

2024/25. õa keemiaolümpiaadi piirkonnavor

11.–12. klass

Lahendused

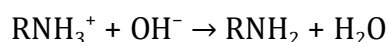
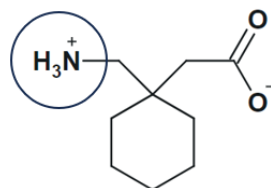
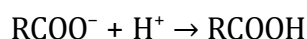
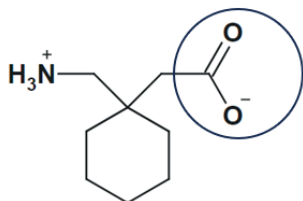
1. Test. Autor: Andreas Päkk

(10 p)

- a) i) $\text{pH} = -\log[\text{H}^+] \Rightarrow [\text{H}^+] = 10^{-\text{pH}} = 10^{-2} = 0,01 \text{ mol} \cdot \text{dm}^{-3}$ (1)
 ii) $\text{pH} = 14 - \text{pOH} = 14 - [-\log(0,02)] = 12,3$ (1)
 b) 1. aste: $\text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{H}^+$ (või $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+$) (0,5)
 2. aste: $\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$ (või $\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_3\text{O}^+$) (0,5)
 c) Võrreldes GABA-ga on GBP lipofiilsem, sest ühend sisaldab mittepolaarset tsüklohelsüülrühma, mis soodustab läbi hüdrofoobsete vastasmõjude rasvlahustuvust. (1)
 d) (1)

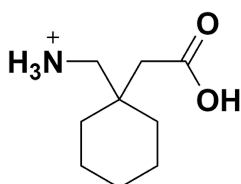
i) Brønstedti alus (liidab prootoni):

ii) Brønstedti hape (loovutab prootoni):

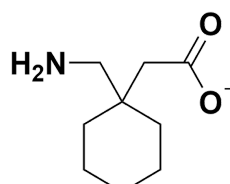


e)

(2×1)



B



C

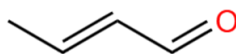
- f) $\text{p}K_a = -\log(K_a) = -\log(2,0 \cdot 10^{-4}) = 3,7$ (0,5)
 $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}]}{[\text{B}]}\right) \Rightarrow 10^{\text{pH}-\text{p}K_a} = \frac{[\text{A}]}{[\text{B}]}$ (1)
 $10^{\text{pH}-\text{p}K_a} = 10^{4,0-3,7} \approx 2$ ehk $\frac{2}{1}$. [A] : [B] suhe on vastavalt 2 : 1. (0,5)
 g) $m_{\text{gabapentiin}} = 300 \text{ mg} \cdot 0,5^4 = 18,75 \text{ mg}$ (1)

2. Heal ühendil mitu isomeeri. Autor: Andreas Päkk

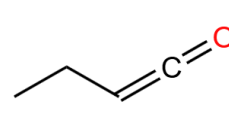
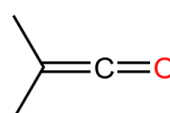
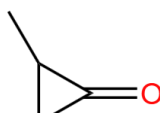
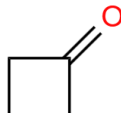
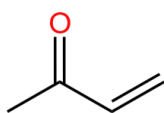
(10 p)

a)

(1)

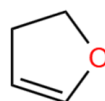
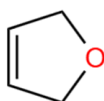


- b) $\text{C}_4\text{H}_6\text{O} + 5\text{O}_2 \rightarrow 4\text{CO}_2 + 3\text{H}_2\text{O}$ (1)
 c) i) Sobivad **kaks** järgmistest variantidest: (2×1)



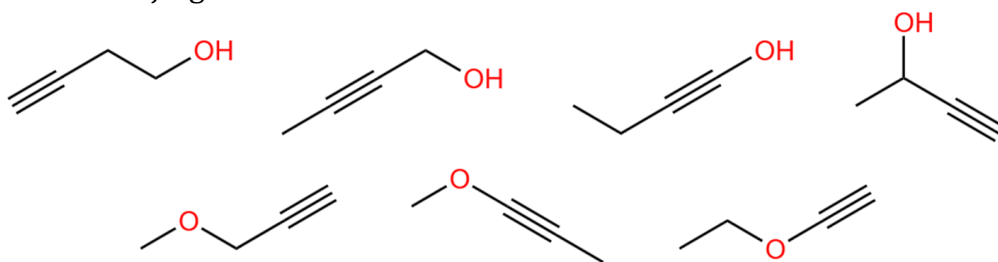
ii) Sobivad järgmised variandid:

(2×1)



iii) Sobivad **kaks** järgmistest variantidest:

(2×1)



d) $n(\text{C}_4\text{H}_6\text{O}) = m/M = (\rho \cdot V)/M = (0,856 \text{ g} \cdot \text{cm}^{-3} \cdot 10,5 \text{ cm}^3)/70,09 \text{ g} \cdot \text{mol}^{-1} = 0,128 \text{ mol}$ (1)

Kahte kaksiksidet (üks C=C kaksiksidi ja üks C=O kaksiksidi) sisaldava ühendi täielikuks hüdrogeenimiseks kulub 2 ekvivalenti H_2 :

$V(\text{H}_2) = n \cdot V_m = 2 \cdot 0,128 \text{ mol} \cdot 22,4 \text{ dm}^3 \cdot \text{mol}^{-1} = 5,73 \text{ dm}^3$ (1)

3. Värvilised olendid. Autor: Anette Kipso

(11,5 p)

a) i) Vesiniksoola valem:

$M_{\text{sool}} = M_{\text{anioon}}/w_{\text{anioon}} = 123,9 \text{ g} \cdot \text{mol}^{-1}/(1 - 0,3391) = 187,5 \text{ g} \cdot \text{mol}^{-1}$ (0,5)

$M_{\text{metall}} = M_{\text{sool}} \cdot w_{\text{katioon}} = 187,5 \text{ g} \cdot \text{mol}^{-1} \cdot 0,3391 = 63,58 \text{ g} \cdot \text{mol}^{-1}$, mis vastab vasele (Cu). (0,5)

Kui vase katiooni laeng on +2, peab aniooni laeng elektroneutraalsuse kohaselt olema -2.

Vesiniksoola anioonile vastab mittemetalli hapnikhape, seega saame välja kirjutada molaarmassi avaldis $M_{\text{anioon}} = x \cdot M(\text{H}) + M_{\text{element}} + y \cdot M(\text{O})$. Kui $x = 1$ ja $y = 3$, siis:

$M_{\text{element}} = 123,9 \text{ g} \cdot \text{mol}^{-1} - 1,008 \text{ g} \cdot \text{mol}^{-1} - 3 \cdot 16,00 \text{ g} \cdot \text{mol}^{-1} = 74,90 \text{ g} \cdot \text{mol}^{-1}$, mis vastab arseenile (As). (0,5)

Aniooni valemile vastab HAsO_3^{2-} . Vesiniksoola valem on **CuHAsO₃**. (1)

ii) Vesiniksoola nimetus: **vask(II)vesinikarseniit** (1)

b) $n(\text{H}_2\text{O}) = (499,4 - 0,0484)/2 \approx 12$ vee molekuli (0,5)

c) i) Kristallhüdraadi valem:

$M_x = 499,4 \text{ g} \cdot \text{mol}^{-1} \cdot 0,1041 \approx 52 \text{ g} \cdot \text{mol}^{-1}$ – metall **X** on Cr. (0,5)

$M_y = 499,4 - 12 \cdot 18,02 - 52 - 2 \cdot 96,06 \text{ (g} \cdot \text{mol}^{-1}) \approx 39 \text{ g} \cdot \text{mol}^{-1}$ – metall **Y** on K. (0,5)

Kristallhüdraadi valem on **CrK(SO₄)₂·12H₂O**. (0,5)

ii) Kristallhüdraadi nimetus: **kaaliumkroom(III)sulfaatdodekahüdraat** (1)

d) Olgu oksidi **Z** üldvalem E_mO_n , kus $w(\text{O}) = n \cdot M(\text{O})/[n \cdot M(\text{O}) + m \cdot M(\text{E})]$.

$0,2071 = n \cdot 16,00/[n \cdot 16,00 + m \cdot M(\text{E})] \Rightarrow M(\text{E}) = 61,26 n/m$ (2)

m	n	$M(\text{E})$	Element
2	1	30,63	–
1	1	61,26	–
2	3	91,89	–
1	2	122,5	–
2	5	153,1	–
1	3	183,8	W (volfram)

Oksidi **Z** valem on **WO₃**. (1)

e) i) Mineraali valem on **Na₂WO₄·2H₂O**. (1)

ii) Mineraali nimetus: **naatriumvolframaatdihüdraat** (1)

4. Hapud viinamarjad. Autor: Astrid Darnell

(9 p)

Allikas:

- Mehta, Lata & Hegde, Amitha & Thomas, Ann & Viridi, Mandeep. (2019). Acidogenic Potential of Packaged Fruit Juices and its Effect on Plaque and Salivary pH. *International journal of clinical pediatric dentistry*. 12(4). 312–317. <https://doi.org/10.5005/jp-journals-10005-1644>



b) $V_{\text{titrant}} = 5,7 \text{ cm}^3$ (1)

c) $n(NaOH) = cV = (5,7 \text{ cm}^3 / 1000 \text{ cm}^3 \cdot \text{dm}^{-3}) \cdot 0,25 \text{ mol} \cdot \text{dm}^{-3} = 1,425 \cdot 10^{-3} \text{ mol}$ (0,5)

$n_{\text{viinhape}} = \frac{1}{2} \cdot n(NaOH) = \frac{1}{2} \cdot 1,425 \cdot 10^{-3} \text{ mol} = 7,125 \cdot 10^{-4} \text{ mol}$ (0,5)

$m_{\text{viinhape}} = nM = 7,125 \cdot 10^{-4} \text{ mol} \cdot 150,9 \text{ g} \cdot \text{mol}^{-1} = 0,108 \text{ g}$ (0,5)

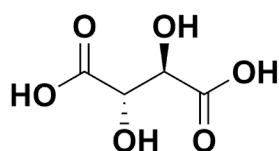
$c_{\text{viinhape}} = m/V = 0,108 \text{ g} / (20 \text{ cm}^3 / 1000 \text{ cm}^3 \cdot \text{dm}^{-3}) = 5,4 \text{ g} \cdot \text{dm}^{-3}$ (0,5)

d) 1. Liiga tumedas proovis ei ole indikaatori värvuse muutus nähtav.

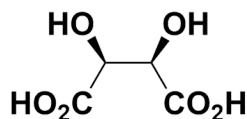
2. Samuti saab potentsiomeetrilise tiitrimise abil määrata lõpp-punkti asukoha täpsemalt kui indikaatoriga tiitrimisel, sest indikaatori nähtav värvimuutus ei pruugi olla täpselt tiitrimise stõhhiomeetriapunkti juures, vaid sellest natuke varem või hiljem. (2)

e) pK_a väärtuse järgi hinnates oleks võimalik kasutada **broomtümoolsinist** või **broomkresoolilillat**. (1,5)

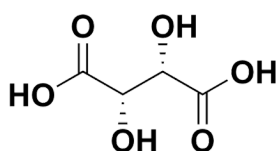
f) (3×0,5)



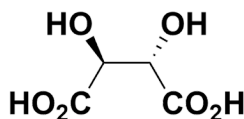
või



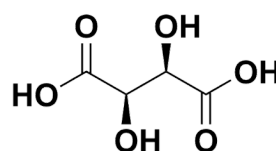
meso



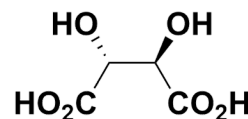
või



S,S



või



R,R

5. Depresso? Joo espressot! Autor: Nikita Žoglo

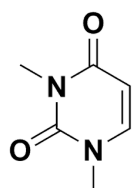
(10 p)

Allikas:

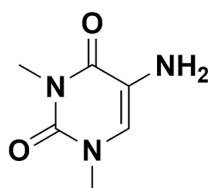
- Zajac, M. A., Zakrzewski, A. G., Kowal, M. G., & Narayan, S. (2003). A Novel Method of Caffeine Synthesis from Uracil. *Synthetic Communications*, 33(19), 3291–3297. <https://doi.org/10.1081/SCC-120023986>

a) Alküülrühm ja laktaam. (2×0,5)

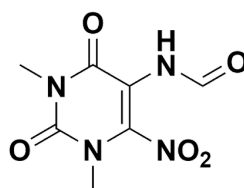
b) (4×1)



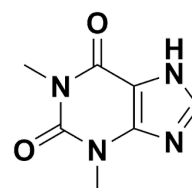
A



B



C



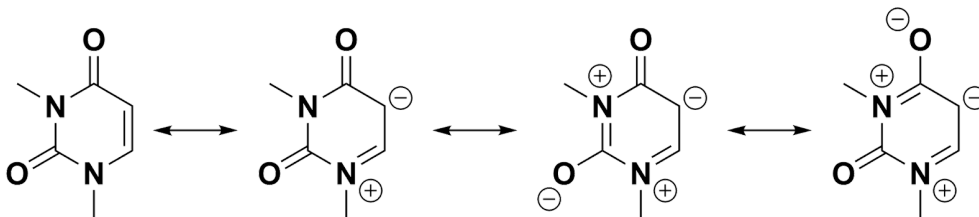
D

c) i) Reaktiivne osake, mis tekib HNO_3 reageerimisel H_2SO_4 -ga, on NO_2^+ . (0,5)



ii)

(0,5)



d) **Fe/CH₃COOH**

(1)

Teised variandid ei sobi. K₂Cr₂O₇ ja KMnO₄ on tugevad oksüdeerijad või pole piisavalt selektiivsed. LiAlH₄ on tugev redutseerija, mis võib ka karbonüülseid rühmi redutseerida.

e) Minimaalne kofeiini kogus on 3 mg/1 kg kehakaalu kohta, järelikut:

$$m_{\text{kofeiin}} = 75,0 \text{ kg} \cdot 3 \text{ mg} \cdot \text{kg}^{-1} = \mathbf{225 \text{ mg}}$$

(1)

f) i) $c_{\text{Coca-Cola}} = 0,100 \text{ g} \cdot \text{l}^{-1} = 0,100 \text{ mg} \cdot \text{ml}^{-1}$

$$V_{\text{Coca-Cola}} = m_{\text{kofeiin}} / c_{\text{Coca-Cola}} = 225 \text{ mg} / (0,100 \text{ mg} \cdot \text{ml}^{-1}) = \mathbf{2250 \text{ ml} = 2,25 \text{ l}}$$

(1)

$$\text{ii) } V_{\text{espresso}} = m_{\text{kofeiin}} / c_{\text{espresso}} = 225 \text{ mg} / (64,0 \text{ mg} / 30 \text{ ml}) \approx \mathbf{105 \text{ ml}}$$

(1)

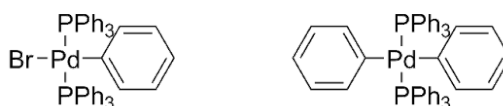
6. Katalüütilised tsüklid. Autor: Nikita Žoglo

(20 p)

Allikas:

- Kim, C.G. and Jun, J.-G. (2015), An Efficient Total Synthesis of Mulberrofuran B and L. Bull. Korean Chem. Soc, 36, 2278-2283. <https://doi.org/10.1002/bkcs.10442>

a) Hindamine: Iga korrektselt joonistatud struktuurivalem (cis/trans) annab 1 p, kokku 2 p. (2×1)



X1

X2

b) Hindamine: Iga korrektne väärtus annab 0,5 p, kokku 5 p.

(10×0,5)

	A1	A2	A3	A4	A5
ΔOS_{Pd}	0	0	+2	0	-2
ΔCN_{Pd}	-2	+2	+2	0	-2

c) Hindamine: Iga korrektselt valitud vastusevariant annab 0,5 p, kokku 2,5 p.

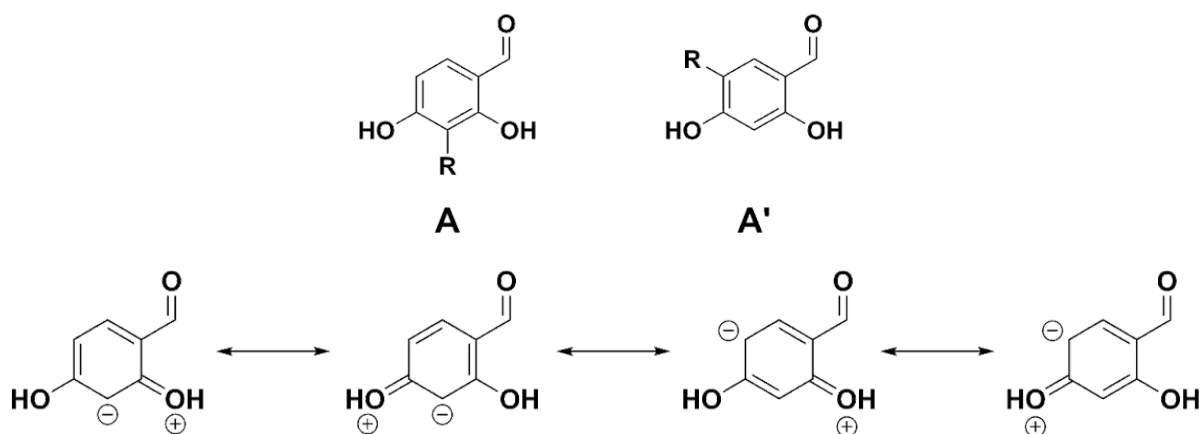
(5×0,5)

	A1	A2	A3	A4	A5
Transmetalleerimine				×	
Redutseeriv elimineerimine					×
Oksüdatiivne liitumine			×		
Ligandide dissotsieerumine	×				
Ligandide assotsieerumine		×			

d) Pd aatomiga seotud rühmad on steeriliselt mahukad

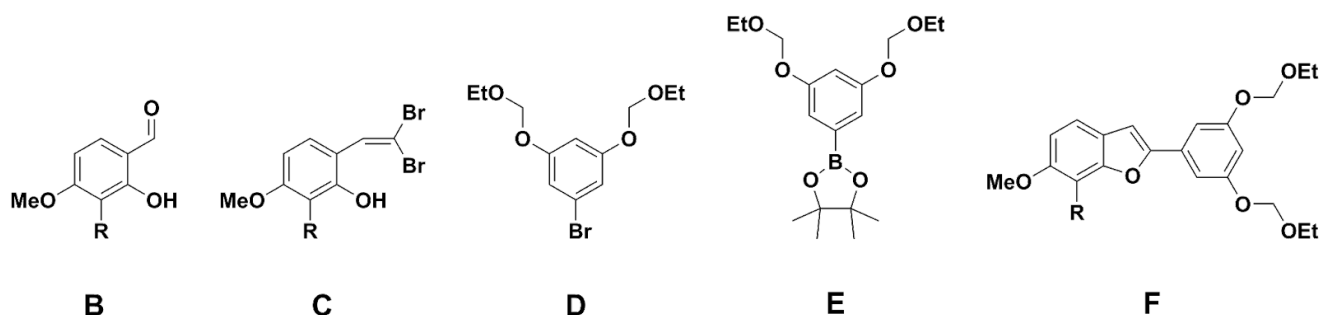
(0,5)

- e) Hindamine: Iga korrektselt joonistatud struktuurivalem ja resonantsstruktuur, kus negatiivne laeng on näidatud metaasendis paikneva aldehüüdrühma suhtes annab 1 p, kokku 4 p. (4×1)



- f) Friedel-Craftsi alküülimine (0,5)

- g) Hindamine: Iga korrektselt joonistatud struktuurivalem annab 1 p, kokku 5 p. (5×1)



- h) Hüdroksüülrühmade kaitsmine (0,5)