

## Valikvõistluse ülesannete lahendused

8. aprill 2004, Tartu

1. a)  $m(\text{kloriid}) = \frac{104}{5} \cdot 0,543 \text{ g} = 11,29 \text{ g} \approx 11,3 \text{ g}$

$m(\text{lisandid}) = 12,2 \text{ g} - 11,3 \text{ g} = 0,9 \text{ g}$

$\%(\text{lisandid}) = \frac{0,9}{12,2} \cdot 100 = 7,38 \approx 7$

b)  $\frac{x}{58,44 \text{ g/mol}} + 2 \cdot \frac{11,3 \text{ g} - x}{133 \text{ g/mol}} = \frac{104}{10} \cdot 2,53 \text{ g} \cdot \frac{1 \text{ mol}}{143,32 \text{ g}}$

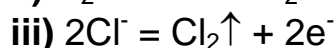
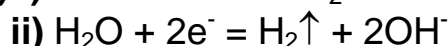
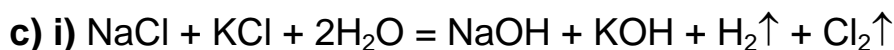
NaCl                      sülviniit                      AgCl

$x = 6,595 \text{ g} \approx 6,6 \text{ g} = m(\text{NaCl})$

$m(\text{sülviniit}) = 11,3 \text{ g} - 6,6 \text{ g} = 4,7 \text{ g}$

i)  $\%(\text{NaCl}) = \frac{6,6}{12,2} \cdot 100 = 54$

ii)  $\%(\text{sülviniit}) = \frac{4,7}{12,2} \cdot 100 = 38,5 \approx 39$



d)  $n(\text{elektronid}) = 5 \text{ A} \cdot 3 \text{ h} \cdot 3600 \text{ s/h} \cdot \frac{1 \text{ mol}}{96500 \text{ A} \cdot \text{s}} = 0,5596 \text{ mol}$

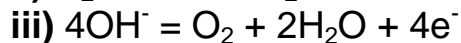
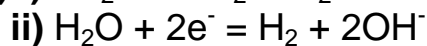
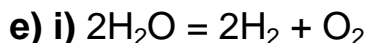
$n(\text{Cl}^-) = 6,6 \text{ g} \cdot \frac{1 \text{ mol}}{58,44 \text{ g}} + 4,7 \text{ g} \cdot \frac{1 \text{ mol}}{133 \text{ g}} \cdot 2 = 0,1846 \text{ mol}$

$V(\text{H}_2) = \frac{1}{2} \cdot 0,5596 \text{ mol} \cdot 22,4 \text{ dm}^3/\text{mol} = 6,27 \text{ dm}^3$

$V(\text{Cl}_2) = \frac{1}{2} \cdot 0,1846 \text{ mol} \cdot 22,4 \text{ dm}^3/\text{mol} = 2,07 \text{ dm}^3 \approx 2,1 \text{ dm}^3$

$n(\text{elektron, O}_2) = 0,5596 \text{ mol} - 0,1846 \text{ mol} = 0,375 \text{ mol}$

$V(\text{O}_2) = \frac{1}{4} \cdot 0,375 \text{ mol} \cdot 22,4 \text{ dm}^3/\text{mol} = 2,1 \text{ dm}^3$



2. a) i) Pb – plii

ii) PbO – plii(II)oksiid

iii) Pb<sub>3</sub>O<sub>4</sub> – pliimennik, plii(II,IV)oksiid

Pb<sub>2</sub>PbO<sub>4</sub> – plii(II)ortoplumfaat

iv) CH<sub>3</sub>COOH – etaanhape

v) Pb(CH<sub>3</sub>COO)<sub>2</sub>·3H<sub>2</sub>O – plii(II)etanaat-3-vesi

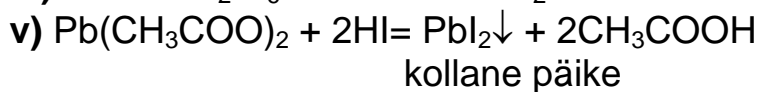
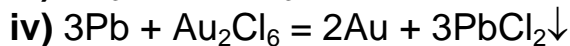
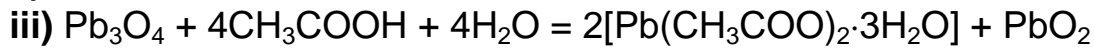
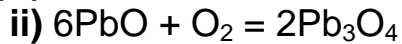
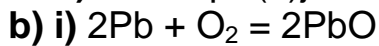
PbO<sub>2</sub> – plii(IV)oksiid

vi) Au<sub>2</sub>Cl<sub>6</sub> – dimeerne kuld(III)kloriid

vii) PbCl<sub>2</sub> – plii(II)kloriid

viii) HI – vesinikjodiidhape

ix)  $\text{PbI}_2$  – plii(II)jodiid



3. a)  $\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0$

$$\Delta G^0 = -91,8 + 298 \cdot 198,1 \cdot 10^{-3} = -32,8 \text{ kJ} \cdot \text{mol}^{-1}$$

$$K_p = \exp\left(-\frac{\Delta G^0}{RT}\right) = \exp\left(\frac{32800}{8,31 \cdot 298}\right)$$

$$\ln K_p = 13,232$$

$$K_p = 5,6 \cdot 10^5$$

Tasakaal on  $\text{NH}_3$  tekke suunas, teoreetiline saagis on hea.

b)  $\Delta C_p = -65,6 + 76,6 \cdot 10^{-3}T - 22,1 \cdot 10^{-6}T^2$

$$\Delta H(773) = -91800 - 65,6 \cdot 475 + \frac{1}{2} \cdot 76,6 \cdot 10^{-3}(773^2 - 298^2) =$$

$$= \frac{1}{3} \cdot 22,1 \cdot 10^{-6}(773^3 - 298^3) = -91800 - 31160 + 19484 - 3207 = -106683 \text{ J} \cdot \text{mol}^{-1}$$

$$\Delta G^0(773) = -106683 + 222,6 \cdot 773 = 65387 \text{ J} \cdot \text{mol}^{-1}$$

$$K_p = \exp\left(-\frac{65387}{8,31 \cdot 773}\right)$$

$$K_p = 3,75 \cdot 10^{-5}$$

Tasakaal on nihutatud lähteainete poole,  $\text{NH}_3$  saagis on väga väike.

Ligikause hinnangu järgi

$$X_{\text{NH}_3} \approx \sqrt{0,1 \cdot K_p} \approx 0,002$$

c) Kui  $\text{NH}_3$  moolimurd on 0,1, siis  $\text{N}_2$  ja  $\text{H}_2$  moolimurrud tasakaalusegus on vastavalt 0,225 ja 0,675. Et  $p_i = X_i \cdot P$

$$K_p = \frac{(0,1 P)^2}{0,225 \cdot P (0,675 P)^3} = 3,75 \cdot 10^{-5}$$

Arvutus annab rõhu  $P$  väärtuseks 62 bar. Arvutustulemus on väga ligikaudne, sest eeldatakse gaaside käitumist ideaalgaasidena.

4. a)  $E_{\text{Cl}_2/2\text{Cl}^-} = 1,360 \text{ V} - \frac{RT}{F} \ln \text{Cl}^-$

$$E_{2\text{H}^+/ \text{H}_2} = 0,000 \text{ V} + \frac{RT}{F} \ln \text{H}^+$$

b)  $\text{EMJ} = E_{\text{Cl}_2/2\text{Cl}^-} - E_{2\text{H}^+/ \text{H}_2}$

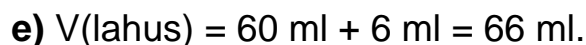
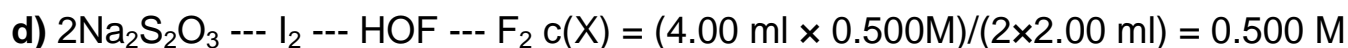
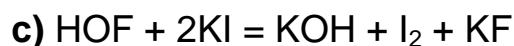
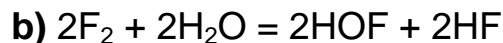
$$1,500 \text{ V} = 1,360 \text{ V} - 0,000 \text{ V} - 0,0259 \text{ V} \ln c - 0,0259 \text{ V} \ln c$$
$$= 2 \cdot (-0,0259 \text{ V}) \cdot \ln c = 0,140 \text{ V}$$

$$\ln c = \frac{0,140}{0,0518} = -2,70$$

$$c = 0,067 \text{ mol/dm}^3$$

5. a) Oletame, et aine X sisaldab ainult ühe fluoriaatomi ning kompleks sisaldab solvendimolekuli. Siis fluori mittersisaldava osa ( $100\% - 24.65\% = 75.35\%$ ) molaarmass võrdub  $= (19 \text{ g/mol} \times 75.35\%) / 24.65\% = 58 \text{ g/mol}$ . Lahutades sellest solvendi molaarmassi, saame  $58 - 41 = 17 \text{ g/mol}$  ehk OH.

Seega, reagent X on **HOF $\times$ CH<sub>3</sub>CN**



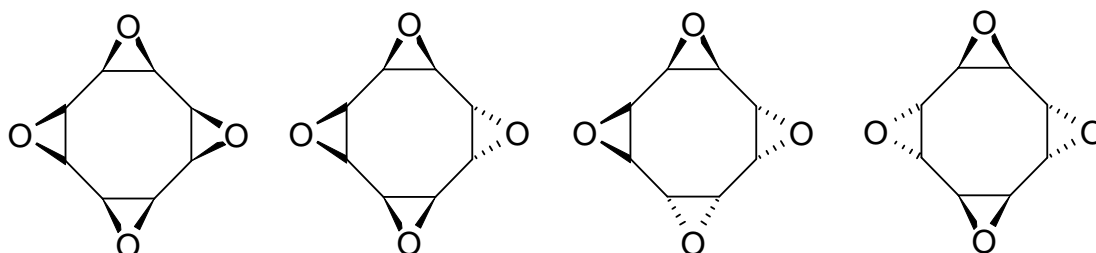
$$n(\text{X}) = 0.500 \text{ M} \times 66 \text{ ml} = 33 \text{ mmol}, n(\text{F}_2) \quad n(\text{X}) = 33 \text{ mmol}$$

Kui saagis on 80%, peab fluori hulk olema  $33 / 0,8 = 41.25 \text{ mmol}$ , mille ruumala on  $= 0.04125 \text{ mol} \times 22.4 \text{ L/mol} = 0.924 \text{ L}$

Kuna segu sisaldab vaid 10% fluori, siis  $V(\text{segu}) = 9.24 \text{ L}$  ning arvestades läbijuhtimise kiirust  $400 \text{ mL/min}$ , saame:  $\text{aeg} = 9.24 \text{ L} / 0.4 \text{ L/min} = 23 \text{ min}$

f) Hapnik. Oksüdatsiooniaste on 0.

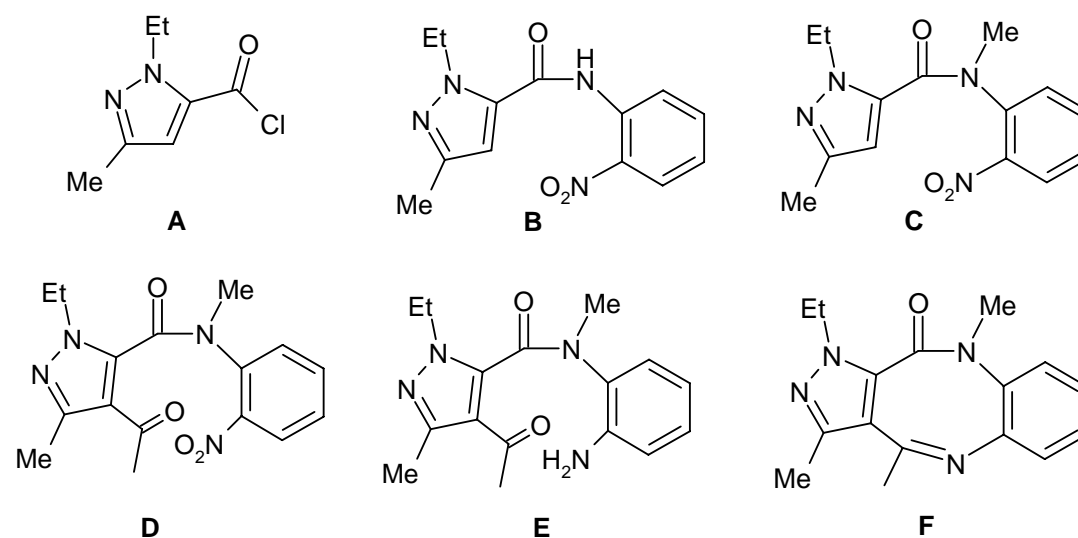
g)



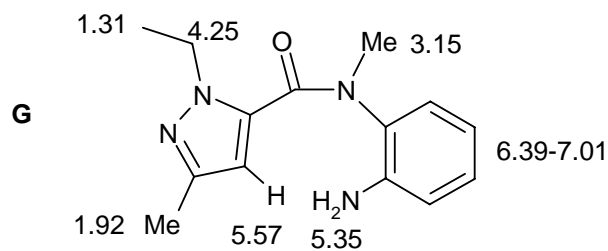
h) Mitte ükski ei ole optiliselt aktiivne, sest igaühes on sümmeetriatasand.

i) Kinoonis on kaksiksideme elektroniühendus väga madal, kuna ta on konjugeeritud karbonüülidega = tugevate (-)R-rühmadega. Pentafenüülsüklopentadieenis on aga probleemiks steeriline takistus.

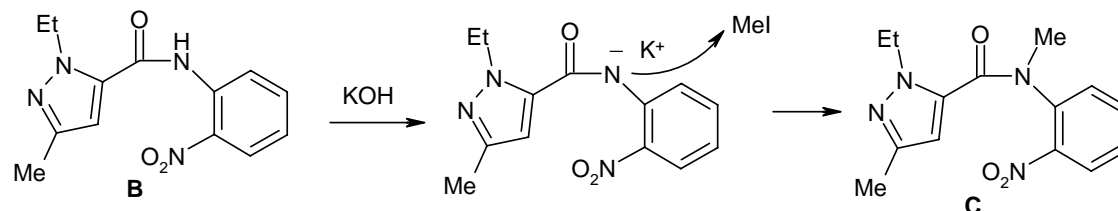
6. a)



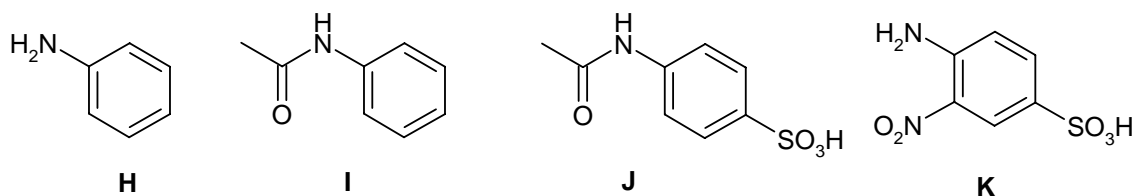
b), c)



d) S<sub>N</sub>2



e)



IP spektris karbonüürühma neeldumise puudumine viitab sellele, et nitreerimise käigus toimus ka amiidi hüdrolüüs.

7.

- 1) PBr<sub>3</sub>
- 2) MCPBA, siis leeliseline või happeline hüdrolüüs
- 3) NaBH<sub>4</sub>
- 4) O<sub>3</sub>, siis redutseeriv hüdrolüüs (lisatakse Me<sub>2</sub>S juurde)
- 5) NaH, siis CH<sub>3</sub>COH, siis kuumutamine kat. H<sub>2</sub>SO<sub>4</sub> juuresolekul.
- 6) CH<sub>3</sub>CH<sub>2</sub>=PPh<sub>3</sub>

8.

$$\text{a) } c(\text{I}_3^-) = \frac{1}{1} \cdot \frac{0,1970\text{g}}{176,13\text{g/mol}} \cdot \frac{1000\text{ml/l}}{29,41\text{ml}} = 0,03803 \text{ M}$$

$$\text{b) } \%(\text{H}_2\text{A}) = \frac{31,63\text{ml}}{1000\text{ml/l}} \cdot 0,03803\text{M} \cdot 176,13\text{g/mol} \cdot \frac{100}{0,4242\text{g}} = 49,95$$

c) muud tingimused =  $-\frac{RT}{nF} \ln[H^+]^m = -\frac{8,3145 \cdot 298 \text{ m}}{96485 \text{ n}} \ln 10^{-7} = 0,414 \text{ m/n}$

d)  $c(\text{H}_2\text{A}) = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}] = [\text{H}_2\text{A}] \left( 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2} \right)$

$$[\text{H}_2\text{A}] = \frac{c(\text{H}_2\text{A})[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

e)  $E = E^0 + \frac{RT}{nF} \ln([\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2) + \frac{RT}{nF} \ln \frac{[\text{D}]}{c(\text{H}_2\text{A})} \Rightarrow E^{0'} = 0,062 \text{ V} \quad ([\text{D}] \approx c(\text{D}))$

f)

