

Uniting Elements, Strengthening Bonds, Shaping Tomorrow!

30th Baltic Chemistry Olympiad Tartu, Estonia, May 4th-6th, 2024

Theoretical exam solutions

Student's code:

May 5^{th} , 2024 Tartu, Estonia

Problem 1. Polygonal chemistry. Author: Siim Kaukver

a) Dinitro(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)palladium(II) *(2 pts)*

b) Structures of **A1−A4** and **B1−B2**: *Each correct structure gives 3 points. (18 pts)*

c) $a = 3, b = 4$ *(2 pts)*

d) First, *ΔH* has to be found using the Van't Hoff equation:

$$
\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)
$$

Substituting $T_1 = 313$ K, $T_2 = 333$ K, $K_1 = 21.5$ and $K_2 = 32.1$ and calculating, we get Δ*H* = 17.38 kJ⋅mol−1. *(3 pts)*

A new equation can now be written to calculate *K*3. It can be assumed Δ*H* is constant in the given temperature range. Whether *K*³ is found via *K*¹ or *K*² makes no difference − both approaches are equally valid.

$$
\ln\left(\frac{K_3}{K_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right)
$$

By substituting known parameters and calculating, we get *K*³ = **26.4**. *(3 pts)*

- **e)** Equilibrium constant *K* for the reaction $3\textbf{A} \rightleftharpoons 4\textbf{B}$ can be written as $K = \frac{[\textbf{B}]^4}{[413]}$ $[A]$ ³ . *(1 pt)*
	- Let the ratio $\frac{[\mathbf{B}]}{[\mathbf{A}]}$ be equal to *x*. Hence, $K = [\mathbf{B}] \cdot x^3$. *(2 pts)*

Mass balance for Pd:
$$
c_0 = 4 \cdot [A] + 3 \cdot [B]
$$
. (2 pts)

By dividing the mass balance equation by $[B]$, the following equation is obtained:

$$
\frac{c_0}{[\mathbf{B}]} = \frac{4}{x} + 3 \text{ , from which } [\mathbf{B}] = \frac{c_0 x}{3x + 4}.
$$
 (2 pts)

Now, *K* can be expressed as: $K = [\mathbf{B}] \cdot x^3 = \frac{c_0 x^4}{2 \pi G}$ $3x + 4$. *(1 pt)*

Finding the exact solution is impossible under exam conditions, but a simplification can be made.

As 3*x* >> 4, it can be assumed that 3*x* + 4 \approx 3*x*. Therefore, $K = \frac{c_0 x^4}{2g}$ $\frac{c_0 x^4}{3x+4} \approx \frac{c_0 x^3}{3}$ 3 . *(3 pts)*

Finally,
$$
x = \sqrt[3]{\frac{3K}{c_0}} = \sqrt[3]{\frac{3 \cdot 26.4}{1.154 \cdot 10^{-3}}} \approx 41.
$$
 (1 pt)

Note: the exact solution is x = 41.38, hence the simplification is justified.

Problem 2. Unknown amino acid. Author: Andreas Päkk

- **a)** $n(N) = n(NH_3) = n(HCl) n(NaOH)$ *(1 pt) n*(N) = 0.1350 mol⋅dm⁻³ ⋅ 0.04000 dm³ − 0.1500 mol⋅dm⁻³ ⋅ 0.01683 dm³ = 0.002875 mol $w(N) = \frac{0.002875 \text{ mol} \cdot 14.01 \text{ g} \cdot \text{mol}^{-1}}{0.3425 \text{ g}} \cdot 100\% \approx 11.76\%$ *(1 pt)*
- **b)** Ammonium ions, which remain in the titrated solution, act as a weak acid: $NH_4^+ \rightleftharpoons NH_3 + H^+$

As the equilibrium is considerably shifted to the left, $[H^+]_{eq} = [NH_3]_{eq}$, therefore:

$$
K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{[H^+]^2}{[NH_4^+]} \implies [H^+] = \sqrt{K_a \cdot c(NH_4^+)} = \sqrt{K_a \cdot \frac{n(HCl) - n(NaOH)}{V(HCl) + V(NaOH)}}
$$
(2 pts)

$$
pH = -\log[H^+] = -\log\left(\sqrt{5.6 \cdot 10^{-10} \cdot \frac{0.002875 \text{ mol}}{0.05683 \text{ dm}^3}}\right) \approx 5.27
$$
 (1 pt)

c) Since **X** has two given dissociation constants, it can be assumed that there is only one ionizable amino group in its structure. The general formula of amino acids is R−CH(NH2)COOH or R-CH(NH₃⁺)COO⁻ (zwitterionic form), where the R group represents a specific side chain. $M(R) = \frac{1.14.01 \text{ g} \cdot \text{mol}^{-1} \cdot 100\%}{11.76\%} - M(C_2H_4NO_2) = 45.07 \text{ g} \cdot \text{mol}^{-1}$ 11.76% *(1 pt)*

R corresponds to the hydroxylated carbon chain CH3CH(OH)−, thus the condensed structural formula of **X** is CH3CH(OH)CH(NH2)COOH or CH3CH(OH)CH(NH³ ⁺)COO[−] (Thr). *(1 pt)*

d) *Each correctly drawn stereochemical structure gives 1 point − in total 4 points. Each pair of correct configuration indications (S/R) gives 0,5 points − in total 2 points.*

e) *Each correctly drawn stereochemical ionic form gives 1 point − in total 3 points.*

f) Two-step dissociation of **X**: *(2 pts)*

1. H₂A⁺
$$
\rightleftharpoons
$$
 H⁺ + HA $K_{a1} = \frac{[H^+][HA]}{[H_2A^+]} \Rightarrow [H_2A^+] = \frac{[H^+][HA]}{K_{a1}}$
\n2. HA \rightleftharpoons H⁺ + A⁻ $K_{a2} = \frac{[H^+][A^-]}{[HA]} \Rightarrow [A^-] = \frac{K_{a2}[HA]}{[H^+]}$

At the isoelectric point [H2A+] = [A−], therefore: *(4 pts)*

$$
\frac{[H^+][HA]}{K_{a1}} = \frac{K_{a2}[HA]}{[H^+]} \implies \frac{[H^+]}{K_{a1}} = \frac{K_{a2}}{[H^+]} \implies [H^+] = \sqrt{K_{a1}K_{a2}} = \frac{K_{a1}K_{a2}}{2}
$$

$$
pH = -\log[H^+] = \frac{-\log K_{a1} - \log K_{a2}}{2} = \frac{pK_{a1} + pK_{a2}}{2} = \frac{2.09 + 9.10}{2} \approx 5.60
$$

Problem 3. Reverse engineering. Author: Ritums Cepītis

- **a)** $\ln[A] = \ln[A]t kt$, where $k = \frac{\ln(0.05) \ln(1)}{30.05}$ $\frac{339 - m(1)}{30 \text{ s}} = 0.1 \text{ s}$ **−1** *(2 pts)*
- **b**) $k_{300} = 0.1 \text{ s}^{-1}$; $k_{2024} = 1.0 \text{ s}^{-1}$ $\ln\left(\frac{k_{300}}{k}\right)$ $\frac{k_{300}}{k_{2024}}$ = $\frac{E_a}{8.314}$ $\left(\frac{1}{202}\right)$ $\frac{1}{2024} - \frac{1}{300}$, where *E*_a = **6.7 kJ⋅mol**⁻¹ *(3 pts)*
- **c)** *T*¹ and *t*2. *(2 pts)*
- **d)** If T_1 is chosen, the answer is $T_1 = 1230$ K. *(2 pts)*
- If t_2 is chosen, the answer is $t_2 = 3.79 \cdot 10^{-8}$ **s**. *(2 pts)*
- **e)** The equations for the missing elementary steps: *(4 pts)*

 $A \rightarrow A' + B$ *k*₁ $A' + B \rightarrow A$ *k*−1 $A' + B \rightarrow B' + B + C$ *k*₂ $A' + B' \rightarrow 2B$ *k*₃

Mechanism correspondance to the given reaction law:

$$
\frac{d(B')}{dt} = 0 = k_2[A'][B] - k_3[A'][B'] \Rightarrow [B'] = \frac{k_2[A'][B]}{k_3[A']} = \frac{k_2[B]}{k_3}
$$

\n
$$
\frac{d(A')}{dt} = 0 = k_1[A] - k_{-1}[A'][B] - k_2[A'][B] - k_3[A'][B'] =
$$

\n
$$
= k_1[A] - k_{-1}[A'][B] - k_2[A'][B] - k_2[A'][B'] =
$$

\n
$$
= k_1[A] - [A'](k_{-1}[B] + 2 \cdot k_2[B])
$$

\n
$$
\Rightarrow [A'] = k_1[A]
$$

\n
$$
-\frac{d(A)}{dt} = k_1[A] - k_{-1}[A'][B] = k_1[A] - \frac{k_{-1}k_1[A]}{(k_{-1} + 2 \cdot k_2)} = (\frac{2 \cdot k_{-1}k_1}{k_{-1} + 2 \cdot k_2}) [A]
$$

Problem 4. Have you heard about cerium? Author: Deimantas Šmigelskas

Part I. Minerals

- **a**) There are 4 tetrahedral PO₄^{3−} ions and 4 Ce atoms in a unit cell which consists of 24 atoms in total. *(1 pt)*
- **b) Th** isotopes are radioactive while La and Nd have stable isotopes. *(1 pt)*
- **c)** $\Delta m = n(U) \cdot M(U) n(Ce) \cdot M(Ce) = 4.53 g$

$$
97.91n = 4.53 \implies n = 0.0463 \tag{1 pt}
$$

$$
\frac{n}{n_0} = \frac{0.0463}{\frac{m(\text{CePO}_4)}{M(\text{CePO}_4)}} = 0.71
$$
 (1 pt)

d) $N_n({}^{238}_{92}U) = N_0 e^{-\lambda_U t}$

Since there was no pre-existing lead in the mineral: $N_0 = N_n \frac{^{238}}{92}U + N_n \frac{^{206}}{82}Pb$ (1 *pt*)

$$
\frac{N_n(^{238}_{92}U)}{N_n(^{238}_{92}U) + N_n(^{206}_{82}Pb)} = e^{-\lambda_U t} \implies \ln\left(\frac{N_n(^{238}_{92}U)}{N_n(^{238}_{92}U) + N_n(^{206}_{82}Pb)}\right) = -\lambda_U t \implies
$$
\n
$$
t = \frac{\ln\left(\frac{N_n(^{238}_{92}U)}{N_n(^{238}_{92}U) + N_n(^{206}_{92}Pb)}\right)}{-\lambda_U} = \frac{\ln\left(\frac{N_n(^{238}_{92}U) + N_n(^{206}_{82}Pb)}{N_n(^{238}_{92}U)}\right)}{\lambda_U} = \frac{\ln\left(1 + \frac{N_n(^{206}_{92}Pb)}{N_n(^{238}_{92}U)}\right)}{\lambda_U}
$$
\n
$$
\lambda = \frac{\ln(2)}{t_{0.5}}
$$
\n(2 pts)

Moles of atoms can be used instead of the number of atoms and Pb mass is 206 because of $238U \rightarrow 206Pb$ decay.

$$
t = \frac{\ln\left(1 + \frac{n_n\left(\frac{206}{82}Pb\right)}{n_n\left(\frac{238}{92}\right)}\right)}{\frac{\ln(2)}{t_{0.5}}} = \frac{\ln\left(1 + \frac{\frac{6.05 \text{ g} \cdot 0.0001}{222 \text{ g} \cdot \text{mol}^{-1}}}{524 \text{ g} \cdot \text{mol}^{-1}}\right)}{\ln(2)} \cdot t_{0.5} = 0.0453 \cdot t_{0.5} = 0.202 \text{ billion}
$$
 (1 pt)

e) 1 mol of CO³ 2− produces 1 mol of CO2, which gives:

$$
n(\text{CO}_3^{2-}) = \frac{m(\text{CO}_2)}{M(\text{CO}_2)} = 0.014224 \text{ mol}
$$
 (0.5 pts)

$$
M(Ce_{0.48}La_{0.37}Nd_{0.1}Pr_{0.04}Sm_{0.01}CO_3F) = \frac{m}{n(CO_3^{2-})} = 219.235 \text{ g} \cdot \text{mol}^{-1}
$$
 (0.5 pts)

Mass balance: *(1.5 pts)*

$$
x \cdot M(La) + y \cdot M(Nd) = 219.235 - n(Ce) \cdot M(Ce) - n(Pr) \cdot M(Pr) - n(Sm) \cdot M(Sm) - n(C)
$$

$$
M(C) - n(0) \cdot M(0) - n(F) \cdot M(F) \tag{0.5 pts}
$$

$$
x \cdot M(\text{La}) + y \cdot M(\text{Nd}) = 65.827 \tag{1 pt}
$$

Charge balance: *(0.5 pts)*

$$
3 \cdot [n(Ce^{3+}) + n(La^{3+}) + n(Nd^{3+}) + n(Pr^{3+}) + n(Sm^{3+})] = 2 \cdot n(CO_3^{2-}) + n(F^-)
$$

(La³⁺) + n(Nd³⁺) = 0.47 (1 pt)

The system of equations yields:

$$
\begin{cases} x \cdot M(\text{La}) + y \cdot M(\text{Nd}) = 65.827 \\ x + y = 0.47 \end{cases} \Rightarrow (x; y) = (0.37; 0.1)
$$

Ce0.48La0.37Nd0.1Pr0.04Sm0.01CO3F *(1 pt)*

- **f)** There are 6 atoms closely located to cerium in the same plane plus 3 above and 3 below the plane − in total 12 atoms, which means the coordination number of Ce is **12**. *(1 pt)*
- **g**) $2CeO₂ + 8HCl → 2CeCl₃ + 4H₂O + Cl₂$ *(1 pt)*

$$
n(HCI) = 4 \cdot n(CeO_2) = 4 \cdot \frac{5.0 \cdot 10^3 \text{ kg} \cdot w(Ce)}{M(Ce) \cdot 100\%} = 45675.14 \text{ mol}
$$

V(HCI) = $\frac{n}{c}$ = 91350.27 dm³ \approx **93 m³** (1 pt)

h) β-cerium (*a* = 0.3681 nm, *c* = 1.1857 nm). DHCP structure can be subdivided into 6 rhombic prism unit cells each of which has 2 atoms inside it: *(2.5 pts)*

$$
\rho = \frac{m(\text{atoms})}{v(\text{unit cell})} = \frac{2 \cdot \frac{M(Ce)}{N_A}}{\frac{\sqrt{3}}{2}a^2 \frac{c}{2}} = 6.69 \text{ g}\cdot\text{cm}^{-3}
$$

γ-cerium (*a* = 0.5161 nm). FCC unit cell contains 4 atoms of Ce: *(2 pts)*

$$
\rho = \frac{m(\text{atoms})}{V(\text{unit cell})} = \frac{4 \cdot \frac{M(\text{Ce})}{N_A}}{a^3} = 6.77 \text{ g}\cdot\text{cm}^{-3}
$$

Thus, γ-cerium is more dense than β-cerium. *(0.5 pts)*

Part II. Cerium loves redox

i) H⁺ + [Ce(NO₃)₆]^{2−} + Fe(OH)₂ + Cu₂O → Ce³⁺ + Fe³⁺ + Cu²⁺ + H₂O + NO₃[−]

Oxidation half-equations:

 $2H^+ + Fe(OH)_2 \rightarrow Fe^{3+} + 2H_2O + e^-$ | · 4 *(0.5 pts)*

 $2H^+ + Cu_2O → 2Cu^{2+} + + 2e^-$ | · 1 *(0.5 pts)*

Reduction half-equation:

 $[Ce(NO₃)₆]²⁻ + e^- \rightarrow Ce³⁺ + 6NO₃$ [−] │· 6 *(0.5 pts)*

The sum of oxidation and reduction half-equations:

10H⁺ + **6**[Ce(NO₃)₆]²⁻ + **4**Fe(OH)₂ + Cu₂O → **6**Ce³⁺ + **4**Fe³⁺ + **2**Cu²⁺ + **9**H₂O + **36**NO₃⁻ (0.5 *pts*) **j)** The structrure of the anion of CAN: *(1 pt)*

k) *Each identified compound A−C gives 1 point. (3 pts)* **A** must contain Ce and O. Hydrogen in water is a weak oxidizing agent, so Ce will be in +3 form, and out of Ce2O3, CeO(OH), Ce(OH)3, or other non-polymeric formulas, Ce(OH)³ gives the right answer. In the second reaction peroxide ion is consumed and water is produced, meaning that the HO² [−] ion has lost its hydrogen and replaced two OH[−] ions in hydroxide resulting in **B**

6

 $Ce(O₂)OH$ (Ce cannot be +4 here because no oxidation occurrs for cerium). However, anhydride $Ce₂(O₂)₂O$ formed after dimerization of $Ce(O₂)OH$ followed by H₂O abstraction is also a possible choice. Ce must be +4 in **C** due to oxidation and since all oxygens have the same oxidation number CeO₂ or Ce(OH)₄ are possible. The absence of stronger base to deprotonate OH⁻ leaves us with the choice of Ce(OH)4.

Balanced reaction equations: *(3 pts)*

- **i)** $2Ce + 6H_2O \rightarrow 2Ce(OH)_3 + 3H_2$
- **ii)** $Ce(OH)_{3} + HO_{2}^{-}$ → $Ce(O_{2})OH + H_{2}O + OH^{-}$ or 2Ce(OH)₃ + 2HO₂[−] → Ce₂(O₂)₂O + 3H₂O + 2OH[−]
- **iii)** $2Ce(O₂)OH + 3H₂O + OH⁻ → 2Ce(OH)₄ + HO₂$ or Ce2(O2)2O + 4H2O + OH⁻ → 2Ce(OH)₄ + HO₂⁻
- **l)** Ceria (CeO₂) plays a special role in heterogeneous catalysis. In the ideal cell of CeO₂, the structure consists of a **face-centered** cubic unit cell of cations with anions occupying the **tetrahedral** holes. In the structure, each cerium cation is coordinated by **8** nearest-neighbor oxygen anions, while each oxygen anion is coordinated by **4** nearest-neighbor cerium cations. Ceria can also be doped with other metal cations to alter electric conductivity. When cerium cations are replaced with lower oxidation state elements (M^2*/M^{3+}) , the lattice oxygen atoms in CeO² are **removed**. The ceria crystal usually exhibits a few defects due to the co-existence of Ce4+ and **Ce3+** ions. /…/ Because the metal surfaces are essentially saturated in CO when excess CO is present, the rate-limiting step for the reaction is **2**. /…/ *(3 pts)*

- **7.** $Ce_2O_3 + H_2O → 2CeO_2 + H_2$ *(1 pt)*
- **o)** Ce(5,5'-(Cl)₂-salen)₂ is a stronger oxidizing agent, because methoxy-substituted aromatic rings are more electron-rich, therefore, stabilizing central Ce(IV). *(1 pt)*

Problem 5. Poisonous chemicals. Author: Denis Sokol

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f) *Each correct structure gives 2 points − in total 8 points. (8 pts)*

Hydrolysis reactions with aqueous sodium hydroxide:

g) G *(2 pts)*

Problem 6. Simple organic chemistry. Author: Nauris Narvaišs

e) Number of possible stereoisomers and products: *1 point for each correct answer. (4 pts)*

f) *1 pt for formation of iodonium, 1 pt for attack on iodonium, 1 pt for cyclization, 1 pt for attack of second carboxylate. If mechanism is just 2 SN2 reactions, then 2 pts total. If relative stereochemistry is incorrect or missing, then 1 pt deduction.*

Simplified mechanism:

h) *1 pt for bromonium formation, 2 pts for rearrangement, 1 point for elimination. 0.5 pts for E² instead of E1CB.*

