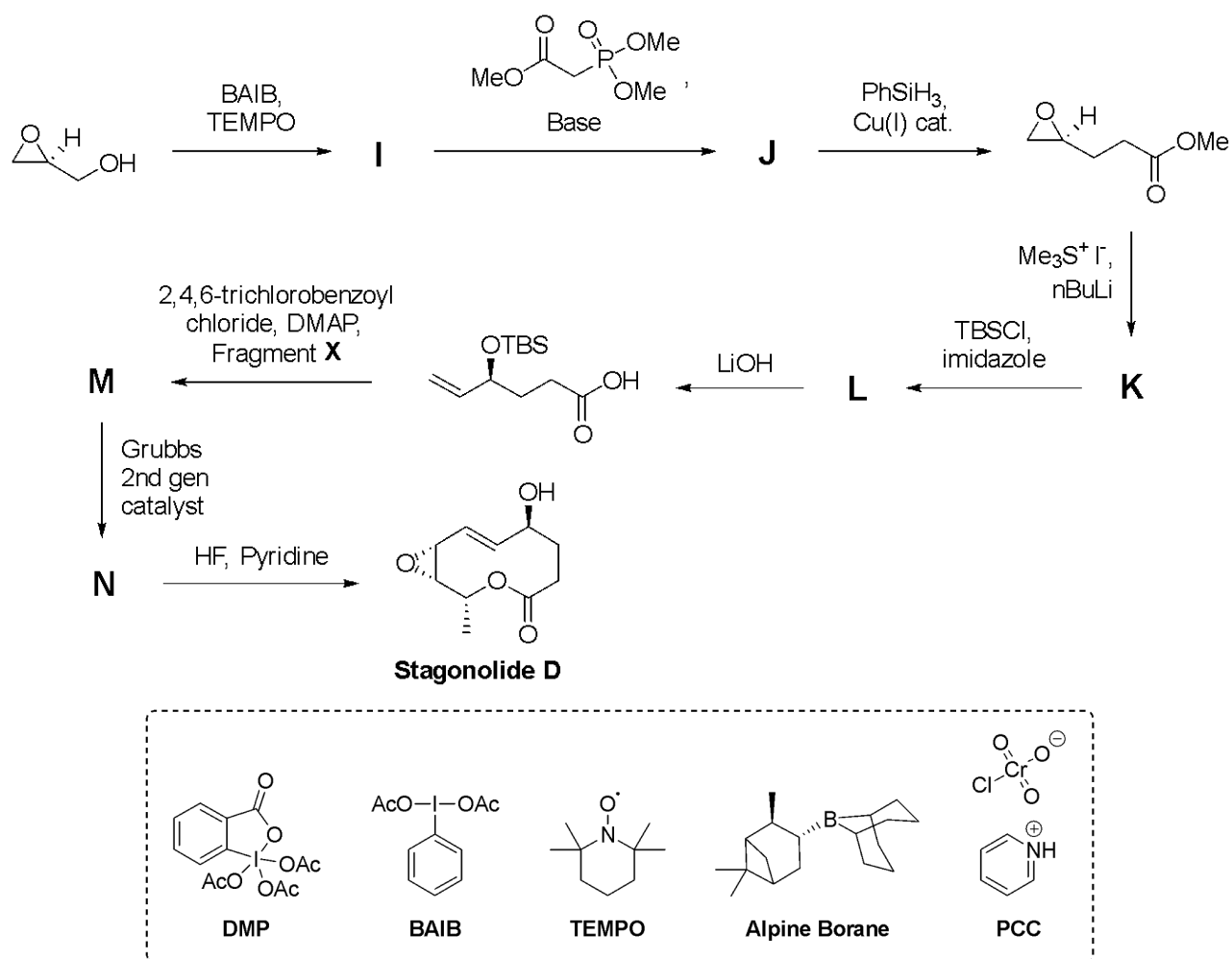
| N-H                      | H-H                      | N-N                      | N-O                      | N=N                      |
|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 391 kJ mol <sup>-1</sup> | 432 kJ mol <sup>-1</sup> | 163 kJ mol <sup>-1</sup> | 201 kJ mol <sup>-1</sup> | 418 kJ mol <sup>-1</sup> |
| N=O                      | O=O                      | O-H                      | N≡N                      |                          |
| 607 kJ mol <sup>-1</sup> | 495 kJ mol <sup>-1</sup> | 467 kJ mol <sup>-1</sup> | 941 kJ mol <sup>-1</sup> |                          |

### Problem 6 – SYNTH – The synthesis of Stagonolide D

During the last decade, there has been a significant interest in 10-membered cyclic macrolides. One such macrolide is Stagonolide D, which in 2007 was isolated from the fungus *Stagnospora Cirsii*. Stagonolide D produces necrotic lesions on leaves and has shown some herbicidal activity. In this problem, we will discuss the total synthesis of Stagonolide D. In order to make Stagonolide D, we first have to make the fragment X, the synthesis of which is shown below.



The obtained fragment X is further used for the synthesis of the Stagonolide D, as shown below and it employs ring-closing metathesis as the key step.



- Draw the structural formulas of compounds **A–N**. Show the appropriate stereochemistry, where necessary.
- Draw a mechanism for the transformation leading to **K**.
- Draw a mechanism for the transformation **F**  $\rightarrow$  **G**.

## 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.

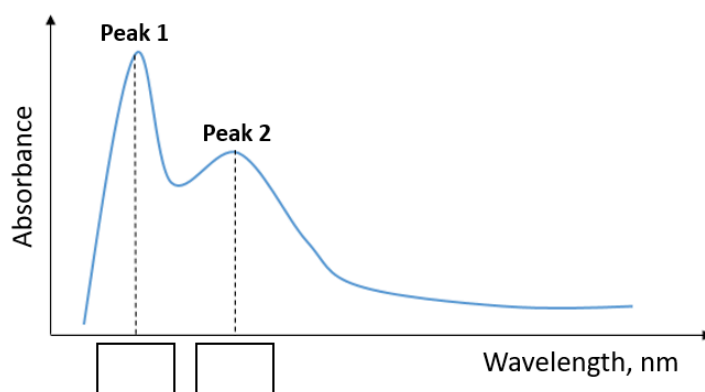
- Write the formulas of **A–G**. Write the equations for all mentioned reactions.
- Draw Lewis structures for compounds **B**, **C**, and **D**. Use VSEPR to determine their geometry at N centers and overall geometry if appropriate.

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.

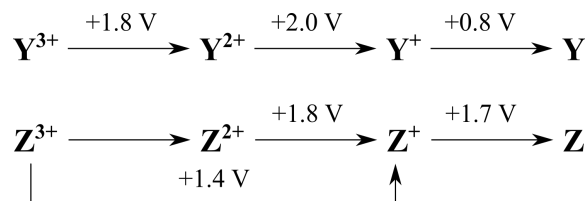


- f) Suggest electronic structures of the excited states corresponding to peaks 1 and 2 using the appropriate  $d$ -orbital splitting pattern from sub-question 3. Note: the overall spin of the molecule has to be preserved upon optical excitation.

### 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.

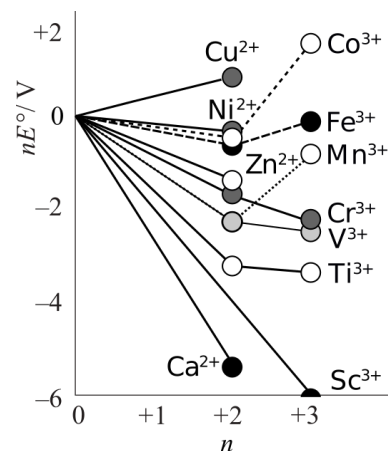
Cations do not occur in solution as bare ions but in a hydrated state as aqua complexes. Other ligands may take the place of water molecules. This way, complex ions are formed in melts and solids.

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.

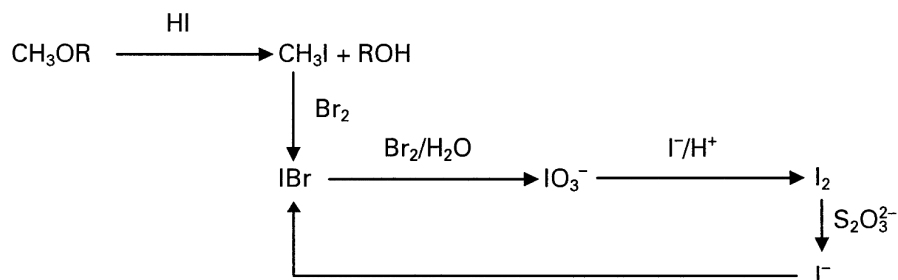
#### Problem 4 – CALC, ELECTRO – Titrimetric determination of methoxyl groups

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:

- A. Formic acid ( $E^\circ(\text{CO}_2/\text{HCOOH}) = -0.1 \text{ V}$ );
- B. Chlorous acid ( $E^\circ(\text{ClO}_3^-/\text{HClO}_2) = +1.2 \text{ V}$ );
- C. 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  $0.03 \text{ cm}^3$ .

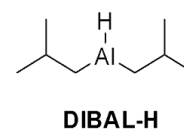
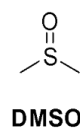
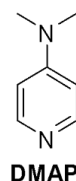
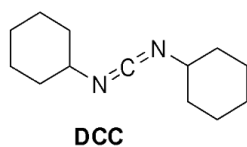
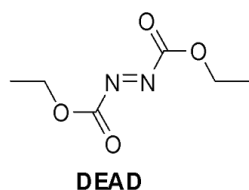
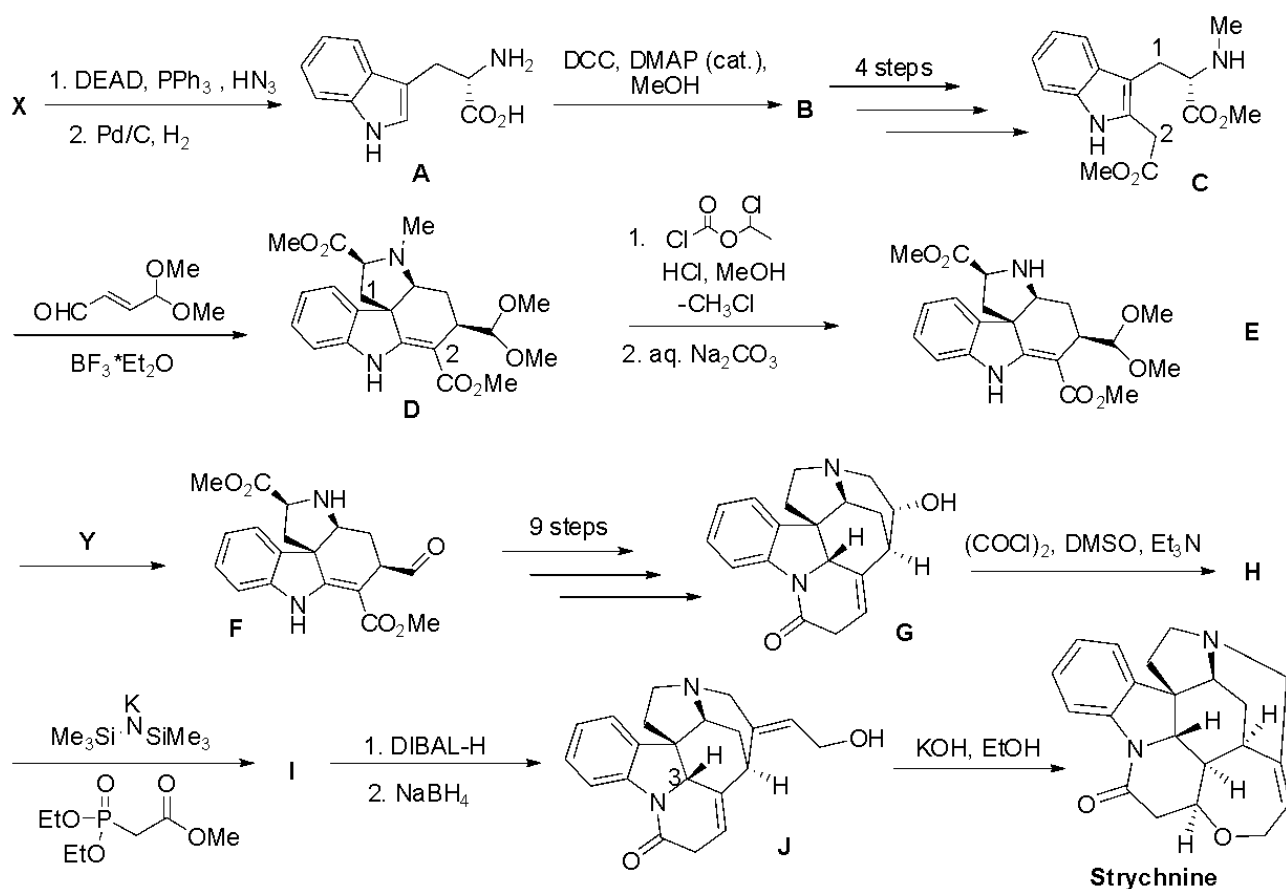
- d) Estimate the minimal theoretical number of multiplication cycles needed to be repeated in order to detect a single molecule of  $\text{R-O-CH}_3$  per 10 g of a sample.

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.



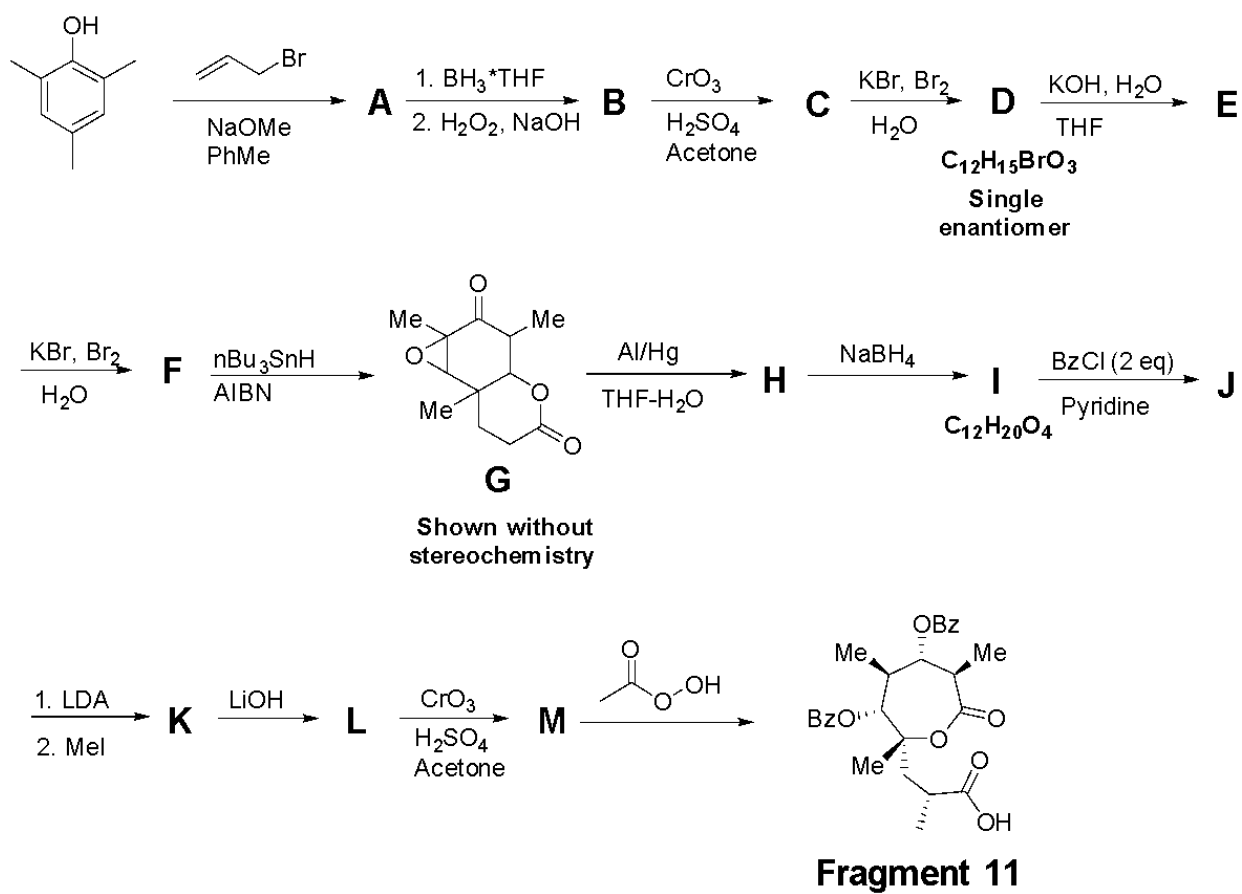
- a) Draw the structure of compound **X** with stereochemistry. Identify the stereocenter(s) using the *R/S* nomenclature.
- b) Draw the structure of compound **B**. During the reaction from **A** to **B**, the reagent DCC is converted to another compound. Draw its structure as well.
- c) Write the suitable 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**.



## 27th BChO 2019, Tartu, Estonia

### Problem 1 – STRUCT – Iron complexes

Iron is an element that makes up the greatest part of Earth by mass (34.6%), constituting 4.65% of Earth's crust. It has been used in the production of various tools. Also, iron complex compounds have been used as pigments. Depending on the pH of the aqueous solution,  $\text{Fe}^{3+}$  ions can form octahedral complexes, which differ in color. Iron(III) ion-containing salt was dissolved in concentrated acid, and the pH of the solution was slowly increased by adding NaOH solution dropwise. During the addition of NaOH solution, there was a gradual change in the color of the solutions, as shown in the table below:

| pH         | The color of the solution | Complex  |
|------------|---------------------------|----------|
| Increase ↓ | Pale violet               | <b>A</b> |
|            | Yellow                    | <b>B</b> |
|            | Green                     | <b>C</b> |

- Write the chemical formulas of the complexes **A–C**. If any isomers exist for **A–C**, draw their structural formulas.
- Provide the equations of formation of **B** from complex **A** and **C** from complex **B**.
- At high pH values,  $\text{Fe}^{3+}$  ions almost could not be found in solution because brown solid substance **D** is formed. Write the chemical formula of substance **D**.

According to the magnetic measurements, it was stated that  $[\text{Fe}(\text{CN})_6]^{3-}$  ion has one unpaired electron, while  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has more than one.

- Draw the crystal field diagrams for both complexes.
- Are  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  ions paramagnetic or diamagnetic?

It is very common for iron ions to interfere with the analysis of other ions. In order to prevent interference of  $\text{Fe}^{2+}$  ions, sodium oxalate is added to the solution.  $\text{Fe}^{2+}$ , combined with oxalate ions, make a very stable octahedral complex (stability constant  $K = 1.7 \cdot 10^5$ ). Equal volumes of solution, where the concentration of  $\text{Fe}^{2+}$  ions is  $0.20 \text{ g dm}^{-3}$  and solution of  $0.20 \text{ M Na}_2\text{C}_2\text{O}_4$ , were mixed.

- Calculate the pH of the  $0.20 \text{ M Na}_2\text{C}_2\text{O}_4$  (oxalic acid's  $\text{p}K_{a1} = 1.27$  and  $\text{p}K_{a2} = 4.27$ ).
- Calculate the percentage of free  $\text{Fe}^{2+}$  ions remaining in the solution after mixing equal volumes of  $0.20 \text{ g dm}^{-3} \text{ Fe}^{2+}$  and  $0.20 \text{ M Na}_2\text{C}_2\text{O}_4$  solutions. *Hint: because  $\text{C}_2\text{O}_4^{2-}$  concentration is relatively high, you can assume that complex formation does not affect it.*

$[\text{Fe}(\text{SCN})_6]^{3-}$  solution shows strong absorbance at  $\lambda = 490 \text{ nm}$ . This characteristic is used for iron concentration determination by absorption spectrophotometry in white wine.  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ , and KSCN are added to wine. Then absorption is measured.

- Draw Lewis dot structures for all  $\text{SCN}^-$  resonance structures.
- Determine the color of  $[\text{Fe}(\text{SCN})_6]^{3-}$  solution.
- Why are  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  added to wine? Answer by writing the net ionic equation/equations for appropriate reaction/reactions.

It was determined that  $100.0 \text{ g}$  of compound  $\text{X}_y[\text{Fe}(\text{CN})_6]_z$  contains  $45.50 \text{ g}$  of iron.

- Identify the element **X** and write the formula of the compound. Show your calculation.

**Problem 2 – EQUIL, THERMO – CaCO<sub>3</sub> in nature and laboratory**

When solving this problem, you will need thermodynamic data from the table below. Assume that all gases and solutions are ideal and enthalpy change of all reactions is temperature-independent. Thermodynamic data at 298 K temperature and 10<sup>5</sup> Pa pressure.

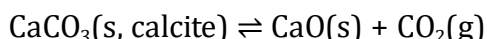
|                                  | $\Delta H_f^\circ [\text{kJ mol}^{-1}]$ | $\Delta G_f^\circ [\text{kJ mol}^{-1}]$ | $S^\circ [\text{J mol}^{-1} \text{K}^{-1}]$ |
|----------------------------------|-----------------------------------------|-----------------------------------------|---------------------------------------------|
| CaO (s)                          | -635.1                                  | -604.0                                  | 39.7                                        |
| Ca <sup>2+</sup> (aq)            | -542.8                                  | -553.6                                  | -53.1                                       |
| Ca(OH) <sub>2</sub> (s)          | -986.1                                  | -898.5                                  | 83.4                                        |
| CaCO <sub>3</sub> (s, calcite)   | -1206.9                                 | -1128.8                                 | 92.9                                        |
| CaCO <sub>3</sub> (s, aragonite) | -1207.1                                 | -1127.7                                 | 88.7                                        |
| CO <sub>2</sub> (g)              | -393.5                                  | -394.4                                  | 213.7                                       |
| H <sub>2</sub> O (l)             | -285.8                                  | -237.2                                  | 69.9                                        |
| OH <sup>-</sup> (aq)             | -230.0                                  | -157.2                                  | -10.7                                       |

Calcium carbonate is found in nature in the form of several polymorphs: calcite, aragonite, vaterite, and ikaite. The first three polymorphs are anhydrous calcium carbonate. Ikaite is a hydrated calcium carbonate – a mineral that is found in the cold waters of Ikka Fjord in Greenland. When heated, ikaite CaCO<sub>3</sub>·xH<sub>2</sub>O readily loses approximately 52% of its initial mass. Under strong heating (1000 °C), it additionally loses approximately 21% of its initial mass.

- a) Determine number  $x$  in CaCO<sub>3</sub>·xH<sub>2</sub>O. Show your calculations.
- b) Predict which polymorph (calcite or aragonite) is more stable at 298 K and 10<sup>5</sup> Pa.

Calcium carbonate minerals are abundant in nature and cause the formation of hard water.

- c) Write the chemical equation depicting calcium carbonate forming hard water.
- d) Calculate equilibrium constant of the following reaction at i) 25 °C and ii) 1070 K:



In the laboratory, a special tightly closed reactor with the possibility to heat substance samples was constructed. This reactor was equipped with a special mechanism that gives the possibility to input samples of solid without any gas leakage. The volume of the reactor is 5.0 dm<sup>3</sup>. Initially, the reactor was filled with argon (25 °C, 1.0·10<sup>5</sup> Pa).

- e) Calculate the pressure (Pa) in the reactor when the temperature was increased to 1070 K. Then, five samples of calcite in consecutive order were introduced into the reactor. The mass of each sample was 1.0 g. Temperature all the time remains at 1070 K. A new sample of calcite was introduced only after constant pressure in the reactor was established.
- f) Calculate the final total gas pressure in the reactor after the introduction of each sample of calcite.

Finally, the reactor was quickly cooled down to 25 °C and flushed with argon gas to expel all carbon dioxide. A mixture of solid compounds from the reactor was transferred into the water. The final volume of the solution is 0.60 dm<sup>3</sup>.

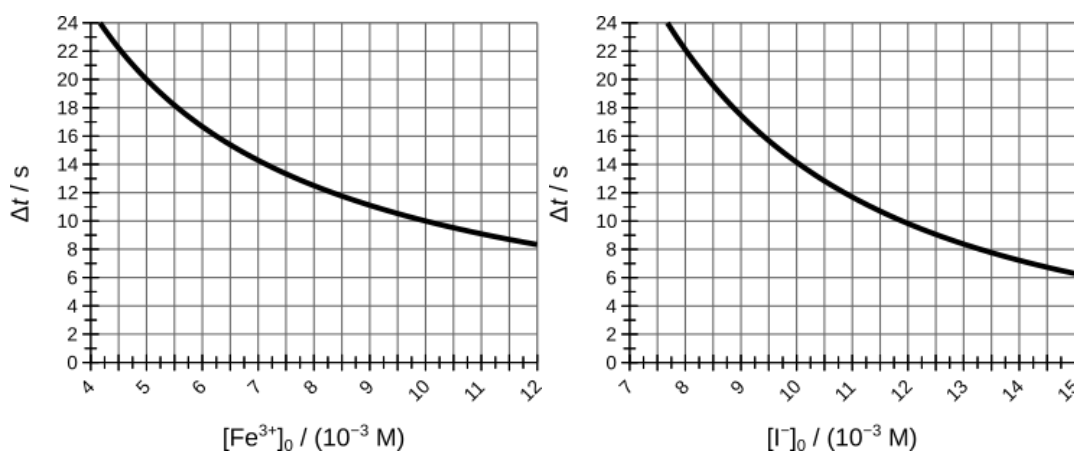
- g) Calculate the pH of this solution (at 25 °C). Show your calculations.

### Problem 3 – ELECTRO, KINETICS – Colorful kinetics

Reactions between iodide ions and iron(III) ions as well as iodine and thiosulfate ions in an aqueous solution are known to occur spontaneously.

- a) Examine the given standard potentials and predict the products of the reactions **i)** between  $\text{Fe}^{3+}$  and  $\text{I}^-$  as well as **ii)** between  $\text{I}_2$  and  $\text{S}_2\text{O}_3^{2-}$ . Show your calculations. Write equations of the feasible reactions.  $E^\circ(\text{Fe}^{3+}/\text{Fe}) = -0.04 \text{ V}$ ;  $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$ ;  $E^\circ(\text{FeO}_4^{2-}/\text{Fe}^{3+}) = +2.20 \text{ V}$ ;  $E^\circ(\frac{1}{2}\text{I}_2/\text{I}^-) = +0.54 \text{ V}$ ;  $E^\circ(\text{IO}_3^-/\frac{1}{2}\text{I}_2) = +1.20 \text{ V}$ ;  $E^\circ(\text{HIO}/\frac{1}{2}\text{I}_2) = +1.44 \text{ V}$ ;  $E^\circ(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}) = +0.08 \text{ V}$ .

Oxidation of iodide by iron(III) ions in the presence of  $\text{S}_2\text{O}_3^{2-}$  ions and starch can run like a clock reaction. The reaction is started by mixing a solution of iron(III) nitrate with a solution containing thiosulfate, iodide, and starch. The solution immediately turns purple due to the formation of  $\text{Fe}(\text{S}_2\text{O}_3)^+$  complex. The color gradually fades until the solution becomes colorless and then suddenly turns dark blue due to the formation of the starch–pentaiodide complex. The kinetics of the reaction between iodide and iron(III) can be studied by the initial rates method by measuring the time ( $\Delta t$ ) elapsed from the mixing of the two solutions to a sudden color change. Under certain conditions, the initial reaction rate is inversely proportional to the measured time:  $v_0 = [\text{S}_2\text{O}_3^{2-}]_0/\Delta t$ . Two graphs given below were obtained measuring  $\Delta t$  after mixing solutions with different initial  $[\text{Fe}^{3+}]_0$  or  $[\text{I}^-]_0$  concentrations while keeping the concentration of all other components constant.



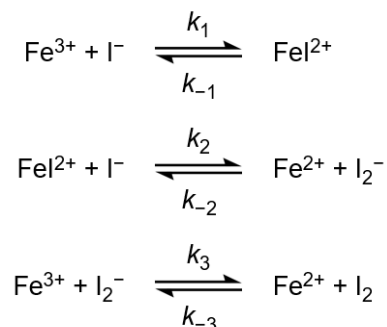
- b) Show how to determine the reaction order with respect to **i)**  $\text{Fe}^{3+}$  and **ii)**  $\text{I}^-$  ions, then calculate the half-life of  $[\text{Fe}^{3+}]$  in solution at experimental conditions.

Some experimental results are summarized in the table below:

| # | $[\text{Fe}^{3+}]_0$ | $[\text{I}^-]_0$ | $v_0 [\text{M s}^{-1}]$ |
|---|----------------------|------------------|-------------------------|
| 1 | 0.09900              | 0.0744           | 0.008836                |
| 2 | 0.09900              | 0.0431           | 0.002978                |
| 3 | 0.04945              | 0.0960           | 0.007319                |
| 4 | 0.00118              | 0.0960           | 0.000175                |
| 5 | 0.00118              | 0.0607           | 0.000070                |
| 6 | 0.00118              | 0.0431           | 0.000035                |

- c) Calculate the rate constant of the reaction.

The following reaction scheme was proposed to explain the mechanism of  $\text{Fe}^{3+}$  reduction by  $\text{I}^-$ :



- d) Derive a rate equation for consumption of  $\text{Fe}^{3+}$  ( $-\text{d}[\text{Fe}^{3+}]/\text{d}t$ ) from the provided scheme, stating any reasonable assumptions made.
- e) Explain whether the provided experimental data confirms the proposed mechanism or not.

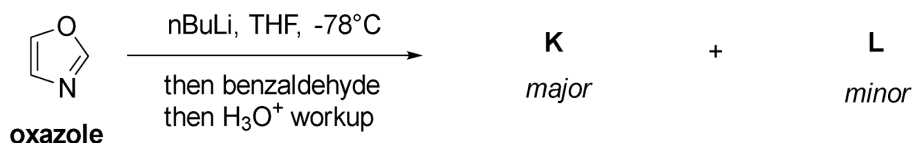
#### Problem 4 – EQUIL – Some penguin chemistry

While in the rookery, Antarctic Adélie penguins may encounter intense solar radiation. Panting during severe heat stress can result in alternations of gas composition and acid–base balance in the blood of brooding adults. Let us examine how the temperature influences the pH by altering the  $\text{HCO}_3^-/\text{CO}_2(\text{aq})/\text{CO}_2(\text{g})$  equilibrium, in which the level of  $\text{CO}_2$  is adjusted by respiration. The following data is available:  $\text{p}K_{\text{a}1} = 6.35$  (25 °C),  $\text{p}K_{\text{a}1} = 6.07$  (38.5 °C),  $\Delta H_{\text{vap}}(\text{CO}_2, \text{blood}) = 19.95 \text{ kJ mol}^{-1}$ ,  $K_{\text{H}}(\text{CO}_2, 38.5 \text{ °C}) = 2.2 \cdot 10^{-4} \text{ mol m}^{-3} \text{ Pa}^{-1}$ .

- a) Calculate the pH of the Adélie penguin blood at a normal body temperature of 38.5 °C if  $[\text{HCO}_3^-] = 29.4 \text{ mM}$  and  $p(\text{CO}_2) = 4.9 \text{ kPa}$ .
- b) Calculate the values of  $\text{p}K_{\text{a}1}$  (40.7 °C) and  $K_{\text{H}}(\text{CO}_2, 40.7 \text{ °C})$ .
- c) Estimate the pH of the Adélie penguin blood at a critical body temperature of 40.7 °C assuming that the  $\text{CO}_2$  pressure remains the same and the concentration of  $\text{HCO}_3^-$  depends on the pH as  $[\text{HCO}_3^-] = (302.4 - 36.4 \cdot \text{pH}) \text{ mM}$ .
- d) Estimate the pH of the Adélie penguin blood at a critical body temperature of 40.7 °C taking into account that due to hyperventilation  $p(\text{CO}_2)$  decreases to 1.5 kPa.
- e) Would you expect the described overheating to cause some of the following conditions: **i)** alkalosis; **ii)** acidosis; **iii)** hypocarbia; **iv)** hypercarbia? “Hypo” and “hyper” originate from the Greek words meaning “below” and “above”, respectively.

#### Problem 5 – MECH, SYNTH – Lithiation gone wrong

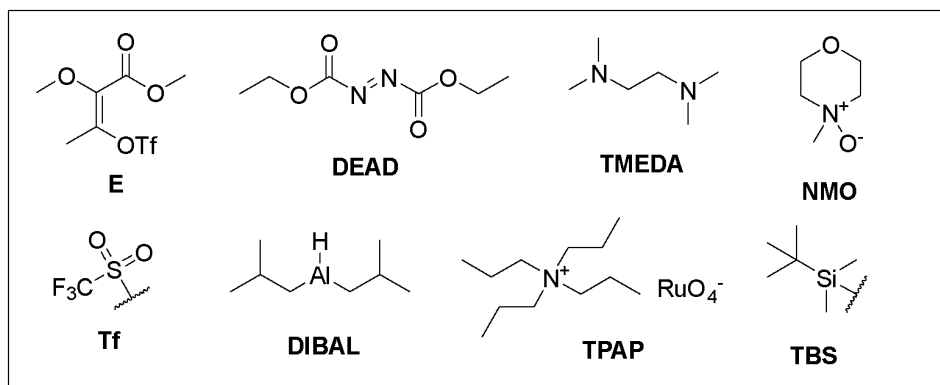
One of the most popular methods for introducing substituents in heterocyclic compounds is lithiation and then subsequential alkylations, acylations, additions etc. The lithiation of oxazole is harder and produces two regioisomers after the addition of benzaldehyde and sequential aqueous workup, where the minor isomer is needed.









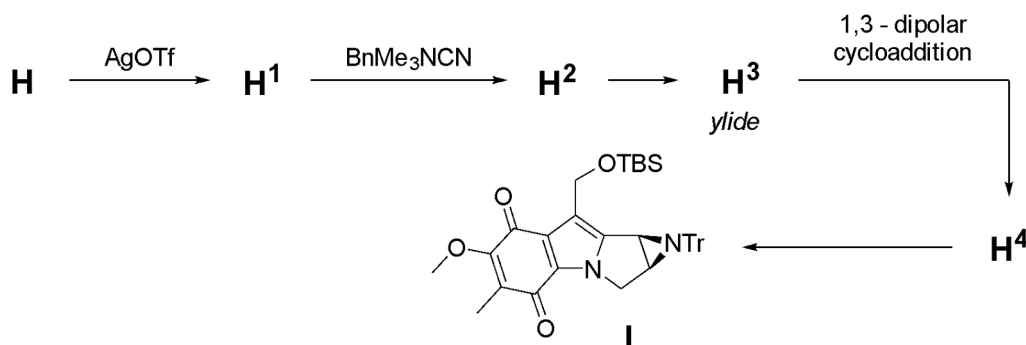


Note:  $\text{Cp}_2\text{ZrCl}_2$ ,  $\text{BuLi}$  are allyl group deprotection conditions.

c) Draw structures **B**<sup>1</sup>, **B**<sup>2</sup>, **C**, **D**, **G**, **H** and indicate the stereochemistry.

d) Draw the mechanism for the transformation **B**<sup>1</sup> → **C**.

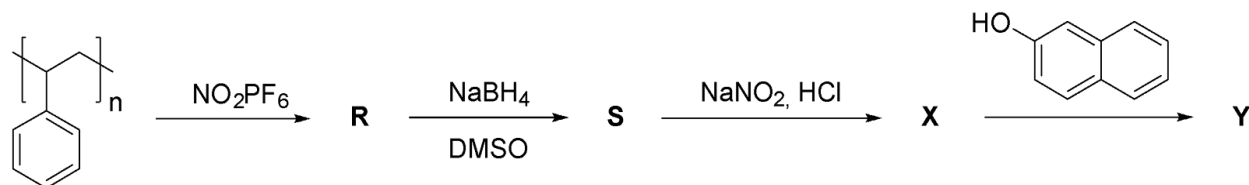
The reaction **H** → **I** is a complex multi-step transformation. First,  $\text{AgOTf}$  is added to **H**, which creates an ionic compound **H**<sup>1</sup> and a yellow salt. To **H**<sup>1</sup>,  $\text{BnMe}_3\text{NCN}$  is added, which is a source of cyanide anions, and additional product **H**<sup>2</sup> is obtained, which reorganizes to azomethine ylide **H**<sup>3</sup>. Ylide **H**<sup>3</sup> undergoes an intramolecular 1,3-dipolar cycloaddition reaction, forming **H**<sup>4</sup>, which subsequently gives **I**.



e) Draw all the missing structures of **H** and **H**<sup>1</sup>–**H**<sup>4</sup>.

### Problem 6 – SPECTRA, SYNTH – Deformed polymers

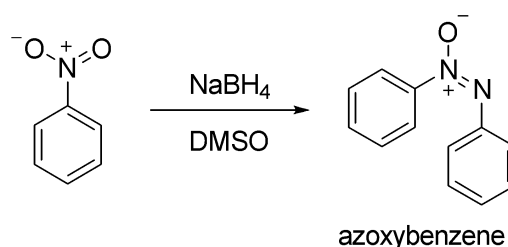
In order to change the color of polystyrene, one may use so-called polymer-analogous reactions that alter only functional groups but leave alkyl chains unaffected. These sorts of reactions may also be useful in the synthesis of polymers that are impossible to make from monomers. Let us look at one of the modifications that could be made with the polymer.



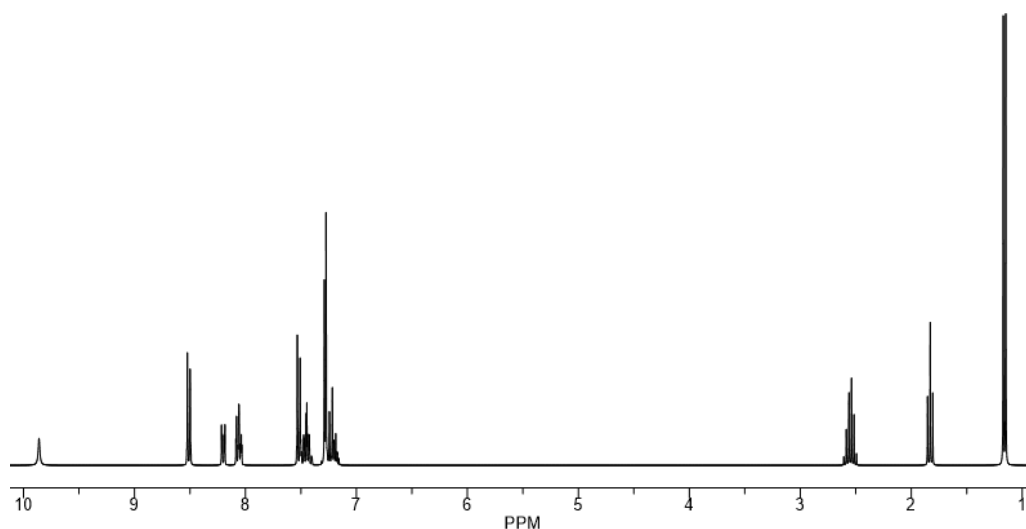
a) Identify product **R** considering that not all benzenes are nitrated.

$\text{NaBH}_4$  is not good for the reduction of aromatic nitro compounds because of the formation of various side products, such as azoxybenzene.

Side products form due to the fact that reduction happens stepwise.

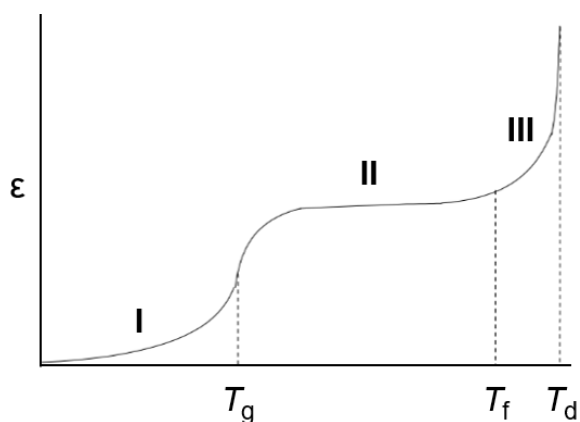


- d) Identify product **S** and four other possible intermediates (**S**<sup>1</sup>, **S**<sup>2</sup>, **S**<sup>3</sup> and **S**<sup>4</sup>), knowing that **S** is fully reduced.
- c) Which two intermediates **S**<sup>1</sup>–**S**<sup>4</sup> lead to the formation of azoxybenzene?
- d) What product is also formed in the reaction of azoxybenzene formation?
- e) Is azoxy-product forming at **i)** low or **ii)** high polystyrene concentrations?
- In the case of a more convenient reduction of **R** (with hydrogen), polymer **P** was obtained. Titration of 1.000 g of **P** required 1.920 cm<sup>3</sup> of 0.2000 M HCl.
- f) Calculate the percentage of nitrated benzene rings, considering that all reactions are quantitative.
- g) Draw the structural formulas of **X** and **Y**, considering the <sup>1</sup>H NMR spectrum of **Y**:



**Y**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.86 ppm (s), 8.51 (d), 8.20–8.05 (m), 7.52–7.43 (m), 7.27–7.19 (m), 2.58–2.53 (m), 1.89–1.83 (m), 1.16 (d).

An important characteristic of the mechanical properties of polymers is the dependence of equilibrium deformation  $\epsilon$  on temperature  $T$ .  $\epsilon$  describes the straightening of polymer chains under calibrated stress. If polymer chains are mobile, then the sample has more developed equilibrium deformations. On the left, you can see the thermomechanical curve for polystyrene. At low temperatures, the polymer has small deformations (**I**). At temperatures higher than  $T_g$ , the polymer becomes highly elastic, in which deformations are determined by the movement of segments of macromolecules (**II**); higher than  $T_f$ , the polymer becomes liquid, and at  $T_d$ , it decomposes.



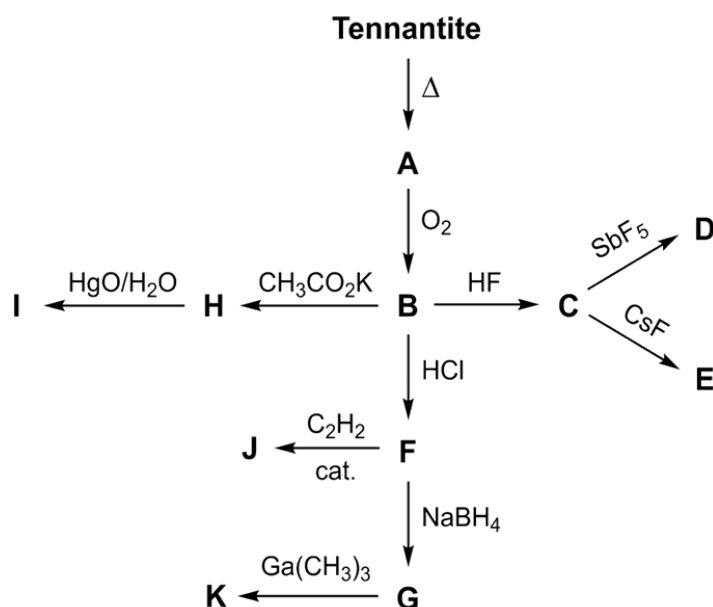
- h) Sketch thermomechanical curves and denote temperature for phase change on the same graph: **i)** For nitrated polystyrene, reduced with excess NaBH<sub>4</sub> at low polymer concentration (nitrated/non-nitrated = 5%); **ii)** For nitrated polystyrene, reduced with excess NaBH<sub>4</sub> at high polymer concentration (nitrated/non-nitrated = 5%); **iii)** For nitrated polystyrene, reduced with excess NaBH<sub>4</sub> at high polymer concentration (nitrated/non-nitrated = 15%).

**Problem 1 – ABC, SPECTRA, STRUCT – Some chemistry of element X**

Element **X** is very important to industry where it is primarily used to manufacture semiconductor electronic devices and as an additive to lead alloys. Not long ago, different compounds of **X** were also used as pesticides and even as green pigments in paint, but these practices had to be abandoned due to the toxicity of **X**. Various minerals of this element are present in the Earth's crust and the majority of them are found in China. One such mineral is tennantite, which consists of three elements – Cu, **X**, and **Y**. Elements **X** and **Y** can be found in groups 15 and 16 of the periodic table, respectively. Crystallographic data for the tennantite unit cell: lattice parameter  $a = 10.186 \text{ \AA}$ , number of formula units per unit cell  $Z = 2$ , density  $\rho = 4.6479 \text{ g cm}^{-3}$ . Assume that the unit cell is cubic. Elemental composition by mass:  $w_{\text{Cu}} = 51.56\%$ ,  $w_{\text{X}} = 20.26\%$ ,  $w_{\text{Y}} = 28.18\%$ .

**a)** Write chemical formulas for **X**, **Y**, and tennantite.

Let us consider the production of **X**-containing compounds starting from this mineral.



The thermal decomposition of tennantite leads to another mineral **A** with a highly symmetric structure consisting of **X** and **Y** only. During the reaction,  $\text{Cu}_2\text{Y}$  and vapors of **Y** are formed as by-products. Further oxidation of **A** leads to oxide **B** ( $w_{\text{X}} = 75.7\%$ ), which is a starting material for the synthesis of almost all **X**-containing compounds. Compound **C** reacts with  $\text{SbF}_5$  in a 1 : 1 ratio to give salt **D** with an **X**-containing cation and Sb-containing anion. **J**, the *anti*-addition product of **F** to acetylene, is an organo-**X** compound known as Lewisite that has been manufactured for use in chemical weapons. In the reaction  $\text{F} \rightarrow \text{G}$ , sodium borohydride acts as a hydride donor. **K** is a semiconductor. **H** ( $w_{\text{C}} = 21.26\%$ ,  $w_{\text{H}} = 5.35\%$ ,  $w_{\text{X}} = 66.31\%$ ,  $w_{\text{O}} = 7.08\%$ ) is known as cacodyl oxide to obtain which potassium acetate has to react with **B**. During the reaction, the evolution of a gas is observed, and a potassium salt is formed as a by-product. Two equivalents of the cacodylic acid **I** are obtained by oxidizing 1 equivalent of **H**.

**b)** Identify the chemical formulas of **A–G** and **K**.

**c)** Draw the structural formulas of compounds **H–J**.

**d)** Write equations of the described reactions.

Similarly to heavy metal poisoning, patients who have been in contact with **J** can be given chelation therapy. A famous example of a covalent drug used specifically in the case of Lewisite poisoning is 2,3-dimercaptopropan-1-ol, also known as British anti-Lewisite (**BAL**).

- e) Draw the structures of **BAL** and a product ( $M = 258.62 \text{ g mol}^{-1}$ ) formed in reaction with **J**.
- f) Using VSEPR theory, determine the geometries of the cation and anion of **D**.

Nuclear magnetic resonance (NMR) spectroscopy is useful beyond organic chemistry and can also be used to study inorganic species. However, this can sometimes be more complicated due to the line-broadening effects of quadrupolar nuclei (i.e. nuclei with a spin quantum number  $I$  greater than  $1/2$ ). Just like for protons ( $I = 1/2$ ) in  $^1\text{H}$  NMR spectra of organic molecules, the number of lines in a multiplet can be predicted for any other NMR-active nucleus using the equation:  $2nI + 1$ , where  $n$  is the number of coupling nuclei. The natural abundances of  $^{19}\text{F}$  ( $I = 1/2$ ) and **X** ( $I = 3/2$ ) are 100%. Two NMR-active nuclei of antimony exist:  $^{121}\text{Sb}$  ( $I = 5/2$ ) and  $^{123}\text{Sb}$  ( $I = 7/2$ ). The natural abundances of  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$  are 57.25% and 42.75%, respectively. In the following questions, assume that any anisotropies resulting from cation-anion interactions average out over the experiment time course and only through-bond couplings are observed.

- g) For solution-state NMR spectra of **D**, predict the number of resonances and their theoretical splitting patterns in the i)  $^{121}\text{Sb}$  NMR spectrum, ii) **X** NMR spectrum, and iii)  $^{19}\text{F}$  NMR spectrum. Include the ratios of peak intensities for any multiplets as predicted by Pascal's triangle.

## Problem 2 – ELECTRO, THERMO – Thermodynamics of electrochemical $\text{CO}_2$ capture

Electrochemical  $\text{CO}_2$  capture is a promising technique for direct air capture, allowing the capture of  $\text{CO}_2$  from the atmosphere and then releasing it in pure, concentrated form for further application.

### Part I. EMCS in the solution

One of the simplest systems is the electrochemically mediated complexation separation (EMCS), where the redox-active adsorbent is activated for  $\text{CO}_2$  capture at the cathode. At the same time, at the anode, it is deactivated and releases  $\text{CO}_2$ . A more specific case is the EMCS in the solution, where the adsorbate is dissolved directly. In the capture process, the first step is an electrochemical reaction:  $\text{A}(\text{aq}) + m\text{e}^- \rightleftharpoons \text{A}^{m-}(\text{aq})$ .

- a) Using the Nernst equation, write an expression for the reduction half-cell potential  $E$ . Furthermore, the reduced  $\text{A}^{m-}$  is capturing  $\text{CO}_2$ :  $\text{A}^{m-}(\text{aq}) + m\text{CO}_2(\text{g}) \rightleftharpoons \text{A}(\text{CO}_2)_m^{m-}(\text{aq})$ .
- b) Write an expression for the equilibrium constant  $K$  for the given reaction, assuming the reference pressure  $P_0$  to be 1.

For convenience, we can define *total adsorbent concentration* –  $A_0$  :  $A_0 = [\text{A}] + [\text{A}^{m-}] + [\text{A}(\text{CO}_2)_m^{m-}]$ ; and *activated fraction*  $x_A$  :  $x_A = ([\text{A}^{m-}] + [\text{A}(\text{CO}_2)_m^{m-}])/A_0$ . We are now equipped to separate expression for half-cell potential  $E$  into terms related to activated fraction and  $\text{CO}_2$  pressure:  $E = E^\circ + RT/mF \cdot f_1(x_A) + RT/mF \cdot f_2(KP_{\text{CO}_2}^m)$ .

- c) Derive expressions for  $f_1(x_A)$  and  $f_2(KP_{\text{CO}_2}^m)$ .

Now if we define  $E_0$  to be the potential when no  $\text{CO}_2$  is present ( $P_{\text{CO}_2} = 0$ ), we can consider the deviation potential  $E^{\text{dev}}$  observed at different  $P_{\text{CO}_2}$  :  $E^{\text{dev}} = E(P_{\text{CO}_2}) - E_0$ .

- d) Write an expression for  $E^{\text{dev}}$  in this case.

## Part II. Thermodynamic analysis

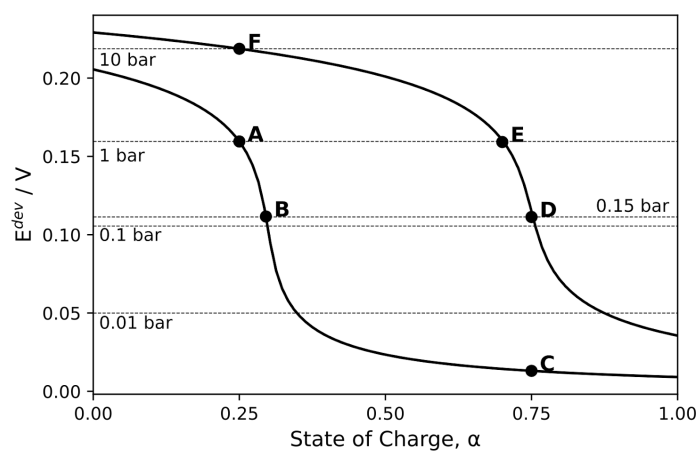
To calculate the work needed to perform the capture-release cycle, we have to consider a diagram analogous to that of the  $p$ - $V$  diagram known from classical thermodynamics. However, in this case, we consider a diagram  $E^{\text{dev}}$  vs.  $\alpha$  (state of charge, which describes the relative amount of reduced species). To construct this diagram, we must first understand the relation between total  $\text{CO}_2$  content ( $x_{\text{CO}_2}$  normalized with respect to A initial concentration) and partial pressure of  $\text{CO}_2$  ( $P_{\text{CO}_2}$ ), which is given by the relation:  $x_{\text{CO}_2} = \alpha \cdot K P_{\text{CO}_2} / (1 + K P_{\text{CO}_2}) + k'_{\text{h,CO}_2} P_{\text{CO}_2}$ . The first term in the sum describes  $\text{CO}_2$  which is bound to the reduced form of A, where  $\alpha$  is the *state of charge*, which in the ECMS case coincides with the activated fraction  $x_A$  defined before. The second term, however, describes the part of  $\text{CO}_2$  that is dissolved in the solution, where  $k'_{\text{h,CO}_2}$  is normalized Henry constant. Assume that  $K = 500$ ,  $P_{\text{CO}_2} = 10^5$  Pa, and  $k'_{\text{h,CO}_2} = 5 \cdot 10^{-7} \text{ Pa}^{-1}$ .

**e)** Calculate the total  $\text{CO}_2$  content  $x_{\text{CO}_2}$  for cases **i)**  $\alpha = 0.25$  and **ii)**  $\alpha = 0.75$ .

During the  $\text{CO}_2$  adsorption and desorption cycle, there are three types of thermodynamic pathways possible:

- Constant state of charge –  $\text{CO}_2$  is adsorbed or released from A with no electrochemical reaction happening.
- Constant total  $\text{CO}_2$  concentration – during the reduction/oxidation process, the  $\text{CO}_2$  in the solution adsorbs to the reduced species/adsorbed  $\text{CO}_2$  is released into the solution, while the total  $\text{CO}_2$  concentration remains constant.
- Constant  $\text{CO}_2$  partial pressure – the external pressure is kept constant; therefore, while the capture/release happens, the total  $\text{CO}_2$  concentration and state of charge change while the partial pressure is constant.

The following plot shows the diagram of  $E^{\text{dev}}$  vs.  $\alpha$ . Solid lines indicate constant total  $\text{CO}_2$  concentration ( $x_{\text{CO}_2}$  is constant), and dashed lines indicate constant  $\text{CO}_2$  partial pressure ( $P_{\text{CO}_2}$  is constant). The labeled points **A–F** show special points during the capture-release cycle, which will be described later. Note that you have already calculated the  $x_{\text{CO}_2}$  for points **A** and **E** in question **e)**.



**f)** Calculate the partial pressure  $P_{\text{CO}_2}$  at point **C**.

The release-capture system can be considered in two extremes. In both cases, the initial state of charge is 0.25, during adsorption, the partial pressure of the feed stream is  $0.15 \cdot 10^5$ , and adsorption continues until the state of charge is 0.75. At the release stage, the  $\text{CO}_2$  is released in a pure stream with a partial pressure of  $10^5$ .

**Four-stage system:**

1. As the absorbent is activated, i.e. the state of charge increases, while the total  $\text{CO}_2$  concentration remains constant.
2. The activated absorbent is in contact with the feed gas until the partial pressure of the feed gas is reached.
3. The absorbent is deactivated as the state of charge decreases. In the end, the free  $\text{CO}_2$  in the solution is at a partial pressure of  $10 \cdot 10^5$  Pa.
4.  $\text{CO}_2$  is removed by desorption as a gas in the flash tank at a pressure of  $10^5$ .

**Two-stage system:**

1. The adsorbent is activated and  $\text{CO}_2$  is captured at the same time.
2. The adsorbent is deactivated and  $\text{CO}_2$  is released at the same time.

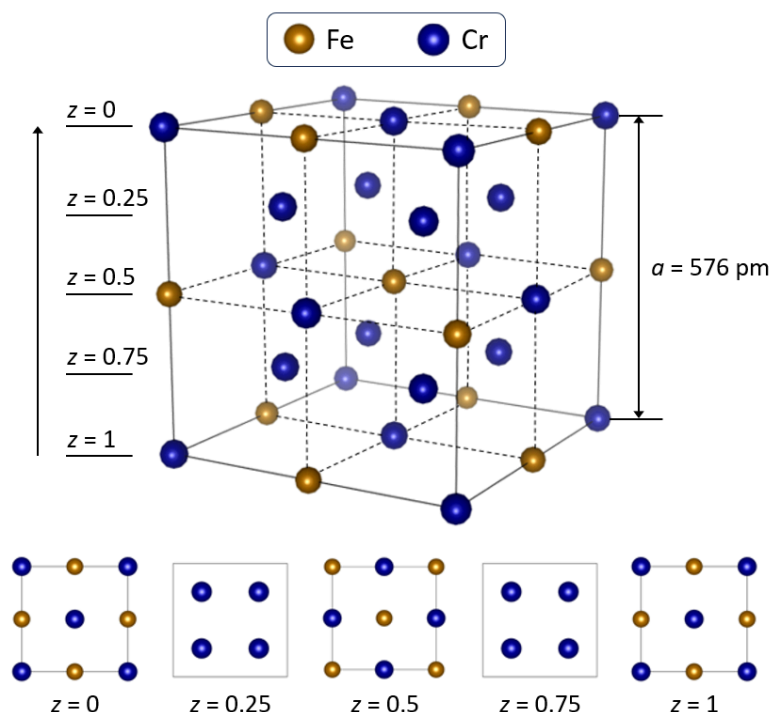
**g)** Assign all the described steps with points shown in the  $E^{\text{dev}}$  vs.  $\alpha$  diagram.

The work required to perform the capture-release cycle is described as the area enclosed by the cycle in the  $E^{\text{dev}}$  vs.  $\alpha$  diagram.

**h)** Which system (four-stage or two-stage) requires less work?

**Problem 3 – CRYSTAL – Solution  $\neq$  liquid**

We are used to the term “solution” in the context of liquid materials. But solid solutions also exist. In solid solutions, different atoms or ions form compounds with different stoichiometric compositions, but the crystal lattice remains the same. Ferrochrome has the empirical formula  $\text{Fe}_x\text{Cr}_{1-x}$ . Both iron and chromium form body-centered cubic (BCC) crystal lattices; therefore, their solid solution has the same lattice if a certain amount of iron atoms are substituted by chromium atoms in the nodes of the crystal lattice. One ferrochrome cubic cell and five planar projections perpendicular to the z-axis are shown in the Figure below.



**a)** Calculate the  $x$  value in the empirical formula  $\text{Fe}_x\text{Cr}_{1-x}$  for the structure in the Figure.

- b)** Calculate the density of ferrochrome if its lattice parameter is 576 picometers.
- c)** The experimental ferrochrome density value differs by 5% compared with your result. Which of the following statements can explain such a difference?

- ☐ Additional Fe or Cr atoms can be intercalated in octahedral or tetrahedral voids.
- ☐ Formation of vacancies in nodes of the crystal lattice.
- ☐ Because of the random distribution of Fe and Cr atoms in the lattice one cubic cell does not ideally correspond to the actual composition of the material.
- ☐ Chemical interactions between Fe and Cr cause a significant change of atomic radii.
- ☐ In solid solutions, lattice parameter values fluctuate significantly.

Ionic solid solutions can be obtained by combining two or more ionic compounds. Substituting cations or anions of different charges in the lattice gives rise to peculiar physical properties of such material. Forsterite is a mineral that has the empirical formula  $\text{Mg}_2\text{SiO}_4$ . Silicon is covalently bound to oxygen atoms, and magnesium ions occupy octahedral holes in the orthorhombic lattice. The reaction between forsterite and lanthanum(III) oxide yields  $\text{La}_x\text{Mg}_y\text{SiO}_4$  solid solution and one more by-product containing no lanthanum.

- d)** Write the chemical formula of the by-product.
- e)** Express index  $y$  as a function of  $x$ .
- f)** When  $\text{La}^{3+}$  ions substitute  $\text{Mg}^{2+}$  ions, a certain concentration of vacancies is formed. Vacancies influence the electrical conductivity of the ionic solid solution. Which electric charge transfer mechanism occurs in  $\text{La}_x\text{Mg}_y\text{SiO}_4$  solid solution?

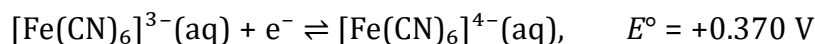
- ☐  $\text{Mg}^{2+}$  migrates to the vacancy, a new vacancy is formed in  $\text{Mg}^{2+}$  node.
- ☐  $\text{La}^{3+}$  migrates to the vacancy, a new vacancy is formed in  $\text{La}^{3+}$  node.
- ☐  $\text{Si}^{4+}$  migrates to the vacancy, a new vacancy is formed in  $\text{Si}^{4+}$  node.
- ☐  $\text{O}^{2-}$  migrates to the vacancy, a new vacancy is formed in  $\text{O}^{2-}$  node.
- ☐  $\text{Mg}^{2+}$  or  $\text{La}^{3+}$  migrates to the vacancy, a new vacancy is formed in  $\text{Mg}^{2+}$  or  $\text{La}^{3+}$  node.
- ☐  $\text{Mg}^{2+}/\text{La}^{3+}/\text{Si}^{4+}$  migrates to the vacancy, a new vacancy is formed in  $\text{Mg}^{2+}/\text{La}^{3+}/\text{Si}^{4+}$  node.
- ☐  $\text{O}^{2-}$  migrates to the vacancy, a new vacancy is formed in  $\text{O}^{2-}$  node.
- ☐ Free electrons migrate from vacancy to vacancy.

- g)** By performing electrical conductivity measurements, it was calculated that the concentration of vacancies in lanthanum-doped forsterite is  $6.2 \cdot 10^{17} \text{ cm}^{-3}$ . The density of the material is  $3.223 \text{ g cm}^{-3}$ . One unit cell contains one silicon and four oxygen atoms. Calculate index  $x$  in the formula  $\text{La}_x\text{Mg}_y\text{SiO}_4$  by assuming that all vacancies are formed because of  $\text{La}^{3+}\text{--Mg}^{2+}$  exchange.

Cations can intercalate in ionic compounds via different mechanisms. For example, ferrous oxide  $\text{FeO}$  can react with lithium oxide  $\text{Li}_2\text{O}$  to yield a solid solution  $\text{Li}_x\text{Fe}_{1-x}\text{O}$ . During the reaction, a fraction of iron atoms oxidize to +3 oxidation state. One of the simplest methods to analyze the composition of such a solid solution is electrochemical  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio determination. We denote the ratio  $r = n(\text{Fe}^{3+})/n(\text{Fe}^{2+})$ ,  $n$  is the molar amount. Reciprocal values of empirical formula index  $x$  and ratio  $r$  are related linearly:  $x^{-1} = a \cdot r^{-1} + b$ , where  $a$  and  $b$  are integer numbers.

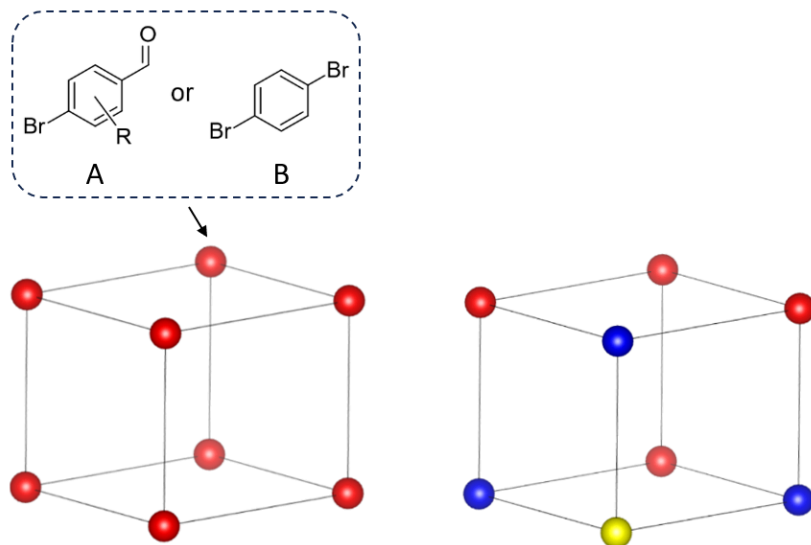
**h)** Calculate values  $a$  and  $b$ .

When  $\text{Li}_x\text{Fe}_{1-x}\text{O}$  is dissolved in a non-oxidizing acid, an excess of sodium cyanide is added to bind all iron atoms to  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  complex ions. Two electrodes are immersed in this solution: a working Pt electrode and a reference  $\text{AgCl} | \text{Ag}, \text{Cl}^-$  electrode, filled with saturated KCl solution. 0.092 V potential difference was measured at the starting moment of the experiment, then an increase of  $[\text{Fe}(\text{CN})_6]^{4-}$  concentration was observed. Redox potentials at 298 K and  $10^5$  Pa are:



**i)** Calculate the ratio  $r$  and  $x$  from electrochemical measurement data.

Organic solid solutions are attractive because of their optical properties. For instance, *p*-bromobenzaldehyde derivatives weakly phosphoresce (emit light) in a crystalline state. However, if the *p*-bromobenzaldehyde derivative (**A**) is co-crystallized with 1,4-dibromobenzene (**B**), a solid phosphorescent solution will form. **B** molecules interrupt interactions between **A** molecules and do not allow for vibrational relaxation of excited **A** molecules. This solid solution has a primitive orthorhombic structure, where nodes can be occupied by either **A** or **B**. In the Figure below, a primitive orthorhombic cell with parameters  $a$ ,  $b$ ,  $c$  and nodal positions marked as red balls is shown; if the yellow molecule is the selected one, blue molecules are in the first coordination shell.



A simple kinetic model can be used to estimate the phosphorescence intensity  $I$  of the material:  $I = \text{CN} \cdot k_{\text{ph}} / [k_{\text{ph}} r_0^2 + k_{\text{vib}} \sum_i (\text{CN}_i^2 r_i^2)]$ , where CN is the coordination number, defining the average count of **A** molecules around selected **A** molecule,  $k_{\text{ph}}$  and  $k_{\text{vib}}$  are phosphorescence and vibrational relaxation rate constants,  $r_0$  is a constant and  $\text{CN}_i$  are average counts of **A** molecules that are at a specific  $r_i$  distance from selected **A** molecule.  $r_0$  and  $r_i$  are in angstroms ( $\text{\AA}$ ). CN,  $\text{CN}_i$ , and  $r_i$  values should be considered only for the first coordination shell.

**j)** Show that for orthorhombic lattice with different unit cell lengths  $a$ ,  $b$ ,  $c$ , phosphorescence intensity can be calculated as  $I = 9 \cdot \text{CN} \cdot k_{\text{ph}} / [9 \cdot k_{\text{ph}} r_0^2 + k_{\text{vib}} \text{CN}^2 (a^2 + b^2 + c^2)]$ .

Solid solution **X** is prepared by co-crystallizing **A** and **B** in ratio  $n(A) : n(B) = 1 : 1$ . Solid solution **Y** is prepared by co-crystallizing **A** and **B** in ratio  $n(A) : n(B) = 2 : 1$ . **X** is 1.25 times more intense compared to **Y**.

**k)** Calculate the diagonal of the orthorhombic unit cell if  $k_{ph}/k_{vib} \approx 10^{-4}$  and  $r_0 = 710 \text{ \AA}$ .

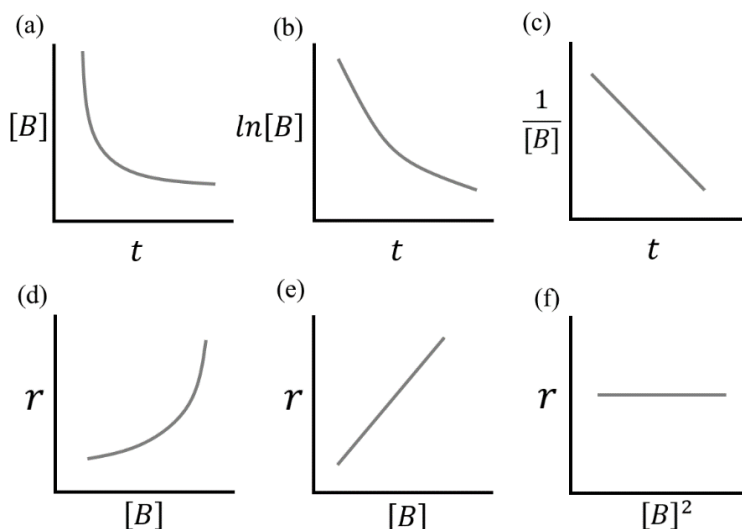
#### Problem 4 – KINETICS – Kinetics ABC

The following reaction proceeds via an unknown mechanism:  $A + 2B \rightarrow AB_2$  (**0**).

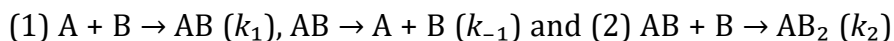
**a)** Choose all appropriate mechanisms that are consistent with the assumption that reaction **0** proceeds in a second-order fashion in relation to  $[B]$ .

- |                                         |                                         |
|-----------------------------------------|-----------------------------------------|
| <b>i)</b> $A + B \rightarrow AB$ slow   | <b>iii)</b> $A + B \rightarrow AB$ fast |
| $AB + B \rightarrow AB_2$ fast          | $AB + B \rightarrow AB_2$ slow          |
| <b>ii)</b> $B + B \rightarrow B_2$ slow | <b>iv)</b> $A + A \rightarrow A_2$ slow |
| $A + B_2 \rightarrow AB_2$ fast         | $B + B \rightarrow B_2$ slow            |
|                                         | $A_2 + B_2 \rightarrow AB_2 + A$ fast   |

**b)** Choose graphs that could depict the relationship between  $[B]$  and both time ( $t$ ) and rate of reaction ( $r$ ). Assume a constant state for  $[A]$ .



In reality, reaction (**0**) proceeds via the following mechanism:



**c)** For each condition listed below, determine whether the rate-limiting step of the mechanism presented above is step (1), step (2) or neither. Assume that  $[A]$  and  $[B]$  are much greater than  $[AB]$  and  $[AB_2]$ .

- i)**  $k_1 \gg k_{-1}$ ;  $k_2 \gg k_1$ , **ii)**  $k_1 \gg k_{-1}$ ;  $k_2 \ll k_1$ , **iii)**  $k_1 \gg k_{-1}$ ;  $k_2 \cong k_1$ , **iv)**  $k_1 \cong k_{-1}$ ;  $k_2 \ll k_1$

Unknown amounts of reagents **A** and **B** were added together to a container under conditions that favor reaction **0**. At time  $t = t_1$ , the concentration of intermediate **AB** has become constant,  $[AB] = [AB]_{\text{const}}$  and the concentration of reagent **A** has reached a certain value,  $[A] = [A]_1$ .

d) Express the ratio  $k_1/k_2$  in terms of  $[A]_1$  and  $[AB]_{\text{const}}$ . Assume that  $k_1, k_2 \gg k_{-1}$ .

At time  $t = t_2$ , and at a different temperature, a certain amount of reagent C was added to the mixture. C interacts with intermediate AB via the following reaction: (3)  $AB + C \rightarrow ABC$  ( $k_3$ ). The experimental rate of production of ABC can be expressed as  $r = ak_{\text{obs}}$ , where  $k_{\text{obs}}$  is the observed rate constant for the production of ABC, and  $a$  is a product of concentration(s) of a certain compound(s).

e) Assuming that under given conditions, steps (1) and (2) proceed much slower than step (3), show that  $k_{\text{obs}}$  is approximately equal to rate constant  $k_1$ .

The temperature of the mixture was increased to a certain value, at which rate constants  $k_2$  and  $k_3$  become equal.

f) Using signs  $>$ ,  $<$  and/or  $\cong$ , denote the relationship between Arrhenius pre-factors ( $A_2$  and  $A_3$ ) and activation energies ( $E_{a2}$  and  $E_{a3}$ ) for reaction  $AB + B \rightarrow AB_2$  and  $AB + C \rightarrow ABC$ . Assume that Arrhenius pre-factors and activation energies of these reactions are independent of temperature.

Certain amounts of B, C, and AB were added to a container under conditions that favor only reactions  $AB + B \rightarrow AB_2$  and  $AB + C \rightarrow ABC$ . Assume that  $[AB]_0$  is greater than  $[B]_0$  and  $[C]_0$ .

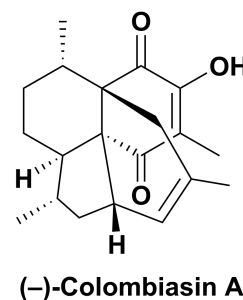
At time  $t = t_3$ , concentrations of compounds  $AB_2$  and ABC became equal.

g) Express the ratio  $[B]_0/[C]_0$  in terms of  $[AB]_0$ ,  $k_2$ ,  $k_3$  and  $t_3$ .

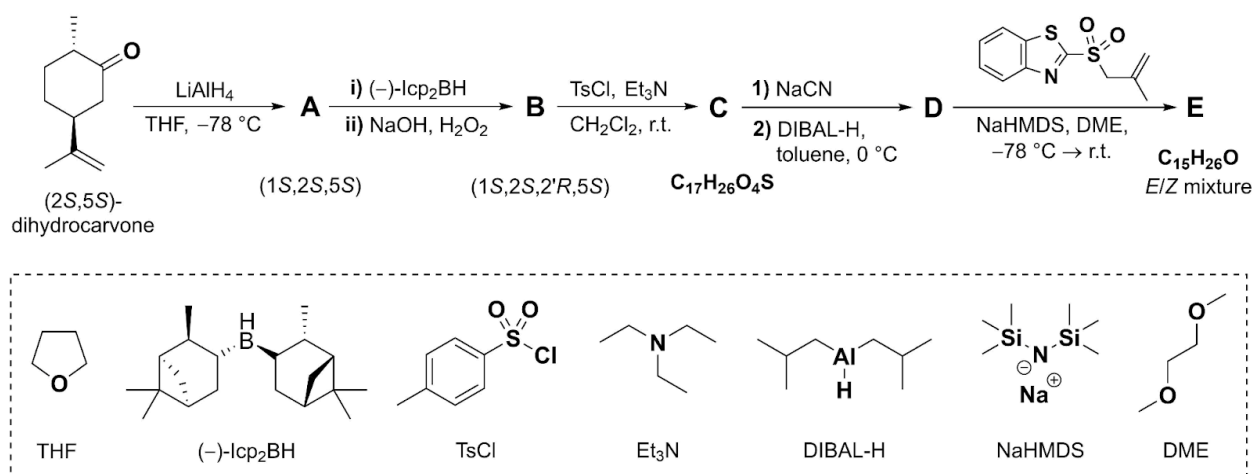
h) Calculate the ratio  $r_2/r_3$  for reactions  $AB + B \rightarrow AB_2$  and  $AB + C \rightarrow ABC$  at time  $t = t_3$  using  $[AB]_0 = 1.20 \cdot 10^{-3}$  M,  $k_2 = 1.40 \cdot 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_3 = 5.60 \cdot 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ , and  $t_3 = 2.50 \cdot 10^3$  s.

### Problem 5 – MECH, SPECTRA, SYNTH – Total synthesis of (–)-Colombiasin A

(–)-Colombiasin A is a marine natural product first isolated from a species of coral found off the coast of San Andres island, Colombia. Following the initial reported total synthesis and structural assignment by K. C. Nicolaou and co-workers in 2001, Colombiasin A and structurally closely related compounds have been prepared via numerous different synthetic approaches. Construction of the carbon skeleton poses, in this case, some rather unique challenges to the synthetic chemist. Most notably, the two adjacent quaternary carbons central to Colombiasin A's carbocycles have been recognized as some of the most challenging aspects of building this natural product.

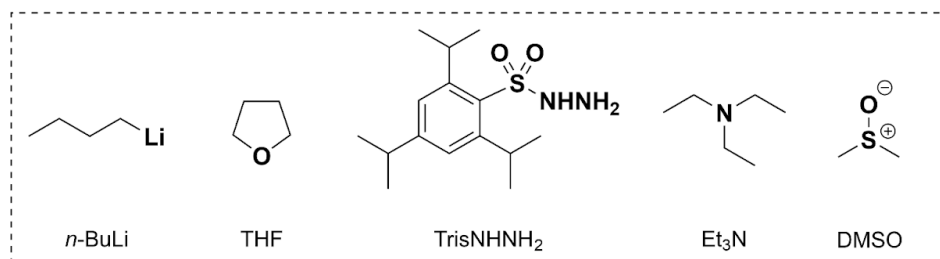
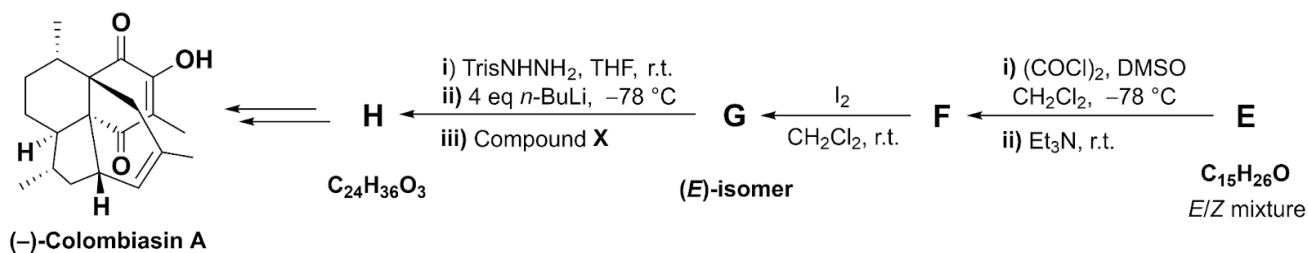


In this task, you will follow the approach of D. C. Harrowven and co-workers, which starts off simple yet concludes in a spectacular fashion. The synthesis begins from enantiomerically pure dihydrocarvone. In the first half of the sequence, a number of simple transformations eventually lead to an *E/Z* mixture of conjugated diene **E**. The stereochemical configurations of compounds **A** and **B** have been provided in the scheme below. In reaction  $C \rightarrow D$ , a partial reduction occurs over steps i)–ii). It is also known that both **C** and **D** contain a secondary hydroxyl group.



- a) Draw the structural formulas of **A–E** with stereochemistry.
- b) From the list below, choose the most suitable solvent for the reaction **C** + NaCN:  
**i)** *n*-hexane, toluene, NH<sub>3</sub> (l), **ii)** 1,2-dichloroethane (DCE), **iii)** dimethylsulfoxide (DMSO),  
**iv)** kefir, **v)** 1 : 1 MeOH/H<sub>2</sub>O with 5% v/v H<sub>2</sub>SO<sub>4</sub>.
- c) Sketch the reaction mechanism for transformation **D** → **E** and clearly indicate the three by-products formed in progress. You may abbreviate parts of molecule(s) irrelevant to this transformation. *Hint: the reaction proceeds via an anionic spirocyclic intermediate. Spiro compounds are molecules containing at least two ring systems and only a single common atom.*
- d) Explain briefly, with reference to relevant <sup>3</sup>J<sub>H-H</sub> coupling constants, how the *E/Z* isomeric ratio of compound **E** could be estimated by <sup>1</sup>H NMR spectroscopy.

In the next part of the synthesis, the *E/Z* mixture of compound **E** is first oxidized into **F** and subsequently, with the aid of catalytic I<sub>2</sub>, converted into stereochemically pure **G**. Compound **G** is then subjected to an interesting sequence of reactions. First, an alkenyl lithium species is formed *in situ* from **G** via a Shapiro reaction, which then undergoes a nucleophilic addition to compound **X**. Following aqueous work-up, the α-hydroxy ketone **H** is obtained. *Hint: the first step in the Shapiro reaction is the formation of a hydrazone via condensation.*



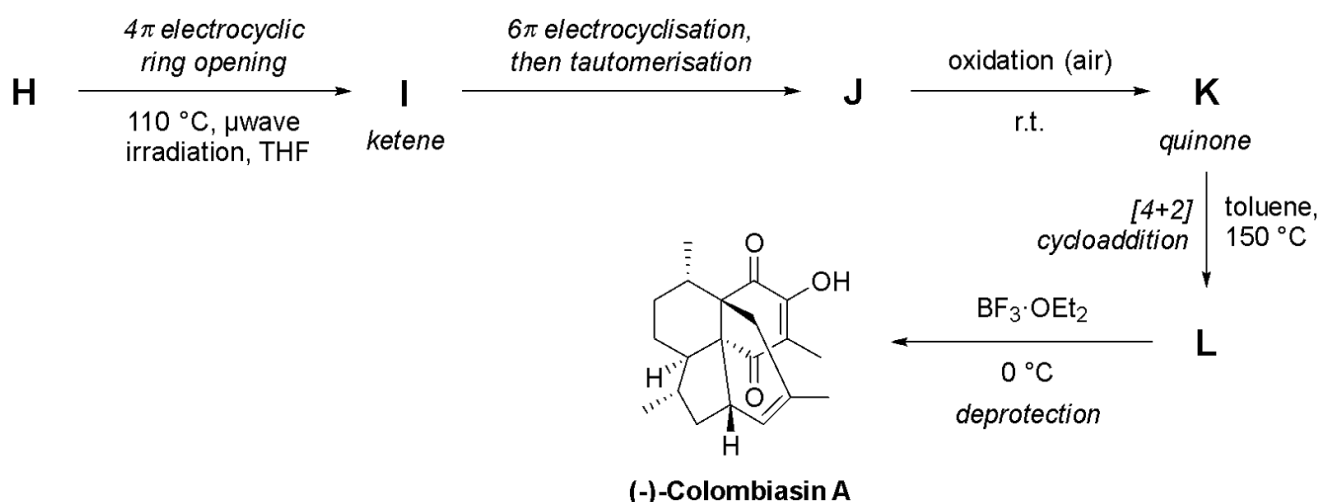
Information about compound **X**:

- Elemental composition: 64.27% C; 7.19% H; 28.54% O.
- $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.19 (s, 1H), 1.62 (s, 3H) ppm. *NB! The listed integrals are relative, not absolute.*
- $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.9, 195.9, 192.8, 182.7, 87.5, 28.7, 9.3 ppm.
- Selected IR spectroscopic data:  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) – 1799, 1748, 1584, 1395.

e) Identify the four low molecular weight by-products formed in step **E**  $\rightarrow$  **F**.

f) Draw the structures of **F**, **G**, **H** and **X** with stereochemistry.

The total synthesis of (–)-Colombiasin A from dihydrocarvone culminates in an impressive cascade, which proceeds from **H** to **K** via intermediates **I** and **J**. In the last steps, a [4+2] cycloaddition furnishes the (–)-Colombiasin A core, and deprotection using  $\text{BF}_3$  etherate reveals the target molecule.



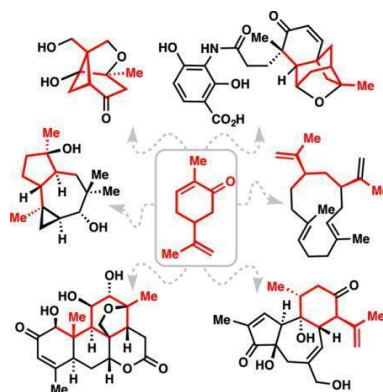
g) Draw the structural formulas of **I–L** with stereochemistry.

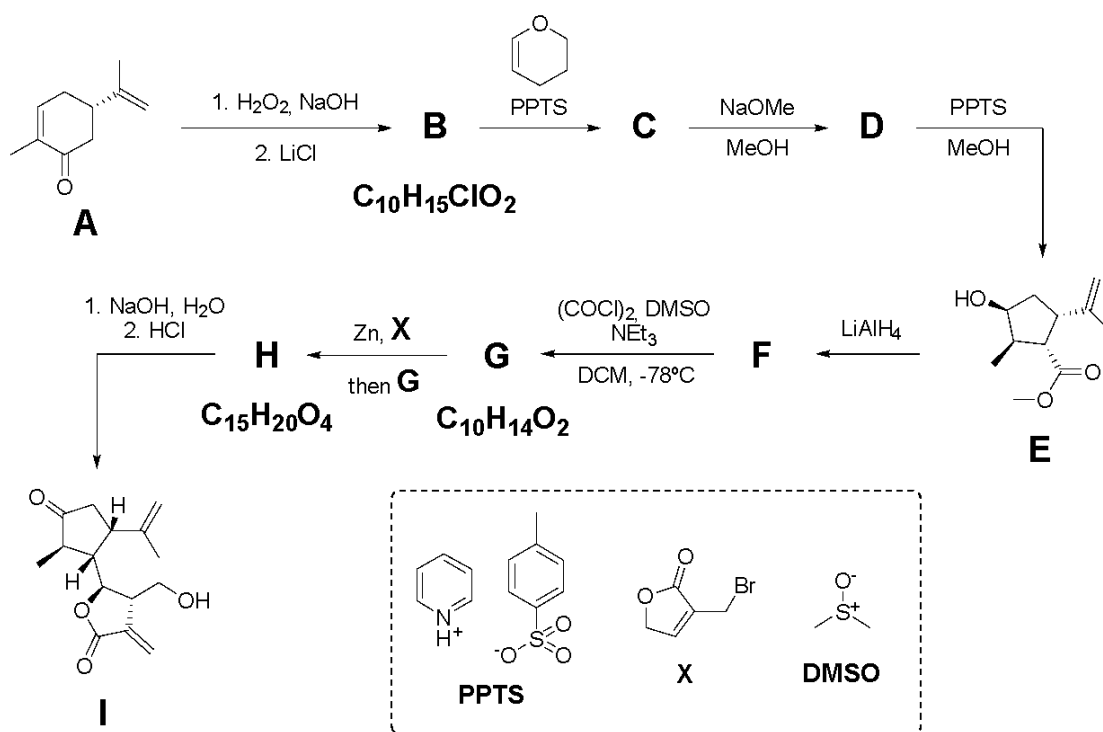
### Problem 6 – SYNTH – Chiral pool

A chiral pool is a collection of enantiopure (thus chiral), cheap compounds that could be used as starting materials in synthesis, creating chiral ligands, reagents, etc. One of the most popular members of the chiral pool is a terpene Carvone. In this problem, we will take a look at the synthesis of sesquiterpene lactone 8-epigosheimin that utilizes (*S*)-carvone (**A**) as a source of chirality.

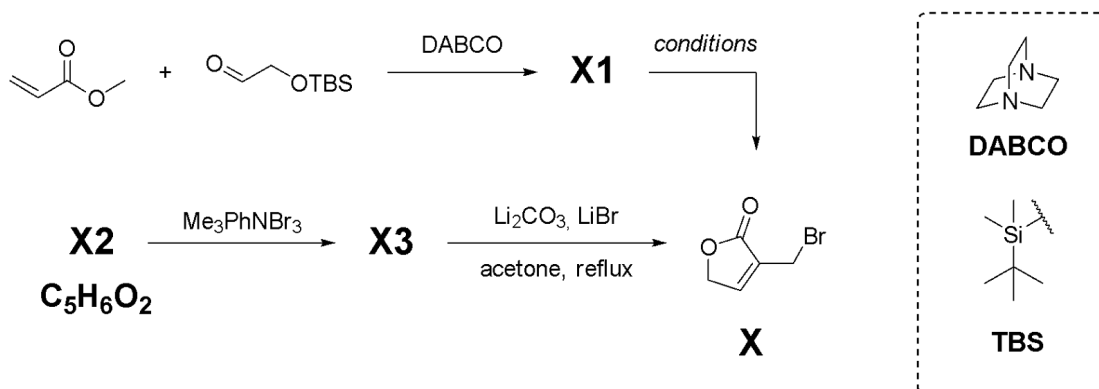
Note that 1) PPTS is a weakly acidic catalyst, and 2) in the reaction **G**  $\rightarrow$  **H**, zinc is required to create organometallic species.

a) Draw the structural formulas of compounds **B–D**, **F–H**.





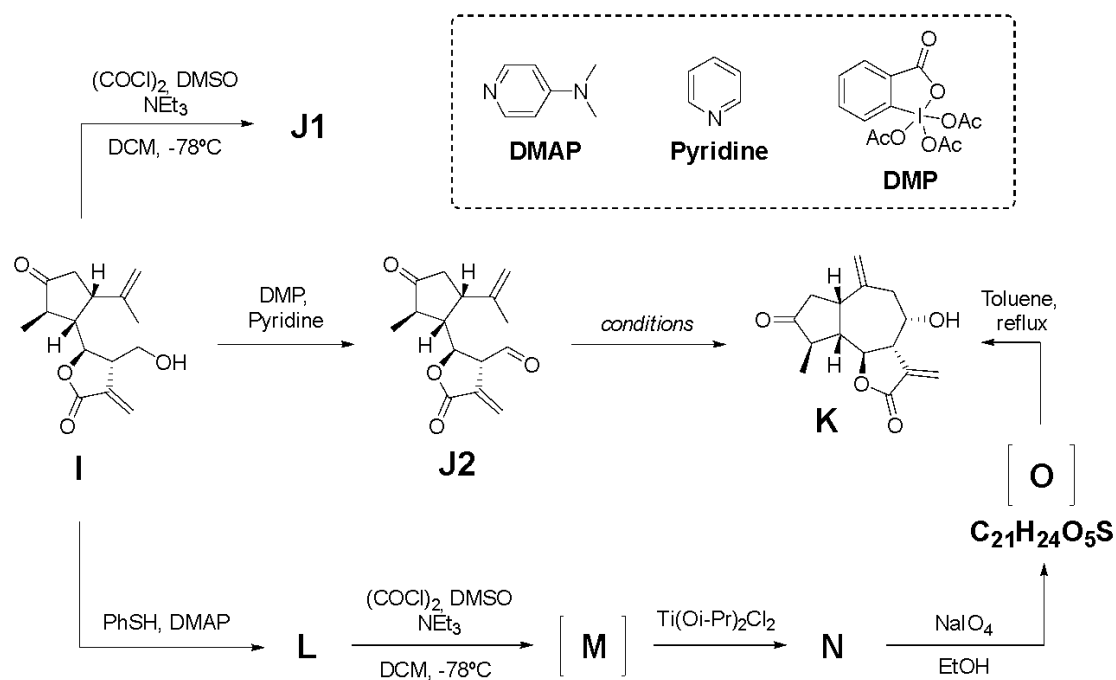
The reagent **X** could be obtained in many ways. In the scheme below, two of the most popular routes are shown.



$^1\text{H}$  NMR spectra of **X2**: 6.08 (t,  $J = 3$  Hz, 1H), 5.63 (t,  $J = 3$  Hz, 1H), 4.30 (t,  $J = 7$  Hz, 2H), 2.97 (m, 2H).

- Draw the structural formulas of compounds **X1**, **X2** and **X3**.
- Propose a mechanism for the synthesis of **X1**.
- Propose a reagent(s) to obtain **X** from **X1** in one step.

The endgame of the synthesis was planned through Swern oxidation followed by cyclization to obtain the 8-epigosheimin (**K**). During the oxidation, an isomer **J1** was formed instead of the necessary **J2**. Although the endgame was quite short, in order to prove the absolute configuration, a different route was taken (through **L**).



Note that Ti(IV) salts are strong oxophilic Lewis acids.

e) Draw the structural formulas of compounds **J1**, **L–O**.

f) Choose the appropriate conditions for the transformation of **J2** to **K**:

- ☐  $n\text{-BuLi}$ , diethylamine
- ☐  $\text{MgSO}_4$ , toluene, reflux
- ☐  $\text{Et}_2\text{O} \cdot \text{BF}_3$
- ☐  $\text{NaOH}$ ,  $\text{H}_2\text{O}_2$
- ☐  $\text{NaClO}_2$ ,  $\text{NaH}_2\text{PO}_4$ ,  $t\text{-BuOH}/\text{H}_2\text{O}$

**Problem 1 – CALC, EQUIL – Determination of protein content by the Kjeldahl method**

The Kjeldahl method was developed in 1883 by the Danish chemist Johan Kjeldahl. It was designed to determine the nitrogen content in organic compounds. Although 140 years have passed, this method is still used to determine protein content in food. The method consists of three stages: digestion, distillation, titration, and calculations.

**Part I. Digestion stage**

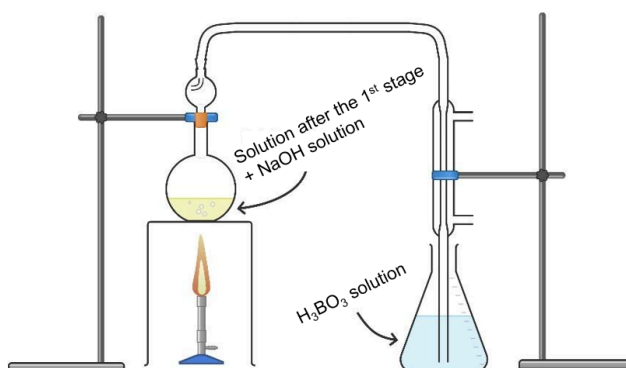
At the digestion stage, nitrogen in a sample is converted into ammonium ions. Digestion is achieved by adding excess concentrated sulfuric acid to the sample and boiling the mixture for a few hours.

- a) Write the equation for the reaction between heated conc.  $\text{H}_2\text{SO}_4$  acid and i) C; ii) S.
- b) Will boiling concentrated sulfuric acid convert nitrate ions into ammonium ions? Circle the correct answer: Yes / No.

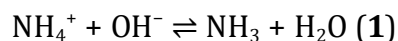
Concentrated sulfuric acid is a 98%  $\text{H}_2\text{SO}_4$  solution. Interestingly, pure, anhydrous sulfuric acid contains not only  $\text{H}_2\text{SO}_4$  molecules. As the equilibrium is reached,  $\text{HSO}_4^-$ ,  $\text{HS}_2\text{O}_7^-$ ,  $\text{H}_2\text{S}_2\text{O}_7$ ,  $\text{H}_3\text{O}^+$ , and  $\text{H}_3\text{SO}_4^+$  species are also found.

- c) 1 kg of 98%  $\text{H}_2\text{SO}_4$  solution contains 8.0 mmol of  $\text{H}_3\text{O}^+$  ions and 4.4 mmol of  $\text{HS}_2\text{O}_7^-$  ions. Determine which ions ( $\text{HSO}_4^-$ ,  $\text{H}_2\text{S}_2\text{O}_7$ ,  $\text{H}_3\text{SO}_4^+$ ) concentration equals to 14.9, 11.3, and 3.6 mmol.
- d) Choose the correct answer.
- ☐ The addition of NaCl and/or  $\text{Na}_2\text{SO}_4$  will increase the boiling point of  $\text{H}_2\text{SO}_4$ . There is little to no difference if NaCl or  $\text{Na}_2\text{SO}_4$  is used.
  - ☐ The addition of NaCl will increase the boiling point of  $\text{H}_2\text{SO}_4$ . For faster digestion, it is significantly better to add NaCl than  $\text{Na}_2\text{SO}_4$ .
  - ☐ The addition of  $\text{Na}_2\text{SO}_4$  will increase the boiling point of  $\text{H}_2\text{SO}_4$ . For faster digestion, it is significantly better to add  $\text{Na}_2\text{SO}_4$  than NaCl.
  - ☐ The addition of NaCl and/or  $\text{Na}_2\text{SO}_4$  will reduce the boiling point of  $\text{H}_2\text{SO}_4$ .
  - ☐ The addition of NaCl and/or  $\text{Na}_2\text{SO}_4$  will reduce the boiling point of  $\text{H}_2\text{SO}_4$ , however, salt will act as a catalyst.

**Part II. Distillation stage**

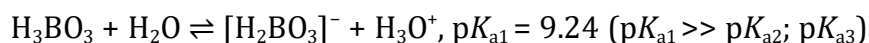


At the distillation stage, the solution from the digestion stage with formed  $(\text{NH}_4)_2\text{SO}_4$  is exposed to an excess NaOH solution. Ammonium ions react with hydroxide ions:

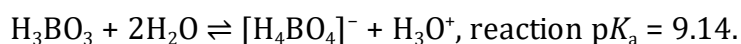


- e) Is the solution with NaOH excess a buffer solution after the first stage? Circle the correct answer: Yes / No.
- f) Calculate the equilibrium constant for **reaction 1**, knowing that the pH of the 0.50 M  $(\text{NH}_4)_2\text{SO}_4$  solution is 4.63.

Generated ammonia reacts with the excess boric acid. Boric acid is very convenient to use since there is no need to know its exact concentration. After the reaction, the solution can be titrated with a strong acid. In solution, boric acid is ionized by water:



However, studies have shown that boric acid solution contains  $[\text{H}_4\text{BO}_4]^-$  ions due to the reaction below:



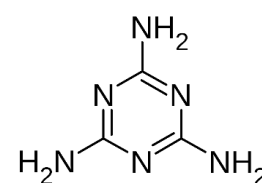
- g) Assume that both reactions occur in the boric acid solution. Calculate the pH of 0.10 M  $\text{H}_3\text{BO}_3$  solution.
- h) Draw  $\text{H}_3\text{O}^+$ ,  $\text{H}_3\text{BO}_3$ , and  $[\text{H}_4\text{BO}_4]^-$  Lewis structures, including formal charges. Determine central atom geometry (by VSEPR).

### Part III. Titration and calculations stage

After titration, the amount of protein in the sample is calculated by multiplying the mass of nitrogen by a specific numeral factor which is 6.38, 5.95, and 6.25 for milk, rice, and meat, respectively.

- i) After testing 10.0 g of rice,  $19.50 \text{ cm}^3$  of the 1.00 M HCl solution was used to titrate the final solution. Calculate how many grams of protein are in the rice sample.

Knowing that the protein content is determined by the Kjeldahl method, the Chinese company "Sanlu Group" added melamine to their production for babies. The aim was to increase the amount of protein to be determined. This led to the deaths of 6 children. After investigation, imprisonments and death penalties were assigned to responsible people.



- j) Assume that all nitrogen atoms in melamine are converted to ammonium ions. Calculate how many grams of protein 1.00 grams of melamine imitates in milk.

## Problem 2 – APPLIED, ELECTRO, STRUCT – Applications of the 7<sup>th</sup> group elements

### Part I. Manganese – coryphaeus among battery materials

Manganese is predominantly used in making alloys and batteries. Interestingly, manganese compounds were used in one of the first rechargeable batteries (Leclanché cell) and are still considered promising materials for future batteries.

Show that novel aqueous Mn-ion battery is comparable to metal-ion and lead-acid batteries from the following considerations. In the case of metal-ion batteries, neglect the electrolytes, respectively; in the case of Pb-acid, account for 35 wt%  $\text{H}_2\text{SO}_4$  aqueous electrolyte.

The theoretical energy density of the Mg-ion battery is  $134 \text{ Wh kg}^{-1}$ ; its pros and cons are X and Y (see below).

a) Calculate the theoretical energy densities of the batteries. Assign letters (A–F) denoting advantages and disadvantages (pros & cons) to the corresponding batteries.

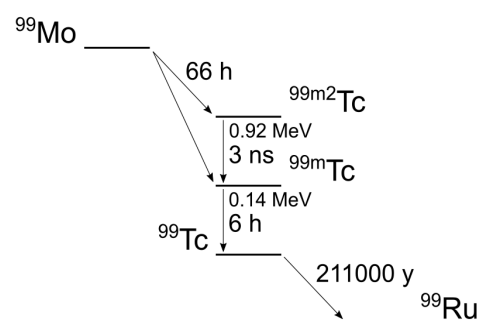
- A. Electrolyte instability and high cost, low abundance of elements used.
- B. Good overall safety, low electrode and electrolyte cost, high abundance of elements used.
- C. Robustness, low electrode and electrolyte cost, and wide temperature range.
- D. High energy density and good overall performance.
- E. Low energy density and environmental issues.
- F. Low voltage and moderate energy density.
- X. Good safety, high energy density, high abundance of Mg.
- Y. Electrolyte instability and high cost, low energy density and voltage.

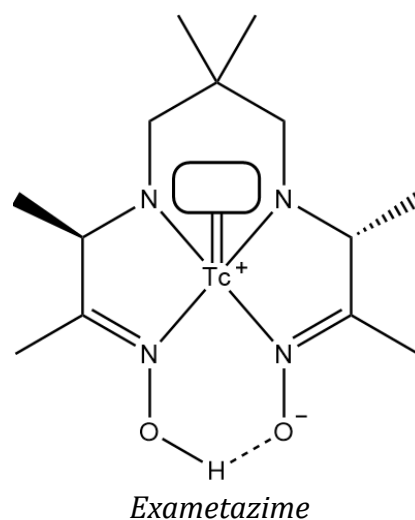
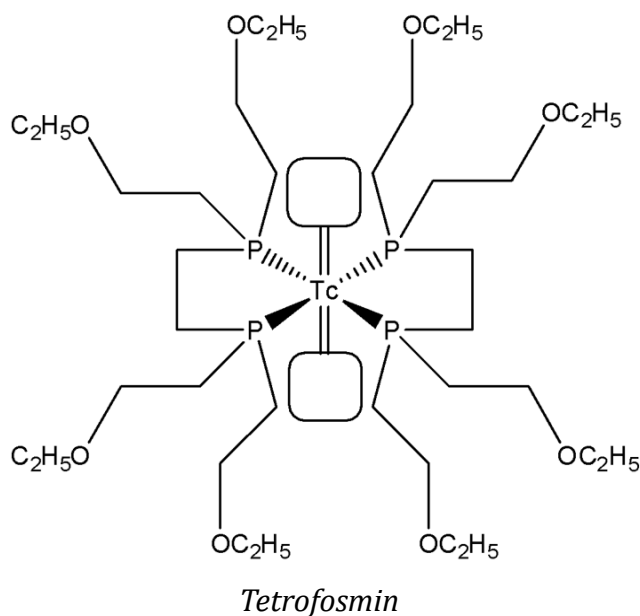
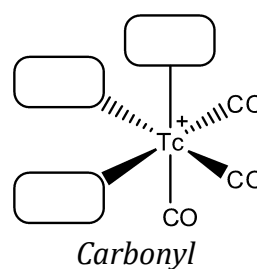
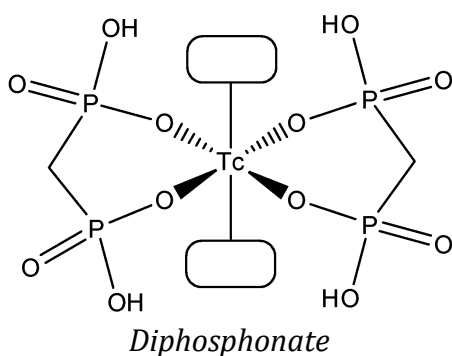
| Battery  | Li-ion                                                                        | Pb-acid                                                                                                     | Mn-ion                                                                                                                                           | Mg-ion                                                                                   |
|----------|-------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Reaction | $\text{LiC}_6 + \text{FePO}_4 \rightleftharpoons \text{LiFePO}_4 + 6\text{C}$ | $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{PbSO}_4 + 2\text{H}_2\text{O}$ | $\text{Mn}_{0.2}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O} + 0.8\text{Mn} \rightleftharpoons \text{MnV}_2\text{O}_5 \cdot \text{H}_2\text{O}$ | $2\text{Mg} + \text{Mo}_6\text{S}_8 \rightleftharpoons \text{Mg}_2\text{Mo}_6\text{S}_8$ |
| EMF [V]  | 3.3                                                                           | 2.1                                                                                                         | 1.3                                                                                                                                              | 1.1                                                                                      |

## Part II. Technetium – the lightest of unstable elements

b) Fill in the blanks in the text and add missing groups (O, OH,  $\text{H}_2\text{O}$ ) to the structures below.

$^{99\text{m}}\text{Tc}$  is one of the most frequently used isotopes in medicinal nuclear imaging. It is prepared in technetium-99m generators as a decay product of  $^{99}\text{Mo}$ , obtained in a nuclear reactor in the fission of uranium-235:  $^{235}\text{U} + ^1_0\text{n} \rightarrow \text{---} + ^{99}\text{Mo} + 3 ^1_0\text{n}$ . Obtained  $^{99}\text{Mo}$  undergoes --- decay into meta-stable isomers  $^{99\text{m}}\text{Tc}$  and  $^{99\text{m}2}\text{Tc}$  according to the generic decay diagram (with half-lives and energy levels).  $^{99\text{m}2}\text{Tc}$  undergoes --- decay of --- keV comparable to the 20–150 keV X-ray range used in conventional radiography. Differently from the latter, detecting the  $^{99\text{m}}\text{Tc}$  radiation from within the patient's body in a gamma camera gives ---dimensional images of tissues and organs. The imaging is taken before half of  $^{99\text{m}}\text{Tc}$  decays, i.e. within --- hours after administrating the radiopharmaceutical.  $^{99\text{m}}\text{Tc}$  radioactivity reduces to 1% of the initial activity in --- hours. The radioactivity of  $^{99}\text{Tc}$  is ---% of the initial activity of  $^{99\text{m}}\text{Tc}$ . In most  $^{99\text{m}}\text{Tc}$  radiopharmaceuticals,  $^{99\text{m}}\text{Tc}$  (eluted from a technetium-99m generator) is turned into a coordination compound with specific biochemical properties: --- attaches to hydroxyapatite and is used to scan bones, --- penetrates lipid membranes and is used to scan the heart, --- crosses the blood-brain barrier and is used to scan the brain.

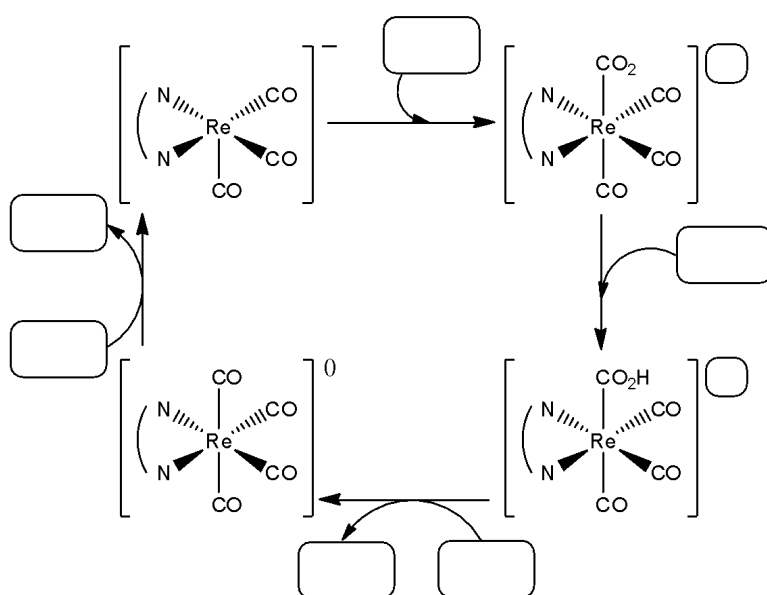




With more targeted imaging and therapy, the future applications of  $^{99\text{m}}\text{Tc}$  for labeling biomolecules will likely be diverse and far-reaching. Technetium \_\_\_\_\_ is an essential precursor to specific coordination compounds: it contains two types of ligands – one is a good leaving group, and the other one is strongly bound to technetium.

### Part III. Rhenium – an element of supermaterials

Rhenium is used in superalloys and catalysts. Rhenium chlorides are precursors for making catalytic coordination compounds. In reaction with chlorine, rhenium forms solid compound **A** ( $w_{\text{Cl}} = 48.77\%$ ), which thermally decomposes into molecular chloride **B** ( $w_{\text{Cl}} = 36.35\%$ ) and chlorine. Chloride **A** is also formed in the decomposition of molecular chloride **C**, which is unstable at room temperature. The coordination number of Re (including Re-Re bonds) is the same in molecules of **A**  $[\text{Cl}_a\text{Re}(\mu\text{-Cl})]_2$ , **B**  $[\text{Cl}_b\text{Re}(\mu\text{-Cl})]_3$ , and **C**, where  $\mu$  denotes that chloride is bridging two rhenium atoms (Re-Cl-Re).



c) Draw the structural formulas of the molecules **A-C**.

Rhenium's possible applications in catalysis include the reduction of CO<sub>2</sub> to CO.

- d) Fill in the blanks (charges, reagents, and products) in the catalytic cycle illustrating the electrochemical reduction mechanism (with H<sup>+</sup> and e<sup>-</sup>).

#### Part IV. Bohrium – probably the most boring element in the Universe

Bohrium belongs to the family of superheavy elements, which could act as powerful nuclear fuel, for example, for future fission-propelled space missions. Isotopes with the "magic" number of protons (114) or neutrons (184) could theoretically have half-lives large enough to be used in nuclear reactors. The half-life of synthesized isotopes (2.9 s for <sup>271</sup>Bh, 8.8 s for <sup>272</sup>Bh, and 54 s for <sup>274</sup>Bh) shows a trend for stabilization ( $\log T_{1/2} = aA^{1/6} + b$ ) towards the "island of stability" near the double-magic <sup>298</sup>Fl.

- e) Estimate the half-life (in years) of the most stable isotope of Bh.  
f) Predict whether bohrium would find any application in the future.

#### Problem 3 – KINETICS – Simple Surface Chemistry

The surface coverage ( $\theta = N_{\text{occ}}/N_{\text{max}}$ , where  $N_{\text{occ}}$  is the number of occupied sites and  $N_{\text{max}}$  is the maximum number of adsorption sites) dependence on pressure is described by adsorption isotherms. The most used adsorption isotherm is the Langmuir adsorption isotherm. To derive the Langmuir isotherm, we consider the following rates for adsorption and desorption:

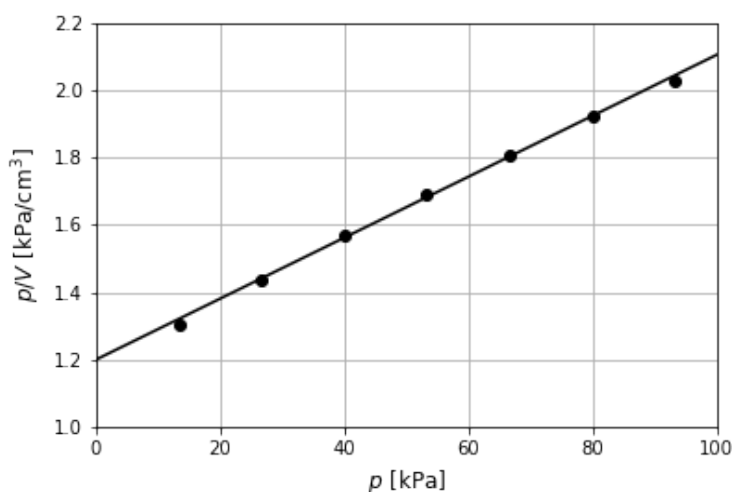
$$r_{\text{ad}} = k_{\text{ad}}p(1 - \theta)^n \text{ and } r_{\text{des}} = k_{\text{des}}\theta^n$$

- a) Assuming steady state, show that the surface coverage  $\theta$  dependence on pressure  $p$  and adsorption/desorption rate constant ratio ( $\alpha = k_{\text{ad}}/k_{\text{des}}$ ) takes the form  $\theta = \frac{(\alpha p)^{1/n}}{1 + (\alpha p)^{1/n}}$ .

Further, we will consider a special case – non-dissociative adsorption – in which the first-order rate law is observed for adsorption and desorption ( $n = 1$ ). In this case, the adsorption isotherm is  $\theta = \frac{\alpha p}{1 + \alpha p}$ . However, in experiments, we cannot measure occupied sites directly.

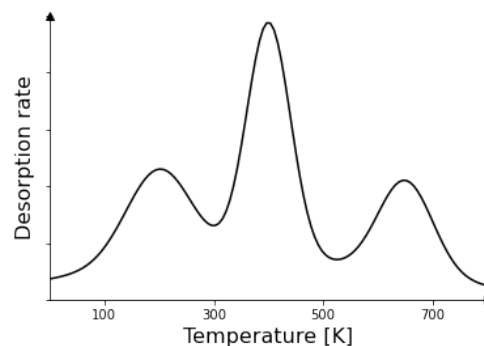
Instead, we consider the volume of gas adsorbed  $V$  versus the volume of gas adsorbed at full coverage  $V_{\text{max}}$ , and therefore, the resulting isotherm in terms of volumes is  $\theta = V/V_{\text{max}} = \frac{\alpha p}{1 + \alpha p}$ . With simple algebra, we can linearize the equation:  $\frac{p}{V} = \frac{1}{\alpha V_{\text{max}}} + \frac{1}{V_{\text{max}}}p$ .

The following plot was obtained in an experiment of CO adsorption on charcoal at 273 K. Solid dots show experimental data points, and the solid line shows the best-fit line.



**b)** Using the plot, determine  $\alpha$  and  $V_{\max}$ .

A useful method to study the kinetics of desorption and determine the desorption activation energy is thermal desorption spectroscopy (TDS). In this method, a sample is heated with a linear change in temperature, and the desorption rate is observed. At the temperature where rapid desorption starts, a peak in rate is observed, but after the sample is heated further, the rate decreases due to a lack of adsorbed species. Schematic representation of spectra observed in the studies is shown in the figure – multiple peaks represent multiple adsorption sites with their respective desorption activation energies.

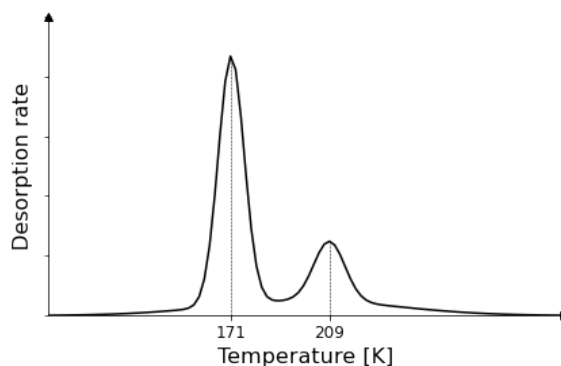


To extract desorption activation energy  $E_d$ , we start from the desorption rate equation and consider that the desorption rate constant follows Arrhenius law, where  $v$  is the pre-exponential factor:  $-d\theta/dt = k_{\text{des}}\theta = v\theta \cdot \exp(-E_d/k_B T)$ . Considering that the temperature change during the experiment is  $T = T_0 + \beta t$ , where  $\beta$  is the heating rate, and integrating the rate law, one obtains the relation, where  $T_{\max}$  is the temperature at the top of the peak:

$$\frac{E_d}{k_B T_{\max}^2} = \frac{v}{\beta} \exp\left(-\frac{E_d}{k_B T_{\max}}\right).$$

**c)** Show that the expression can be rewritten as  $E_d = k_B T_{\max}(\ln(vT_{\max}/\beta) - 3.64)$ , where  $\ln(E_d/k_B T_{\max}) \approx 3.64$ .

A TDS experiment was performed to investigate the desorption of ethylbenzene on pyrolytic graphite. Two peaks in the spectra were observed, one at 171 K and one at 209 K. The peak at 209 K corresponds to desorption from the adsorption layer directly on the surface, while the peak at 171 K corresponds to desorption from further layers.



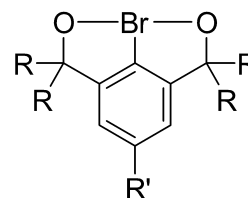
**d)** Calculate the desorption activation energies (expressed in  $\text{kJ mol}^{-1}$ ) for ethylbenzene desorption from pyrolytic graphite. Assume heating rate  $\beta = 1 \text{ K s}^{-1}$ , pre-exponential factor  $v = 10^{12} \text{ s}^{-1}$ . *Hint: the formula from c) provided results for desorption activation energy per atom.*

One of the method's shortcomings is that it relies on a good guess of the pre-exponential factor.

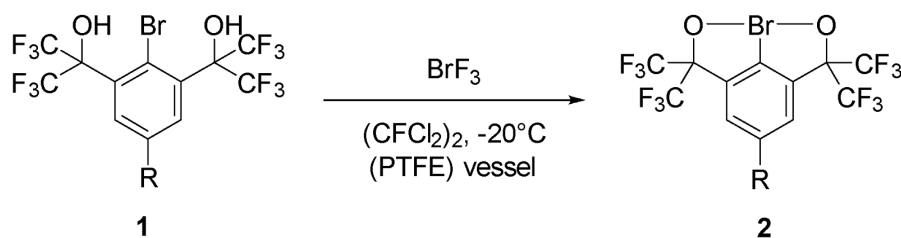
**e)** Calculate the error in the predicted desorption activation energy for desorption at 209 K if the actual pre-exponential factor is 1000 times larger.

#### Problem 4 – INORG, STRUCT – Bromine goes hyper mode

Bromine(III) reagents are fascinating compounds in the realm of organic chemistry due to their unique attributes. While their stability and high oxidizing power can make them difficult to handle, they have also served as tools for innovative synthetic conversions. In this problem, you will explore the synthesis of some hypervalent bromine(III) reagents (such as the one on the right), some of which have been investigated at the Latvian Institute of Organic Synthesis (LIOS).



Traditionally, compounds like **2** have been synthesized from  $\text{BrF}_3$  and an aryl bromide **1** according to the following scheme:



Preparation of  $\text{BrF}_3$  through a chemical process is difficult since it involves using two dangerous compounds,  $\text{Br}_2$  and  $\text{F}_2$ , which require special safety measures. Additionally, the reaction produces two other substances that need to be separated using fractional distillation, which adds to the complexity of the process.

**a)** Write the formulas for the two side products.

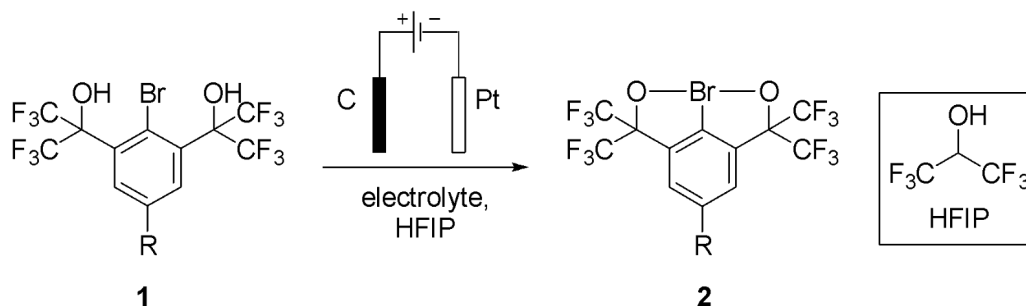
Another complication arises from the fact that  $\text{BrF}_3$  is highly reactive and can react not only with water (forming two acids and oxygen) but also with other common solvents like acetonitrile  $\text{CH}_3\text{CN}$  (yielding a fluoroalkane and two elementary substances) and even glass (yielding two gases and a brown liquid) at room temperature.

**b)** Write equations of the reactions of  $\text{BrF}_3$  with **i)** water; **ii)** acetonitrile; **iii)** silicon dioxide.

**c)** Another complication arises from the ability of  $\text{BrF}_3$  to homolyse into radicals and promote unwanted side reactions. Provide a radical mechanism (should consist of three separate radical reactions) of potential fluorination of a generic alkane  $\text{RCH}_3$ . Note that any other trivalent bromine compounds are highly unlikely to form.

**d)** Provide two more side products that might form from different termination steps.

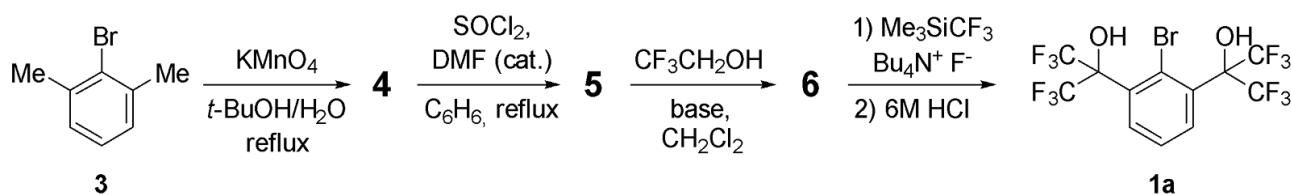
A novel method of synthesizing compound **2** has been developed at LIOS, which involves the oxidation of **1** in an undivided electrochemical cell:



**e)** Write a half-reaction equation for the process occurring on the opposite electrode. Circle the correct answers in the text.

The reaction occurs on the (carbon / platinum) electrode and it is the (anode / cathode). In reaction  $\text{1} \rightarrow \text{2}$ , the bromine's hybridization changes from ( $sp$  /  $sp^2$  /  $sp^3$  /  $sp^3d$  /  $sp^3d^2$  /  $sp^3d^3$ ) to ( $sp$  /  $sp^2$  /  $sp^3$  /  $sp^3d$  /  $sp^3d^2$  /  $sp^3d^3$ ), while its geometry (according to VSEPR) changes from (linear / bent / T-shaped / tetrahedral / octahedral / trigonal bipyramidal) to (linear / bent / T-shaped / tetrahedral / octahedral / trigonal bipyramidal) with the angle  $\text{O}-\text{Br}-\text{C}$  in compound **2** being close to ( $45^\circ$  /  $60^\circ$  /  $75^\circ$  /  $90^\circ$  /  $105^\circ$  /  $120^\circ$ ).

The synthesis of compound **1a** can be implemented starting from compound **3** according to the following scheme:



- f) Draw the structures of the intermediate compounds **4–6**. Note that the molecular formula of compound **6** is  $\text{C}_{12}\text{H}_7\text{BrF}_6\text{O}_4$ .

The electrochemical modification is also appealing due to its non-intrusive nature to monitor the reaction's progress without external interference. By interrupting the chemical reaction and conducting a cyclic voltammetry experiment, we can obtain a cyclic voltammogram that shows the relationship between current and the electric potential. Since the same redox event is being observed, the potential will be the same, enabling the comparison of the peak current  $i_p$  at various time points. The peak current  $i_p$  is proportional to the surface area  $A$ , and the potential sweep rate  $v$ . This relationship is represented by the Randles-Sevcik equation:

$$i_p = 2.69 \cdot 10^5 \cdot z^{\frac{3}{2}} \cdot A \cdot c \cdot D^{\frac{1}{2}} \cdot v^{\frac{1}{2}},$$

where  $z$  – number of electrons transferred;  $A$  – reactive surface area;  $c$  – concentration;  $D$  – diffusion coefficient;  $v$  – potential sweep rate.

- g) Assume that you have acquired peak currents of the oxidation of **1** before starting the experiment ( $i_{p,0}$ ) and at a certain time point  $t$  ( $i_{p,t}$ ). Derive an equation for calculating the reaction yield at a time point  $t$ .

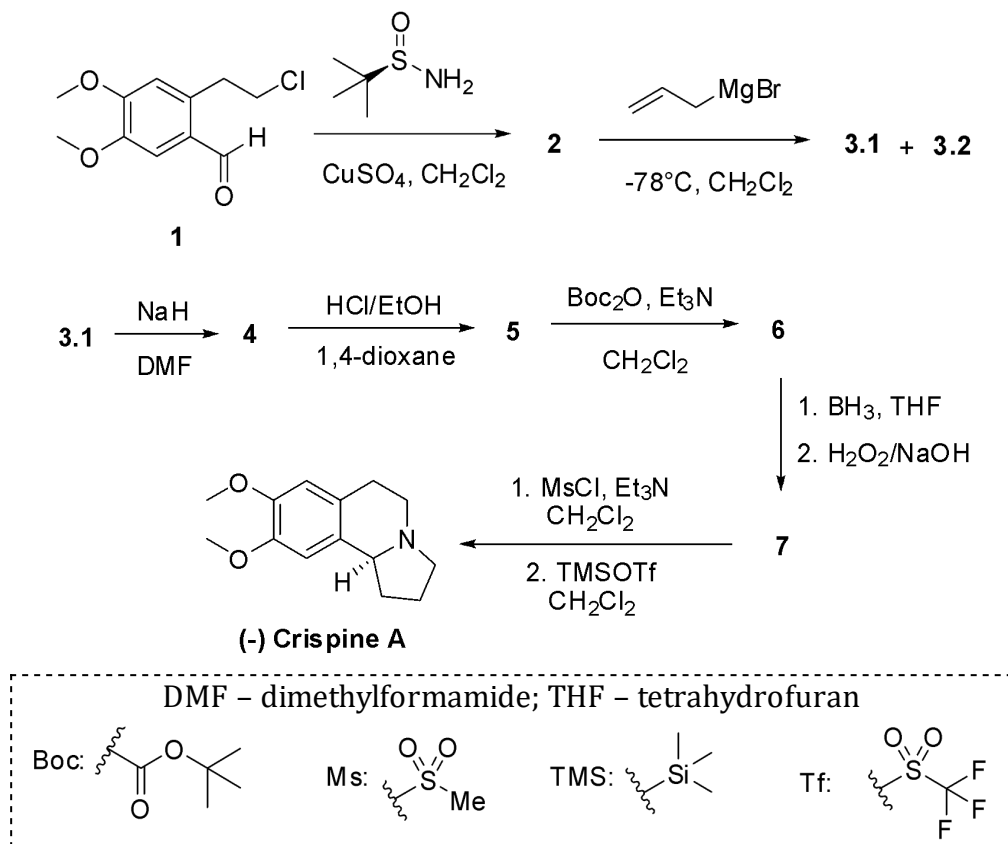
However, the Randles-Sevcik equation only applies to reversible systems. Experimental evidence suggests that the functional group  $R$  could alter whether a particular compound for this reaction will undergo reversible oxidation, therefore rendering this method unsuitable for monitoring reaction progress. An alternative technique involves utilizing quantitative IR spectroscopy to monitor the formation of the  $\text{Br-O}$  bond by measuring its absorption (at a constant  $\lambda$ ) using the Beer-Lambert equation. However, there are a few issues: ambiguity regarding the molar extinction coefficient and path length; background absorption; a synthetic chemist's laziness in calculating intermediate values. These challenges may be overcome by: obtaining absorption values of the product at a known concentration; acquiring background absorption; deriving the equation for them.

- h) Derive the equation for calculating the yield of the reaction  $\mathbf{1} \rightarrow \mathbf{2}$  and calculate it for a reaction with a starting concentration of **1**,  $c_0 = 1 \text{ mM}$ , where the measured absorption at a time point  $t$  is  $A_t = 0.986 \text{ AU}$ , if the background absorption  $A_0 = 0.054 \text{ AU}$  and the measured absorption of a  $0.5 \text{ mM}$  sample of **2** is  $A_x = 0.729 \text{ AU}$ .

### Problem 5 – SYNTH – Synthetic alkaloids

Alkaloids crispine A and crispine B have been isolated as bioactive constituents from the plant *Carduus crispus* L. which has been used for the treatment of cold, stomach ache, and rheumatism. Significant cytotoxic activities of these compounds on some human cancer cells have also been reported. Crispine A and crispine B both are very similar in structure, both belong to a family of pyrroloisoquinoline alkaloids.

Synthesis of enantiopure (–)-crispine A started from aldehyde **1**. Treatment of this aldehyde **1** with (*R*)-*tert*-butanesulfinamide in the presence of anhydrous CuSO<sub>4</sub> afforded compound **2**. Addition of allylmagnesium bromide to compound **2** at –78 °C in CH<sub>2</sub>Cl<sub>2</sub> gave the mixture of two diastereomers, **3.1** (major) and **3.2** (minor). The diastereomeric mixture was easily separated by column chromatography, and only compound **3.1** was used in further synthesis steps. Over the next several steps, compound **3.1** was finally converted to (–)-crispine A, as shown below.

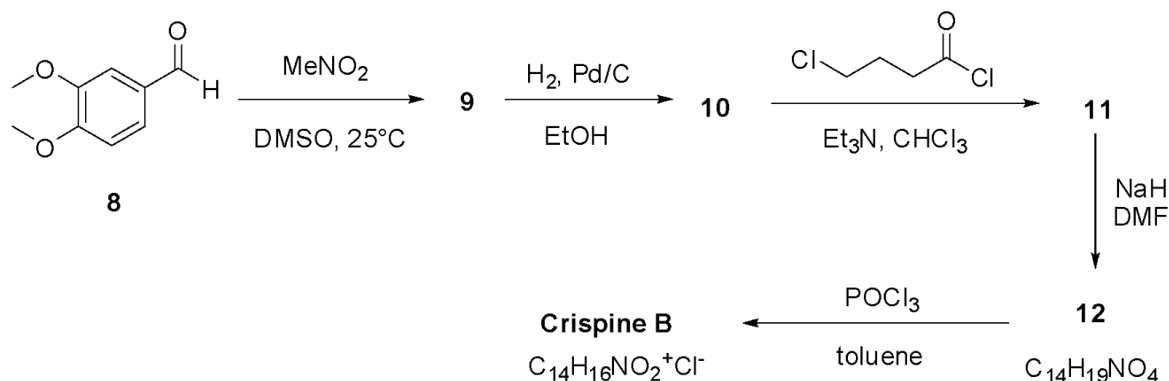


- Provide structures of compounds **2**, **3.1**, and **3.2** with stereochemistry.
- Provide structures of compounds **4**, **5**, **6**, and **7** with stereochemistry.
- Write the absolute configuration of (–)-crispine A stereocenter using *R/S* nomenclature.

If the mixture of compounds **3.1** and **3.2** was used in the synthesis without separation, the liquid mixture of two enantiomers (–)-crispine A and (+)-crispine A would be finally obtained. This mixture has a specific rotation of –72.8°. Enantiopure (–)-crispine A has a specific rotation of –91.0°. The formula for enantiomeric excess calculation:  $ee = (\omega_1 - \omega_2)/(\omega_1 + \omega_2)$ , where  $\omega_1$  is a fraction of one enantiomer in the mixture, and  $\omega_2$  is a fraction of the other enantiomer in the mixture.

- Calculate the enantiomeric excess of this mixture of (–)-crispine A and (+)-crispine A. Calculate the ratio of enantiomers in the mixture and clearly indicate which enantiomer is major and which is minor.
- Choose the correct statement(s).
  - ☐ (–)-enantiomer is always (*R*)-isomer.
  - ☐ (–)-enantiomer is always (*S*)-isomer.
  - ☐ (–)-enantiomer always has a positive specific rotation value.
  - ☐ (–)-enantiomer always has a negative specific rotation value.
  - ☐ There are no correct statements.

Synthesis of crispine B started from aldehyde **8**. After several chemical transformations, crispine B was obtained. It is known that crispine B is a salt whose cation has the molecular formula  $C_{14}H_{16}NO_2^+$ . DMSO – dimethyl sulfoxide.



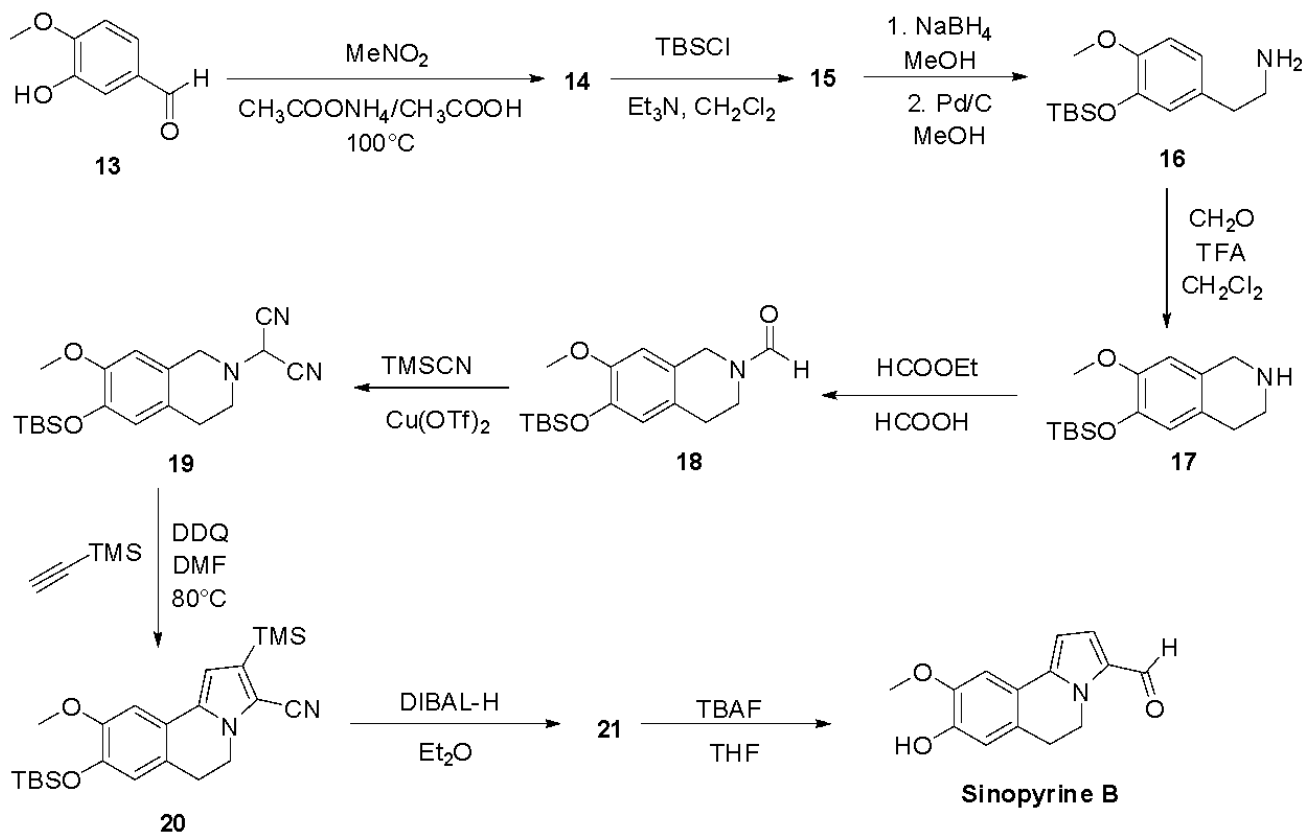
$^1H$  NMR spectral data of compounds **9** and crispine B:

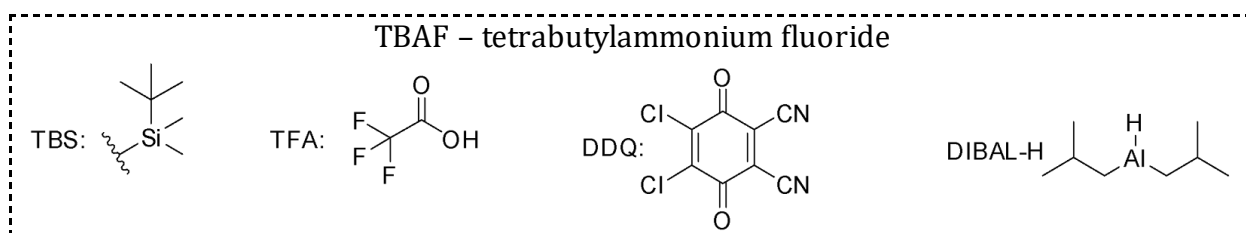
Compound **9**  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 2.74 (br. s., 1H), 3.88 (s, 3H), 3.90 (s, 3H), 4.50 (dd,  $J = 3.2, 13.2$  Hz, 1H), 4.62 (dd,  $J = 9.6, 13.2$  Hz, 1H), 5.42 (dd,  $J = 3.2, 9.6$  Hz, 1H), 6.86-6.94 (m, 3H).

Crispine B  $^1H$  NMR (deuterated MeOH)  $\delta$ : 2.63 (q, 2H), 3.89 (t, 2H), 4.08 (s, 3H), 4.10 (s, 3H), 4.91 (t, 2H), 7.57 (s, 1H), 7.65 (s, 1H), 8.07 (d,  $J = 6.8$  Hz, 1H), 8.36 (d,  $J = 6.8$  Hz, 1H).

f) Provide structures of compounds **9**, **10**, **11**, **12**, and crispine B. Stereochemical information is not required.

Another alkaloid structurally very similar to crispine A and crispine B is sinopyrine B, which is found in the plant *Sinomenium acutum*. It can be synthesized from aldehyde **13**.





Compound **14**  $^1\text{H}$  NMR (deuterated DMSO)  $\delta$ : 3.81 (s, 3H), 6.84 (d,  $J$  = 8.2 Hz, 1H), 7.28 (d,  $J$  = 8.2 Hz, 1H), 7.46 (s, 1H), 8.01 (d,  $J$  = 13.4 Hz, 1H), 8.13 (d,  $J$  = 13.4 Hz, 1H), 10.00 (br. s., 1H).

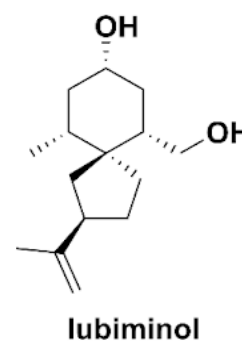
- g)** Draw structural formulas of compounds **14**, **15** and **21**.
- h)** The reaction **16**  $\rightarrow$  **17** is called Pictet-Spengler isoquinoline synthesis reaction. Draw the mechanism of **16**  $\rightarrow$  **17**.
- i)** One of the key steps in this synthesis is a three-stage reaction **19**  $\rightarrow$  **20** when a pyrrole ring is formed. Everything starts with a ylide formation after HCN removal. Then, a cycloaddition reaction occurs. And finally, the pyrrole ring is formed in the presence of DDQ. Draw the correct resonance structure of the most stable intermediate ylide which is formed after HCN removal and which actually participates in further reaction steps. Also, draw the structure of the compound which forms just after the cycloaddition reaction (before DDQ starts acting).
- j)** Write the name for the cycloaddition reaction using two different systems by writing appropriate numbers instead of letters  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ . When written in parentheses (...), numbers indicate the number of atoms in each reactant that participated in the cycloaddition reaction. When written in brackets [...], numbers indicate the number of electrons in each reactant that participated in the cycloaddition reaction.
- k)** What is the role of DDQ in this reaction: **i)** Oxidizing agent; **ii)** Reducing agent; **iii)** Catalyst; **iv)** Inhibitor?

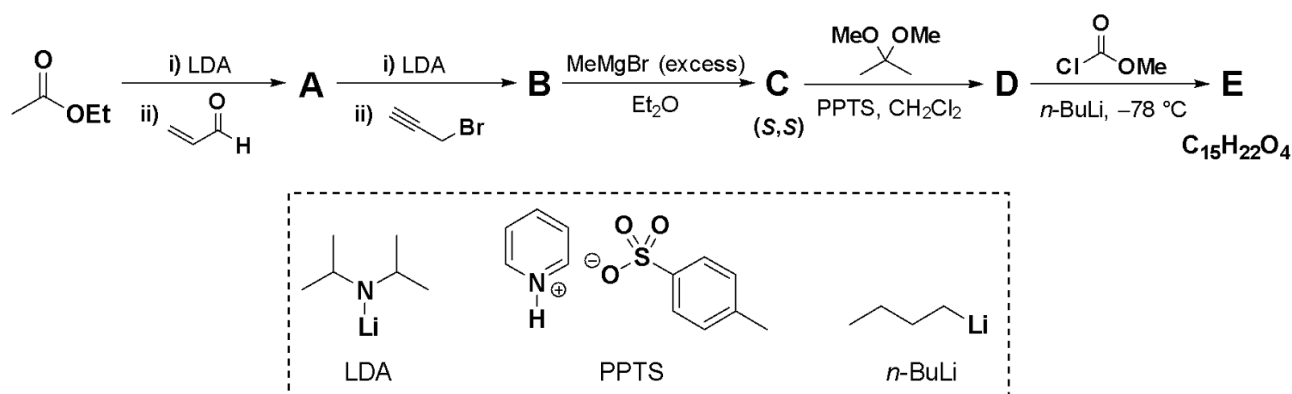
### Problem 6 – MECH, STEREO, SYNTH – Lubiminol

Phytoalexins are naturally occurring antimicrobial compounds produced by plants in response to pathogens at the site of infection. In this way, they serve an essential role in the general defense mechanism against plant diseases. Phytoalexins can counter the invading organism in various ways, including delaying the maturation, disrupting metabolism, breaking down cell walls, or inhibiting its reproduction.

Lubiminol is a spirocyclic phytoalexin first isolated from potato plants infected with a particular species of fungus (*Phytophthora infestans* or *Glomerella cingulata*). Although lubiminol has bioactive properties itself, it is an intermediate in the biosynthetic pathway of more substantial and potent antifungal agents.

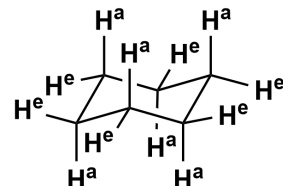
In this task, you will look into the highly stereoselective total synthesis of lubiminol utilizing a radical cascade as the key step in constructing its spirocyclic core. The sequence began with a stereoselective aldol addition of ethyl acetate lithium enolate to acrolein, which gave the  $\beta$ -hydroxy ester **A** predominantly as its *R*-isomer. Propargylation with propargyl bromide in the presence of LDA then yielded **B**, which in turn was converted into **C** with an excess of methyl Grignard. Protection of **C** as an acetone acetal and subsequent treatment with methyl chloroformate gave compound **E**.





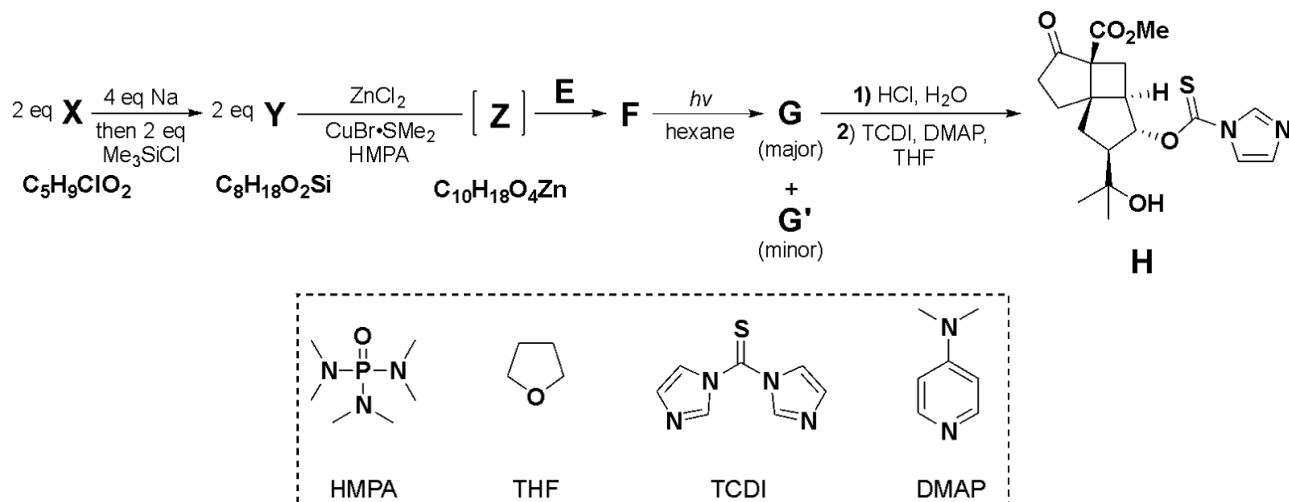
a) Draw the structural formulas of **A–E** with stereochemistry.

The stereoselectivity of the formation of **A** derives from the energetic differences in the two possible transition states and the outcome can be rationalized by the Zimmerman-Traxler model. By this rationale, the addition of the lithium enolate proceeds via a cyclic six-membered chair-like transition state, resembling of the chair-conformation of cyclohexane (see the figure). The stereochemical outcome is ultimately determined by the spatial arrangement of the electrophile in the transition state. The lowest energy transition state is such where the electrophile's bulkiest substituent is positioned equatorially, and the smallest substituent is positioned axially. In the figure, axial protons of  $\text{C}_6\text{H}_{12}$  are denoted as  $\text{H}^a$ , and equatorial protons as  $\text{H}^e$ .



b) Account for the stereochemistry of **A** by applying the Zimmerman-Traxler model. Denote bonds which are being formed or broken with a dashed line (---).

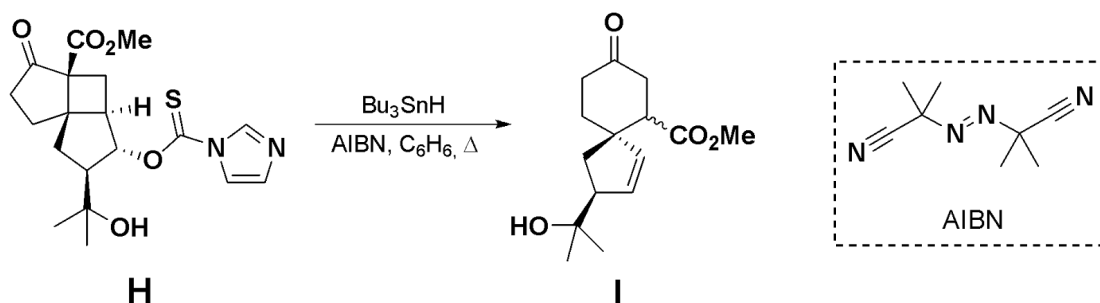
Next, compound **E** was converted into enone **F** via a formal [3+2] cycloaddition. For this purpose, a zinc homoenolate **Z** was generated in situ from 2 equivalents of **Y** and 1 equivalent of  $\text{ZnCl}_2$ . Note that 1 equivalent of **Z** can react with up to 2 equivalents of **E**. Compound **Y** can be formed by treating **X** with sodium and trapping the resulting alkoxide with trimethylsilyl chloride. It is known that **Y** is cyclic, whereas **X** and **Z** are not. Irradiation of **F** with UV light yielded **G** and **G'** as the major and minor products, respectively. Upon deprotection and carbamothioate formation, compound **H** was obtained.



c) Draw the structures of **X**, **Y**, **Z**, **F**, **G** and **G'**, taking stereochemistry into account.

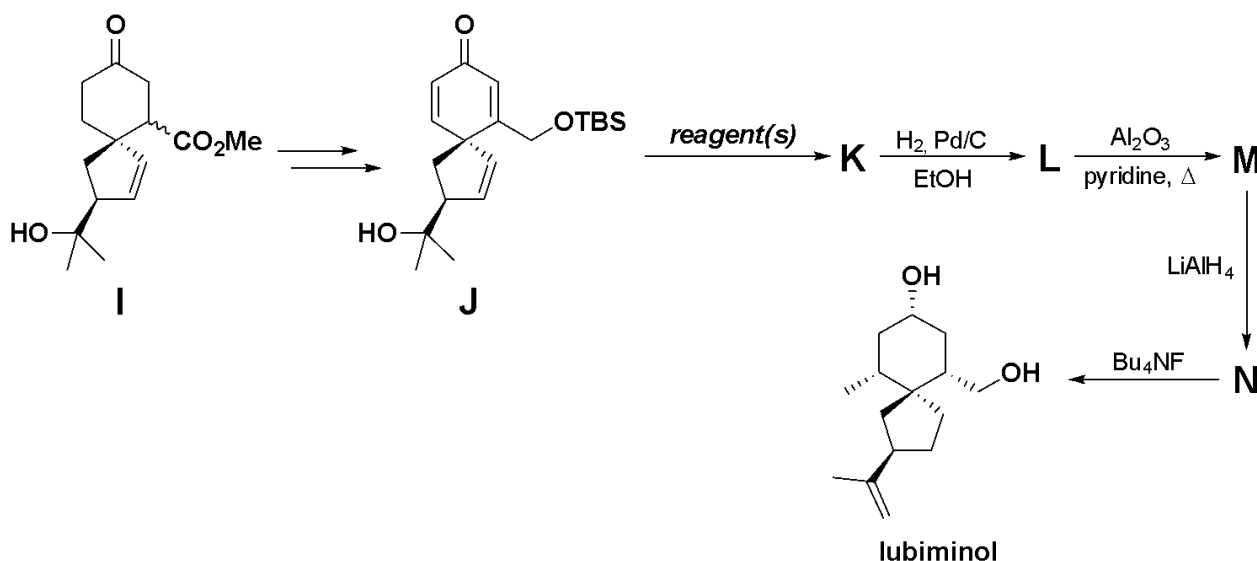
- d) Circle the correct classification for the pericyclic reaction **F** → **G**:  
 electrocyclization / cycloaddition / sigmatropic rearrangement / cycloreversion /  
 cheletropic reaction / ene reaction / the correct answer is not listed
- e) Circle the correct answer. Based on Woodward-Hoffman rules, reaction **F** → **G** is:  
 conrotatory / disrotatory / neither conrotatory nor disrotatory

Compound **H** paved the way to the key step: a radical cascade that gave access to spirocycle **I**. The first step of the cascade is a well-known name reaction.



- f) The first step of the radical cascade is called a: **i)** Barton–McCombie reaction; **ii)** Mitsunobu reaction; **iii)** Wolff–Kishner reduction; **iv)** Corey–Fuchs reaction.
- g) Sketch the mechanism of the reaction **H** → **I** using curly fish-hook arrows to indicate the flow of electrons. Clearly indicate any by-products that are formed in the process.

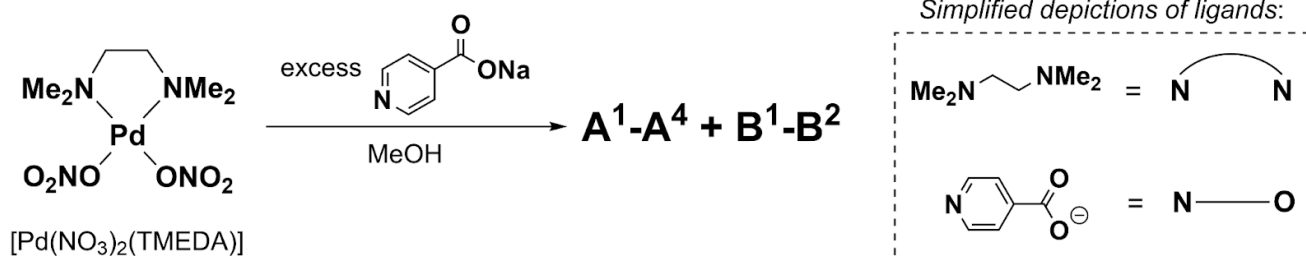
From compound **I**, precursor **J** was prepared over 7 steps. Subjecting **J** to *conditions* gave compound **K** stereoselectively. That was hydrogenated to give compound **L**, where all carbon-carbon bonds are saturated. From there, only two trivial steps remained to complete the synthesis.



- h) Choose the appropriate reagent(s) for converting **J** into **K**: **i)** *i*-Pr<sub>2</sub>NLi, MeI, **ii)** MeMgBr, **iii)** (Me<sub>3</sub>O)BF<sub>4</sub>, **iv)** Me<sub>2</sub>CuLi, **v)** Me<sub>3</sub>Si, NaH.
- i) Draw the structural formulas of **K–N** with stereochemistry.

**Problem 1 – EQUIL, STRUCT, THERMO – Polygonal chemistry**

The palladium complex  $[\text{Pd}(\text{NO}_3)_2(\text{TMEDA})]$  reacts with sodium isonicotinate (simplified as  $\text{NaL}$ ) in a 1 : 1 ratio to yield a mixture of multinuclear complexes **A** and **B**, which resemble the simplest equilateral polygons by structure. The empirical formula of both complexes is  $[\text{PdL}(\text{TMEDA})]\text{NO}_3$ , where **A** can exist as four different isomers ( $\text{A}^1\text{--A}^4$ ) and **B** as two isomers ( $\text{B}^1\text{--B}^2$ ).



- Write the systematic name for the complex  $[\text{Pd}(\text{NO}_3)_2(\text{TMEDA})]$ .
- Sketch the structures of inner coordination spheres of complexes  $\text{A}^1\text{--A}^4$  and  $\text{B}^1\text{--B}^2$  using the provided structural simplifications to represent TMEDA and the isonicotinate anion ( $\text{L}^-$ ). Ignore overall charges and counterions in your structures.

Complexes **A** and **B** can interconvert in solution. Their chemical equilibrium is described by the equation  $a\text{A} \rightleftharpoons b\text{B}$ , where  $a$  and  $b$  are integer coefficients. The forward equilibrium constant has a value  $K_1 = 21.5$  at  $t_1 = 40.0\text{ }^\circ\text{C}$  and  $K_2 = 32.1$  at  $t_2 = 60.0\text{ }^\circ\text{C}$ . For the sake of simplicity, assume all isomers of **A** have the same Gibbs free energy of formation and all isomers of **B** also have the same Gibbs free energy of formation.

- Determine the smallest possible integer values for coefficients  $a$  and  $b$ .
- Calculate the value of the forward equilibrium constant  $K_3$  at  $t_3 = 50\text{ }^\circ\text{C}$ .
- Approximate the ratio  $[\text{B}] : [\text{A}]$  in solution at  $t_3 = 50\text{ }^\circ\text{C}$  if the analytical concentration of palladium in solution is  $c_0 = 1.154\text{ mM}$ . Assume that in solution,  $\text{Pd}^{2+}$  exists only as part of complexes **A** and **B**.

**Problem 2 – ABC, EQUIL – Unknown amino acid**

0.3425 g of unknown amino acid **X** sample was treated with hot concentrated sulfuric acid, which converts organically bound nitrogen to ammonium salt. Then, an excess of concentrated sodium hydroxide solution was added to the previously obtained solution containing ammonium ions. Generated ammonia was distilled into  $40.00\text{ cm}^3$  of  $0.1350\text{ M}$  hydrochloric acid. Finally, the excess of hydrochloric acid was titrated with  $16.83\text{ cm}^3$  of  $0.1500\text{ M}$  sodium hydroxide solution. In the following calculations, assume that all ammonia produced reacts with hydrochloric acid.

- Calculate the mass percentage (%) of nitrogen in the sample.
- Calculate the pH value of the hydrochloric acid solution after the titration when  $16.83\text{ cm}^3$  of  $0.1500\text{ M}$  sodium hydroxide solution has been added.  $\text{p}K_a(\text{NH}_4^+) = 9.25$ .

In nature, **X** occurs in its *L*-isomer form, which has two adjacent stereocenters. The dissociation constants of **X** are  $K_{a1} = 8.13 \cdot 10^{-3}$  and  $K_{a2} = 7.94 \cdot 10^{-10}$  ( $25\text{ }^\circ\text{C}$ ).

- Determine the condensed structural formula of **X**.

- d) Draw all the possible stereochemical structures for **X** using wedge-dash notation. Indicate the absolute configurations (*R/S*) of the stereocenters on all the structures.
- e) Draw the stereochemical structures of **X** *L*-isomer for the major ionic forms in aqueous solution at (i) pH 1.50, (ii) pH 6.00, and (iii) pH 11.00.
- f) Calculate the pH value of the aqueous **X** solution at its isoelectric point, where the overall charge of the ionic amino acid species is zero.

### Problem 3 – KINETICS – Reverse engineering

A teacher is making a standard kinetics task for an exam, starting from desired answers that are easy to grade – 30 s and 60 kJ mol<sup>-1</sup>. Assist him in making the task! Consider a first-order kinetic reaction  $A \rightarrow B$  at  $T_1 = 300$  K. The initial concentration  $[A]_0$  is 1 M, and the concentration  $[A]_t$  after time  $t$  is 0.05 M.

- a) Calculate the reaction rate constant  $k$  value corresponding to  $t = 30$  s.
- b) Calculate the activation energy  $E_a$  value corresponding to  $t = 3$  s at  $T_2 = 2024$  K.

The calculated  $E_a$  value turns out to be too small. Which parameters (if changed individually) can the teacher adjust to make up a more reasonable activation energy?

- c) Choose parameters that affect activation energy  $E_a$ :  $T_1$ ,  $[A]_0$ ,  $[A]_t$ ,  $t$ .
- d) Recalculate the values of the selected parameters to give  $E_a = 60$  kJ mol<sup>-1</sup>.

The teacher continued reverse engineering by designing a four-step mechanism that gives the desired reaction law ( $-d[A]/dt = 2k_1k_2[A]/(k_{-1}+2k_2)$ ) assuming a steady state for  $A'$  and  $B'$ :

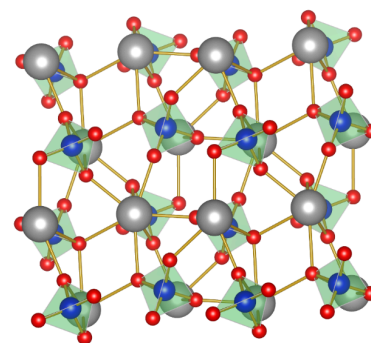


- e) Write the equations for the missing elementary steps. Show that your mechanism corresponds to the given reaction law.

### Problem 4 – CRYSTAL, RADIO – Have you heard about cerium?

#### Part I. Minerals

Monazite (Ce,La,Nd,Th)PO<sub>4</sub> and Bastnäsite (Ce,La)CO<sub>3</sub>F are the most common natural sources for cerium and other lanthanides such as lanthanum or neodymium. The monazite structure is made up of the arrangement of separate PO<sub>4</sub> tetrahedra, which are somewhat distorted but joined to one another by Ce (or other lanthanide) atoms. Monazite has a primitive monoclinic lattice system with  $\alpha = \gamma = 90^\circ$  and  $\beta = 103.63^\circ$ . The structure of this mineral is shown (colors of atoms: Ce – gray, P – blue, O – red).



- a) How many atoms are in the unit cell of monazite-(Ce)?
- b) Presence of which element makes the natural monazite radioactive: i) La, ii) Nd, iii) Th?

Part of the Ce atoms were artificially substituted by U atoms in the pure CePO<sub>4</sub> monazite crystal of 15.23 g. The mass of the resulting mineral was 19.76 g.

- c) Calculate the fraction of Ce atoms that were replaced.

U–Pb dating is one of the oldest and most refined of the radiometric dating schemes. The method relies on two separate decay chains, the uranium series from <sup>238</sup>U to <sup>206</sup>Pb, with

a half-life of 4.47 billion years, and the actinium series from  $^{235}\text{U}$  to  $^{207}\text{Pb}$ , with a half-life of 710 million years. Since the exact rate at which uranium decays into lead is known, the current ratio of lead to uranium in a sample of the mineral can be used to reliably determine its age if any lead found in the mineral is radiogenic. Consider a monazite rock (from Kollam, India) of 6.05 g which has 0.37%  $^{238}\text{U}_2\text{O}_3$  and 0.01%  $\text{PbO}$  by mass.

- d)** Calculate the approximate age of this mineral. Assume that only the uranium series decay chain occurs, and the presence of  $\text{Pb}$  is only due to the decay of radioactive  $^{238}\text{U}$ .

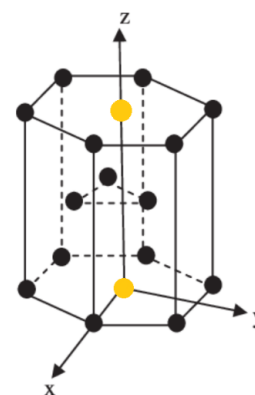
Bastnäsite usually occurs in a reddish brown color and can be even yellow depending on the ratio of metal ions present in the mineral. To identify the empirical formula of bastnäsite, the specimen with the formula of  $\text{Ce}_{0.48}\text{La}_x\text{Nd}_y\text{Pr}_{0.04}\text{Sm}_{0.01}\text{CO}_3\text{F}$  and weighing 3.1184 g was taken from Gallinas Mountains in New Mexico, USA. During mineral analysis 0.6260 g of  $\text{CO}_2$  after acidic treatment with dilute  $\text{H}_2\text{SO}_4$  was captured.

- e)** Calculate an empirical formula for this mineral sample if all metal atoms have an oxidation number +3.

The crystal structure of bastnäsite is quite complex. Yet, one can simplify it to hexagonal closest-packed (HCP). In the Figure, Ce atoms are orange, and all other atoms (whether they are C, O, or F) are black.

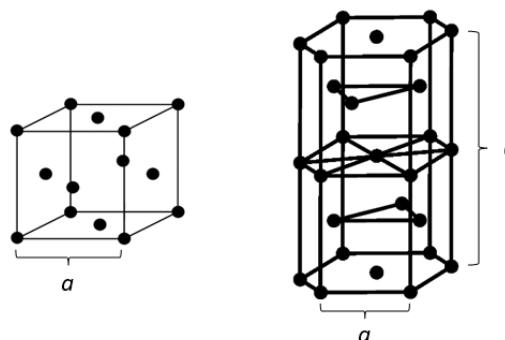
- f)** What is the coordination number of Ce in this structure?

Among lanthanides, cerium is the easiest to extract from its minerals because it is the only one that can reach a stable +4 oxidation state in aqueous solutions. While roasting the bastnäsite, most of the lanthanides are oxidized to  $\text{Ln}_2\text{O}_3$ , except cerium which forms the water-insoluble dioxide  $\text{CeO}_2$ .



- g)** Calculate the volume  $\text{m}^3$  of 0.50 M  $\text{HCl}$  needed to leach  $\text{CeO}_2$  after roasting  $5.00 \cdot 10^3$  kg of bastnäsite with 32% Ce by mass. Write the equation of this extraction reaction in the tank.

Four allotropic forms of cerium exist at standard pressure. The stable form below 726 °C to approximately room temperature is  $\gamma$ -cerium, with a face-centered cubic (FCC) crystal structure. The double hexagonal close-packed form, known as  $\beta$ -cerium, is the equilibrium structure approximately from room temperature to -150 °C. Upon cooling below -15 °C,  $\gamma$ -cerium starts to change to  $\beta$ -cerium, but the transformation proceeds slowly.



FCC unit cell

DHCP unit cell

- h)** Calculate and compare the density of  $\beta$ -cerium ( $a = 0.3681$  nm,  $c = 1.1857$  nm) and  $\gamma$ -cerium ( $a = 0.5161$  nm) in  $\text{g cm}^{-3}$ .

## Part II. Cerium loves redox

Cerium extracted from the ores is used to produce certain laboratory reagents such as ceric ammonium nitrate (abbreviated as CAN)  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ . CAN is often used in redox reactions for quantitative analysis, especially iron determination. Consider the reaction of CAN with the soil sample.

- i)** Write the equation of this one-electron oxidizing reagent reacting with green rust  $\text{Fe}(\text{OH})_2$  and 4 times smaller amounts of cuprite  $\text{Cu}_2\text{O}$  in acidic conditions.

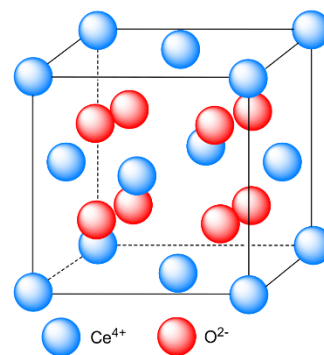
j) Draw the structure of CAN if the central atom and its neighbors form an icosahedron.

A is a pale white powder and contains 25.11% O by mass. By modifying the oxidation state of oxygen atoms in A, a reddish-brown color substance B is formed. B contains oxygens that differ in their oxidation states. B is converted to C by heating the solution and can also be prepared using strong oxidizers like PbO<sub>2</sub>. All oxygen atoms in C have the same oxidation number.

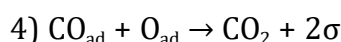
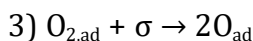
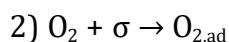
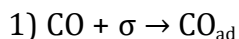
k) Identify A–C and write the equations: i)  $\text{Ce} + \text{H}_2\text{O} \rightarrow \text{A} + \text{H}_2$ , ii)  $\text{A} + \text{HO}_2^- \rightarrow \text{B} + \text{H}_2\text{O} + \text{OH}^-$ , iii)  $\text{B} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{C} + \text{HO}_2^-$ .

l) Fill in the gaps in the text and choose correct answers.

Ceria (CeO<sub>2</sub>) plays a special role in heterogeneous catalysis. In the ideal cell of CeO<sub>2</sub>, the structure consists of a **primitive cubic** / **body-centered cubic** / **face-centered cubic** unit cell of cations with anions occupying the **cubical** / **tetrahedral** / **octahedral** holes. In the structure, each cerium cation is coordinated by \_\_\_ nearest-neighbor oxygen anions, while each oxygen anion is coordinated by \_\_\_ nearest-neighbor cerium cations. Ceria can also be doped with other metal cations to alter electric conductivity. When cerium cations are replaced with lower valent elements (M<sup>2+</sup>/M<sup>3+</sup>), the lattice oxygen atoms in CeO<sub>2</sub> are **incorporated** / **removed**. The ceria crystal usually exhibits a few defects due to the co-existence of Ce<sup>4+</sup> and \_\_\_\_\_ ions.



One of the applications of CeO<sub>2</sub> resides in automotive catalysis and offers a more efficient way to convert CO to CO<sub>2</sub>. The challenging part here is that the oxidation of CO and hydrocarbons must be carried out simultaneously with the reduction of pollutant I. The harsh conditions experienced in the catalytic converter dictate that the catalysts be based on precious metals (e.g., Pt, Rh, and Pd), but precious metals are not selective for oxidizing CO and hydrocarbons using I in the presence of J. However, an altered catalyst is made by vapor depositing catalytic metals onto polycrystalline ceria films to improve the situation. When excess J is present in the exhaust stream, it is removed by adsorption onto reduced ceria so that CO and hydrocarbons are oxidized by reducing J. When there are insufficient amounts of I and J in the exhaust to oxidize the CO and hydrocarbons, ceria releases K. K transfer from ceria to precious metal is important for catalysis. In excess CO, the kinetics for this reaction over bulk Pt, Pd, and Rh are very well understood and are described by Reactions 1–4 (written in the end), where σ represents an empty site on the metal. Because the metal surfaces are essentially saturated in CO when excess CO is present, the rate-limiting step for the reaction is \_\_\_. With ceria-supported metals, there is an additional pathway 5 for forming O<sub>ad</sub> by the transfer of oxygen from ceria to the metal that speeds up the overall conversion. Because ceria does not adsorb CO, the reoxidation of L, reaction 6, is not affected by the coverage of CO on the metal. Using steam as the oxidant, 6 is replaced by 7 which is a very important reaction for the production of M.

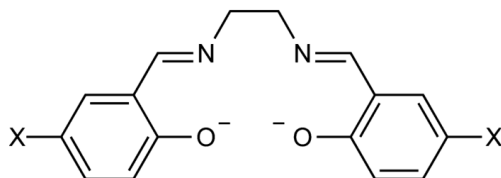


m) Identify formulas of compounds and elements I, J, K, L, and M.

n) Write equations of reactions 5, 6, and 7.

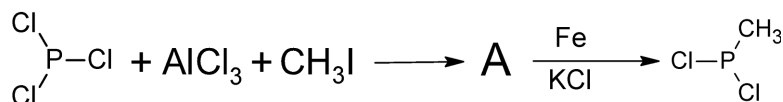
Ce(IV) forms 8-coordinate bis(salen) complexes. A 5,5'-X<sub>2</sub>-salen ligand is shown.

- o) Which complex – Ce(5,5'-(OMe)<sub>2</sub>-salen)<sub>2</sub> or Ce(5,5'-(Cl)<sub>2</sub>-salen)<sub>2</sub> – is a stronger oxidizing agent?

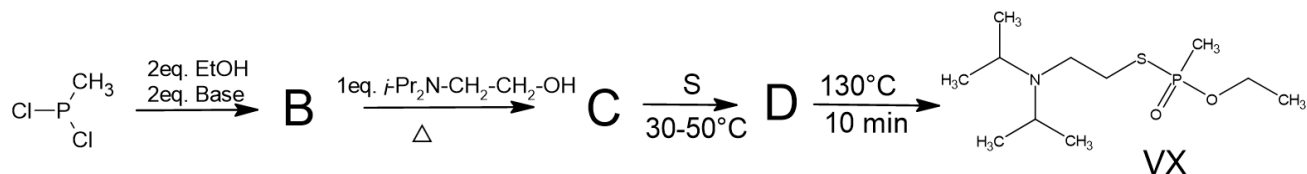


### Problem 5 – SPECTRA, STRUCT, SYNTH – Poisonous chemicals

S-[2-(diisopropylamino)ethyl]-O-ethyl methylphosphonothioate (**VX**) is an odorless, colorless, human-made chemical developed in 1952. It is the most toxic, rapidly acting of all compounds classified as nerve agents. Not found naturally in the environment, **VX**'s only application is in chemical warfare. It is classified as a weapon of mass destruction by the United Nations in UN Resolution 687, and the production and stockpiling of **VX** was outlawed by the Chemical Weapons Convention of 1993. Synthesis of **VX** starts from a two-step reaction of phosphorus trichloride with methyl iodide.



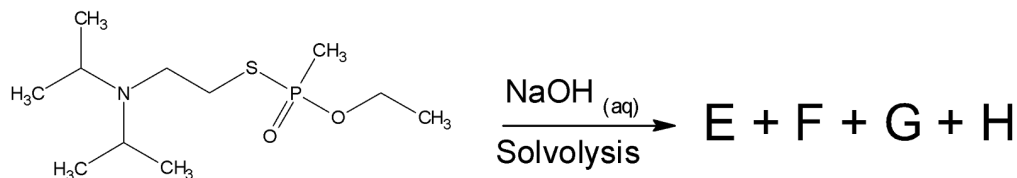
- a) Draw the structural formula of intermediate **A**.  
b) Draw the structural formulas of compounds **B–D**.



Affected by high temperature product **D** starts isomerisation to **VX**.

- c) Draw the isomerization mechanism from product **D** to **VX**.  
**VX** is produced *via* the thermal process, which gives a racemic mixture of enantiomers.  
d) Mark the chiral centers in the **VX** molecule.  
e) How many possible stereoisomers does **VX** have?

Like other organophosphorus nerve agents, **VX** may be destroyed by a reaction with strong nucleophiles. The reaction of **VX** with concentrated aqueous sodium hydroxide results in two competing solvolysis reactions giving four different compounds (**E–H**).



- f) Write structural formulas of compounds **E–H**.  
g) Which one of the **E–H** compounds is still highly toxic?

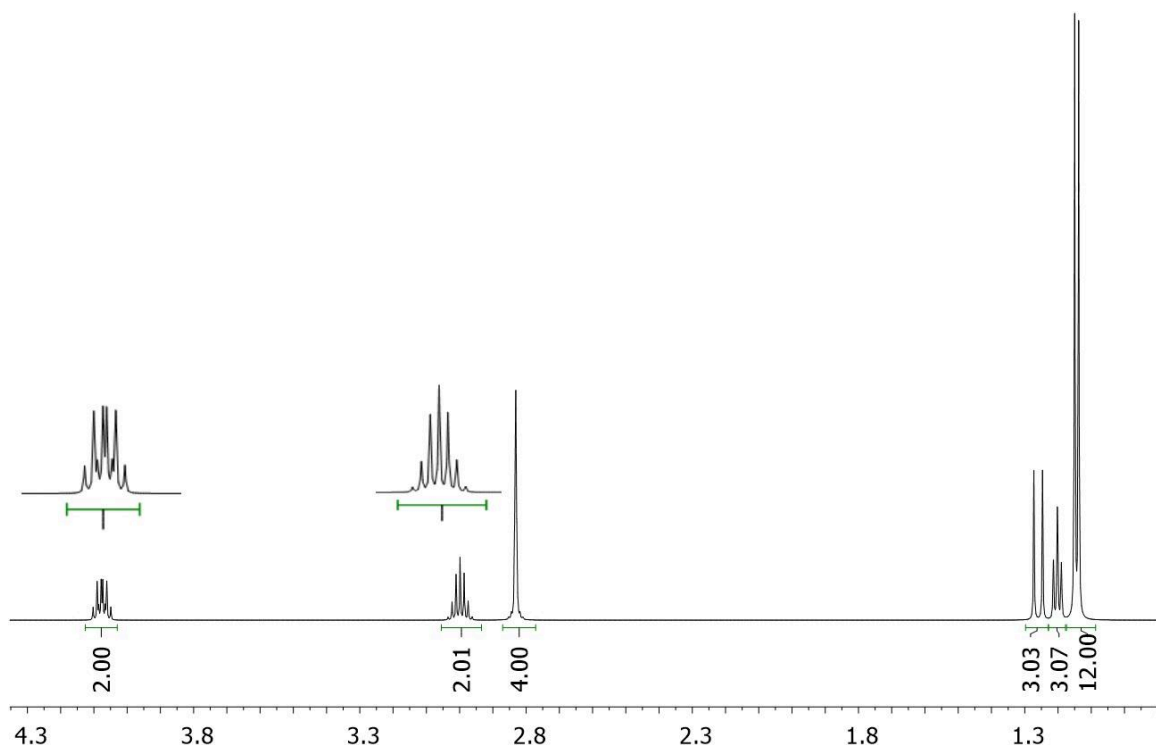
Despite solvolysis, it was found that **VX** can go the third way of degradation. Cucurbituril's third degradation pathway becomes dominant under certain conditions. It involves the C-S bond cleavage.

**h)** Draw the structural formulas of compounds **I** and **J**.

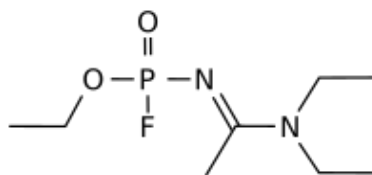


The  $^1\text{H}$  NMR spectrum of the **VX** gas (in  $\text{CDCl}_3$ ) is given below.

- Assign the corresponding  $^1\text{H}$  NMR signals for **VX**.
- Indicate all elements that cause peak splitting in compound **VX**  $^1\text{H}$  NMR spectrum.
- Assign the multiplicity of peaks in both  $^1\text{H}$  NMR spectra.



The agent A-234 is supposedly around five to eight times more potent than **VX** gas.

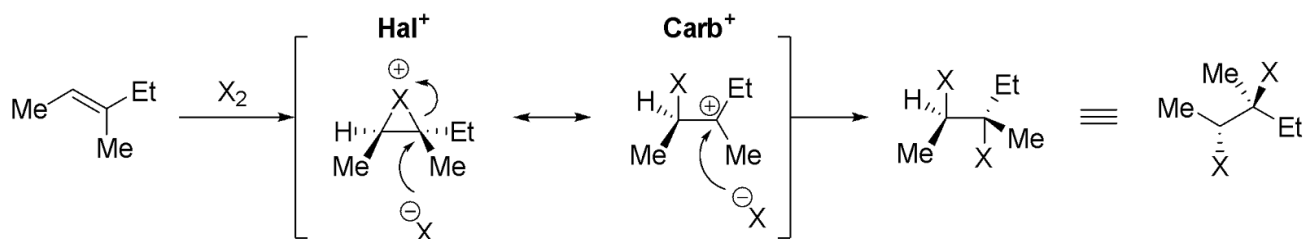


The median inhaled A-234 lethal dose for an 80 kg person has been estimated as  $7 \text{ mg m}^{-3}$  for two-minute exposure when the person inhales  $15 \text{ dm}^3$  per minute.

- Calculate the lethal dose of agent A-234 in grams.
- Calculate the lethal dose in grams per kilogram of a person's weight.
- How many lethal doses are in 1 gram of this compound for a 100 kg person?

## Problem 6 – SPECTRA, SYNTH – Simple organic chemistry

Alkenes react with halogens through a three-membered cationic halonium ion intermediate **Hal<sup>+</sup>**, which is in resonance with a carbocation **Carb<sup>+</sup>**. Both resonance forms explain selectivity in this reaction: halonium **Hal<sup>+</sup>** dictates that the addition of  $X_2$  is anti (on opposite sides), and carbocation **Carb<sup>+</sup>** dictates that attack of halide anion (or a different nucleophile) takes place at the most substituted carbon atom.



Let us look at monoalkenes with a molecular formula of  $C_5H_8$ . Assume that all these isomers are stable and obtainable.

- a) Determine the number of **i)** 5-membered ring, **ii)** 4-membered ring, and **iii)** 3-membered ring isomers, considering stereochemistry.

A symmetrical isomer of this group reacted with  $Br_2$  in a nonpolar solvent and formed only one stereoisomer.

- b) Draw the structural formula of this isomer.  
c) What would be the product of bromination in methanol?

A monoalkene **H1** with a molecular formula  $C_4H_6$  reacted with bromine and produced three structural isomers **B1–B3**. The  $^1H$  NMR data of **B1–B3** (in  $CDCl_3$ ) are given below.

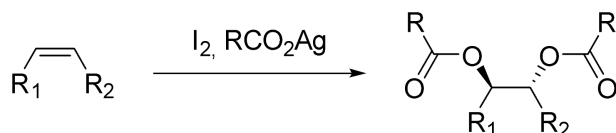
**B1:**  $^1H$  NMR 4.02 (s, 2H), 1.38–1.32 (m, 2H), 1.10–1.03 (m, 2H)

**B2:**  $^1H$  NMR 5.67 (s, 2H), 4.31 (s, 4H)

**B3:**  $^1H$  NMR 3.24 (m, 4H), 2.20 (m, 2H)

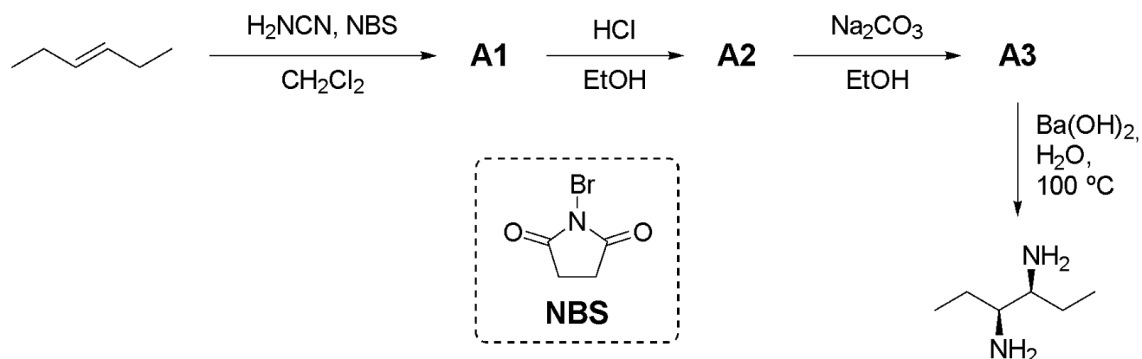
- d) Draw the structural formulas of compounds **H1** and **B1–B3**.

The formation of halonium ion is typically used as an intermediate in more complex transformations. For example, the Prevost reaction allows to obtain diesters in an anti-fashion:



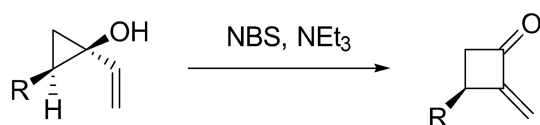
- e) How many stereoisomers are formed in this reaction if **i)**  $(R_1 = R_2) \neq H$  and **ii)**  $(R_1 \neq R_2) \neq H$ ? Since the product (diester) has 2 chiral carbon atoms, how many stereoisomers exist in total if **i)**  $(R_1 = R_2) \neq H$  and **ii)**  $(R_1 \neq R_2) \neq H$ ?  
f) Draw the mechanism of the Prevost reaction. Note that the relative configuration of the product is anti.

Halonium ion can also be used as an intermediate in the synthesis of 1,2-diamines:



**g)** Draw the structural formulas of compounds **A1–A3** with stereochemistry.

Halonium ion is also an intermediate in some rearrangements, such as semipinacol rearrangement, which leads to a ring expansion:



**h)** Draw the reaction mechanism.