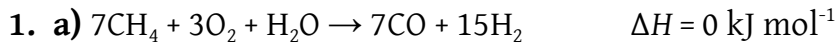


Valikvõistlus (teoreetiline voor)

Lahendused

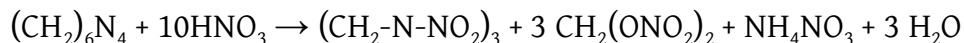
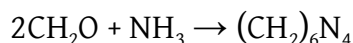
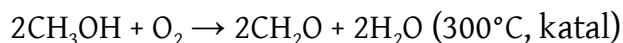
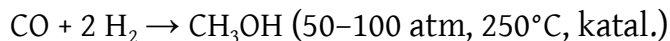
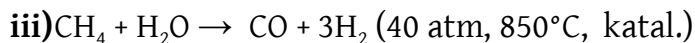
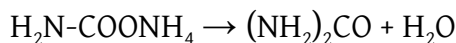
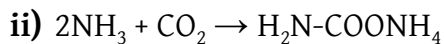
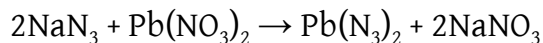
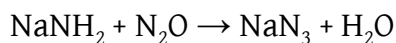
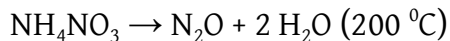
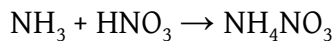
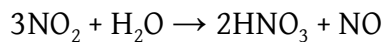
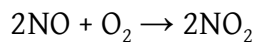
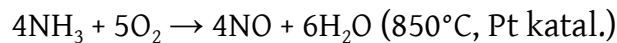
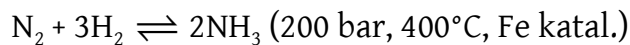
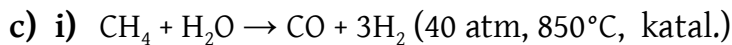
31. märts 2011 a., Tartu

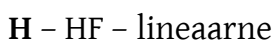
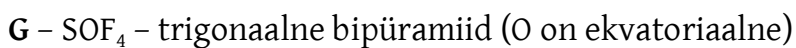
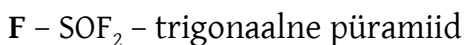
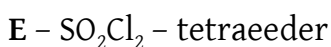
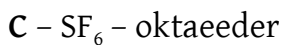
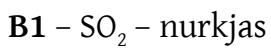
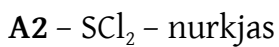
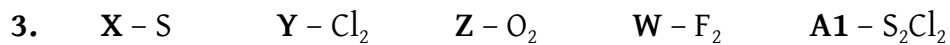
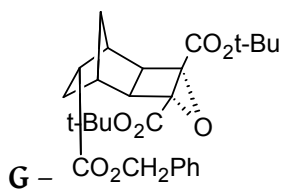
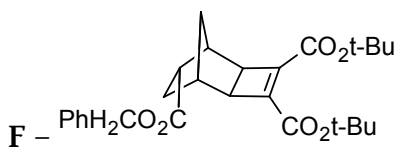
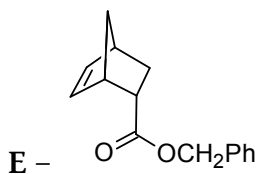
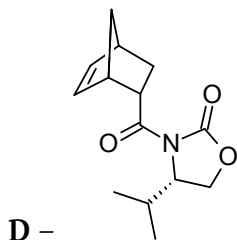
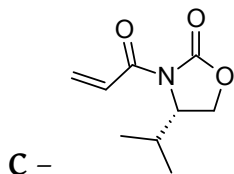
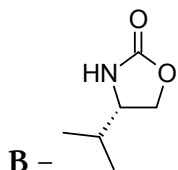
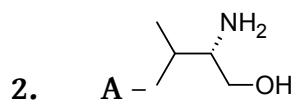


b) 1) $w_2 = n_1 RT \ln \frac{p_1}{p_0} + n_2 RT \ln \frac{p_1}{p_0} = n_1 RT \left(\ln \frac{p_1}{p_0} + 2 \ln \frac{p_2}{p_0} \right)$

$$100 \text{ mol} \cdot 8,314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 500 \text{ K} \cdot \left(\ln \frac{3 \text{ MPa}}{0,1 \text{ MPa}} + 2 \ln \frac{6 \text{ MPa}}{3 \text{ MPa}} \right) = 1,99 \text{ MJ}$$

2) $w_1 = n_2 RT \ln \frac{p_2}{p_0} = 200 \text{ mol} \cdot 8,314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 500 \text{ K} \cdot \ln \frac{6 \text{ MPa}}{0,1 \text{ MPa}} = 3,40 \text{ MJ}$





Sidemetevaheline nurk on väiksem **A2**-s (SCl_2), kuna ta on (elektronpaare arvesse võttes) tetraeedrilise struktuuriga (nurk umbes 109°), aga **B1** (SO_2) on (elektronpaare arvesse võttes) tasandilise struktuuriga (nurk umbes 120°).

Toatemperatuuril on **C** (SF_6) gaasiline aine. Seletus - ta ei ole polaarne, molekulidevaheline vastastikmõju on nõrk tänu kompaktsale F aatomite kihile.

4. a)

Katse nr.	[NO] / M	[O ₂] / M	v / mol dm ⁻³ s ⁻¹
1	A ₁	B ₁	v ₁
2	A ₂ = 2A ₁	B ₁	v ₂ = 4v ₁
3	2A ₁	2B ₁	v ₃ = 8v ₁

Üldjuhul $v = k[\text{A}]^a[\text{B}]^b$

1. ja 2. katses [B] ei muutu, seega

$$\frac{v_2}{v_1} = 4 = \left(\frac{(2A_1)}{(A_1)} \right)^a = 2^a$$

$$\ln 4 = a \ln 2$$

$$a = 2$$

2. ja 3. katses [A] ei muutu, seega

$$\frac{v_3}{v_2} = 2 = \left(\frac{(2B_1)}{(B_1)} \right)^b = 2^b$$

$$\ln 2 = b \ln 2$$

$$b = 1$$

vastus: järk NO suhtes on 2 ja O₂ suhtes 1 ning reaktsiooni üldine järk on 2+1=3

b) reaktsiooni kineetiline võrrand on $v = k [\text{NO}]^2[\text{O}_2]$

$$c) v = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt},$$

$$\text{millest } \frac{d[\text{O}_2]}{dt} = -v, \quad \frac{d[\text{NO}_2]}{dt} = 2v \text{ ja } \frac{d[\text{NO}]}{dt} = -2v$$

d)

(I) sobib:

$$K = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]}, \text{ siit avaldame } [\text{NO}_3] \text{ ja paneme järgmise avaldisse:}$$

$$v = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} k_2 [\text{NO}_3][\text{NO}] = \frac{1}{2} k_2 K [\text{NO}]^2 [\text{O}_2], \text{ millest } k = k_2 K / 2$$

(II) on vähetõenäoline, sest kolme osakese korraga kohtumine on vähetõenäoline.

(III) reaktsiooni üldise kiiruse määrab aeglane staadium:

$$\frac{d[\text{NO}_3]}{dt} = k_1 [\text{NO}][\text{O}_2] - k_2 [\text{NO}_3][\text{NO}], \text{ järelikult } k_1 [\text{NO}][\text{O}_2] = k_2 [\text{NO}_3][\text{NO}]$$

reaktsiooni kiirus

$$v = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_2 [\text{NO}_3][\text{NO}] = k_1 [\text{NO}][\text{O}_2], \text{ mis on NO suhtes esimest järku ja seega ei sobi.}$$

(IV) sobib:

$$K = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}, \text{ siit avaldame } [\text{N}_2\text{O}_2] \text{ ja paneme järgmisse avaldisse:}$$

$$v = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} k_2 [\text{N}_2\text{O}_2][\text{O}_2] = \frac{1}{2} k_2 K [\text{NO}]^2 [\text{O}_2], \text{ millest } k = k_2 K / 2$$

5. a) $\frac{10^{-7} \text{ g}}{50000 \text{ g/mol} \cdot 10^{-3} \text{ l}} = 2 \cdot 10^{-9} \text{ M} = 2 \text{ nM}$

b) $V_{\max} = 600 \text{ nM/min}; K_M = 5 \mu\text{M}$

c) $v = \frac{V_{\max} \cdot [S]}{K_M + [S]} = \frac{600 \text{ nM/min} \cdot 25 \mu\text{M}}{5 \mu\text{M} + 25 \mu\text{M}} = 0,833 \cdot V_{\max} = 500 \text{ nM/min}$

d) $\frac{600 \cdot 10^{-9} \text{ mol} \cdot 10^{-3} \text{ l} \cdot \text{g}}{\text{l} \cdot \text{min} \cdot 10^{-7} \text{ g} \cdot 10^3 \text{ mg}} = 6 \cdot 10^{-6} \frac{\text{mol}}{\text{min} \cdot \text{mg}} = 6 \frac{\mu\text{mol}}{\text{min} \cdot \text{mg}}$

e) $\frac{600 \cdot 10^{-9} \text{ mol} \cdot \text{l} \cdot \text{min}}{\text{l} \cdot \text{min} \cdot 2 \cdot 10^{-9} \text{ mol} \cdot 60 \text{ s}} = 5 \text{ s}^{-1}$

f) Kontsentratsioonid reaktsioonisegus: ensüüm $E_0 = 4 \mu\text{L} \cdot 10 \text{ nM} / 40 \mu\text{L} = 1 \text{ nM}$,
Inhibiitor $I_0 = 36 \mu\text{L} \cdot 50 \text{ nM} / 40 \mu\text{L} = 45 \text{ nM}$.

a) kuna $I_0 \gg E_0$, siis $[I] \approx I_0$ ja ensüümi kontsentratsioonist tulemus ei sõltu:

$$K_i = \frac{[E][I]}{[EI]} = \frac{(E_0 - [EI])I_0}{[EI]} = 10^{-8},$$

$$\frac{(E_0 - [EI])45 \cdot 10^{-9} \text{ M}}{[EI]} = 10^{-8},$$

$$E_0 - [EI] = 0,222[EI],$$

$$\frac{[EI]}{E_0} \cdot 100\% = \frac{100\%}{1,222} = 81,8\% \approx 82\%.$$

b) kui teha täpse võrrandi järgi:

$$K_i = \frac{[E][I]}{[EI]} = \frac{(E_0 - [EI])(I_0 - [EI])}{[EI]} = 10^{-8},$$

$$\frac{(10^{-9} M - [EI])(45 \cdot 10^{-9} M - [EI])}{[EI]} = 10^{-8},$$

$$[EI]^2 - 5,6 \cdot 10^{-8} [EI] + 4,5 \cdot 10^{-17} = 0$$

$$[EI] = 8,15 \cdot 10^{-10} M$$

$$\frac{[EI]}{E_0} = 0,815 = 81,5\% \approx 82\%,$$

seega lihtsustus punktis **a)** oli õigustatud.

- g)** Ensüüm esineb kahes vormis, E^{aktiivne} ja $E^{\text{inaktiivne}}$. Tasakaalulises sidumises inhibiitoriga osaleb ainult E^{aktiivne} :

$$I_0 = 20 \cdot 10^{-9} M,$$

$$E_0^{\text{kogu}} = 20 \cdot 10^{-9} M,$$

$$E_0^{\text{aktiivne}} \leq E_{\text{kogu}},$$

$$K_i = 10^{-8} = \frac{[E][I]}{[EI]} \text{ ja } \frac{[EI]}{I_0} = 0,155$$

$$[EI] = 20 \cdot 10^{-9} M \cdot 0,155 = 3,1 \cdot 10^{-9} M$$

$$[I] = 20 \cdot 10^{-9} M - 3,1 \cdot 10^{-9} M = 16,9 \cdot 10^{-9} M$$

$$10^{-8} = \frac{(E_0^{\text{aktiivne}} - 3,1 \cdot 10^{-9} M) \cdot 16,9 \cdot 10^{-9} M}{3,1 \cdot 10^{-9} M}$$

$$E_0^{\text{aktiivne}} = 4,9 \cdot 10^{-9} M$$

$$\frac{E_0^{\text{aktiivne}}}{E_0^{\text{kogu}}} \cdot 100\% = 24,5\%$$

$$[E^{\text{aktiivne}}] = E_0^{\text{aktiivne}} - [EI] = 1,8 \cdot 10^{-9} M$$

$$[E^{\text{inaktiivne}}] = E_0^{\text{kogu}} - E_0^{\text{aktiivne}} = 15,1 \cdot 10^{-9} M$$

$$I_0 = 20 \cdot 10^{-9} M,$$

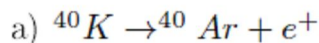
$$E_0 = 20 \cdot 10^{-9} M,$$

$$K_i = 10^{-8} = \frac{[E][I]}{[EI]} = \frac{(E_0 - [EI])(I_0 - [EI])}{[EI]} = \frac{(20 \cdot 10^{-9} - [EI])^2}{[EI]}$$

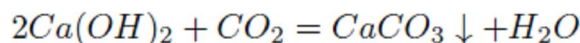
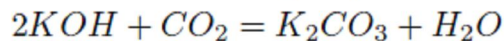
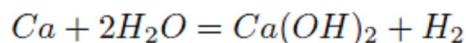
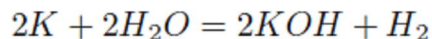
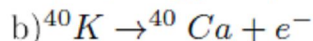
$$[EI] = 10^{-8} M$$

$$\frac{[EI]}{I_0} \cdot 100\% = 50\%$$

6.



$$n_0(\text{Ar}) = \frac{p_0 V}{RT}, n(\text{Ar}) = \frac{pV}{RT}, \Delta n(\text{Ar}) = \frac{V(p-p_0)}{RT} = 1.44 \cdot 10^{-6} \text{ mol}$$



$$n(\text{Ca}) = 1.233 \cdot 10^{-3} \text{ g} / (100.09 \text{ g/mol}) = 1.232 \cdot 10^{-5} \text{ mol}$$

$$n(\text{K}) = 1 \text{ g} / (39.964 \text{ g/mol}) - 1.232 \cdot 10^{-5} \text{ mol} - 1.44 \cdot 10^{-6} \text{ mol} = 0.025009 \text{ mol}$$

$$m(\text{K}) = 0.025009 \text{ mol} \cdot 39.964 \text{ g/mol} = 0.99945 \text{ g}$$

$$\text{c) } \ln \frac{[K]}{[K]_0} = -\frac{\ln 2 \cdot t}{T_{1/2}}, T_{1/2} = \frac{-\ln 2 \cdot 10^6 \text{ a}}{\ln(0.99945)} = 1.26 \cdot 10^9 \text{ a}, k = \frac{\ln 2}{T_{1/2}}$$

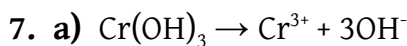
$$\text{Ca ja Ar moodustavad suhes } 1.44 \cdot 10^{-6} : 1.232 \cdot 10^{-5} \text{ mol} = 1 : 8.54$$

$$[K] = [K]_0 e^{-kt}, [Ar] + [Ca] = [K]_0 (1 - e^{-kt})$$

$$[Ar] = \frac{[K]_0 (1 - e^{-kt})}{9.54}$$

$$\frac{[Ar]}{[K]} = \frac{[K]_0 (1 - e^{-kt})}{9.54 [K]_0 e^{-kt}} = \frac{1}{9.54}, \text{ seega } 1 - e^{-kt} = 9.54 e^{-kt}, 1 = 10.54 e^{-kt}, -kt = \ln\left(\frac{1}{10.54}\right),$$

$$t = \frac{-T_{1/2} \ln\left(\frac{1}{10.54}\right)}{\ln 2} = 4.28 \cdot 10^9 \text{ a}$$



$$[\text{Cr}^{3+}][\text{OH}^-]^3 = 6,3 \cdot 10^{-31}$$

$$[\text{Cr}^{3+}] = 0,01 \text{ M}$$

$$0,01 \cdot [\text{OH}^-]^3 = 6,3 \cdot 10^{-31}$$

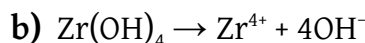
$$[\text{OH}^-] = ((6,3 \cdot 10^{-31}) / 0,01)^{1/3} = 3,98 \cdot 10^{-10} \quad \text{pOH} = -\log[\text{OH}^-] = 9,4 \quad \text{pH} = 4,6$$

$$[\text{Cr}^{3+}] = 0,01 \text{ M} / 1000 = 10^{-5} \text{ M}$$

$$10^{-5} \cdot [\text{OH}^-]^3 = 6,3 \cdot 10^{-31}$$

$$[\text{OH}^-] = ((6,3 \cdot 10^{-31}) / 10^{-5})^{1/3} = 3,98 \cdot 10^{-9} \quad \text{pOH} = -\log[\text{OH}^-] = 8,4 \quad \text{pH} = 5,6$$

pH 4,6 juures hakkab kroom hüdroksiidina välja sadenema, ning pH 5,6 juures on 99,9% kroomist sadenenud.



$$[\text{Zr}^{4+}][\text{OH}^-]^4 = 1,1 \cdot 10^{-54}$$

$$[\text{Zr}^{4+}] = 0,01 \text{ M}$$

$$0,01 \cdot [\text{OH}^-]^4 = 1,1 \cdot 10^{-54}$$

$$[\text{OH}^-] = ((1,1 \cdot 10^{-54}) / 0,01)^{1/4} = 1,02 \cdot 10^{-13} \quad \text{pOH} = -\log[\text{OH}^-] = 13,0 \quad \text{pH} = 1,0$$

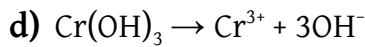
$$[\text{Zr}^{4+}] = 0,01 \text{ M} / 1000 = 10^{-5} \text{ M}$$

$$10^{-5} \cdot [\text{OH}^-]^4 = 1,1 \cdot 10^{-54}$$

$$[\text{OH}^-] = ((1,1 \cdot 10^{-54}) / 10^{-5})^{1/4} = 5,76 \cdot 10^{-13} \quad \text{pOH} = -\log[\text{OH}^-] = 12,2 \quad \text{pH} = 1,8$$

pH 1,0 juures hakkab tsirkoonium hüdroksoidina välja sadenema, ning pH 1,8 juures on 99,9% kroomist sadenenud.

c) Saab küll eraldada. Kui Cr^{3+} ja Zr^{4+} ionide tugevalt happelisele segule lisada alust, siis pH 1,0...1,8 vahemikus sadeneb tsirkoonium(IV)hüdroksoid. Samas ei sadene selles pH vahemikus kroom(III)hüdroksoid.



$$[\text{Cr}^{3+}][\text{OH}^-]^3 = 6,3 \cdot 10^{-31}$$

$[\text{Cr}^{3+}] = x$ tähistame lihtsuse mõttes muutujatega- x on kroom(III)hüdroksoidi molaarne lahustuvus

$$[\text{OH}^-] = 3x \quad \text{sest laengubilanss on: } 3[\text{Cr}^{3+}] = [\text{OH}^-]$$

$$x \cdot (3x)^3 = 6,3 \cdot 10^{-31}$$

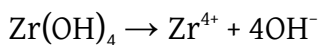
$$27x^4 = 6,3 \cdot 10^{-31}$$

$$x = ((6,3 \cdot 10^{-31}) / 27)^{1/4} = 1,2 \cdot 10^{-8} \text{ mol/L}$$

$$M[\text{Cr}(\text{OH})_3] = 103 \text{ g/mol}$$

$$n(\text{Cr}(\text{OH})_3) = c \cdot V = 1,2 \cdot 10^{-8} \cdot 0,1 = 1,2 \cdot 10^{-9} \text{ hüdroksoidi moolide arv 100 g vees}$$

$$m(\text{Cr}(\text{OH})_3) = 103 \cdot 1,2 \cdot 10^{-9} = 1,27 \cdot 10^{-7} \text{ g/100 g vees}$$



$$[\text{Zr}^{4+}][\text{OH}^-]^4 = 1,1 \cdot 10^{-54}$$

$[\text{Zr}^{4+}] = x$ tähistame lihtsuse mõttes muutujatega- x on kroom(III)hüdroksoidi molaarne lahustuvus

$$[\text{OH}^-] = 4x \quad \text{sest laengubilanss on: } 4[\text{Zr}^{4+}] = [\text{OH}^-]$$

$$x \cdot (4x)^4 = 1,1 \cdot 10^{-54}$$

$$256x^5 = 1,1 \cdot 10^{-54}$$

$$x = ((1,1 \cdot 10^{-54}) / 256)^{1/5} = 5,33 \cdot 10^{-12} \text{ mol/L}$$

$$M[\text{Zr}(\text{OH})_4] = 159 \text{ g/mol}$$

$$n(\text{Zr}(\text{OH})_4) = c \cdot V = 5,33 \cdot 10^{-12} \cdot 0,1 = 5,33 \cdot 10^{-13} \quad \text{hüdroksoidi moolide arv 100 g vees}$$

$$m(\text{Zr}(\text{OH})_4) = 159 \cdot 5,33 \cdot 10^{-13} = 8,47 \cdot 10^{-11} \text{ g/100 g vees}$$