2006/2007 õa keemiaolümpiaadi lõppvooru ülesannete lahendused
11. klass

1. a) Oletame, et mineraali valem on $(FeSO_4)_x[Fe_2(SO_4)_3]_y \cdot zH_2O$, siis
M_r(mineraal) = 152 · x + 400 · y + 18 · z

$M_r(\text{melanteriit}) = \frac{55{,}85}{0{,}2009} = 278$ **$FeSO_4 \cdot 7H_2O$** (x = 1, y = 0, z = 7)

$M_r(\text{szomolnokiit}) = \frac{55{,}85}{0{,}3286} = 170$ **$FeSO_4 \cdot H_2O$** (x = 1, y = 0, z = 1)

$M_r(\text{römeriit}) = \frac{55{,}85(x+2y)}{0{,}2084} = 268(x + 2y)$

Kui x = y = 1, siis M_r(römeriit) = 804 ja z = 14 **$FeFe_2(SO_4)_4 \cdot 14H_2O$**

$M_r(\text{korneliit}) = \frac{55{,}85(x+2y)}{0{,}2123} = 263(x + 2y)$

Kui x = 0 ja y = 1, siis M_r(korneliit) = 526 ja z = 7 **$Fe_2(SO_4)_3 \cdot 7H_2O$**

b) M_r(kopiapiit) = 152 · x + 400 · y + 18 · y – w · (96,07 – 2 · 17,02)

$M_r(\text{kopiapiit}) = \frac{55{,}85(x+2y)}{0{,}2234} = 250(x + 2y)$ **$FeFe_4(SO_4)_6(OH)_2 \cdot 20H_2O$**

(x = w = 1, y = 2, z = 20)

Oletame, et mineraali valem on $Fe_k(H_3O)_l(SO_4)_m \cdot nH_2O$, siis
M_r(romboklaas) = 55,85 · k + 19,03 · l + 96,07 · m + 18 · n
(laengubilanss: 3 · k + l = 2 · m)

$M_r(\text{romboklaas}) = \frac{55{,}85 \cdot k}{0{,}1739} = 321k$ **$(H_3O)Fe(SO_4)_2 \cdot 3H_2O$**

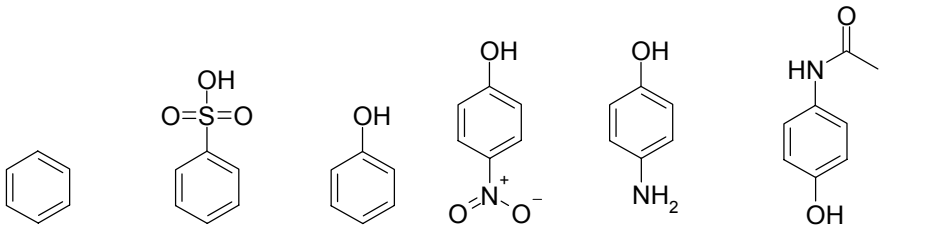
(k = l = 1, m = 2, n = 3)

c) $FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$
$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O$

d) i) $Fe^{2+} + 4Fe^{3+} + 6SO_4^{2-} + 22H_2O = 2H^+ + FeFe_4(SO_4)_6(OH)_2 \cdot 20H_2O$
pH alaneb
ii) $Fe^{3+} + 2SO_4^{2-} + H^+ + 4H_2O = (H_3O)Fe(SO_4)_2 \cdot 3H_2O$, pH kasvab

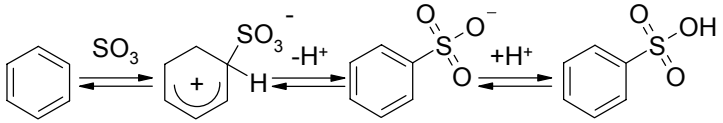
e) 90WA109 – melanteriit või szomolnokiit
90WA110A – römeriit

2. a)

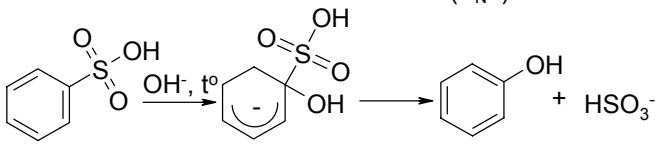


A - benseen **B** - benseen-sulfoonhape **C** - fenool **D** - p-nitro-fenool **E** - p-amino-fenool **Paratsetamool**

b) **A** → **B** elektrofiilne aromaatne asendus (S_E2)

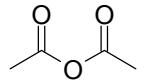


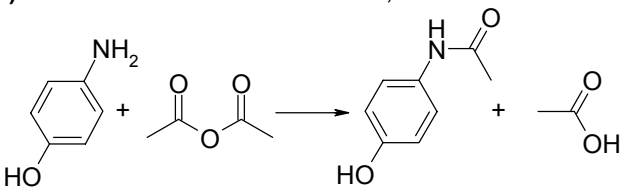
B → **C** nukleofiilne aromaatne asendus (S_N2)



c) o-nitrofenool

d) i) Aineks **F** sobib atseetanhüdriid,





ii) Kuna tegemist on bimolekulaarse reaktsiooniga kuluks reaktsiooni lõpuni kulgemiseks reagentide stöhhiomeetriliste koguste korral lõpmatu aeg, sellepärast kasutatakse atsüülimisreaktsioonides ca 10% atsüüliva reagendi ülehulka.

3. a) i) $Zn = Zn^{2+} + 2e^-$ **ii)** $Cu^{2+} + 2e^- = Cu$

b) (-) Zn | $ZnSO_4$ || CuSO4 | Cu (+)

c) $EMJ = E(Cu^{2+}/Cu) - E(Zn^{2+}/Zn) = E^0(Cu^{2+}/Cu) - E^0(Zn^{2+}/Zn) - \frac{RT}{zF}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$

EMJ = 0,340 V – (-0,763 V) – RT/2F ln 1 **= 1,103 V**

d) Galvaanielement töötab kuni kogu Cu^{2+} on redutseerunud.

$$\mathbf{q} = \frac{2}{1} \cdot 1\,\mathrm{dm^3} \cdot 0{,}1\,\frac{\mathrm{mol}}{\mathrm{dm^3}} \cdot 96485\,\frac{\mathrm{A \cdot s}}{\mathrm{mol}} \cdot \mathbf{= 19\ 300\ C}$$

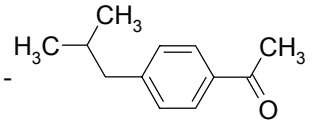
e) Tartu Ülikool

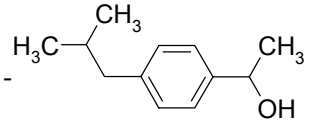
4. a) i) C : H : O <=> $\frac{75{,}68}{12{,}0} : \frac{8.81}{1{,}01} : \frac{15{,}51}{16{,}0}$ <=> 6,31 : 8,72 : 0,97<=> 13:18:2

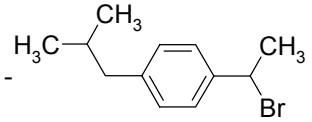
ibuprofeeni brutovalem $\mathbf{C_{13}H_{18}O_2}$

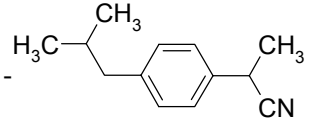
ii) 1-isobutüülbenseen

b)

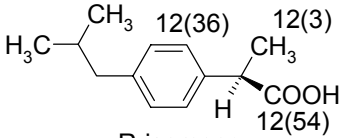
A - 

B - 

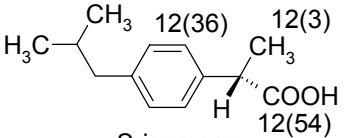
C - 

D - 

c)



R-isomeer



S-isomeer

5. a) i) $7{,}4 = 6{,}86 - \log\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} \quad \frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = 0{,}288$

$$\mathbf{\%(H_2PO_4^-)} = \frac{0{,}288}{1+0{,}288} \cdot 100 \mathbf{\ = 22{,}4 \approx 22}$$

$$\mathbf{\%(HPO_4^{2-})} = \frac{1}{1+0{,}288} \cdot 100 \mathbf{\ = 77{,}6 \approx 78}$$

ii) $\mathbf{[H_2PO_4^-]} = 0{,}224 \cdot 1{,}2\ \mathrm{mmol/l} = 0{,}269\ \mathrm{mmol/l} \mathbf{\approx 0{,}27\ mmol/l}$

$\mathbf{[HPO_4^{2-}]} = 0{,}776 \cdot 1{,}2\ \mathrm{mmol/l} = 0{,}931\ \mathrm{mmol/l} \mathbf{\approx 0{,}93\ mmol/l}$

b) $6{,}4 = 6{,}86 - \log\frac{[H_2PO_4^-] + \beta_{H^+}}{[HPO_4^{2-}] - \beta_{H^+}} \qquad \frac{0{,}269 + \beta_{H^+}}{0{,}931 - \beta_{H^+}} = 2{,}88$

$\mathbf{\beta_{H^+} = 0{,}65\ mmol/l}$

$8{,}4 = 6{,}86 - \log\frac{[H_2PO_4^-] - \beta_{OH^-}}{[HPO_4^{2-}] + \beta_{OH^-}} \qquad \frac{0{,}269 - \beta_{OH^-}}{0{,}931 + \beta_{OH^-}} = 0{,}0288$

$\mathbf{\beta_{OH^-} = 0{,}24\ mmol/l}$

c) Piimhapet, sest fosfaatpuhvri puhvermahtuvus on suurem happe järgi ($\beta_{H^+} > \beta_{OH^-}$).

6. a) i) $Cu_2SO_4(OH)_2$ – divask(II)dihüdroksiidsulfaat

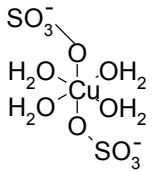
ii) $[Cu(NH_3)_4]SO_4$ – tetraammiinvask(II)sulfaat

b) $2CuSO_4 + 2NH_3 + 2H_2O = Cu_2SO_4(OH)_2\downarrow + (NH_4)_2SO_4$ (**reakts. 1**)

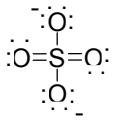
$Cu_2SO_4(OH)_2 + (NH_4)_2SO_4 + 6NH_3 = 2[Cu(NH_3)_4]SO_4 + 2H_2O$ (**reakts. 2**)

$[Cu(NH_3)_4]SO_4 + 2H_2SO_4 = CuSO_4 + 2(NH_4)_2SO_4$ (**reakts. 3**)

c)



d)



e) kokku on 10 vesiniku aatomit, järelikult on kristallis **10** vesiniksidet

f) Vase aatomiga koordineerunud 4 vee molekuli saavad anda 8 vesiniksidet: kaks nendest lähevad sideme andmiseks vaba vee molekuliga ja ülejäänud kuus seostuvad sulfaatioonidega. Iga sulfaatioon võib vastavalt anda 8 vesiniksidet.