

Valikvõistlus 2008 – Tartu, Eesti – Ülesanne 1

1. 2 puuduolevat E väärust:

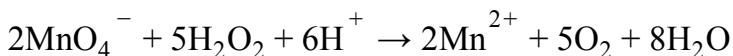
$$E_{\text{Mn}^{3+}/\text{Mn}^{2+}}^{\circ} = 2E_{\text{MnO}_2/\text{Mn}^{2+}}^{\circ} - E_{\text{MnO}_2/\text{Mn}^{3+}}^{\circ} = 1,51 \text{ V}$$

$$E_{\text{MnO}_2^{-}/\text{MnO}_2}^{\circ} = \frac{1}{3} \cdot \left[E_{\text{MnO}_4^{-}/\text{MnO}_4^{2-}}^{\circ} + 2E_{\text{MnO}_4^{2-}/\text{MnO}_2}^{\circ} \right] = 1,70 \text{ V}$$

2. Disproportioneeruma kalduvad happelises lahuses MnO_4^{2-} ja Mn^{3+} , kuna mõlemal $E_{\text{ox}}^{\circ} > E_{\text{red}}^{\circ}$ (parempoolne E° on suurem kui vasakpoolne), seega on nad tugevad oksüdeerijad ja ühtlasi suhteliselt tugevad redutseerijad, mis muudab nad ebastabiilseks.

$$K = \exp\left(-\frac{\Delta G^{\circ}}{RT}\right) = \exp\left(\frac{F}{RT}(E_{\text{ox}}^{\circ} - E_{\text{red}}^{\circ})\right) = e^{21,8}$$

3. Kuna $E_{\text{MnO}_4^{-}/\text{Mn}^{2+}}^{\circ} > E_{\text{O}_2/\text{H}_2\text{O}_2}^{\circ}$, kulgeb reaktsioon



$$E^{\circ} = E_{\text{MnO}_4^{-}/\text{Mn}^{2+}}^{\circ} - E_{\text{O}_2/\text{H}_2\text{O}_2}^{\circ} = (1,51 - 0,695) \text{ V} = 0,815 \text{ V}$$

4. Lahustuvuskorrutis: $K_L = [\text{Mn}^{2+}][\text{OH}^{-}]^2$

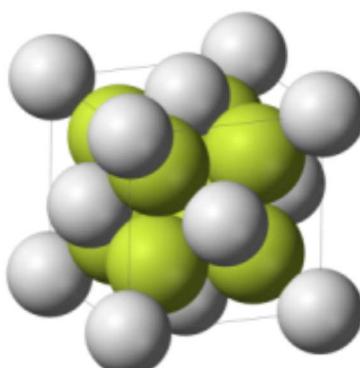


$$\Delta G^{\circ} = -nF(E_{\text{Mn}(\text{OH})_2/\text{Mn}}^{\circ} - E_{\text{Mn}^{2+}/\text{Mn}}^{\circ}) = 71,4 \frac{\text{kJ}}{\text{mol}}$$

$$K = \exp\left(-\frac{\Delta G^{\circ}}{RT}\right) = e^{-28,8}$$

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1. Katioonide kordinatsiooniarv on 8 ja anionidel 4.



2. Tabelväärustus: $\rho = 3.18 \cdot 10^3 \text{ kg/m}^3$

$$\rho = \frac{m}{V} = \frac{n(\text{Ca}) \cdot A(\text{Ca}) + n(\text{F}) \cdot A(\text{F})}{N_A \cdot a^3}$$

$$\rho = \frac{(4 \cdot 40.08 + 8 \cdot 19.00) \text{ g}}{6.022 \cdot 10^{23} \cdot (5.462 \cdot 10^{-10} \text{ m})^3} = 3.183 \cdot 10^3 \frac{\text{kg}}{\text{m}^3}$$

3. Vastus: $\rho = 3.159 \cdot 10^3 \text{ kg/m}^3$

$$\rho = \frac{m}{V} = \frac{n(\text{Ca}) \cdot A(\text{Ca}) + n(\text{F}) \cdot A(\text{F})}{N_A \cdot a^3}$$

$$\rho = \frac{(4 \cdot 40.08 + 4 \cdot 1.97 \cdot 19.00) \text{ g}}{6.022 \cdot 10^{23} \cdot (5.462 \cdot 10^{-10} \text{ m})^3} = 3.159 \cdot 10^3 \frac{\text{kg}}{\text{m}^3}$$

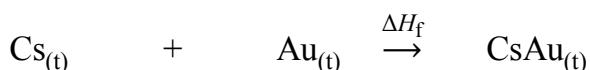
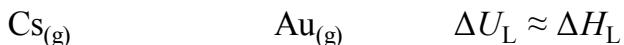
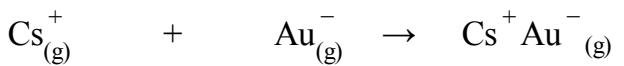
4. $\text{CaF}_{1,97}$ koostis massiosades:

$$w(\text{Ca}) = \frac{40.08}{40.08 + 1.97 \cdot 19.00} = 0,5171$$

$$w(\text{F}) = 1 - w(\text{Ca}) = 0,4829$$

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1. Diagramm



2. Kui $r = r_{\max}$, $\Delta H_{\text{f}} = 0$.

$$\Delta H_{\text{at}} + \text{IE} + \text{EA} = 1072 \cdot \frac{(|z_-| + |z_+|)|z_-||z_+|}{r_- + r_+}$$

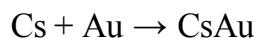
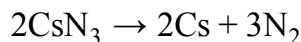
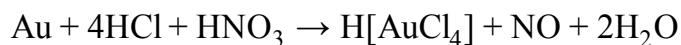
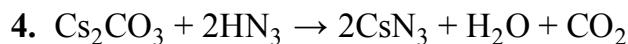
$$r_{\max} = 1072 \cdot \frac{(|z_-| + |z_+|)|z_-||z_+|}{\Delta H_{\text{at}} + \text{IE} + \text{EA}} - r_+$$

$$1. \quad r_{\max}(\text{CsAu}) = 2144 / 597 \text{ \AA} - 1,67 \text{ \AA} = 1,92 \text{ \AA}$$

$$2. \quad r_{\max}(\text{BaAu}_2) = 6432 / 1940 \text{ \AA} - 1,35 \text{ \AA} = 1,97 \text{ \AA}$$

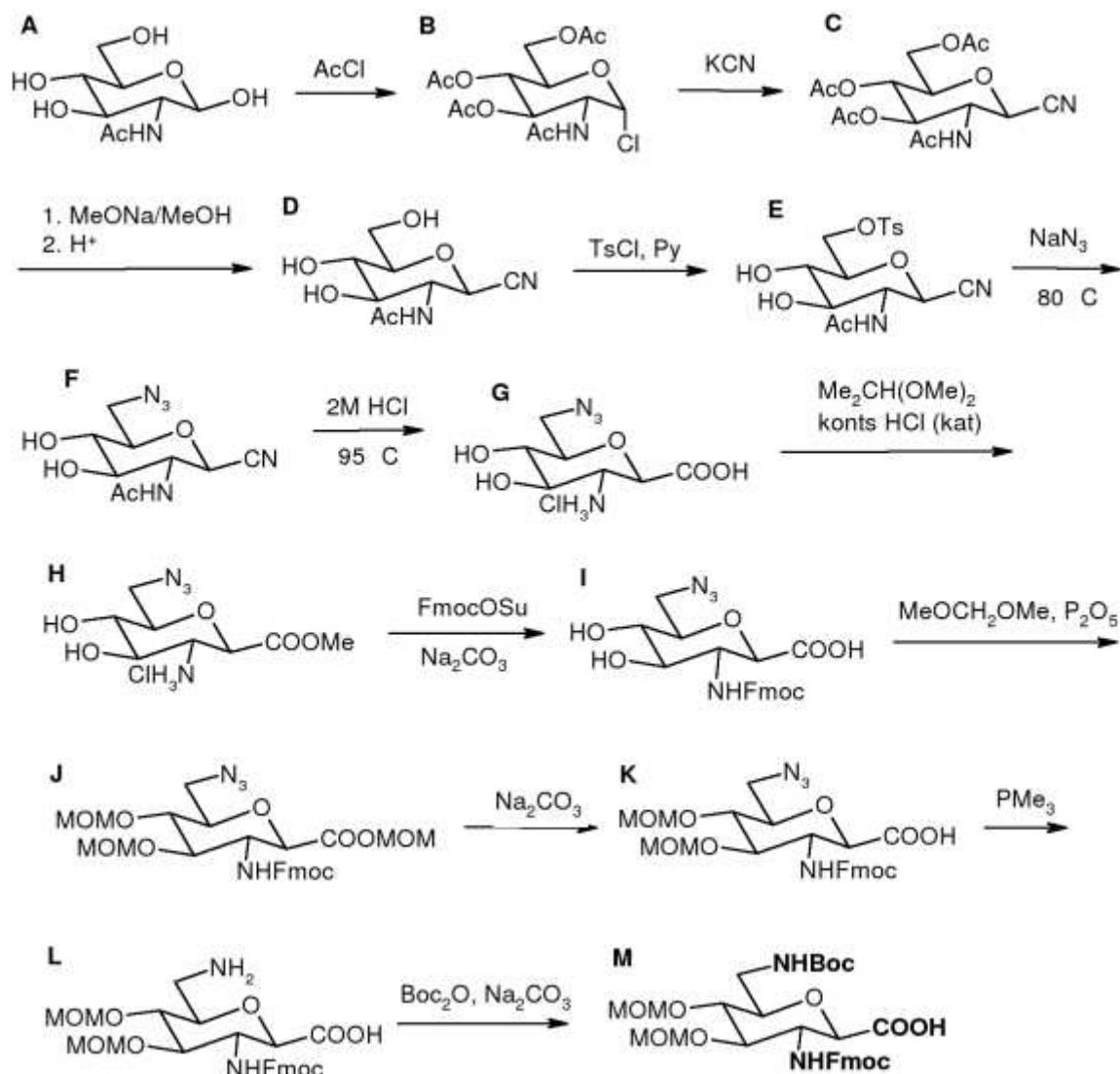
3. $\text{IE} = \text{EA} + kq_1q_2/r$

$$r = \frac{kq_1q_2}{IE - EA} = \frac{8.99 \cdot 10^9 \frac{m}{F} \cdot (1.602 \cdot 10^{-19} C)^2 \cdot 6.022 \cdot 10^{23} \frac{1}{mol}}{(376 - 223) \cdot 10^3 \frac{J}{mol}} = 9.08 \cdot 10^{-10} m$$

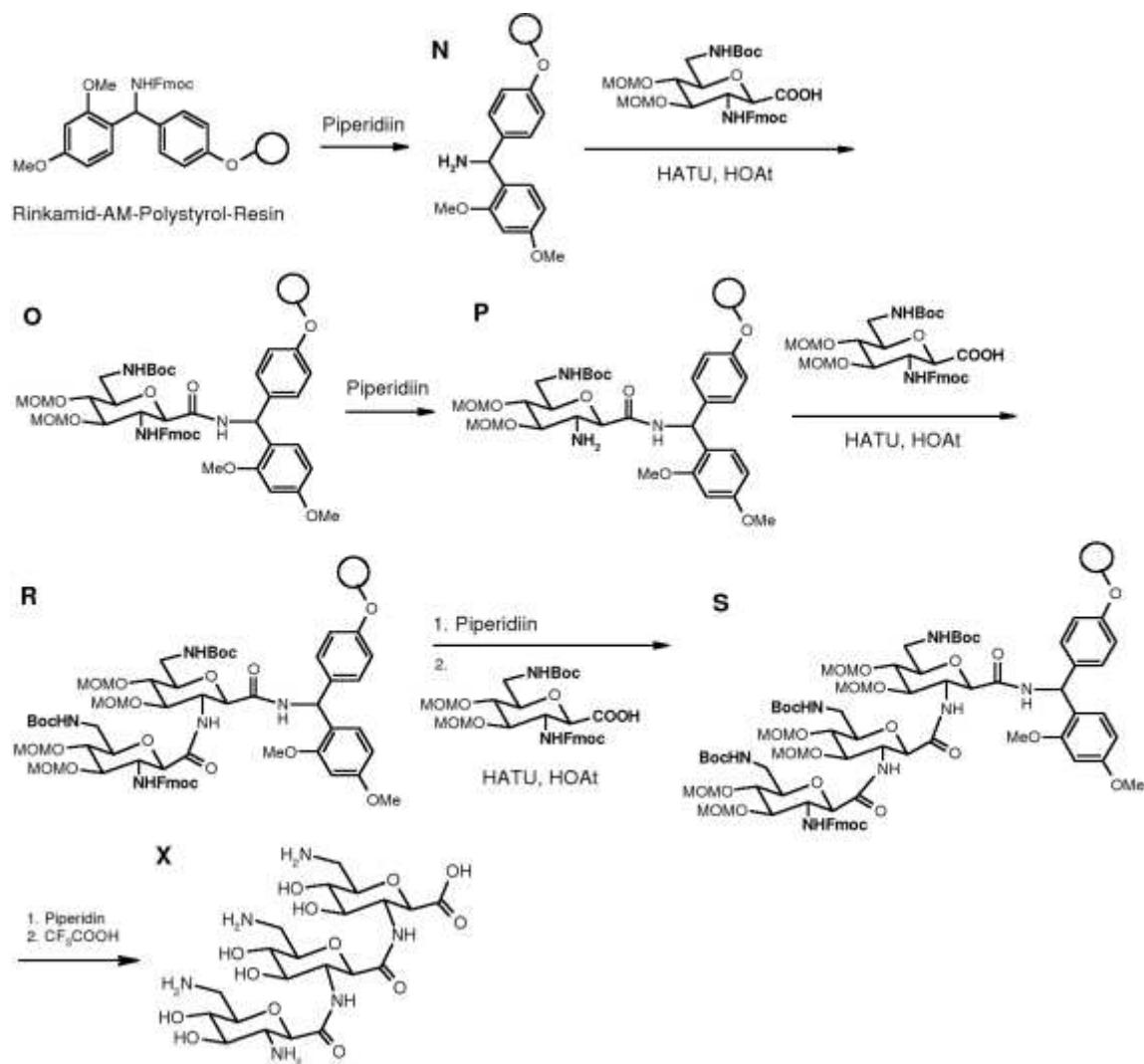


5. K, Rb, Cs, Ca, Sr, Ba

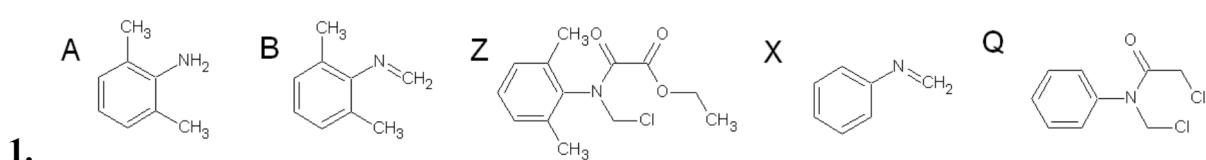
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1.



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2. Phe-*H* – 7,1–7,3 ppm; N-CH₂-Cl – 5,45 ppm; O-CH₂-Me – 3,97 ppm; Phe-CH₃ – 2,34 ppm; OCH₂-CH₃ – 0,93 ppm.

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1. Vastus: 52.87 mg/l

	<i>c</i> (TC)	<i>c</i> (CTC)	<i>C/C</i> _{std}	<i>A</i> (TC)	<i>A</i> (CTC)	<i>A/A</i> _{std}
proov		100	0	55	35	1,571
50	50	100	0,5	55	37	1,486
100	100	100	1	86	29	2,966

$$\frac{A}{A_{\text{std}}} = 2,958 \cdot \frac{C}{C_{\text{std}}} + 0,007456$$

$$C = \frac{1,571 - 0,007456}{2,958} \cdot 100 = 52,87$$

2. Eeldusi on mitmeid, toodud on olulisemad

- proov ega kalibreerimiseks kasutatav maatriks ei tohi sisaldada sisestandardiks kasutatavat ainet
- proovi ettevalmistuse käigus käituvald nii analüüt kui sisestandard sarnaselt.
- kontsentratsiooni ja analüütilise signaali vahel on lineaarne seos

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A	Xe	H	NH ₃	O	N ₂ O
B	O ₂	I	XeF ₆	P	Na
C	N ₂	J	XeO ₃	R	NH ₂ ⁻
D	F ₂	K	HClO	S	HN ₃
E	H ₂	L	N ₂ H ₄	T	[N ₂ H ₅ ⁺][N ₃ ⁻]
F	HF	M	HNO ₃		
G	H ₂ O	N	NH ₄ NO ₃		