

VALIKVÕISTLUSE ÜLESANNETE LAHENDUSED
19. aprill 1997, Tartu

4. a) Järk puhverlahuses on 1.

b) I $v = k_1 [NH_2NO_2]$
 II $v = k_2 [NO_2NH_3^+] = k_2 K_t [NH_2NO_2] [H^+]$
 III $v = k_3 [NO_2NH^-] = k_3 K_t \frac{[NH_2NO_2]}{[H^+]}$

Otsitav mehhanism III

c) pH suurenemisel reaktsiooni kiirus kasvab

d) $k' = \frac{1}{t} \ln \frac{c_0}{c_t} = \frac{1}{t} \ln \frac{p^\infty}{p^\infty - p}$

$$k' = \frac{1}{5} \ln \frac{40}{40 - 6,8} = 0,0162 \cdot 2,3 = 0,0373$$

$$k' = \frac{1}{10} \ln \frac{40}{40 - 12,4} = 0,0370$$

$$k' = \frac{1}{15} \ln \frac{40}{40 - 17,2} = 0,0374$$

$$k' = \frac{1}{20} \ln \frac{40}{40 - 20,8} = 0,0366$$

$$k' = \frac{1}{25} \ln \frac{40}{40 - 24} = 0,0366$$

Keskmine $0,037 \text{ min}^{-1}$

e)

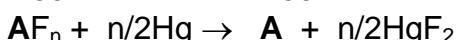
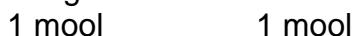
$$\frac{100}{100 - x} = e^{k' t}$$

$$\frac{100}{100 - 99,9} = \frac{100}{0,1} = 1000$$

$$t = \frac{1}{k'} \ln 1000 = \frac{3 \cdot 2,3}{0,037} = 186,7 \text{ min} = 3,11 \text{ h}$$

5. a) Ainete A, B, C ja D identifitseerimine
 $B, C, D \rightarrow AF_n$

C + Hg:



450 mg

$$n(A) = \frac{pV}{RT} = \frac{101,000 \cdot 5,325 \cdot 10^{-2}}{8,314 \cdot 298} = 2,17 \cdot 10^{-3} \text{ mooli A ning ka } AF_n$$

$$M(AF_n) = 0,45 / 2,17 \cdot 10^{-3} = 207,3 \text{ g/mol} = M(A) + nM(F) = M(A) + n \cdot 19,0$$

$$nM(F) = 0,367M(AF_n) = 0,367 \cdot 207,3 = 76,08 = n_F \cdot 19,0; \quad n_F = 4$$

$$M(A) = 207,3 - 4 \cdot 19 = 131,3 \text{ g/mol}$$

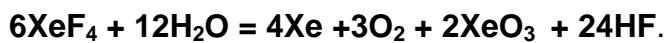
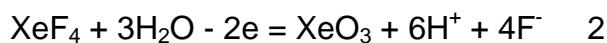
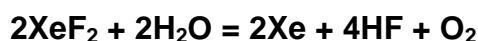
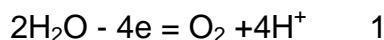
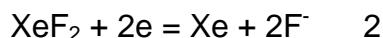
A = Xe; C = XeF₄

$$\frac{n \cdot 19}{131,3 + n \cdot 19} = 0,465; \quad n \cdot 19 = 0,465 \cdot 131,3 + 0,465 \cdot n \cdot 19$$

$$0,535 \cdot 19n = 0,465 \cdot 131,3$$

$$n = \frac{0,465 \cdot 131,3}{0,535 \cdot 19} = 6 \quad \mathbf{B = XeF_6}$$

$$\frac{245,3 \cdot 0,690 - 131,3}{2} \approx 2 \quad \mathbf{B = XeF_2}$$



c) Olgu XeF_2 a mooli

XeF_4 b mooli

XeF_6 c mooli

a mooli $XeF_2 \rightarrow b/2$ mooli O_2 ; a mooli Xe .

b mooli $XeF_4 \rightarrow b/2$ mooli O_2 ; $2b/3$ mooli Xe ; $b/3$ mooli XeO_3 .

c mooli $XeF_6 \rightarrow$

c mooli XeO_3 .

$$n(O_2) = a/2 + b/2$$

$$n(Xe) = a + 2b/3$$

$$n(XeO_3) = b/3 + c$$

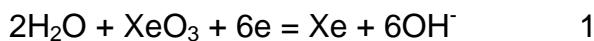
$$n(\text{gaas}) = \frac{100 \cdot 60,2 \cdot 10^{-3}}{8,314 \cdot 289,6} = 2,50 \cdot 10^{-3}$$

$$n(O_2) = 0,4 \cdot 2,50 \cdot 10^{-3} = 1 \cdot 10^{-3} \text{ mooli}$$

$$n(Xe) = 1,5 \cdot 10^{-3} \text{ mooli}$$

$$2 \cdot 10^{-3} = a + b$$

$$4,5 \cdot 10^{-3} = 3a + 2b \quad \rightarrow a = 0,5 \cdot 10^{-3} \text{ mooli}; \quad b = 1,5 \cdot 10^{-3} \text{ mooli}$$



$$n(\text{XeO}_3) = 1/6n(\text{Fe}^{2+})$$

$$n(\text{Fe}^{2+}) = 0,1 \cdot 0,036 = 3,6 \cdot 10^{-3} .$$

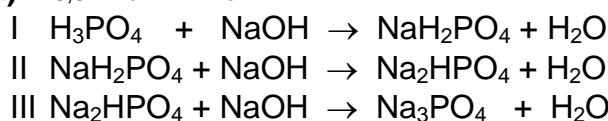
$$n(\text{XeO}_3) = 0,6 \cdot 10^{-3} \text{ mooli} = c + 0,5 \cdot 10^{-3} \quad c = 0,1 \cdot 10^{-3} = 1 \cdot 10^{-4} \text{ mooli}$$

$$\text{XeF}_2 = 5 \cdot 10^{-4} \rightarrow 23,8\%$$

$$\text{XeF}_4 = 15 \cdot 10^{-4} \rightarrow 71,4\%$$

$$\text{XeF}_6 = 1 \cdot 10^{-4} \rightarrow 4,8\%$$

7. a) 0,01 mol x mol



Enne NaOH lisamist

$$E_{ke} = 0,2000 + 0,059 \log [\text{H}^+] = \\ = 0,2000 + 0,059 \log \sqrt{K_1 \cdot c} = 0,2000 + 0,059 \log \sqrt{7,5 \cdot 10^{-3} \cdot 0,1} = 0,1078 \text{ V}$$

Pärast NaOH lisamist:

$$E_{ke} = 0,1078 - 0,3000 = -0,1922 \text{ V} \\ -0,1922 = 0,2000 + 0,059 \log [\text{H}^+]$$

$$\log [\text{H}^+] = \frac{-0,1922 - 0,2000}{0,059} = -6,647; \quad \text{pH} = 6,647$$

$$[\text{H}^+] = K_2 \frac{[\text{NaH}_2\text{PO}_4]}{[\text{Na}_2\text{HPO}_4]}$$

$$\log [\text{H}^+] = \log K_2 + \log \frac{[\text{NaH}_2\text{PO}_4]}{[\text{Na}_2\text{HPO}_4]}$$

$$-6,647 = -7,208 + \log \frac{[\text{NaH}_2\text{PO}_4]}{[\text{Na}_2\text{HPO}_4]}$$

$$\log \frac{[\text{NaH}_2\text{PO}_4]}{[\text{Na}_2\text{HPO}_4]} = 0,56; \quad \frac{[\text{NaH}_2\text{PO}_4]}{[\text{Na}_2\text{HPO}_4]} = 3,64$$

(I) alusel kulub NaOH 0,01 mooli
 (II) alusel:

$$\text{NaH}_2\text{PO}_4 = 3,64 \cdot \text{Na}_2\text{HPO}_4$$

$$\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4 = 0,01 \text{ mol}$$

$$4,64 \text{ Na}_2\text{HPO}_4 = 0,01 \text{ mol}$$

$$\text{Na}_2\text{HPO}_4 \text{ on } \frac{0,01}{4,64} = 0,002155 \text{ mol}$$

$$\text{NaH}_2\text{PO}_4 \text{ on } 0,01 - 0,002155 = 0,007845 \text{ mol}$$

II reaktsioonile kulus seega 0,002155 mol NaOH

Kokku: $0,01 + 0,002155 = 0,012155 \text{ mol}$

lahust 100 ml, seega **c = 0,12155 M**

b) $E_{\text{Ag}/\text{AgCl}} = E_{\text{Ag}/\text{AgCl}}^0 - 0,059 \log(\text{Cl}^-) = 0,2220 - 0,059 \log 0,1 = \mathbf{0,2810 \text{ V}}$

Enne $\Delta E = 0,1078 - 0,2810 = - \mathbf{0,1732 \text{ V}}$

Pärast $\Delta E = - 0,1922 - 0,2810 = - \mathbf{0,4732 \text{ V}}$

EMJ : Enne: $E = 0,2810 - 0,1078 = \mathbf{0,1732 \text{ V}}$

Pärast: $E = 0,2810 - (-0,1922) = \mathbf{0,4732 \text{ V}}$

ehk $E = 0,1732 + 0,3000 = \mathbf{0,4732 \text{ V}}$