**40th Austrian Chemistry Olympiad**

**National Competition**





**Solution**

**Task 1 15 points**

**Titanium and other metals**

**A. From the ore to the element**

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| *1.1. Calculate the empirical formula of titanite.* |
| *formula:* CaTiSiO5 |
| *calculations:* Ti: Ca: Si: = 0.5101 O: proportion 1:1:1:5 |

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| *1.2. Write down balanced equations for the reactions in the scheme and derive from them an overall equation for the depicted process.* |
| *A:* FeTiO3 + C → Fe + CO + TiO2 |
| *B:* TiO2 + 2 C + 2 Cl2 → TiCl4 + 2 CO |
| *C:* TiCl4 + 2 Mg → Ti + 2 MgCl2 |
| *D:* MgCl2 → Mg + Cl2 |
| *overall:* FeTiO3 + 3 C → Fe + 3 CO + Ti |

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| *1.3. 1000 kg of the reaction mixture according to the overall equation were used. Which maximum mass of titanium may be generated starting from these 1000 kg?*  |
| *mass of Ti:* 255 kg Ti |
| *calculations:* *M*(FeTiO3) = 151.72 g/mol *n*·151,72 + 3n·12,01 = 106 g therefore *n* = 5326 mol  *m*(Ti) = 5326·47.87 = 255 kg Ti |

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| *1.4. Which process is used to execute reaction D?* |
|  electrolyis, [fused-salt](http://dict.leo.org/ende/index_de.html#/search=fused-salt&searchLoc=0&resultOrder=basic&multiwordShowSingle=on) [electrolysis](http://dict.leo.org/ende/index_de.html%22%20%5Cl%20%22/search%3Delectrolysis%26searchLoc%3D0%26resultOrder%3Dbasic%26multiwordShowSingle%3Don) |

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| *1.5. Complete the equation for the synthesis of barium titanate(IV) from TiO2:* |
| BaCO3 + TiO2 → BaTiO3 + CO2 |

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| *1.6. Write down the complete equation for the radioactive decay of 45Ti.* |
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| *1.7. What was the specific activity of the sample put aside after 3.0 hours?*  |
| *specific activity after 3.0 hours:* 33.54 Bq/g |
| *calculations:*  |

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| *1.8. Calculate the overall yield of Ti of the reaction sequence (A,B,C,D) based on the starting amount of FeTiO3.* |
| *yield in %:* 80.0 % |
| *calculations:* total activity at the beginning: 82.6 g · 65.91 = 5681.4 Bq After some time – activity after 210 min (3.5h)  yield:  |

**B. Other Ti-compounds – crystal lattice**

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| *1.9. Write down the electron configuration of Ti3+.* |
|  1s2 2s2 2p6 3s2 3p6 3d1 |

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| *1.10. Calculate the ionic radius of N3− using the Kapustinskii-equation. Show your calculations. (d\* = 34.5 pm; κ = 1.21·105 kJ·pm/mol)* |
| *Ionic radius of nitride N3−:* 1.64Å |
| *calculations:* *r0* = 2.31Å = *r*Ti + *r*N therefore *r*N = 1.64Å |

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| *1.11. Calculate the lengths of x and y using this information.* |
| *x = 3,562* Å  | *y = 3,548* Å |
| *calculations:*Looking at the front plane: and |

**C. Complexes of chromium and cobalt**

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| *1.12. Write down the missing name or formula respectively for each of the compounds (a) to (e).* |
| *(a)* pentaamminbromidocobalt(III)-sulfate |
| *(b)* pentaamminsulfatocobalt(III)-bromide |
| *(c)* [CrCl2(OH2)4]Cl · 2 H2O |
| *(d)* [CrCl(OH2)5]Cl2 · H2O |
| *(e)* potassium hexafluoridocobaltat(III) |

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| *1.13. Assign (a) to (e) with the roman numbers I to V.* |
| *I: (a)* | *II: (e)* | *III: (c)*  | *IV: (b)* | *V: (d)* |
| *Give your reasoning for the classification using either calculations or chemical equations.* Vessels III, IV and V must contain bromide, and twice chloride respectively. Vessel I: SO42- + Ba2+ → BaSO4 M(c) = M(d) = 266.47 g/mol → vessel III contains (c) *Mass loss by drying* → crystal water → have only (c) and (d) → vessel V must (d).molar mass 290.23 g/mol → (e) |

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| *1.14. How do you call the constitution isomerism of (a) and (b)?* |
|  *ionisation isomersm* |
| *1.15. How many diastereomeres may occur in the case of the cation of (c)? Give also the prefixes which you use in naming them.*  |
| two -- *cis* and *trans* |

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| *1.16. Calculate Δ*O *in kJ/mol.* |
| *Δ*O =  |
| *calculation:* *E =*  |

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| *1.17. Sketch a d-orbital scheme for the complex in (e)* |
| *GS MBP HD:Users:schoeb:Documents:Chemie:Olympiade:OECHO 40:Bewerb:CoKomplexOrbitalschema.jpg* |

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| *1.18. Calculate the magnetic moment in units of μB.* |
| *μ=*  |
| *calculation:* |

**Task 2 13 points**

**Some Equilibria**

**A. Electrochemical Equilibria – Alkaline Cell**

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| *2.1. Write down the reaction equations for the generation of MnOOH and Mn(OH)3 respectively, starting from Mn2O3 using water as reaction partner.* |
|  *Mn2O3 + H2O ⇌ 2 MnOOH*  *Mn2O3 + 3 H2O ⇌ 2 Mn(OH)3* |

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| *2.2. Calculate the free standard reaction enthalpy for the reaction Mn2O3 → Mn(OH)3.* |
| *ΔG0= 77 kJ* |
| *calculation:* *2 Mn(OH)3 + 2e- ⇌ 2 Mn(OH)2 + 2 OH- E03 = 0.15 V* *Mn2O3 + 3 H2O + 2e- ⇌ 2 Mn(OH)2 + 2 OH- E04 = -0.25 V* *Mn2O3 + 3 H2O ⇌ 2 Mn(OH)3 E07 = E04 – E03 = -0.40 V* *ΔG07 = -z·F·E07 = 77 k*  |

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| *2.3. Calculate the free standard reaction enthalpy for the reaction Mn2O3 → MnOOH.* |
| *ΔG0= 5.8 kJ* |
| *calculation:* *2 MnOOH + H2O + Zn ⇌ 2 Mn(OH)2 + ZnO E02 = 1.06 V* *Zn + 2 OH- ⇌ ZnO + H2O + 2e- E01 = 1.28 V* *2 MnOOH + 2 H2O + 2e- ⇌ 2 Mn(OH)2 + 2 OH- E08 = E02 – E01 = -0.22 V* *Mn2O3 + 3 H2O + 2e- ⇌ 2 Mn(OH)2 + 2 OH- E04 = -0.25 V* *Mn2O3 + H2O ⇌ 2 MnOOH E09 = E04 – E08 = -0.03 V* *ΔG09 = -z·F·E09 = 5.8 kJ* |

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| *2.4. Calculate the solubility product of Mn(OH)2.* |
| *KL = 1.42·10-13*  |
| *calculation:**Mn2+ + 2e- ⇌ Mn E05 = -1.18 V ΔG05 = -z·F·E05 =228 kJ**Mn(OH)2 + 2e- ⇌ Mn + 2 OH- E06 = -1.56 V ΔG06 = -z·F·E06 =301 kJ**Mn(OH)2 ⇌ Mn2+ + 2 OH- ΔG010 = ΔG06 - ΔG05 = 73.3 kJ* |

**B. The coral reef**

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| *2.5. Calculate the minimum concentration of carbonate ions in sea water in order to build the lime frame.* |
|  *8.3·10-7 mol/L* |
| *calculation:**[Ca2+]·[CO32-] = 8.7·10-9 ⟶*  |

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| *2.6. Calculate the highest pH, where the lime frame dissolves.*  |
| *pH = 6.92* |
| *calculation:* *⟶*  *⟶* *⟶ [H3O+] = 1.21·10-7* *⟶ pH = 6.92* |

**C. A mixture of acids**

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| *2.7. Calculate the pH of this solution. Neglect the autoprotolysis of water.* |
| *pH = 2.88* |
| *calculation:* |

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| *2.8. Give for the concentrations of all particles in this mixture numbers or terms with variables, whereby you should show reasonable assumptions about negligible species.*  |
| *[HAc] ≈ 0.05 [Ac-] = x [H2SO4] ≈ 0 [HSO4­-] = a [SO42-] = b**[H3O+] = 10-(2.88-0.300) = 10-2.58 = 0.00263 mol/L* |

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| *2.9. Calculate the concentration of the diluted sulphuric acid, which is added to the acetic acid solution.* |
| *c = 0.00251 mol/L* |
| *calculation:* *⟶ x = 0.0003303 mol/L**[H3O+] = x + a + 2b ⟶ 0.00263 = 0.0003303 + a + 2b* *⟶*  *⟶ 0.00263 = 0.0003303 + a + 2·4.571·a* *⟶ a = 0.000227 mol/L* *⟶ b = 0.00104 mol/L**Before dilution: c = 0.00251 mol/L* |

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| *2.10. Give reasoning for your assumptions in 2.8.* |
| *[HAc] = 0.05 – x x = 0.0003303 mol/L*  *⟶ assumption [HAc] ≈ 0.05 true* *⟶ assumption [H2SO4] ≈ 0 true* |

**Task 3 15 points**

**Kinetics and Thermodynamics**

**A. Two kinetic problems**

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| *3.1. Write down the differential rate law for reaction (1) and give proof by a short calculation.* |
| *rate law:*  |
| *calculation:**;*  *⇒ 1st order* *⇒ zero order* |

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| *3.2. Calculate the initial concentration of t-butyl bromide.* |
| *exp1: c0 (t-BuBr) = 0.212 mol/L* | *exp2: c0 (t-BuBr) = 0.318 mol/L* |
| *calculation for one example:* |

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| *3.3. Calculate the concentration of t-butyl bromide after one hour for experiment (1) and (2).* |
| *ct (1) = 0.201 mol/L* | *ct (2) = 0,302 mol/L* |
| *calculation for one example:*    |

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| *3.4. Calculate the rates in experiment 1 and 2 using the differential rate law, and thereby find also a mean value for the rate constant.* |
| *v(1) = 0.0106 mol/L·h* | *v(2) = 0,0159 mol/L·h* |
| *k = 5.00·10-2 h-1* |
| *calculation:* |

**Concerning reaction (2):**

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| *3.5. Which reaction order do you suppose based on the chemical system in question?* |
| *reaction order: 2nd order* |

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| *3.6. Calculate the initial concentrations of the starting products.*  |
| *c0(methyl bromide) = 1.00 mol/L* | *c0(sodium methylate) = 1,00 mol/L* |
| *calculation:* |

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| *3.7. Calculate the concentrations of methyl bromide and sodium methylate respectively after 30, 60, 90, 120 and 150 minutes.* |
| *ct(30) = 0.984 mol/L* | *ct(60) = 0.968 mol/L* | *ct(90) = 0.953 mol/L* |
| *ct(120) = 0.938 mol/L* | *ct(150) = 0.923 mol/L* |  |
| *calculation for one example:* |

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| *3.8. Proof your assumption in part 2.7. by a calculation and find a mean value of the rate constant.* |
| *k (30) = 5.56·10-4 L/mol·min* | *k (60) = 5.55·10-4 L/mol·min* | *k (90) = 5.53·10-4 L/mol·min* |
| *k (120) = 5.53·10-4 L/mol·min* | *k (150) = 5.55·10-4 L/mol·min* | *kM = 5.54·10-4 L/mol·min* |
| *calculation for one example:**k remains constant ⇒ 2nd order* |

**B. Four (extraordinary?) compounds**

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| *3.9. What is element X?*  |
| *X: Fluorine, F2*  |

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| *3.10. Give the formulae of A, B, C, and D. Show your calculations, if this is possible.*  |
| *A: CF4*  | *B: PF3* |
| *C: XeF4* | *D: SF4* |
| *Calculation:**A:* *3 fluorine: M(element) ⇒ P**4 fluorine: M(element) ⇒ C**PF3 or CF4, the description of properties and the fact that B obviously is PF3, lead to CF4.**C: 207 - 3·19 = 150 g/mol, could be M of samarium, SmF3 possible, but not a molecule!**207-4·19 = 131, is M of Xe, therefore XeF4**D: could be Mg, but MgF3 does not exist*.  *sulphr, SF4 makes sense* |

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| *3.11.At first sight, A and C have very similar fornulae. In fact, their three dimensional structures are quite different. Sketch the three dimensional structures of both molecules using the VSEPR-theory, and find for both structures the point groups.*  |
| *TD* | *D4h*  |

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| *3.12. Write down a balanced equation for this synthesis.*  |
| *P4 + 6 H2 ⇄ 4 PH3* |

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| *3.13.Calculate the standard reaction enthalpy of process 3.12., and consequently the standard formation enthalpy of phosphane at 298 K.*  |
|  *1.25 kJ/mol* |
| *Calculation:**The equation in 3.6. follows from: (a) + (b) + 3×(c) - 4×(d)**-2984 – 415 - 3·572 + 4·1280 = 5.0 kJ for 4 mol ⇒ 1.25 kJ/mol* |

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| *3.14. Calculate the equilibrium constant of the phosphane synthesis at 300°C.*  |
| *K = 4,9·10-9* |
| *Calculation:* |

**Task 4 17points**

**Nitrogen-Heterocycles**

**Cimetidin, an antagonist for histamine receptors**

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| *4.1. Draw the constitutional formulae of* ***A, B, D****,* ***E,*** *and* ***F****.*  |
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| *4.2. Which type of reaction is meant by the conversion from* ***C*** *to* ***E****, and from* ***E*** *to cimetidine (Look at the –CN-group!)* |
| *1,4-nucleophilic addition to a conjugated system, then elimination* |

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| *4.3. Draw the mechanism of the reaction* ***C****→****E****. Use for* ***C*** *R-NH2, and arrows to show the positions of the respective attacks.* |
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**B: Ketorolac, an inflammation inhibitor**

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| *4.4. Draw the structural formulae of* ***U, V, X****, and* ***Y****.* |
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| *4.5. What is the mechanism of the reaction* ***X***→***Y****? Think about AIBN.* |
| *radical cyclisation* |

**Ketorolac** appears as racemic mixture, whereby only the (*S*)-enantiomere has a medical effect.

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| *4.6. Draw the structure of the (S)-enantiomere of ketorolac.*  |
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**C. Norflurazon and Diclomezin, two herbicides belonging to the pyridazinon-type**

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| *4.7. Draw the structural formulae of* ***G, H,*** *and* ***J****.* |
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| *4.8. Write down the formula of the reaction product of a carboxylic acid RCOOH with hydrazine. How do you call this class of substances?* |
| *formula:**RCONHNH*2 | *name:**acid hydrazides, hydrazides* |

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| *4.9. Write down the formula of the reaction product of an aldehyde RCHO with hydrazine.*  *How do you call this class of substances?* |
| *formula:**RCH=NNH2* | *name:**hydrazone* |

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| *4.10. Allocate the two N-atoms in compound* ***I*** *to the classes of compounds from above.* |
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In reaction **H** →**I**, mucochloro acid is involved. Some sub-tasks for this issue:

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| *4.11. Draw the possible stereo isomers of mucochloro acid.* |
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| *4.12. Write down a balanced equation for this reaction.*  |
| *C5H4O2 + 5 Cl2 + 3 H2O → C4H2Cl2O3 + CO2 + 8 HCl*  |

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| *4.13. Mucochloro acid may also occur in a tautomeric cyclic form* ***K****.*  *Draw the structural formulae of* ***K****.*  |
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| *4.14. Write down the molecular formula for the particle which causes the peak at 126 m/e.* |
| *[C3H235Cl37ClO]+* |

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| *4.15. Draw the structure formulae of the compounds* ***L****,* ***M****,* ***N****, and* ***O****.* |
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