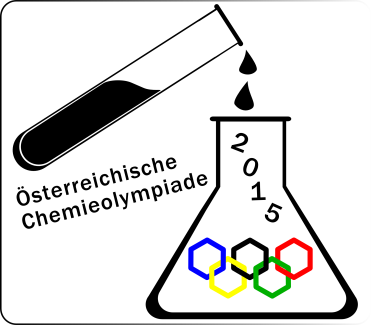
**41st Austrian Chemistry Olympiad**

**National Competition**



**SOLUTIONS**

**Task 1 28/ 7.5 points**

**Chemistry around a purification plant**

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| *1.1. Write balanced reaction equations in ionic form for the single steps as well as for the overall reaction of nitrification.* |
| NH4+ + 1,5 O2 → HNO2 + H2O + H+ ***1bp*** |
| HNO2 + 0,5 O2 → NO3- + H+ ***1bp*** |
| NH4+ + 2 O2 ⇄NO3- + 2 H+ + H2O ***1bp*** |

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| *1.2. Calculate the mass of Ca(OH)2, which is needed hourly to hold a constant pH in the nitrification zone.* |
| *g*  *≙*  g/d ⇒ ***2bp*** |
| *1.3. Calculate the standard potential of the half cell NO3-/ NH4+* |
| **V** ***1bp*** |

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| *1.4. What is the potential of the half cell of 1.3., if the pH is brought to 7.0, while all other concentrations remain unchanged? T = 298 K. Show your calculations.* |
| For: NO3- + 8e- + 10 H+ → NH4+ + 3 H2O  V***2bp*** |

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| *1.5. Write a balanced reaction equation for the reaction nitrate-methanol in ionic form.* |
| 6 NO3- + 6 H+ + 5 CH3OH → 5 CO2 + 13 H2O + 3 N2 ***2bp*** |

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| *1.6. Show by calculation, that NO may disproportionate into N2 and NO3-.* |
| V ***3bp***  V  NO → N2: 1.68 V and NO → NO3-: -0.956 V give for NO→N2 + NO3-: 0.724 V  ⇒ equilibrium on the right side, NO disproportionates |

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| *1.7. What is the lowest pH, at which iron(III) hydroxide will start to precipitate, if the solution contains 10 g/m3 Fe3+? Show your calculations. pKL(Fe(OH)3) = 38.7* |
| ***3bp***  10 g/m3 = 10 mg/L ⇒ 0.179 mmol/L Fe3+  ⇒ mol/L  ⇒ |

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| *1.8. Calculate the proportion of amount Fe:P in the above case.* |
| ***1.5bp***  P: g ⇒ 3.552·103 mol  Fe: 250 kg ⇒ 4.476·103 mol  Fe:P = 1.26:1 |

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| *1.9. Calculate the solubility product of AlPO4 assuming that no protolysis takes place.* |
| ***1.5bp***  μg/m3 = 9.64·10-8 g/L *M*(AlPO4) = 122 g/mol  mol/L |

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| *1.10.Calculate the solubility of AlPO4 at the pH mentioned.*  *hint: you may calculate accurately or you may use sensible simplifications. In the latter case you have to prove mathematically, that the simplifications were valid. If you did not get a value in 1.9. you may use 9,0·10-19 for KS.*  *H3PO4: pKA1 = 2.15; pKA2 = 7.20; pKA3 = 12.4;* |
| ***9bp***  with we have    ⇒  ⇒  ⇒  mol/L  mol/L  mol/L  mol/L ⇒ q.e.d.  mol/L |

**Task 2 27/ 7.5 points**

**Thermodynamics and Equilibrium**

**A. A thermodynamic cycle**

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| *2.1. Calculate the efficiency of the machine.* |
| Calculation: ***1bp*** |
| *2.3. Calculate the p- and V-values of the points A, B, C, and D, and give a sketch of this thermodynamic cycle using the p-V-diagram at hand (the form of the hyperbolic curves should be estimated).*  *Mark the geometrical part by shading, which corresponds to the net-work of the system.* |
| Calculation: ***4bp***  A: L ⇒ bar  B: bar ⇒ L  C: L ⇒ bar  D: L ⇒ bar    sketch:        Shaded area = ***3bp*** |
| *2.4. Calculate the work of the reversible isothermal expansion at 800°C and the heat which is released to the surrounding of the machine.* |
| Calculation: ***2bp***  kJ  kJ |

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| *2.5. Calculate the final temperature and the final pressure of this adiabatic expansion.* |
| Calculation: ***3bp***  und  bar  K |

**B. Boudouard‘s Equilibrium**

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| *2.6.What is the molar percentage of CO in the equilibrium mixture at 727°C and 1 bar?* |
| 70% ***0.5bp*** |
| *2.7. Calculate KP of the reaction at 727°C and a total pressure of 0.80 bar.* |
| Calculation:  pressure of the diagram(!): ***1bp*** |
| *2.8. Calculate the percentage of CO at 727°C and a total pressure of 2.0 bar.* |
| Calculation: ***4.5bp***   |  |  |  | | --- | --- | --- | |  | CO2 | CO | | *n0* | 1 | 0 | | *Δn* | -a | +2a | | *neq* | 1-a | 2a | | *xeq* |  |  |     ⇒  ⇒ mol  ⇒ 58.3% CO |

**C. An Isomerisation**

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| *2.9. Calculate the equilibrium constant of the reaction and the composition of the equilibrium mixture at 25°C.* |
| Calculation: ***2.5bp***    ⇒ ⇒  0.33 mol F6P and 0.67 mol G6P |
| *2.10. Calculate the free reaction enthalpy of this reaction depending on the fraction of fructose-6-phosphat in optional reaction mixtures (at least 6 values), and draw a sketch of this dependency in the given diagram.* |
| kJ   |  |  | | --- | --- | | *x* | (kJ) | | 0 | -∞ | | 0.1 | -3.75 | | 0.2 | -1.74 | | 0.33 | 0 | | 0.4 | 0.69 | | 0.6 | 2.71 | | 0.8 | 5.14 | | 0.9 | 7.15 | | 1.0 | +∞ |   ***5.5bp*** |

**Task 3 54/ 15 points**

**Three Elements out of the Copper Mine**

**A. Copper itself**

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| *3.1. Calculate the lattice constant in Angström (*1Å = 100 pm*)* |
| *lattice constant a =* ***2bp*** |
| *Your calculation:* |

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| *3.2. Calculate the radius of this statistical atom.* |
| *calculated radius r =* |
| *Your calculation:*  ***1bp***  ***1bp***  ***1bp*** |

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| *3.3. Write down the empirical formulae of these two compunds.* | |
| **A: CuAu *1bp*** | **B: Cu3Au *1bp*** |

**B. Copper minerals and the production of copper**

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| *3.4. Determine the formulae of the compounds* **X** *and* **Y***.* | |
| **X: SiO2 *1bp*** | **Y: Fe2SiO4 *1bp*** |
| *Your calculation:*  N not possible (NO2 not difficult to melt)  Si matches → **X** is SiO2  **Y**: O ... 1.9631 mol ... 4  13.78 % Si ... 0.4906 mol ... 1  54.81% Fe ... 0.9814 mol ... 2 | |
| *3.5. Give balanced equations for the reactions in steps a. to d.:* | |
| a. 6 Cu5FeS4 + 13 O2  → 15 Cu2S + 2 Fe3O4 + 9 SO2 ***2bp*** | |
| b. 2 Fe3O4 + 2 CO + 3 SiO2 → 3 Fe2SiO4 + 2 CO2 ***1bp*** | |
| c. 2 Cu2S + 3 O2 → 2 Cu2O + 2 SO2 ***1bp*** | |
| d. 1 Cu2S + 2 Cu2O → 6 Cu + SO2 ***1bp*** | |

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| *3.6. In the empty plot denote the compositons of* ***pyrite*** *(FeS2) (46,5 % Fe) and* ***cubanite*** *(CuFe2S3)(23,4% Cu, 41,1% Fe).*  *GS MBP SSD:Users:schoeb:Desktop:ternary plot3.pdf*  FeS2 ***3bp***  CuFe2S3 ***3bp***  gray region: Cu-Fe-S- compositions useable for pyrometallurgy |
| *3.7. For the Cu-Fe-S-compositions useable in pyrometallurgy denote:* |
| *a) the maximum percentage of Fe such a mixture may have 56.5 %* ***2bp***  *b) the minimum percentage of S such a mixture must have 16.5 %* ***1bp*** |

**C. Strange copper compounds**

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| *3.8. Give a balanced equation for the formation of potassium hexafluoridocuprate(III).* | |
| 6 KCl + 2 CuCl2 + 6 F2 → 2 K3[CuF6] + 5 Cl2 ***2bp*** | |
| *3.9. Write down the entire electron configuration for Cu(III) in its ground state.* | |
| ***1bp*** | |
| *3.10. Depict the splitting of the d-orbitals for the complex and tick the right box:* | |
| *Scheme of the d-Orbitals:*  eg —— ——  t2g —— —— ——  ***2bp*** | 🞏 diamagnetic  **X** paramagnetic  ***1bp*** |

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| *3.11. Draw a Lewis – formula and tick the right box:* | |
| *structure of H5IO6:*  ***2bp*** | geometry according to VSEPR  🞏 linear  🞏 trigonal planar  🞏 tetrahedral  🞏 square pyramidal  **X** octahedral  ***1bp*** |
| *3.12. Write down the molecular formula of the copper-containing complex anion:* | |
| *Formula:* [Cu(O6IH)2]5- ***2bp*** | |
| *Justify by calculation*  *M* (HIO64-) = 224 M(complex with 12.4%Cu) = 63,55/0.124 = 513  → two HIO64- needed | |
| *3.13. Propose a structure for this anion:* | |
| ***3bp*** | |

**D. Arsenic**

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| *3.14. Write down complete, balanced equations for both decays. Denote the nuclids with the appropriate mass numbers.* |
| β+: ***1bp*** |
| β–: ***1bp*** |
| *3.15. Calculate the decay constant for the* β+ *decay in .* |
| β+: *λ1* = ***2bp*** |
| *Your calculation:*  β+: |

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| *3.16. Indicate the mass number of the Ge-isotope, that gets converted according to the equation given above.* |
| Mass number A = 72 ***1bp*** |
| *3.17. Calculate the total activity of the sample (β+ and β-) immediately after the irradiation.* |
| activity *A* = 1.80 MBq ***3bp*** |
| *Your calculation:*  0.743 g GeO2 → 7.101 mmol Ge → 1.946 mmol 72Ge = atoms of 72Ge  atoms were converted |

**E. Reactions of square planar platinum(II) complexes**

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| *3.18. Indicate which letter stands for which ligand.* | | |
| A: Cl- B: NO2- C: NH3 D: py je*1bp* ***= 4 bp*** | | |
| *3.19. Draw configuration formulae for the complexes IV - VI.* | | |
| **IV**  ***1bp*** | **V**  ***2bp*** | **VI**  ***1bp*** |
| *3.20. How many isomers are possible for complex VI?* | | |
| There are \_\_\_\_\_ 3 \_\_\_\_\_\_\_\_ possible isomers. ***1bp*** | | |

**Task4 15 points**

**Synthesis of different drugs**

**A. Verapamile**

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| *4.1. Write down the absolute configuration of this sterogenic center.* |
| *S* |

|  |  |
| --- | --- |
| *4.2. Draw constitution formulae of* ***B*** *and* ***C*** *and a possible formula of the reagent a.* | |
| *reagent a:* LiAlH4 or H2/catalyst***0,5 bp*** | |
| ***B*** | ***C*** |

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| *4.3. Draw the constitution formula of compound* ***D****. Draw a formula of reagent* ***b*** *and suggest two conditions of the reaction from* ***D*** *to* ***E****.* | |
| ***D*** | ***b:*** CH3OH    *2 conditions:*  H+, heat |

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| *4.4. Write possible formulae of reagents* ***c, d, e, f*** *,* ***g*** *and* ***h****.* | |
| ***c:*** strong base, NaOEt, LDA etc. | ***f:*** CH2=CH-CH2Br |
| ***d:*** (CH3)2CH-Br (I) | ***g:*** OH-, H2O |
| ***e:*** strong base, NaOEt, LDA etc. | ***h:*** H3O+ |

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| *4.5. Draw constitution formulae of the compounds* ***I, J, K****,* ***L*** *and* ***M*.** | |
| ***I*** | ***J*** |
| ***K*** | ***L*** |
| ***M*** |  |

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| *4.6. Which type of reaction is meant in the reaction of* ***M*** *and* ***C*** *to Verapamile?*  *What is the reason for adding Et3N?* |
| nucleophile substitution, SN2 |
| for capturing HCl, moves the equilibrium to the right. |

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| *4.7. Assign absolute configurations to the stereogenic centres in the formula above.* |



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| *4.8. What is the name of the reaction of* ***N*** *with diethyl oxalate?* | |
| Claisen-ester-condensation | |
| *4.9. Draw a mechanism of the 1st step of attack on diethyloxalate.* | |
|  | |
| *4.10. Draw constitution formulae of compounds* ***N, O****,****P*** *and* ***Q.*** | |
| ***N*** | ***O*** |
| ***P*** | ***Q*** |

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| *4.11. Draw steric formulae of the compounds* ***R, S*** *and* ***T*** *and suggest a possible reagent for* ***i.*** | | |
| ***R*** | ***S*** | |
| ***T*** | ***Reagenz i:***  LiAlH4 | |
| *4.12. Draw the species which is formed in the reaction of* ***R*** *with the base NaH. By using a curly arrow show the attack which finally leads to the formation of the bicyclus.* | | |
|  | | |
| *4.13. Draw constitution formulae of the compounds* ***W, X, Y*** *and* ***Z.*** | | |
| ***W*** | | ***X*** |
| ***Y*** | | ***Z:*** |
| *4.14. Name the reaction type of the transformation of* ***V*** *to* ***W****.* | | |
| elektrophilic substitution, SE | | |

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| *4.15. Write a balanced equation for this reaction.* |
|  |

**Task 5 25/ 7.5 Punkte**

**A synthetic nucleoside functions as HI-virustatica**

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| *5.1. Name the three building blocks of a nucleotide.* |
| organic, heterocyclic base; saccharide (usual a pentose), phosphoric acid ***1.5bp*** |
| *5.2. Design the structure of a 3-Deoxy-“purine nucleotide“.* |
| ***4bp***  *C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\5.2.png*  alternatively: guanine as base and / or 2´ -ester; also di-or triphosphate are correct |
| *5.3. Show the equation leading from the chain form of (2S, 3R, 4 R)-2,3,4,5-Tetrahydroxypentanal to α-D-arabinofuranose. Depict the reactant in Fischer projection and the product in Haworth projection.* |
| *C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\5.3.png* ***3bp*** |
| *5.4. Name the reaction type leading from the open chain to the ring form.* |
| nucleophilic addition (AN) ***1bp*** |

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| *5.5. Calculate the sum-formula of A.* |
| C3.67H4.90O1.63N1.22F0.41  🡪 C9H12O4N3F ***2bp*** |
| *5.6. Design the structure formula of A.* |
| ***4bp***  *C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\5.6.png* |

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| *5.7. Write down the structural formulae of the substances B to G into the boxes. Abbreviate Phenyl with Ph as usual. If the base is not involved in a reaction, use the abbreviation ”base“.*  *Use a Guanine-nucleoside with a common sugar with a primary hydroxyl group if you are not able to derive the formula for A.* | |
| *C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\5.7.B.png****B: 1bp*** | *C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\5.7.C.png****C: 1bp*** |
| ***C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\5.7.D.pngD: 1bp*** | ***C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\5.7.E.pcxE: 1bp*** |
| ***F: 1bp***  ***C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\5.7.F.png*** | ***G: 1bp***  ***C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\5.7.G.png*** |

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| *5.8. Write down the letters t (true statement) and w (wrong statement) in the boxes. Randomly placed crosses lead to a deduction according to the scores.* |
| ***3.5bp***  f  *The absence of the 2´ hydroxyl group causes the way of molecular action.*  w *The nucleoside analogue G vies competitively with dCTP.*  f *The nucleoside analogue G vies competitively with CTP.*  f *The nucleoside analogue G vies competitively with TTP.*  w *Chain termination at the DNA elongation is the key factor of the inhibitory effect.*  f  *The reverse transcriptase is a DNA-dependent DNA polymerase. This enzyme uses the   wrong nucleotide for transcription.*  w  *The reverse transcriptase is an RNA-dependent DNA polymerase. This enzyme uses the  wrong nucleotide for transcription.* |

**Task 6 25.5/ 7.5 points**

**The horse-radish Enzyme**

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| *6.1. Using the partial equations, derive a law for the rate of the reaction.* |
| ***4bp*** |

**Enzymkinetik**

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| *6.2. Write down the unit of KM..* |
| ***1,5bp*** |
| *6.3. Calculate the maximum rate of this reaction.* |
| ***2bp*** |
| *6.4. Draw a graph of eq. 1 by plotting v against [S]. It is not necessary to scale the axes.* |
| ***3bp***  *C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\6.4.jpg* |
| *6.6. Show by calculation which condition leads to v = vmax.* |
| ***3bp*** |

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| *6.7. A linear transformation of eq. I leads to the equation of Lineweaver and Burk.*  *Perform a linear transformation of eq. I and show your calculation by forming the reciprocal of the Michaelis-Menten-equation.*  *Sketch a graph. It is not necessary to scale the axes.*  *Name the axes and highlight the ordinate axis*, *when x = 0.*  *Find an expression for the slope of the function.* |
| ***5bp***  *C:\Users\mathias\Desktop\neuesordningsystemschule\Schule\Chemie\Bundeskoordinatorenteam_Olympiade\ÖCHO2015\Wettbewerb\6.7.jpg* |

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| *6.8. Derive the rate law (Michaelis-Menten eq.) and show your calculation step by step (application of the steady state model).* |
| ***7bp*** |