

Valikvõistluse ülesanded

14. aprill 2017, Tartu

- 1. a)** Dissotsiaatsioonireaktsioon: $\text{COCl}_2 \rightleftharpoons \text{CO} + \text{Cl}_2$ ($\Delta n = 1$)

Esialgus oli $n_0 = 2,5 \text{ g}/99 \text{ g/mol} = 0,0253 \text{ mol}$

$$n_T = pV/(RT) = n_0 \cdot (\alpha - 1) + 2 \cdot n_0 \cdot \alpha \Rightarrow \alpha = n_T / n_0 - 1$$

$$[\text{COCl}_2] = n_0 \cdot (\alpha - 1)/V$$

$$[\text{CO}] = [\text{Cl}_2] = n_0 \cdot \alpha/V$$

$$K_c = [\text{CO}][\text{Cl}_2]/[\text{COCl}_2] = (n_0/V) \cdot \alpha^2 / (\alpha - 1)$$

$$K_p = K_c (RT)^{\Delta n}$$

Temperatuuril 400°C, tasakaalu sabumisel:

$$n_{673\text{K}} = 101,325 \text{ kPa} \cdot 1,7 \text{ dm}^3 / (8,314 \text{ J}/(\text{mol}\cdot\text{K}) \cdot 673 \text{ K}) = 0,0308 \text{ mol}$$

$$\alpha_{673\text{K}} = \frac{0,0308 \text{ mol}}{0,0253 \text{ mol}} - 1 = 0,22$$

$$K_{c, 673\text{K}} = \frac{0,0253 \text{ mol}}{1,7 \text{ dm}^3} \cdot \frac{0,217^2}{0,783} = 8,95 \cdot 10^{-4} \text{ M} \approx 9,0 \cdot 10^{-4} \text{ M}$$

$$K_{p, 673\text{K}} = 8,95 \cdot 10^{-4} \text{ M} \cdot (8,314 \text{ J}/\text{mol}\cdot\text{K} \cdot 673 \text{ K})^1 = 5010 \text{ Pa}$$

$$K_p^\circ = 5010 \text{ Pa}/101325 \text{ Pa} = 0,049$$

Temperatuuril 550°C, tasakaalu sabumisel:

$$n_{823\text{K}} = 101,325 \text{ kPa} \cdot 2,8 \text{ dm}^3 / (8,314 \text{ J}/(\text{mol}\cdot\text{K}) \cdot 823 \text{ K}) = 0,0415 \text{ mol}$$

$$\alpha_{823\text{K}} = \frac{0,0415 \text{ mol}}{0,0253 \text{ mol}} - 1 = 0,64$$

$$K_{c, 823\text{K}} = \frac{0,0253 \text{ mol}}{2,8 \text{ dm}^3} \cdot \frac{0,640^2}{0,360} = 1,03 \cdot 10^{-2} \text{ M} \approx 1,0 \cdot 10^{-2} \text{ M}$$

$$K_{p, 823\text{K}} = 1,03 \cdot 10^{-2} \text{ M} \cdot (8,314 \text{ J}/\text{mol}\cdot\text{K} \cdot 823 \text{ K})^1 = 70500 \text{ Pa}$$

$$K_p^\circ = 70500 \text{ Pa}/101325 \text{ Pa} = 0,70$$

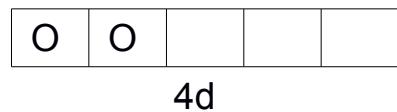
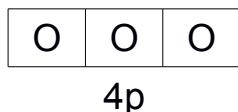
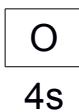
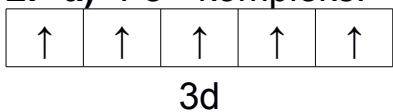
b) $\ln\left(\frac{K_{p2}}{K_{p1}}\right) = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 \cdot T_2} \right)$

$$\Delta H^\circ = \ln\left(\frac{70500}{5010}\right) \cdot 8,314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \cdot \left(\frac{673 \cdot 823 \text{ K}}{150} \right) = 8,12 \cdot 10^4 \text{ J/mol} \approx 81 \text{ kJ/mol}$$

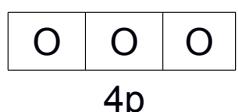
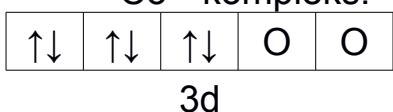
$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -RT \ln K_p$$

$$\Delta S^\circ = \frac{\Delta H^\circ}{T} + R \ln K_p = \frac{8,12 \cdot 10^4 \text{ J/mol}}{823} + 8,314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \cdot \ln 0,70 = 96 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

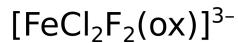
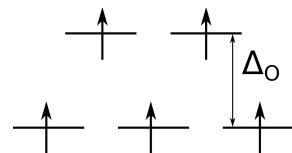
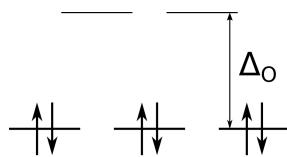
- 2. a)** Fe^{3+} kompleks:



- Co^{3+} kompleks:

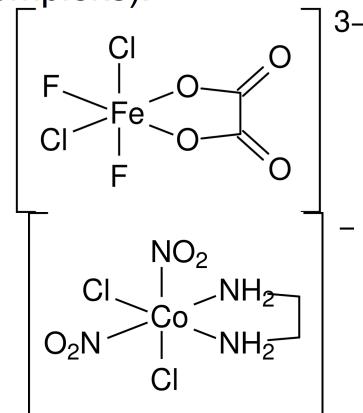
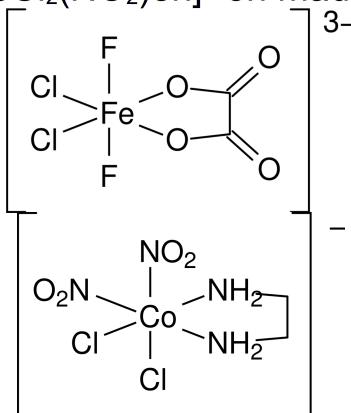


b)



Δ_0 on kõrgem Co^{3+} kompleksil, sest ligandid on tugevama mõjuga. Nad on spektrokeemilises reas kõrgemal kohal, lämmastikuühendid on paremad elektronpaari doonorid kui halogeniidid või hapnikuühendid, mida näitab ka see, et $[\text{CoCl}_2(\text{NO}_2)\text{en}]^-$ on madalaspinniline kompleks).

c) i)

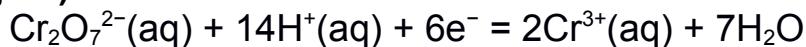


3. a) $E_{\text{rakk}}^0 = E^0(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{2+}, \text{H}^+) - E^0(\text{Br}_2/\text{Br}^-)$

$$E_{\text{rakk}}^0 = 1,36 \text{ V} - 1,07 \text{ V} = 0,29 \text{ V}$$

b) Topeltkriipsu || kasutamine galvaanielemendi skeemis tähistab, et **difusioonipotentsiaal** kahe elektrolüudi lahuse vahel (katoodi- ja anoodiruumi lahuste) on **kõrvaldatud**. Selleks võib kasutada näiteks **soolasilda**, mis on täidetud KCl küllastatud lahusega.

c) ja d)



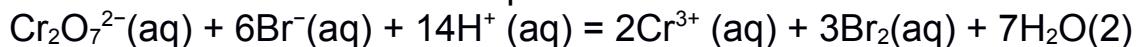
oksüdeerija redutseerub (katood) (+)



redutseerija oksüdeerub (anood) (-)

Elektronid liiguvad **anoodilt katoodile**.

Kuna redutseerumise ja oksüdeerumise käigus läheb üle sama arv elektrone, siis teist võrrandit korrutatakse kolmega. Summaarse reaktsiooni võrrandi saamiseks liidetakse poolreaktsioonid:



e) $\Delta_r G^0 = -RT \ln K = -nFE_{\text{rakk}}^0$

$$\ln K = \frac{nF}{RT} E_{\text{rakk}}^0$$

$$n = 6$$

$$\ln K = \frac{6 \cdot 96485 \text{ C mol}^{-1}}{8,314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 298,15 \text{ K}} \cdot 0,29 \text{ V} = 67,72$$

$$K = 2,6 \cdot 10^{29}$$

Reaktsiooni tasakaal on nihutatud tugevalt saaduste suunas s.t. protsess on

isevooluline ($K \gg 1$, $\Delta_r G^0 < 0$).

- f) Nernsti võrrand on kujul:

$$E_{\text{rakk}} = E_{\text{rakk}}^0 - \frac{RT}{nF} \ln Q = E_{\text{rakk}}^0 - \frac{RT}{nF} \ln \frac{a_{\text{Cr}^{3+}}^2 a_{\text{Br}_2}^3 a_{\text{H}_2\text{O}}^7}{a_{\text{Cr}_2\text{O}_7^{2-}}^6 a_{\text{Br}^-}^6 a_{\text{H}^+}^{14}}$$

(Vee aktiivsus on üks.)

$$E_{\text{rakk}} = 0,29 \text{ V} - \frac{0,02569 \text{ V}}{6} \ln(0,2)^{-16} = 0,44 \text{ V} - \frac{-16 \cdot 0,02569 \text{ V}}{6} \ln(0,2)$$

$$E_{\text{rakk}} = 0,29 \text{ V} - 0,11 \text{ V} = 0,18 \text{ V} > 0$$

Reaktsioon on antud tingimustes isevooluline ($\Delta_r G < 0$).

- g) Tasakaaluolekus $E = 0$.

$$0 = E_{\text{rakk}}^0 - \frac{RT}{nF} \ln Q$$

$$\ln Q = \frac{nFE_{\text{rakk}}^0}{RT} = 67,72$$

$$\ln(Q) = 2,3 \log Q = 2,3 \log \frac{a_{\text{Cr}^{3+}}^2 a_{\text{Br}_2}^3 a_{\text{H}_2\text{O}}^7}{a_{\text{Cr}_2\text{O}_7^{2-}}^6 a_{\text{Br}^-}^6 a_{\text{H}^+}^{14}} = 2,3 \left(\log \frac{a_{\text{Cr}^{3+}}^2 a_{\text{Br}_2}^3 a_{\text{H}_2\text{O}}^7}{a_{\text{Cr}_2\text{O}_7^{2-}}^6 a_{\text{Br}^-}^6} + 14 \text{ pH} \right)$$

$$2,303 \left(\log \frac{a_{\text{Cr}^{3+}}^2 a_{\text{Br}_2}^3 a_{\text{H}_2\text{O}}^7}{a_{\text{Cr}_2\text{O}_7^{2-}}^6 a_{\text{Br}^-}^6} + 14 \text{ pH} \right) = 67,72$$

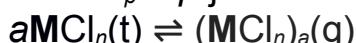
$$\text{pH} = \frac{1}{14} \left(\frac{67,72}{2,303} - \log \frac{a_{\text{Cr}^{3+}}^2 a_{\text{Br}_2}^3 a_{\text{H}_2\text{O}}^7}{a_{\text{Cr}_2\text{O}_7^{2-}}^6 a_{\text{Br}^-}^6} \right) = \frac{1}{14} \left(\frac{67,72}{2,303} - \log 0,2^{-2} \right) = 2,0$$

Muutmaks reaktsiooni suunda peab Gibbsi energia muut olema positiivne ja $E_{\text{rakk}} < 0$.

Reaktsiooni suuna muutmiseks tuleb **pH-d tõsta üle 2,0** ehk siis vähendada prootonite aktiivsust alla 0,01.

4. a) $\ln(p)$ vs. $1/T$

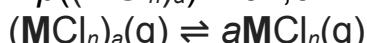
kuna $K_p = p$ ja $-RT \cdot \ln K_p = \Delta H - T\Delta S \Rightarrow \ln(p) = \Delta S/R - \Delta H/R \cdot 1/T$



$$\Delta H_1 = (-654 + 397a) \text{ kJ/mol}$$

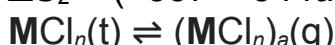
$$\Delta S_1 = (537 - 142a) \text{ J/(mol K)}$$

$$\ln p((\text{MCl}_n)_a) = 64,6 - 17,1a + 78662/T - 47751a/T$$



$$\Delta H_2 = (654 - 253a) \text{ kJ/mol}$$

$$\Delta S_2 = (-537 + 344a) \text{ J/(mol K)}$$



$$\Delta H_2 = (397 - 253) \text{ kJ/mol} = 144 \text{ kJ/mol}$$

$$\Delta S_2 = (-142 + 344) \text{ J/(mol K)} = 202 \text{ J/(mol K)}$$

$$\ln p(\text{MCl}_n) = 24,3 - 17320/T$$

- b) $p(\text{MCl}_n) = \exp(24,3 - 17320/T) = 7,5 \cdot 10^{-4} \text{ atm}$

$$p((\text{MCl}_n)_a) = p_{\text{tot}} - p(\text{MCl}_n) = 0,8054 \text{ atm}$$

$$\ln p((\text{MCl}_n)_a) = 64,6 - 17,1a + 78662/T - 47751a/T \Rightarrow a \Rightarrow 2$$

$$n((\text{MCl}_n)_2) \approx 0,8054 \text{ atm} \cdot 101,325 \text{ kPa/atm} \cdot 0,100 \text{ dm}^3 / (8,314 \text{ J/(mol K)} \cdot 550 \text{ K})$$

$$n((\text{MCl}_n)_2) \approx 1,785 \cdot 10^{-3} \text{ mol}$$

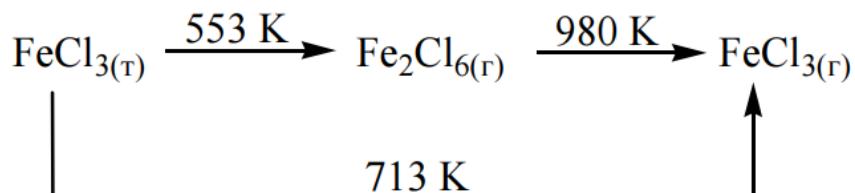
$$m((\text{MCl}_n)_2) = 5,8370 \text{ g} - 5,2561 \text{ g} = 0,5809 \text{ g}$$

$$m((\text{MCl}_n)_2) = 0,5809 \text{ g} / 1,785 \cdot 10^{-3} \text{ mol} = 325 \text{ g/mol} = 2 \cdot M(\text{M}) + 71 \cdot n$$

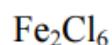
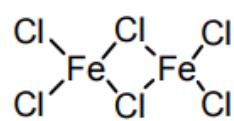
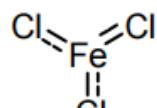
$$M(\text{M}) = 162,7 - 35,5 \cdot n$$

kui $n = 3$, $M(\text{M}) = 56$; M on raud.

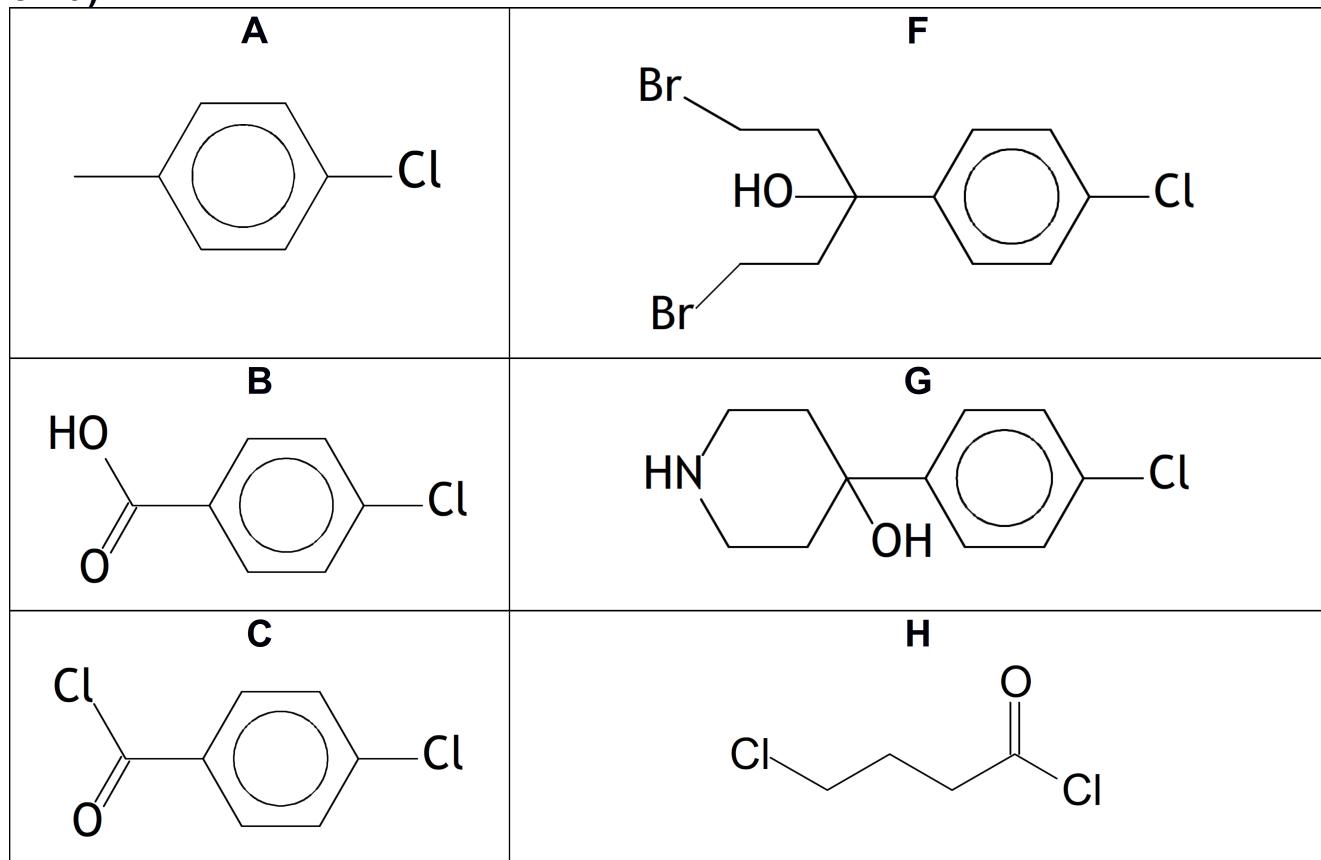
c) $T = \Delta H / \Delta S$, $T_1 = 553 \text{ K}$, $T_2 = 980 \text{ K}$, $T_3 = 713 \text{ K}$

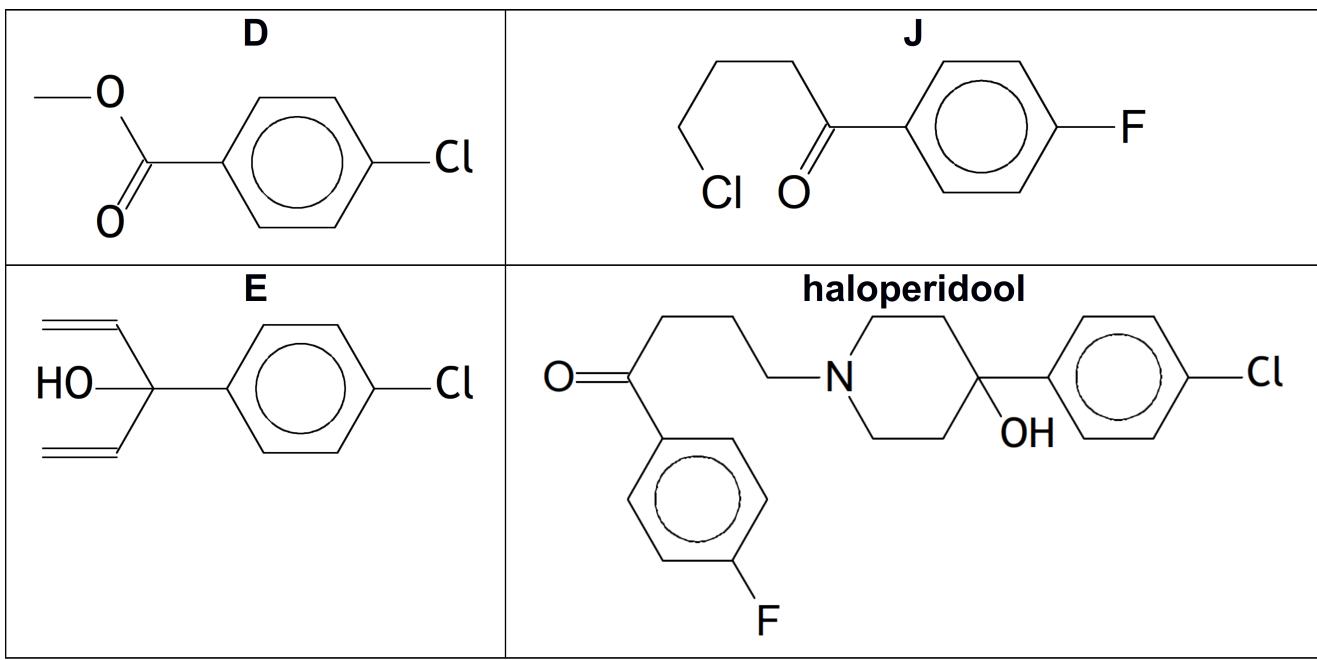


d)



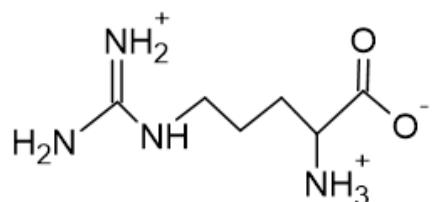
5. a)



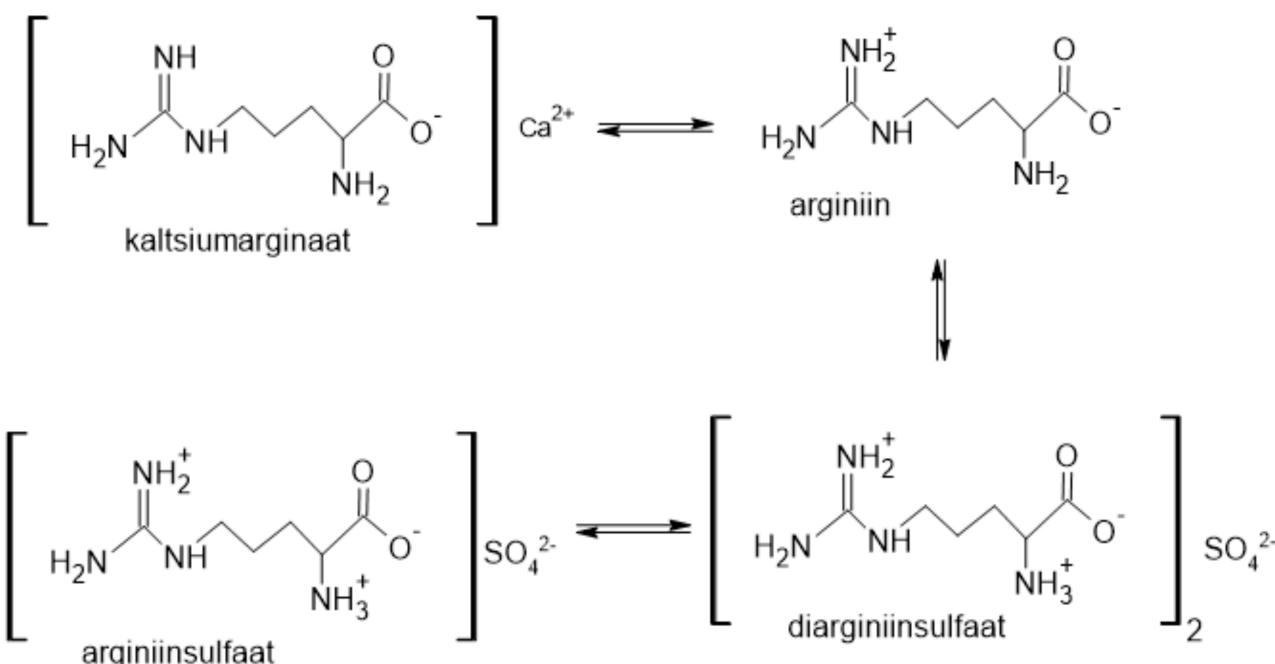


- b) Bensoüülperoksiid on radikaalide generaator ja reaktsioon toimub anti-Markovnikovi mehhaniزمi järgi ainult üle radikaalide.
- c) Nukleofiilne asendus.

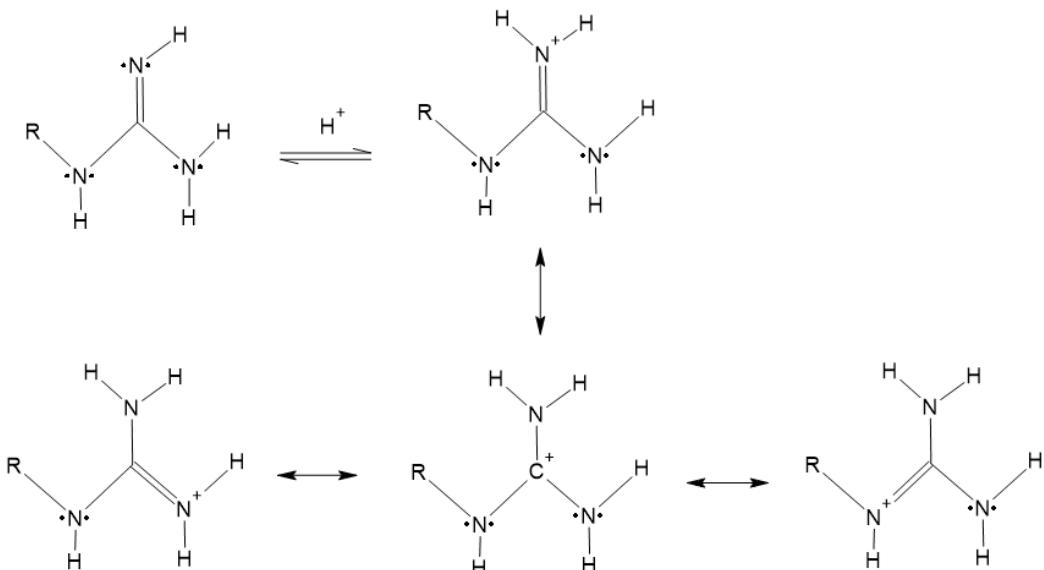
6. a)



b)

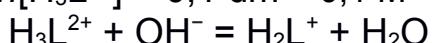


c)

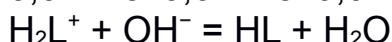


Tänu arginiinis olevale guanidiinrühmale, millel on mitu resonantspiirstruktuuri, on protoneeritud kõrvalahel stabilsem (K on väiksem) kui lüsiini kõrvalahela protoneeritud aminorühm.

d) $n[H_3L^{2+}] = 0,1 \text{ dm}^3 \cdot 0,1 \text{ M} = 0,01 \text{ mol}$



$$0,01 \text{ mol} \quad 0,01 \text{ mol} \quad 0,01 \text{ mol}$$



$$0,01-x \text{ mol} \quad x \text{ mol} \quad x \text{ mol}$$

$$K_{a2} = \frac{[H^+][HL]}{[H_2L]}$$

$$pH = pK_{a2} + \log \frac{[HL]}{[H_2L^+]} = pK_{a2} + \log \frac{x}{0,01-x} \Rightarrow 9,4 = 9,04 + \log \frac{x}{0,01-x}$$

$$\log \frac{x}{0,01-x} = 0,36 \Rightarrow x = n(NaOH) = 0,00691 \text{ mol} \text{ (kulub } H_2L^+ \text{ tiitrimiseks)}$$

$$n(OH^-)_{\text{kokku}} = 0,0100 \text{ mol} + 0,00691 \text{ mol} = 0,0170 \text{ mol}$$

$$V(NaOH) = 0,0170 \text{ mol} / 0,400 \text{ M} = 0,0425 \text{ dm}^3 = 42,5 \text{ cm}^3$$

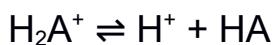
e) $M(\text{Arg}) = 174,20 \text{ g/mol}; n(\text{Arg}) = 4$



$$K_w = [H^+][OH^-] \quad (\text{valem 1})$$



$$K_1 = \frac{[H^+][H_2A^+]}{[H_3A^{2+}]} \quad (\text{valem 2})$$



$$K_2 = \frac{[H^+][HA]}{[H_2A^+]} \quad (\text{valem 3})$$



$$K_3 = \frac{[H^+][A^-]}{[HA]} \quad (\text{valem 4})$$

$$c(Arg^+) = [H_3A^{2+}] + [H_2A^+] + [HA] + [A^-] \quad (\text{valem 5})$$

$$H^+ + 2[H_3A^{2+}] + [H_2A^+] = [A^-] + [OH^-] \quad (\text{valem 6})$$

$$[OH^-] = \frac{K_w}{H^+}$$

$$(\text{valem 1'})$$

$$[\text{H}_2\text{A}^+] = \frac{[\text{H}^+][\text{HA}]}{K_2} \quad \text{asendame } \text{H}_2\text{A}^+ \text{ valemissee 2} \quad (\text{valem 3}')$$

$$[\text{H}_3\text{A}^{2+}] = \frac{[\text{H}^+]^2[\text{HA}]}{K_1 K_2} \quad (\text{valem 2}')$$

$$[\text{A}^-] = \frac{K_3[\text{HA}]}{[\text{H}^+]} \quad (\text{valem 4}')$$

$$[\text{H}^+] + \frac{2[\text{H}^+]^2[\text{HA}]}{K_1 K_2} + \frac{[\text{H}^+] [\text{HA}]}{K_2} = \frac{K_3 [\text{HA}]}{[\text{H}^+]} + \frac{K_w}{[\text{H}^+]} \quad (\text{valem 6}') | [\text{H}^+] K_1 K_2$$

$$[\text{H}^+]^2 K_1 K_2 + 2[\text{H}^+]^3 [\text{HA}] + [\text{H}^+]^2 K_1 [\text{HA}] = K_1 K_2 K_3 [\text{HA}] + K_w K_1 K_2$$

$$[\text{H}^+]^2 K_1 K_2 + [\text{H}^+]^2 K_1 [\text{HA}] = K_1 K_2 K_3 [\text{HA}] + K_w K_1 K_2 | : K_1$$

$$[\text{H}^+]^2 (K_2 + [\text{HA}]) = K_2 K_3 [\text{HA}] + K_w K_2$$

$$[\text{H}^+] = \sqrt{\frac{K_2 K_3 [\text{HA}] + K_2 K_w}{K_2 + [\text{HA}]}} \quad K_2 \ll \text{HA ja } K_2 K_w \ll K_2 K_3 [\text{HA}]$$

$$[\text{H}^+]^2 = \sqrt{K_2 K_3}$$

$$\text{pH} = \frac{pK_2 + pK_3}{2} = \frac{9,04 + 12,43}{2} = 10,7$$

f) $c(\text{HA}) = [\text{H}_3\text{A}^{2+}] + [\text{H}_2\text{A}^+] + [\text{HA}] + [\text{A}^-] = \frac{4,00 \text{ g}}{174,2 \text{ g/mol} \cdot 0,150 \text{ dm}^3} = 0,153 \text{ M}$



$$K_3 = 10^{-12,43}$$

$$K_{b2} = \frac{K_w}{K_2} = \frac{10^{-14}}{10^{-9,04}} = 10^{-4,96}$$

$$[\text{H}^+] \text{ punktist e)} = 10^{-10,7} \text{ M}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{10^{-10,7}} = 10^{-3,30} \text{ M} = 5,01 \cdot 10^{-4} \text{ M}$$

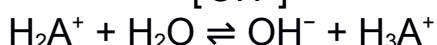
$$K_3 = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]}$$

$$[\text{HA}] \approx c(\text{HA}) = 0,153 \text{ M}$$

$$[\text{A}^-] = \frac{[\text{HA}] K_3}{[\text{H}^+]} = 0,153 \text{ M} \cdot \frac{10^{-12,43}}{10^{-10,7}} = 0,153 \cdot 10^{-1,73} \text{ M} = 2,85 \cdot 10^{-3} \text{ M}$$

$$K_{b2} = \frac{[\text{H}_2\text{A}^+][\text{OH}^-]}{[\text{HA}]}$$

$$[\text{H}_2\text{A}^+] = \frac{K_{b2}[\text{HA}]}{[\text{OH}^-]} = 0,153 \text{ M} \cdot \frac{10^{-4,96}}{10^{-3,30}} = 3,34 \cdot 10^{-3} \text{ M}$$



$$K_{b3} = K_w / K_1 = 10^{-14} / 10^{-2,17} = 10^{-11,83}$$

$$K_{b3} = \frac{[\text{OH}^-][\text{H}_3\text{A}^{2+}]}{[\text{H}_2\text{A}^+]}$$

$$[\text{H}_3\text{A}^{2+}] = \frac{[\text{H}_2\text{A}^+][K_{b3}]}{[\text{OH}^-]} = 3,34 \cdot 10^{-3} \text{ M} \cdot \frac{10^{-11,83}}{10^{-3,30}} = 9,86 \cdot 10^{-12} \text{ M}$$