

Valikvõistluse ülesannete lahendused

7. aprill 2005, Tartu

1.
 - a) Diagrammi punktid: O_2 (oks. aste 0) $nE^{\circ} = 0$;
 HO_2^{-} (oks. aste -I) $nE^{\circ} = 0,065$ V; OH^{-} (oks. aste -II) $nE^{\circ} = -0,802$ V.
 - b) $E^{\circ}(O_2/2OH^{-}) = 0,401$ V.
 - c) On isevooluline. Frosti diagrammi põhjal: HO_2^{-} asub kõrgemal tema naaberühendeid ühendavast sirgest, st. on ebapüsiv; arvutuste põhjal: reaktsiooni $2 HO_2^{-} \rightarrow O_2 + 2 OH^{-}$ korral on $E^{\circ} = 0,932$ V, st. $E^{\circ} > 0$.
 - d) Happelises keskkonnas on O_2 tugevam oksüdeerija, sest happelises lahuses on vastava poolreaktsiooni E° väärtus kõrgem.
 - e) $E \approx 0,82$ V.

2.
 - a) SF_4 – väävlil on lisaks neljale sidemele valentskihis 1 vaba elektronipaar, valentskihis on kokku 5 elektronipaari, vaba elektronipaar paikneb kolmnurkses bipüramiidis ekvatoriaalselt;
 - b) ClF_3 – klooril on lisaks kolmele sidemele valentskihis 2 vaba elektronipaari, valentskihis on kokku 5 elektronipaari, molekul on ligikaudu T-kujuline, vabad elektronipaarid paiknevad kolmnurkses bipüramiidis ekvatoriaalselt;
 - c) IF_5 – joodil on lisaks 5 sidemele 1 vaba elektronipaar, valentskihis on kokku 6 elektronipaari, molekul on ligikaudu nelinurkse püramiidi kujuline.

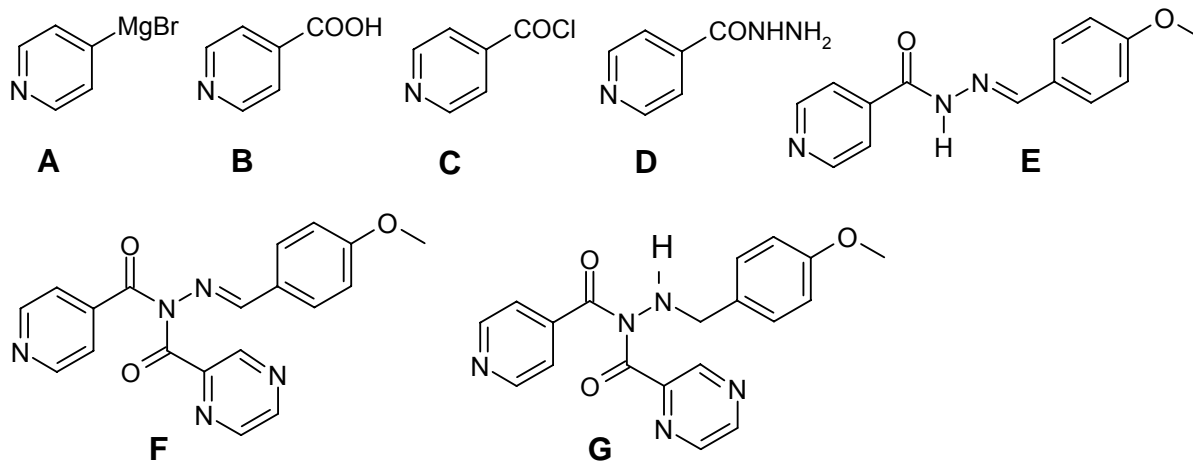
3.
 - a) $CH_3-CO-COO^{-} + NADH + H^{+} \rightarrow CH_3-CHOH-COO^{-} + NAD^{+}$
 - b) Reaalselt on rakus $pH \sim 7$, karboksüülhapped on sel pH -l dissotsieerunud
 - c) 2 elektroni
 - d) $A = b \cdot \epsilon \cdot C$, $C = A / (b \cdot \epsilon) = 0,5 / (1 \text{ cm} \cdot 6220 \text{ M}^{-1} \text{ cm}^{-1}) = 8,04 \cdot 10^{-5} \text{ M}$, ümardatuna $80 \mu\text{M}$
 - e) $K_m = 40 \mu\text{M}$, $10 \times K_m = 400 \mu\text{M}$. Reaktsioonisegusse viiakse $80 \mu\text{M}$ NADH, kuna reaktsioon on 1:1 oleks sobiv algkontsentratsioon vähemalt $480 \mu\text{M}$, ümardatuna $500 \mu\text{M}$ ehk $0,5 \text{ mM}$
 - f) NADH: $2 \text{ ml} \cdot 80 \mu\text{M} / 1000 \mu\text{M} = 0,16 \text{ ml}$
Püruvaat: $2 \text{ ml} \cdot 0,5 \text{ mM} / 10 \text{ mM} = 0,1 \text{ ml}$
puhvrit: $2 \text{ ml} - 0,5 \text{ ml} - 0,16 \text{ ml} - 0,1 \text{ ml} = 1,24 \text{ ml}$
 - g) $\Delta A = b \cdot \epsilon \cdot \Delta C$, $\Delta C = \Delta A / (b \cdot \epsilon) = 0,035 / (1 \text{ cm} \cdot 6220 \text{ M}^{-1} \text{ cm}^{-1}) = 5,63 \cdot 10^{-6} \text{ M}$, mõlema substraadi jaoks
 - h) kontsentratsioonimuut $\Delta C = 5,63 \cdot 10^{-6} \text{ M/sekundis}$ vastab

$$\Delta n = \Delta C \cdot V = 5,63 \cdot 10^{-6} \text{ M} \cdot 0,002 \text{ l} = 1,13 \cdot 10^{-8} \text{ mol/s} = 0,0113 \text{ } \mu\text{mol/s}$$

$$\text{aktiivsus } U = 0,0113 \text{ } \mu\text{mol/s} \cdot 60 \text{ s/min} = 0,676 \text{ U}$$

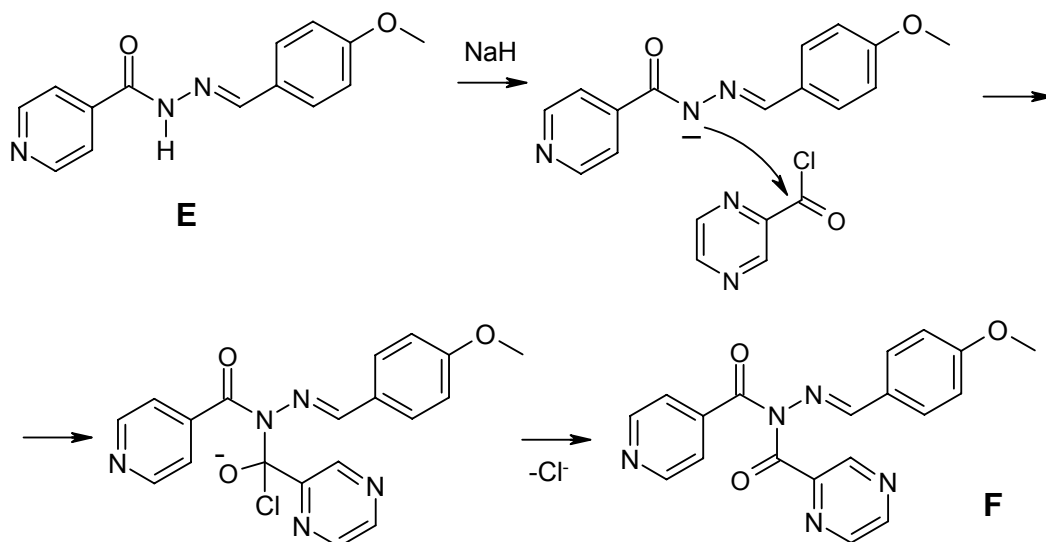
i) kontsentratsioon vereseerumis oli $0,676 \text{ U} / 0,0005 \text{ l} = 1350 \text{ U/l}$, selgelt üle normi

4.

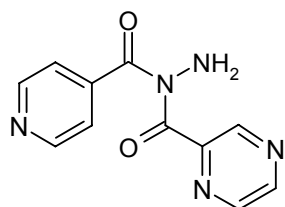


2. $\sim 3300 \text{ cm}^{-1}$ NH
 $\sim 1650 \text{ cm}^{-1}$ CO (amiidne, konjugeeritud)

3.

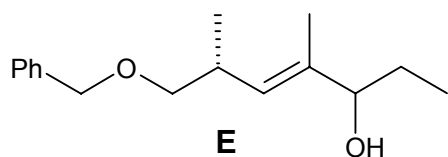
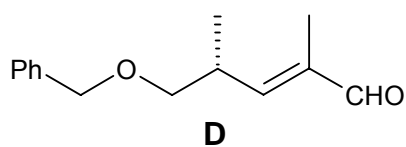
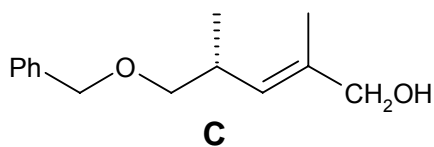
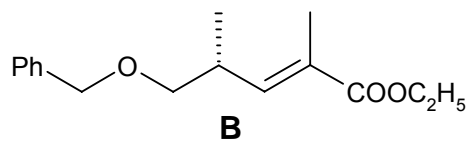
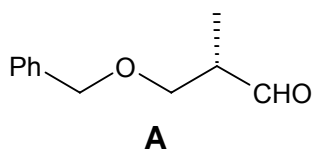


4.

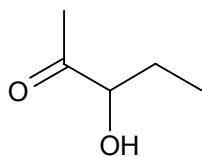
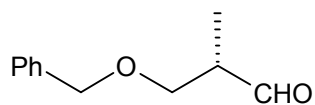


5.

a)



b)



B.

KMnO_4

Zn/Hg/HCl või $\text{N}_2\text{H}_4/\text{digl\u00fc\u00fcm/KOH}$

$\text{C}_5\text{H}_9\text{COCl} + \text{AlCl}_3$

$\text{P} + \text{I}_2$

LiAlH_4

6.

a) $[A] = [A]_0 - kt,$

$$k = \{[A]_0 - [A]\}/t = (1.000 \text{ M} - 0.600 \text{ M})/16 \text{ min} = 0.025 \text{ M/min} = 0,00042\text{M/s}$$

$$t_{100\%} = \{[A]_0 - [A]_{\infty}\}/k = 1.000 \text{ M}/(0.025 \text{ M/min}) = 40 \text{ min}$$

b) $[A] = [A]_0 \cdot e^{-kt},$ $100\% - [A]/[A]_0 = (1 - e^{-0.000050 \cdot 2 \cdot 60 \cdot 60}) \cdot 100\% = 30\%$

c) $\ln(k_1/k_2) = E_a/R (1/T_2 - 1/T_1),$

$$E_a = \ln(1.66/0.037) \cdot 8.314 \cdot ((650 + 273) \cdot (550 + 273)) / (650 - 550) = 240 \text{ kJ}$$

$$k_{600} = \exp\{\ln 1.66 + 240222/8.314(1/923 - 1/873)\} = 0.276 \text{ (bar s)}^{-1}$$

$$p^{-1} = p_0^{-1} + kt,$$

p_0 – NO₂ algröhk

$p = p_0/(1 + ktp_0)$ – NO₂ löpp osaröhk

$3/2(p_0 - p)$ – produktide osaröhk

$p' = p + 3/2(p_0 - p)$ – üldröhk

$$p' = 3/2p_0 - 1/2p = 3/2 \cdot 600 - 1/2 \cdot 600 / (1 + 0,276 \cdot 60 \cdot \frac{600}{760} \cdot \frac{101325}{100000}) = 897 \text{ mm Hg}$$

~ 900 mm Hg

7.

$$\text{a) } W = -nRT \ln \frac{V_2}{V_1} = -0,1 \cdot 8,31 \cdot 298 \cdot \ln 0,5$$

$$W = \mathbf{171,5 \text{ J}}$$

$$\text{b) } p_2 = \left(\frac{V_1}{V_2}\right)^\gamma p_1; \quad p_2 = 2^{1,4} \cdot 1 = \mathbf{2,64 \text{ bar}}$$

$$V_1 = 0,1 \cdot \frac{0,0831 \cdot 298}{1} = 2,475 \text{ l}$$

$$V_2 = 0,5 V_1 = \mathbf{1,238 \text{ L}}$$

$$T_2 = \frac{p_2 V_2}{nR} = \frac{2,64 \cdot 1,238}{0,1 \cdot 0,0831} = 393 \text{ K}$$

$$W = n \cdot c_v \cdot (T_2 - T_1) = 0,1 \cdot \frac{5}{2} \cdot 8,31(393 - 298)$$

$$W = \mathbf{198 \text{ J}}$$