

2022/23. õa keemiaolümpiaadi piirkonnavooru ülesanded

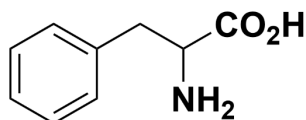
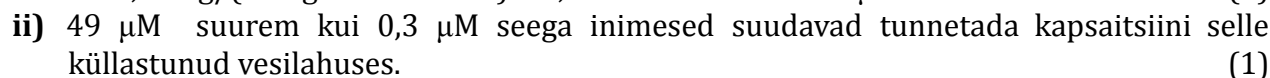
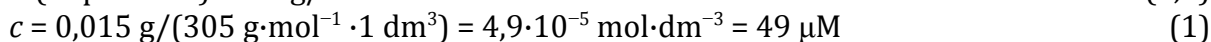
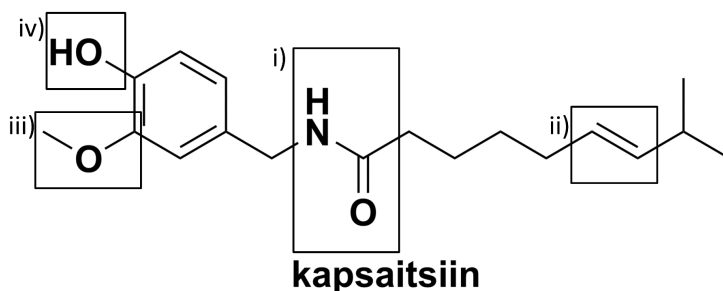
11.–12. klass

Lahendused

1. Kuum keemia (10 p)

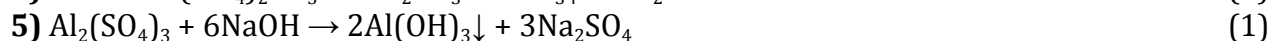
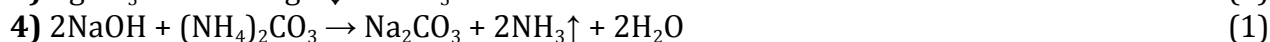
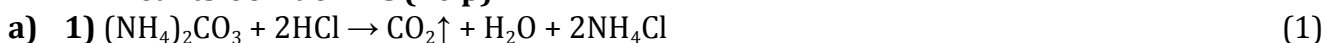
Allikas: Han, P., Müller, L. & Hummel, T. Peri-threshold Trigeminal Stimulation with Capsaicin Increases Taste Sensitivity in Humans. *Chem. Percept.* 15, 1–7 (2022).

<https://doi.org/10.1007/s12078-021-09285-4>



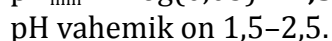
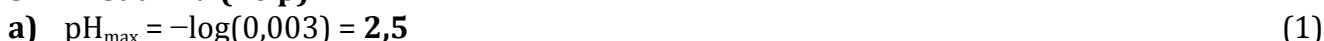
10 p

2. Tilkreaktsioonide ABC (10 p)



10 p

3. Ensüümid (10 p)



b) pH vahemik kattub pepsiini isoensüümide pH optimumi vahemikuga (1,9–2,9). Seega, osa pepsiini isoenüümidest on maomahlas maksimaalselt aktiivsed. (1)

c) i) Oletame et meil on 1 dm³ äädikat, siis 4% oleks $V_{\text{äädikhape}} = 0,04 \text{ dm}^3$. Äädika tihedus on $\sim 1 \text{ g}\cdot\text{cm}^{-3}$. Seega äädika kontsentratsioon on

$$c \approx 0,04 \text{ dm}^3 \cdot 1000 \text{ g}\cdot\text{dm}^{-3} / (60 \text{ g}\cdot\text{mol}^{-1}) = 0,7 \text{ mol}\cdot\text{dm}^{-3} \quad (1)$$

Kuna tegemist on nõrga happega siis $[\text{CH}_3\text{COOH}] \approx [\text{happe üldkontsentratsioon}]$, ning $[\text{CH}_3\text{COO}^-] \approx [\text{H}^+] = x$.

$$K_a = x^2 / 0,7 = 1,74 \cdot 10^{-5} \Rightarrow x = 0,0034 \quad (1)$$

$$\text{pH} = -\log(0,0034) = 2,5 \quad (0,5)$$

ii) $c \approx 0,18 \text{ dm}^3 \cdot 1000 \text{ g}\cdot\text{dm}^{-3} / (60 \text{ g}\cdot\text{mol}^{-1}) = 3 \text{ mol}\cdot\text{dm}^{-3}$ (1)

$$K_a = x^2 / 3 = 1,74 \cdot 10^{-5} \Rightarrow x = 0,0072 \quad (1)$$

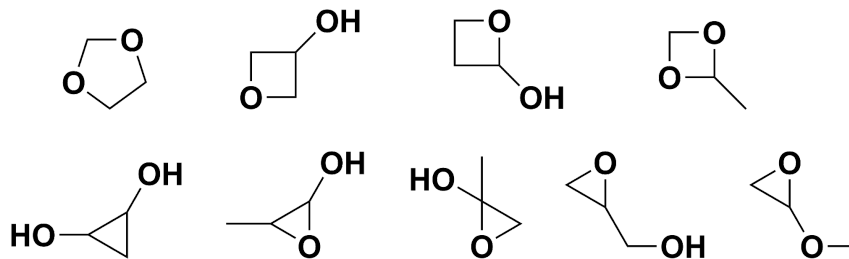
$$\text{pH} = -\log(0,0072) = 2,1 \quad (0,5)$$

d) Amülaas ja lipaas ei ole äädikas maksimaalselt aktiivsed (2)

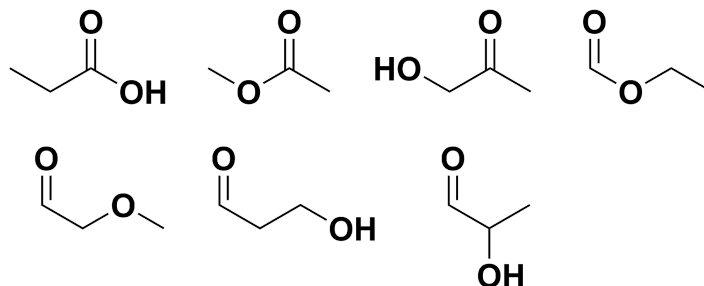
10 p

4. Tautomeeria (10 p)

a) (8×0,5)



b) (7×0,5)



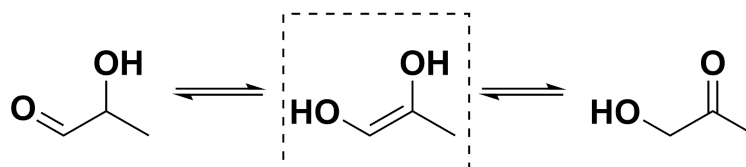
c) i) jah (1)

ii) ei (deprotoneerimine) (1)

iii) jah (1)

iv) ei (Beckmanni ümberasetus) (0,5)

d) (0,5)



10 p

5. Radikaalkaskaadreakstioon (10 p)

Allikas: *J. Am. Chem. Soc.*, **107**(5): 1448–1449. 1985.

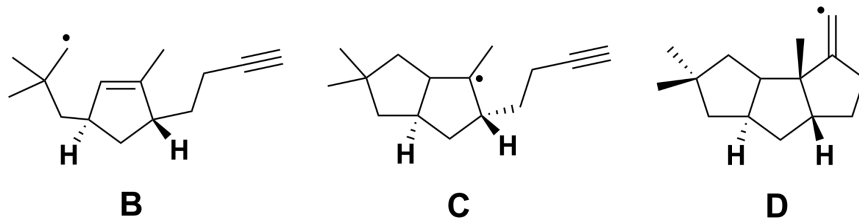
a) Gaas X on lämmastik - N₂ (0,5)

b) UV-kiirgusega kiiritamisel (0,5)

c) i) AIBN on **plahvatusohtlik**. Lisaks on nii AIBN kui ka selle lagunemisel tekkivate radikaalide ühinemisel moodustuvad ühendid **mürgised**.

ii) Bu₃SnH on **mürgine** lenduv äärmiselt ebameeldiva lõhnaga ühend. (2)

- d) Keemilised sidemed tekivad süsinikuaatomite **15 ja 8** ning **9 ja 2** vahel.
 e) Kuna AIBN on initsiaator, piisab ka **vähem kui stöhhiomeetrilisest kogusest.** (1)
 f) **Y** – Bu₃SnI ehk (CH₃CH₂CH₂CH₂)₃SnI ehk C₁₂H₂₆SnI. (1)
 g)



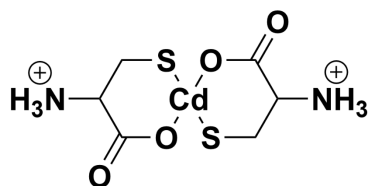
10 p

6. Kvanttäpid (20 p)

Allikas: Adapteeritud 55. Mendelejevi keemiaolümpiaadi I vooru ülesanne.

- a) $M(X) = 1,00 \text{ g} \cdot 2,96485 / (1,00 \text{ A} \cdot 28,6 \cdot 60 \text{ s}) = \mathbf{112 \text{ g} \cdot \text{mol}^{-1}}$ (1)
 X on Cd
 $M(\text{H}_2\text{Y}) = 3,26 \text{ g} \cdot \text{dm}^{-3} \cdot 8,314 \text{ dm}^3 \cdot \text{kPa} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 298,15 \text{ K} / (10^3 \text{ kPa}) = \mathbf{80,8 \text{ g} \cdot \text{mol}^{-1}}$ (1)
 Y on Se
 $M(\text{XY}) = 4/3 \cdot 3,1416 \cdot (3,3 \cdot 10^{-7} \text{ cm})^3 \cdot 5,81 \text{ g} \cdot \text{cm}^{-3} \cdot 6,022 \cdot 10^{23} / 2730 = \mathbf{193 \text{ g} \cdot \text{mol}^{-1}}$ (1)
 XY on CdSe
- b) 1) $2\text{Se} + 4\text{NaBH}_4 + 7\text{H}_2\text{O} = 2\text{NaHSe} + \text{Na}_2\text{B}_4\text{O}_7 + 14\text{H}_2$ (1)
 2) $2\text{NaHSe} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{Se}$ (1)
 3) $\text{H}_2\text{Se} + \text{CdCl}_2 + 2\text{NaOH} = \text{CdSe} + 2\text{NaCl} + 2\text{H}_2\text{O}$ (1)
 4) $\text{CdCl}_2 + 2\text{CH}_3\text{MgCl} = \text{Cd}(\text{CH}_3)_2 + 2\text{MgCl}_2$ (1)
 5) $\text{Se}[\text{Si}(\text{CH}_3)_3]_2 + \text{Cd}(\text{CH}_3)_2 = \text{CdSe} + 2\text{Si}(\text{CH}_3)_4$ (1)
 6) $\text{CdCl}_2 + 4\text{NH}_3 = [\text{Cd}(\text{NH}_3)_4]\text{Cl}_2$ (1)
 7) $\text{SeO}_2 + 2\text{NaOH} = \text{Na}_2\text{SeO}_3 + \text{H}_2\text{O}$ (1)
 8) $2\text{Na}_2\text{SeO}_3 + 2[\text{Cd}(\text{NH}_3)_4]\text{Cl}_2 + 3\text{N}_2\text{H}_4 = 2\text{CdSe} + 8\text{NH}_3 + 3\text{N}_2 + 4\text{NaCl} + 6\text{H}_2\text{O}$ (1)
- c) i) $E_g^{mp} = 3,35 \cdot 10^{-19} \text{ J} - (6,63 \cdot 10^{-34})^2 / (8 \cdot (3,30 \cdot 10^{-9} \text{ m})^2 \cdot 0,730 \cdot 10^{-31} \text{ kg}) +$
 $+ 2 \cdot (1,60 \cdot 10^{-19} \text{ C})^2 / (4 \cdot 3,1416 \cdot 10,6 \cdot 8,854 \cdot 10^{-12} \text{ F} \cdot \text{m}^{-1} \cdot 3,30 \cdot 10^{-9} \text{ m}) =$
 $= \mathbf{2,79 \cdot 10^{-19} \text{ J}}$ (1)
 $\lambda(\text{mp}) = 6,63 \cdot 10^{-34} \text{ J} \cdot \text{s} / (2,79 \cdot 10^{-19} \text{ J}) \cdot 3,00 \cdot 10^8 \text{ m} \cdot \text{s}^{-1} \cdot 10^9 \text{ nm} \cdot \text{m}^{-1} = 713 \text{ nm}$ (1)
 Pooljuhul on **punane värv** (0,5)
- ii) $E_g^{kt}(2,0 \text{ nm}) = 2,79 \cdot 10^{-19} \text{ J} + (6,63 \cdot 10^{-34})^2 / (8 \cdot (2,00 \cdot 10^{-9} \text{ m})^2 \cdot 0,730 \cdot 10^{-31} \text{ kg}) -$
 $- 2 \cdot (1,60 \cdot 10^{-19} \text{ C})^2 / (4 \cdot 3,1416 \cdot 10,6 \cdot 8,854 \cdot 10^{-12} \text{ F} \cdot \text{m}^{-1} \cdot 2,00 \cdot 10^{-9} \text{ m}) =$
 $= \mathbf{4,54 \cdot 10^{-19} \text{ J}}$ (1)
 $\lambda(\text{mp}) = 6,63 \cdot 10^{-34} \text{ J} \cdot \text{s} / (4,54 \cdot 10^{-19} \text{ J}) \cdot 3,00 \cdot 10^8 \text{ m} \cdot \text{s}^{-1} \cdot 10^9 \text{ nm} \cdot \text{m}^{-1} = 438 \text{ nm}$ (1)
 Kvanttäpil on **sinine värv** (0,5)
- d) $\Delta G_1^\circ = -8,314 \cdot 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot (298 \text{ K} - 2,9 + 2,9 \cdot 10^4) = \mathbf{-234 \text{ kJ/mol}}$ (1)
 $\Delta G_2^\circ = -8,314 \cdot 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot (298 \text{ K} - 3,5 + 3,7 \cdot 10^4) = \mathbf{-199 \text{ kJ/mol}}$ (1)
- e) *Hindamine: mõlema õige struktuuri eest 1 p.* (2)

Peamine kompleks pH = 9 juures:



Peamine kompleks pH = 12 juures:

