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Mangāna savienojumu šķīšanas, protolīzes un reducēšanas-oksidēšanas Prigožina elektroķīmiskie atraktori.

$MnO_2+4OH^-=MnO_4^-+2H_2O+\mathbf{3e^-}$; Expression of absolute potential has
standard $E°_{classic}$=0,595 V [1], water logarithm -0,0591/3*log(55,3^2)=-0,068663 and sum ΔE°=0,10166-0,37239:

$E°_{MnO2/MnO4-}=E°_{MnO2/MnO4-}-0{,}0591/3\cdot\log([H_2O]^2)+\Delta E°=0{,}595-0{,}0591/3*\log(55{,}3\verb|^|2)+0{,}10166-0{,}37239=\mathbf{0{,}2556}$ V

$\Delta \mathbf{G}_{\mathbf{eq}MnO2/MnO4-}=E°_{MnO2/MnO4-}\bullet F\bullet 3=\mathbf{-0{,}25561}*96485*3=\mathbf{73{,}9876}$ kJ/mol,

$\Delta \mathbf{G}_{\mathbf{eq}MnO2/MnO4-}=G_{MnO4-}+2G_{H2O}\mathbf{-}(G_{MnO2}+4G_{OH-})=\underline{\mathbf{476{,}95}}+2*0\mathbf{-}(\mathbf{93{,}5224}+4*77{,}36)=\mathbf{73{,}9876}$ kJ/mol,

$G_{MnO2}=G_{MnO4-}+2G_{H2O}-(\Delta \mathbf{G}_{\mathbf{eq}MnO2/MnO4-}+4G_{OH-})=\underline{\mathbf{476{,}95}}+2*0\mathbf{-}(\mathbf{73{,}9876}+4*77{,}36)=\mathbf{93{,}5224}$ kJ/mol,

$MnO_2+6H_2O=MnO_4^-+4H_3O^++\mathbf{3e^-}$; Expression of potential has standard $E°_{classic}$=1,679 V [1], water logarithm -0,0591/3*log(1/55,3^6)=+0,20599 and ΔE°=0,10166-0,37239:

$E°_{MnO2/H+}=E°_{MnO2/H+}-0{,}0591/3\cdot\log(1/[H_2O]^6)+\Delta E°=1{,}679-0{,}0591/3*\log(1/55{,}3\verb|^|6)+0{,}10166-0{,}37239=\mathbf{1{,}61426}$ V

$\Delta \mathbf{G}_{\mathbf{eq}MnO2/H+}=E°_{MnO2/H+}\bullet F\bullet 3=\mathbf{1{,}61426}*96485*3=\mathbf{467{,}2556}\ \ \mathbf{487{,}1296}$ kJ/mol,

$\Delta \mathbf{G}_{\mathbf{eq}MnO2/H+}=G_{MnO4-}+4G_{H3O+}\mathbf{-}(G_{MnO2}+6G_{H2O})=\underline{\mathbf{476{,}95}}+4*22{,}44\mathbf{-}(\mathbf{99{,}4544}+6*0)=\mathbf{467{,}2556}$ kJ/mol,

$G_{MnO2}=G_{MnO4-}+4G_{H3O+}-(\Delta \mathbf{G}_{\mathbf{eq}MnO2/H+}+6G_{H2O})=\underline{\mathbf{476{,}95}}+4*22{,}44\mathbf{-}(\mathbf{467{,}2556}+6*0)=\mathbf{99{,}4544}$ kJ/mol,

| *Viela* | $\Delta H°_H$, kJ/mol | $\Delta S°_H$, J/mol/K | $\Delta G°_H$, kJ/mol | $G_{BioChem\mathbf{H2O}}$=237,191**-151,549=85,642** kJ/mol. |
|---|---|---|---|---|
| $\mathbf{H_2O}$ | -285,85 | 69,9565 | -237,191 | CRC Handbook of Chemistry and Physics, [1] |
| $\mathbf{H_2O}$ | **-286,65** | **-453,188** | **-151,549** | Biochem.Thermodyn., Massachusetts Technology Inst.[8] pH=7,36 |
| $\mathbf{H_3O^+}$ | $G_{AlbertyH3O}$= | **22,44** | **-257,46** | $\Delta G°_{H3O+\_absolute}=G_{H3O+}\mathbf{-}(0{,}5G_{\mathbf{H2}}^{gas}+1{,}5*G_{O2}^{gas})=\mathbf{-257{,}46}$ kJ/mol; |
| $\mathbf{H_3O^+}$ | –285,809 | -168,8 | -217,2345 | $\mathbf{\Delta G°}_{H3O+}=\Delta H-T*\Delta S=-285{,}809-298{,}15*-168{,}8/1000=-235{,}48$ kJ/mol; |
| $G_{e-}$ $H_3O^+$ | formation | -235,48 | **22,029** | $G_{e-}=\mathbf{\Delta G°}-G_{H3O+}+(1{,}5*G_{H2}^{gas}+0{,}5*G_{\mathbf{O2}}^{gas})=\mathbf{22{,}029}$ kJ/mol; [1,8,26]. |
| $\mathbf{H_2}^{gas}$ | Alberty | pH=7,36 | **85,64** | Biochem.Thermodyn., Massachusetts Technology Inst.[8] pH=7,36 |
| $\mathbf{H_{2(aq)}}$ | 23,4 | -130 | 99,13 | $\Delta H°_{\mathbf{H3O+}}$=-285,809 kJ/mol Mischenko 1972, Himia, Leningrad [26,1] |
| $\mathbf{H_{2(aq)}}$ | **-5,02** | **-363,92** | **103,483** | Biochem.Thermodyn., Massachusetts Technology Inst.[8] pH=7,36 |
| $\mathbf{H(Pt)_{aq}}$ | - | - | **48,56** | $\Delta G_{eq}$=**-847,7** kJ/mol ; $\Delta \mathbf{G}_{Hess}$=-1044,2 kJ/mol |
| $MnO_4^-$ | -541,4 | -191,2 | -447,2 | [1] |
| $MnO_4^-$ | formation | -447,2 | **391,572** | [1,8] $G_{MnO4-}=\mathbf{\Delta G°}_{MnO4-}+(G_{Mn}+\mathbf{2G_{O2}}+G_{e-})=\mathbf{391{,}572}$ kJ/mol; |
| $MnO_4^-$ | $E°_{Mn2+/MnO4-}$ | **1,483458V** | **714,133** | $G_{MnO4-}=\Delta \mathbf{G}_{\mathbf{eq}Mn2+/MnO4-}\mathbf{-}8G_{H3O+}+(G_{Mn2+}+12G_{H2O})=\mathbf{714{,}133}$ kJ/mol; |
| $MnO_4^-$ | $\Delta E°_{H/MnO4-}$=**-** | **1,754188V** | **714,133** | $G_{MnO4-}=G_{Mn2+}+7G_{H2O}-(\Delta G_{HessPt)H}+3G_{H3O}+5G_{H(Pt)})=\ \mathbf{714{,}133}$ kJ/mol; |
| $MnO_4^{2-}$ | -653,0 | 59,0 | -500,7 | [1] |
| $MnO_4^{2-}$ | formation | -500,7 | **359,294** | [1,8] $G_{MnO42-}=\mathbf{\Delta G°}_{MnO42-}+(G_{Mn}+\mathbf{2G_{O2}}+2G_{e-})=\mathbf{359{,}294}$ kJ/mol; |
| $MnO_4^{2-}$ | =**0,25561** | **457,396** | **449,233** | $G_{MnO42-}=\mathbf{\Delta G}_{\mathbf{eq}MnO4-/MnO42-}+G_{MnO4-}=\mathbf{-27{,}717}+(\mathbf{714{,}13})=\mathbf{449{,}23}$ kJ/mol; |
| MnO | -385,2 | 59,7 | -362,9 | ΔG°=ΔH–T*ΔS=-385,2-298,15*-0,0592=-367,5495 kJ/mol; [1] |
| MnO | formation | -362,9 | **0** | $G_{MnO}=\mathbf{\Delta G°}_{MnO}+(G_{Mn}+G_{\mathbf{O2}}^{gas})=-362{,}9+(\mathbf{211{,}35}+0{,}5*\mathbf{303{,}1})=\mathbf{0}$ kJ/mol; |
| $MnO_2$ | -520 | 53,1 | -465,1 | ΔG°=ΔH–T*ΔS=-520-298,15*-0,0531=-504,168 kJ/mol; [1] |
| $MnO_2$ | formation | -465,1 | **49,35** | $G_{MnO2}=\mathbf{\Delta G°}_{MnO2}+(G_{Mn}+G_{\mathbf{O2}}^{gas})=465{,}1+(\mathbf{211{,}35}+\mathbf{303{,}1})=\mathbf{49{,}35}$ kJ/mol; |
| $MnO_2$ | $G_{MnO2}$=**0** | kJ/mol [1,8] | $G_{Mn}$=**162** | $G_{MnO2}=0=\mathbf{\Delta G°}_{MnO2}+G_{Mn}+G_{\mathbf{O2}}^{gas}=-465{,}1+G_{Mn}+\mathbf{303}$ kJ/mol; [1,8] |
| $MnO_2$ | $E°_{MnO2/OH}$ | **0,25561 V** | **330,7054** | OH- $G_{MnO2}=G_{MnO4-}+2G_{H2O}-(\Delta \mathbf{G}_{\mathbf{eq}MnO2/MnO4-}+4G_{OH})=\mathbf{330{,}7054}$ kJ/mol; |
| $MnO_2$ | $E°_{MnO2/H}$ | **1,61426** | **336,6374** | H+ $G_{MnO2}=G_{MnO4-}+4G_{H3O+}-(\Delta \mathbf{G}_{\mathbf{eq}MnO2/H+}+6G_{H2O})=\mathbf{336{,}6374}$ kJ/mol; |
| MnOOH | $E°_{MnOOH/MnO2}$ | **1,072265V** | **255,62** | $G_{MnOOH}=\Delta \mathbf{G}_{\mathbf{eq}MnOOH/MnO2}+G_{H2O}\mathbf{-}(G_{MnO2}+G_{H3O+})=\mathbf{255{,}62}$ kJ/moll; |
| MnOOH | Formation | **1,072265V** | **256,042** | $G_{MnOOH}=\mathbf{\Delta G°}_{MnOOH}+(G_{Mn}+G_{\mathbf{O2}}^{gas}+0{,}5G_{H2})=\mathbf{256{,}042}$ kJ/mol; |
| $Mn^{2+}$ | –220,8 | -73,6 | -228,1 | ΔG°=ΔH–T*ΔS=-220,8-298,15*-0,073=-199,035 kJ/mol; [1] |
| $Mn^{2+}$ | $E°_{Mn(H2O)6/Mn}$ | **-1,146745** | **227,684** | $G_{Mn2+}=\mathbf{\Delta G}_{Mn2+H2O/Mn}+G_{Mn}+G_{H2O}=\mathbf{-221{,}287}+\mathbf{448{,}97}=\mathbf{227{,}684}$ kJ/mol; |
| $Mn^{2+}$ | $E°_{Mn2+/Mn}$ | **-1,404233** | **177,996** | $G_{Mn2+}=\mathbf{\Delta G}_{Mn2+H2O/Mn}+(G_{Mn}+G_{H2O})=\mathbf{-270{,}97474}+\mathbf{448{,}97}=\mathbf{178}$ kJ/mol; |
| $Mn^{2+}$ | $E°_H-E°_{MnO4-}$ | **-1,754188** | **177,989** | $G_{Mn2+}=\Delta G_{HessPt)H}-7G_{H2O}+(G_{MnO4}+3G_{H3O}+5G_{H(Pt)})=\mathbf{177{,}989}$ kJ/mol; |
| $G_{e-}Mn^{2+}$ | formation | -228,1 | **21,44** | $G_{Mn2+}$=**448,97** ; $2G_{\mathbf{e-}}=\mathbf{\Delta G°}_{Mn2+}-G_{Mn2+}+(G_{Mn})=2*\mathbf{21{,}44}$ kJ/mol; |
| $Mn_{H2O}^{2+}$ | **1,483458 V** | -228,1 | **177,996** | $G_{[Mn(\mathbf{H2O})]2+}=\mathbf{\Delta G°}_{Mn2}-2G_{\mathbf{e-}}+(G_{Mn}+G_{H2}+0{,}5G_{\mathbf{O2}}/2)=\mathbf{177{,}996}$ kJ/mol; |
| $Mn_{H2O}^{2+}$ | formation | -228,1 | **415,181** | $G_{[Mn(\mathbf{H2O})]2+}=\mathbf{\Delta G°}_{Mn2+}-2G_{\mathbf{e-}}+(G_{Mn}+G_{H2}+0{,}5G_{\mathbf{O2}}/2)=\mathbf{415{,}181}$ kJ/mol; |
| Mn | $G_{MnOOH}$= | 32,0 CRC | **211,4** | $G_{Mn}=-\mathbf{\Delta G°}_{MnO2}-G_{\mathbf{O2}}^{gas}=362{,}9-0{,}5*\mathbf{303{,}1}=\mathbf{211{,}35}$ kJ/mol. [1,8] |
| Mn $G_{Mn2+}$=**227,684** | | **-1,146745** | **448,971** | $G_{Mn}=G_{Mn2+}-(\Delta \mathbf{G}_{\mathbf{eq}Mn2+/Mn}+G_{H2O})=\mathbf{227{,}684}+\mathbf{221{,}287}=\mathbf{448{,}971}$ kJ/mol,; |
| Mn $G_{Mn2+}$=**177,996** | | **-1,404233** | **448,971** | $G_{Mn}=G_{Mn2+}-(\Delta \mathbf{G}_{\mathbf{eq}Mn2+/Mn}+G_{H2O})=\mathbf{448{,}971}$ kJ/mol; |
| $\mathbf{O_{2\,aqua}}$ | **-11,7** | **-94,2** | **16,4** | Biochem.Thermodyn., Massachusetts Technology Inst.[8] pH=7,36 |

Formation $Mn+2\mathbf{O_2}^{gas}+e^-=MnO_4^-$;

$\Delta G°_{MnO4-}=G_{MnO4-}-(G_{Mn}+\mathbf{2G_{O2}}+G_{e-})=\mathbf{714{,}133}-(\mathbf{211{,}35}+2*\mathbf{303{,}1}+\mathbf{21{,}222})=-447{,}2$ kJ/mol;

$G_{MnO4-}=\Delta G^\circ_{MnO4-}+(G_{Mn}+2G_{O2}+G_{e-})=-447,2+(211,35+2*303,1+21,222)=714,133$ kJ/mol;

$G_{e-}=G_{MnO4-}-(G_{Mn}+2G_{O2}+\Delta G^\circ_{MnO4-})=714,133-(211,35+2*303,1-447,2)=21,222$ kJ/mol;

$\Delta G^\circ_{MnO4-}=G_{MnO4-}-(G_{Mn}+2G_{O2}+G_{e-})=476,957-(211,35+2*303,1+21,222)=-447,2$ kJ/mol;

$G_{MnO4-}=\Delta G^\circ_{MnO4-}+(G_{Mn}+2G_{O2}+G_{e-})=-447,2+(211,35+2*303,1+21,222)=476,957$ kJ/mol;

$G_{e-}=G_{MnO4-}-(G_{Mn}+2G_{O2}+\Delta G^\circ_{MnO4-})=476,957-(211,35+2*303,1-447,2)=21,222$ kJ/mol;

Formation $Mn+2O_2^{gas}+2e^-=MnO_4^{2-}$;

$\Delta G^\circ_{MnO42-}=G_{MnO42-}-(G_{Mn}+2G_{O2}+2G_{e-})=359,294-(211,35+2*303,1+2*21,222)=-500,7$ kJ/mol;

$G_{MnO42-}=\Delta G^\circ_{MnO42-}+(G_{Mn}+2G_{O2}+2G_{e-})=-500,7+(211,35+2*303,1+2*21,222)=359,294$ kJ/mol;

$2G_{e-}=G_{MnO42-}-(G_{Mn}+2G_{O2}+\Delta G^\circ_{MnO42-})=359,294-(211,35+2*303,1-500,7)=2*21,222=42,444$ kJ/mol;

Formation $1,5H_2^{gas}+0,5O_2^{gas}=H_3O^++e^-$; $\Delta G^\circ_{H3O+}=\Delta H-T*\Delta S=-285,809-298,15*-168,8/1000=-235,48$ kJ/mol;

$\Delta G^\circ=G_{H3O+}+G_{e-}-(1,5*G_{H2}^{gas}+0,5*G_{O2}^{gas})=22,44+G_{e-}-(1,5*85,6+0,5*303,1)=-235,48$ kJ/mol;

$G_{e-}=\Delta G^\circ-G_{H3O+}+(1,5*G_{H2}^{gas}+0,5*G_{O2}^{gas})=-235,48-22,44+(1,5*85,6+0,5*303,1)=22,029$ kJ/mol;

Formation $Mn+O_2^{gas}=MnO_2$; $\Delta G^\circ_{MnO2}=G_{MnO2}-(G_{Mn}+G_{O2}^{gas})=49,35-(211,35+303,1)=-465,1$ kJ/mol;

$G_{MnO2}=\Delta G^\circ_{MnO2}+(G_{Mn}+G_{O2}^{gas})=-465,1+(211,35+303,1)=49,35$ kJ/mol;

$G_{Mn}=G_{MnO2}-(\Delta G^\circ_{MnO2}+G_{O2}^{gas})=49,35-(-465,1+303,1)=211,35$ kJ/mol. [1,8]

Formation $Mn+0,5O_2^{gas}=MnO$; $\Delta G^\circ_{MnO}=G_{MnO}-(G_{Mn}+G_{O2}^{gas}/2)=0-(211,35+0,5*303,1)=-362,9$ kJ/mol;

$G_{MnO}=\Delta G^\circ_{MnO}+(G_{Mn}+G_{O2}^{gas})=-362,9+(211,35+0,5*303,1)=0$ kJ/mol;

$G_{Mn}=G_{MnO}-(\Delta G^\circ_{MnO}+G_{O2}^{gas})=-0-(-362,9+0,5*303,1)=211,35$ kJ/mol;

$Mn^{2+}+12H_2O=MnO_4^-+8H_3O^++5e^-$; Absolūtais aprēķins satur standarta $E^\circ_{klasisko}=1,507$ V [1], ūdens logaritmu un $\Delta E^\circ$: $E^\circ_{Mn2+/MnO4-}=E_o-0,0591/5\bullet\log(1/[H_2O]^{12})=1,507-0,0591/5\bullet\log(1/55,3\text{^}12)+0,10166-0,37239=1,483458$ V.

$\Delta G_{eqMn2+/MnO4-}=E^\circ_{Mn2+/MnO4-}\bullet F\bullet 5=1,483458*96485*5=715,657$ kJ/mol,

$\Delta G_{eqMn2+/MnO4-}=G_{MnO4-}+8G_{H3O+}-(G_{Mn2+}+12G_{H2O})=\underline{476,95}+8*22,44-(-59,187+12*0)=715,657$ kJ/mol,

$G_{MnO4-}=\Delta G_{eqMn2+/MnO4-}-8G_{H3O+}+(G_{Mn2+}+12G_{H2O})=715,657-8*22,44+(-59,187+12*0)=476,95$ kJ/mol,

$G_{Mn2+}=G_{MnO4-}+8G_{H3O+}-(\Delta G_{eqMn2+/MnO4-}+12G_{H2O})=\underline{476,95}+8*22,44-(715,657+12*0)=-59,187$ kJ/mol,

$\Delta G_{eqMn2+/MnO4-}=G_{MnO4-}+8G_{H3O+}-(G_{Mn2+}+12G_{H2O})=714,133+8*22,44-(177,996+12*0)=715,657$ kJ/mol,

$G_{MnO4-}=\Delta G_{eqMn2+/MnO4-}-8G_{H3O+}+(G_{Mn2+}+12G_{H2O})=715,657-8*22,44+(177,996+12*0)=714,133$ kJ/mol,

$G_{Mn2+}=G_{MnO4-}+8G_{H3O+}-(\Delta G_{eqMn2+/MnO4-}+12G_{H2O})=714,133+8*22,44-(715,657+12*0)=177,996$ kJ/mol,

Formation $Mn+6H_2^{gas}+3O_2^{gas}=[Mn(H_2O)_6]^{2+}+2e-$;

One coordinative bond has $190,5255$ kJ/mol$=H_2O=>\square\Delta Mn^{2+}$;

but six coordinative bonds have sum of six times $6*190,5255=1143,153$ kJ/mol $[Mn(H_2O)_6]^{2+}$;

$\Delta G^\circ_{Mn26H2O/}=G_{Mn26H2O}+2G_{e-}-(G_{Mn}+6G_{H2}+3G_{O2})=G_{Mn2+6H2O}+2*21,222-(448,97+6*85,64+3*303,1)=-228,1$ kJ/mol;

$G_{Mn26H2O}=\Delta G^\circ_{Mn26H2O}+2G_{e-}-(G_{Mn}+6G_{H2}+3G_{O2})=-228,1-2*21,222+(448,971+6*85,64+3*303,1)=1601,567$ kJ/mol;

Formation $Mn=Mn^{2+}+2e-$;

$\Delta G^\circ_{Mn2}=G_{Mn2+}+2G_{e-}-(G_{Mn})=177,989+2*21,44-(448,971)=-228,1$ kJ/mol;

$2G_{e-}=\Delta G^\circ_{Mn2+}-G_{Mn2+}+(G_{Mn})=-228,1-(177,989)+(448,971)=42,44=2*21,44$ kJ/mol;

Formation $Mn+0,5O_2^{gas}+H_2^{gas}=[Mn(H_2O)]^{2+}+2e^-$;

$\Delta G^\circ_{Mn2+}=G_{[Mn(H2O)]2+}+2G_{e-}-(G_{Mn}+G_{H2}+0,5G_{O2}/2)=415,181+2*21,44-(448,971+85,64+303,1/2)=-228,1$ kJ/mol;

$G_{[Mn(H2O)]2+}=\Delta G^\circ_{Mn2+}-2G_{e-}+(G_{Mn}+G_{H2}+0,5G_{O2}/2)=-228,1-2*21,44+(448,971+85,64+303,1/2)=415,181$ kJ/mol;

$Mn+6H_2O=[Mn(H_2O)_6]^{2+}+2e^-$; E° satur standarta potenciālu $E^\circ_{klasisko}=-1,185$ V [1], ūdens logaritmu un $\Delta E^\circ$: $E^\circ_{Mn2+/Mn}=E_o-0,0591/2\bullet\log(1/[H_2O]^6)=-1,185-0,0591/2\bullet\log(1/55,3\text{^}6)+0,10166-0,37239=-1,146745$ V.

$\Delta G_{Mn2+H2O/Mn}=E^\circ_{Mn2+/Mn}\bullet F\bullet 2=-1,146745*96485*2=-221,287$ kJ/mol,

$\Delta G_{Mn2+H2O/Mn}=G_{Mn2+}-(G_{Mn}+G_{H2O})=-9,937-(211,35+0)=-221,287$ kJ/mol,

$G_{Mn2+}=\Delta G_{Mn2+H2O/Mn}+(G_{Mn}+G_{H2O})=-221,287+(211,35+0)=-9,937$ kJ/mol,

$G_{Mn}=G_{Mn2+}-(\Delta G_{eqMn2+/Mn}+G_{H2O})=-9,937-(-221,287+0)=211,35$ kJ/mol,

$\Delta G_{Mn2+H2O/Mn}=E^\circ_{Mn2+/Mn}\bullet F\bullet 2=-1,146745*96485*2=-221,287$ kJ/mol,

$\Delta G_{Mn2+H2O/Mn}=G_{Mn2+}-(G_{Mn}+G_{H2O})=177,996-(399,283+0)=-221,287$ kJ/mol,

$G_{Mn2+}=\Delta G_{Mn2+H2O/Mn}+(G_{Mn}+G_{H2O})=-221,287+(399,283+0)=177,996$ kJ/mol,

$G_{Mn}=G_{Mn2+}-(\Delta G_{eqMn2+/Mn}+G_{H2O})=177,996-(-221,287+0)=399,283$ kJ/mol,

$\Delta G_{Mn2+H2O/Mn}=E^\circ_{Mn2+/Mn}\bullet F\bullet 2=-1,146745*96485*2=-221,287$ kJ/mol,

$\Delta G_{Mn2+H2O/Mn}=G_{Mn2+}-(G_{Mn}+G_{H2O})=227,684-(448,971+0)=-221,287$ kJ/mol,

$G_{Mn2+}=\Delta G_{Mn2+H2O/Mn}+(G_{Mn}+G_{H2O})=-221,287+(448,971+0)=227,684$ kJ/mol,

$G_{Mn}=G_{Mn2+}-(\Delta G_{eqMn2+/Mn}+G_{H2O})=227,684-(-221,287+0)=448,971$ kJ/mol,

$Mn+H_2O=[Mn(\mathbf{H_2O})]^{2+}+2e^-$; Expression of potential has standard $E°_{classic}=-1{,}185$ V [1], water logarithm and $\Delta E°$: $E°_{Mn2+H2O/Mn}=E_o-0{,}0591/2•log(1/[\ H_2O]^6)=-1{,}185-0{,}0591/2*log(1/55{,}3^{\wedge 1})+0{,}10166-0{,}37239=$**-1,4042325 V**.

$\mathbf{\Delta G}_{Mn2+H2O/Mn}=E^{\circ}{}_{Mn2+/Mn}•F•2=$**-1,40423247**$*96485*2=$**-270,97474** $^{kJ}/_{mol}$,

$\mathbf{\Delta G}_{Mn2+H2O/Mn}=G_{Mn2+}-(G_{Mn}+G_{H2O})=$**-59,6247-(211,35**+0)=**-270,97474** $^{kJ}/_{mol}$,

$G_{Mn2+}=\mathbf{\Delta G}_{Mn2+H2O/Mn}+(G_{Mn}+G_{H2O})=$**270,97474**+(**211,35**+0)=**-59,6247** $^{kJ}/_{mol}$,

$G_{Mn}=G_{Mn2+}-(\mathbf{\Delta G}_{\mathbf{eq}Mn2+/Mn}+G_{H2O})=$**-59,6247-(-270,97474**+0)=**211,79** $^{kJ}/_{mol}$,

$\mathbf{\Delta G}_{Mn2+H2O/Mn}=E^{\circ}{}_{Mn2+/Mn}•F•2=$**-1,40423247**$*96485*2=$**-270,97474** $^{kJ}/_{mol}$,

$\mathbf{\Delta G}_{Mn2+H2O/Mn}=G_{Mn2+}-(G_{Mn}+G_{H2O})=$**177,996-(448,971**+0)=**-270,97474** $^{kJ}/_{mol}$,

$G_{Mn2+}=\mathbf{\Delta G}_{Mn2+H2O/Mn}+(G_{Mn}+G_{H2O})=$**-270,97474**+(**448,971**+0)=**177,996** $^{kJ}/_{mol}$,

$G_{Mn}=G_{Mn2+}-(\mathbf{\Delta G}_{\mathbf{eq}Mn2+/Mn}+G_{H2O})=$**177,996-(-270,97474**+0)=**448,971** $^{kJ}/_{mol}$,

$MnO_4^{2-}=MnO_4^-+\mathbf{e^-}$; Absolūtais aprēķins satur standarta potenciālu $E°_{klasisko}=0{,}558$ V [1], ūdens logaritmu un $\Delta E°$:

$E°_{MnO4/MnO4-}=E°-0{,}0591/1•log([\ H_2O]^0)+0{,}10166-0{,}37239=0{,}558-0{,}000+0{,}10166-0{,}37239=$**0,28727** V;

$MnO_4^-+\mathbf{e}^-=MnO_4^{2-}$; inverse $\mathbf{\Delta G}_{\mathbf{eqeq}MnO4-MnO42-}=E^{\circ}{}_{\mathbf{eq}MnO4-MnO42-}•F•1=$**-0,28727**$*96485*1=$**-27,717** $^{kJ}/_{mol}$,

$\mathbf{\Delta G}_{\mathbf{eq}MnO4-/MnO42-}=G_{MnO42-}-G_{MnO4-}=$**449,233-(714,133)=-27,717** $^{kJ}/_{mol}$,

$G_{MnO42-}=\mathbf{\Delta G}_{\mathbf{eq}MnO4-/MnO42-}+G_{MnO4-}=$**-27,717+(714,133)=449,233** $^{kJ}/_{mol}$,

$Mn\underline{O_2}+4OH^-=MnO_4^-+2H_2O+\mathbf{3e^-}$; Absolūtais aprēķins satur standarta potenciālu $E°_{klasisko}=0{,}595$ V [1],

ūdens logaritmu -0,06866 V un $\Delta E°$: $E°_{MnO2//OH}=$**0,25561** V

$E°_{MnO2//OH}=E°_{classic}-0{,}0591/3•log([H_2O]^2)+0{,}10166-0{,}37239=$ =

$=0{,}595-0{,}0591/3•log(55{,}3^{\wedge 2})+0{,}10166-0{,}37239=$**0,25561** V

$\mathbf{\Delta G}_{MnO2//OH}=E°_{MnO2//OH}•F•3=$**0,25561**$*96485*3=$**73,9876** $^{kJ}/_{mol}$,

$\mathbf{\Delta G}_{\mathbf{eq}MnO2/MnO4-}=G_{MnO4-}+2G_{H2O}-(G_{MnO2}+4G_{OH-})=$**714,133**+2*0-(**93,5224**+4*77,36)=**73,9876** $^{kJ}/_{mol}$,

$G_{MnO2}=G_{MnO4-}+2G_{H2O}-(\mathbf{\Delta G}_{\mathbf{eq}MnO2/MnO4-}+4G_{OH-})=$**714,133**+2*0-(**73,9876**+4*77,36)=**330,7054** $^{kJ}/_{mol}$,

$Mn\underline{O_2}+6H_2O=MnO_4^-+4H_3O^++\mathbf{3e^-}$; Expression of potential has standard $E°_{classic}=1{,}679$ V [1],

water logarithm $-0{,}0591/3*log(1/55{,}3^{\wedge 6})=+0{,}20599$ and $\Delta E°=0{,}10166-0{,}37239$

$E°_{MnO2/H+}=E°_{MnO2/H+}-0{,}0591/3•log(1/[H_2O]^6)+\Delta E°=1{,}679-0{,}0591/3*log(1/55{,}3^{\wedge 6})+0{,}10166-0{,}37239=$**1,61426** V

$\mathbf{\Delta G}_{\mathbf{eq}MnO2/H+}=E^{\circ}{}_{MnO2/H+}•F•3=$**1,61426**$*96485*3=$**467,2556** $^{kJ}/_{mol}$,

$\mathbf{\Delta G}_{\mathbf{eq}MnO2/H+}=G_{MnO4-}+4G_{H3O+}-(G_{MnO2}+6G_{H2O})=$**714,133**+4*22,44-(**336,6374**+6*0)=**467,2556** $^{kJ}/_{mol}$,

$G_{MnO2}=G_{MnO4-}+4G_{H3O+}-(\mathbf{\Delta G}_{\mathbf{eq}MnO2/H+}+6G_{H2O})=$**714,133**+4*22,44-(**467,2556**+6*0)=**336,6374** $^{kJ}/_{mol}$,

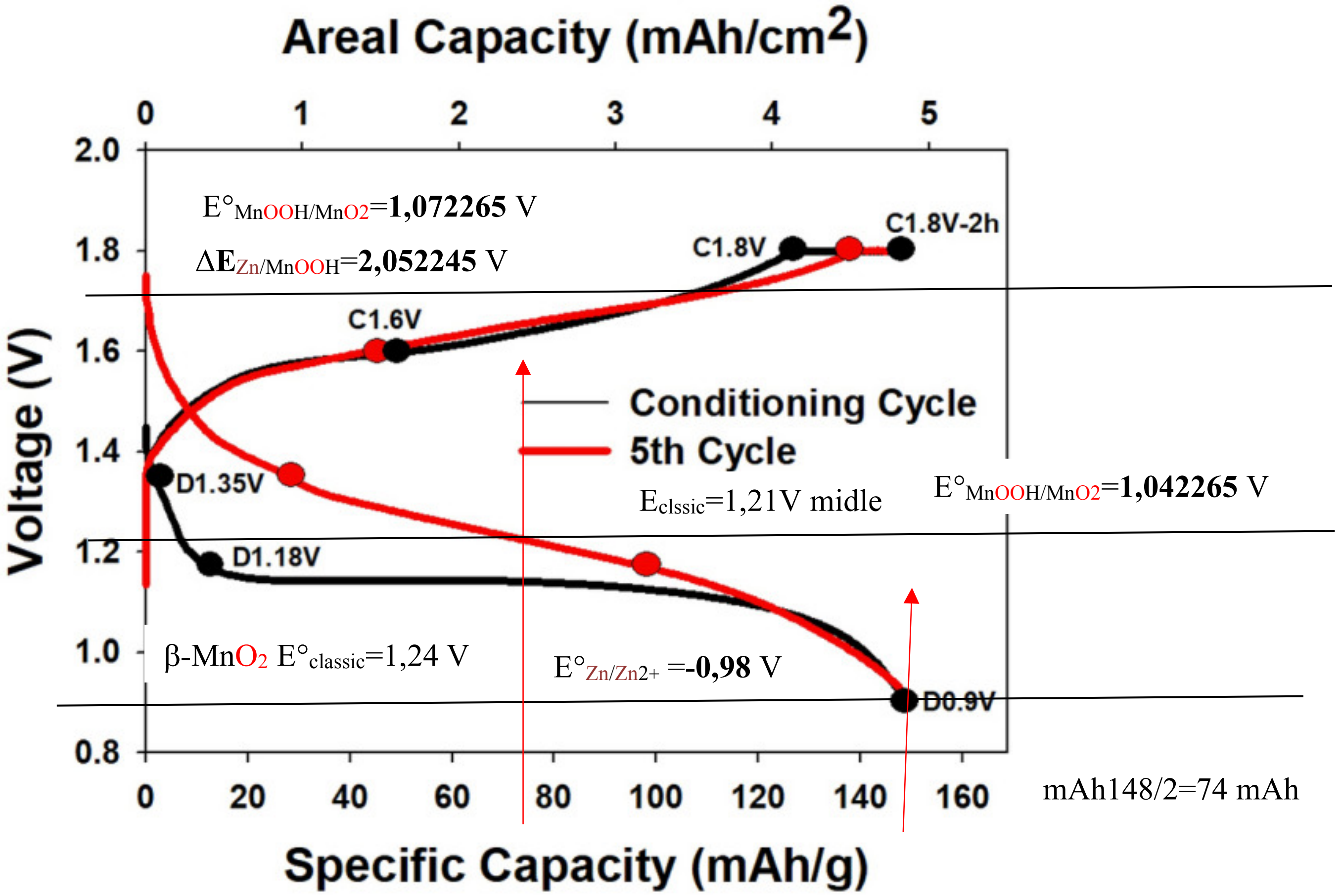



**Figure 2.** Discharge/charge voltage profiles for the first and fifth cycles of a Zn||EMD cell showing where electrodes were extracted for characterization. $\underline{MnO_2}+H_3O^++\mathbf{e^-}=MnOOH+H_2O$; $Zn+H_2O=Zn^{2+}+\mathbf{2e^-}$;

Manganese(III) oxyhydroxide $MnOOH+H_2O=\beta\text{-}MnO_2+H_3O^++e^-$; oxidation Nernst's half reaction Average standard potential has $E°_{classic}$=1,24 V [36], water logarithm and sum $\Delta E°$:

$E°_{MnOOH/MnO2}=E°-0{,}0591/1\cdot\log(1/[H_2O]^1)+0{,}10166-0{,}37239=1{,}24+0{,}103+0{,}10166-0{,}37239=\mathbf{1{,}072265}$ V;

$\beta\text{-}MnO_2+H_3O^++e^-=MnOOH+H_2O$;inverse $\Delta\mathbf{G}_{MnOOH/MnO2}=E°_{MnOOH/MnO2}\cdot F\cdot 1=\mathbf{-1{,}072265}*96485*1=\mathbf{-103{,}4575}$ $^{kJ}/_{mol}$,

$\Delta\mathbf{G}_{\mathbf{eq}MnOOH/MnO2}=G_{MnOOH}+G_{H2O}-(G_{MnO2}+G_{H3O+})=\mathbf{255{,}62}+0-(\mathbf{336{,}6374}+22{,}44)=\mathbf{-103{,}4575}$ $^{kJ}/_{mol}$,

$G_{MnOOH}=\Delta\mathbf{G}_{\mathbf{eq}MnOOH/MnO2}+G_{H2O}-(G_{MnO2}+G_{H3O+})=\mathbf{-103{,}4575}-0+(\mathbf{336{,}6374}+22{,}44)=\mathbf{255{,}62}$ $^{kJ}/_{mol}$,

Formation $\Delta G°_{MnOOH}=G_{MnOOH}-(G_{Mn}+G_{\mathbf{O2}}{}^{gas}+0{,}5G_{H2})=\mathbf{255{,}62}-(\mathbf{448{,}971}+\mathbf{303{,}1}+0{,}5*\mathbf{85{,}64})=\mathbf{-538{,}849}$ $^{kJ}/_{mol}$.

$G_{MnOOH}=\Delta G°_{MnOOH}+(G_{Mn}+G_{\mathbf{O2}}{}^{gas}+0{,}5G_{H2})=\mathbf{-538{,}849}+(\mathbf{448{,}971}+\mathbf{303{,}1}+0{,}5*\mathbf{85{,}64})=\mathbf{256{,}042}$ $^{kJ}/_{mol}$.

$\mathbf{K}_{\mathbf{eq}MnOOH/MnO2}=[MnOOH]*[H_2O]/[\underline{MnO_2}]/[H_3O^+]=([MnOOH]/[\underline{MnO_2}])*(55{,}3/10^{\wedge(-7{,}36)})=10^{\wedge 18{,}125}=$

$=\mathbf{exp(-\Delta G_{eq\,MnOOH/MnO2}/R/T)}=\exp(\mathbf{103457{,}5}/8{,}3144/298{,}15)=10^{\wedge 18{,}125}$;

In water medium and pH=7,36 ratio is $([MnOOH]/[\underline{MnO_2}])=10^{\wedge 18{,}125}/(55{,}3/10^{\wedge(-7{,}36)})=1052627880$;

$\varepsilon\text{-}MnO_2$ E°=1,322 V; $\beta\text{-}MnO_2$ E°=1,238 to 1,242 V; average $E°_{classic}$=1,24 V; $\gamma\text{-}MnO_2$ E°=1,322 V; [36] standard Gibbs energies of formation are calculated to $\beta\text{-}MnO_2$ be -462,7 $^{kJ}/_{mol}$ and $\varepsilon\text{-}MnO_2$ -427,3 $^{kJ}/_{mol}$, rand from CRC 2017 [1] $\Delta G°_{MnO2}$=-465,1 $^{kJ}/_{mol}$ like$\beta\text{-}MnO_2$ be -462,7 $^{kJ}/_{mol}$ respectively.

Formation shows more deep stability $\Delta G°_{MnOOH}$=**-535,5297** $^{kJ}/_{mol}$ between manganesium oxides, where one mol manganesium invest free energy $G_{Mn}$=**448,971** $^{kJ}/_{mol}$, as in formation of $\beta\text{-}MnO_2$ just $G_{Mn}$=**162** $^{kJ}/_{mol}$.

Since $\beta\text{-}MnO_2$ is the thermodynamically most stable in phase of $MnO_2$, these formation energies indicate that the $\varepsilon\text{-}MnO_2$ is less stable by -35,4 $^{kJ}/_{mol}$, i. e., $\varepsilon\text{-}MnO_2$ => $\beta\text{-}MnO_2$ $\Delta G°$ transform: -35:4 $^{kJ}/_{mol}$ ;

$Zn+H_2O=Zn^{2+}+\mathbf{2e^-}$, $2\beta\text{-}MnO_2+2H_3O^++\mathbf{2e^-}=2MnOOH+2H_2O$; $Zn+2\beta\text{-}MnO_2+2H_3O^+=Zn^{2+}+2MnOOH+2H_2O$,

Absolute potential has $E°_{Classic}$=-0,7618 V [32], water logarithm -0,0515 and sum $\Delta E°$ summa

$\Delta E°$: $E°_{Zn/Zn2+}=E°_{classic}-0{,}0591/2*\log(1/([H_2O]))+\Delta E°=-0{,}7618+0{,}051497+0{,}10166-0{,}371339=\mathbf{-0{,}97998}$ V.

$\Delta\mathbf{G}_{\mathbf{eq\_}Zn}=E°_{Zn}\cdot F\cdot 2=\mathbf{-0{,}97998}*96485*2=\mathbf{-189{,}10674}$ $^{kJ}/_{mol}$,

$\Delta\mathbf{G}_{\mathbf{eq}Zn}=G_{Zn2+}-(G_{Zn}+G_{H2O})=\mathbf{215{,}55}-(\mathbf{404{,}657}+\mathbf{0})=\mathbf{-189{,}107}$ $^{kJ}/_{mol}$;

$G_{Zn2+}=\Delta\mathbf{G}_{\mathbf{eq}Zn}+(G_{Zn}+G_{H2O})=\mathbf{-189{,}107}+(\mathbf{404{,}657}+\mathbf{0})=\mathbf{215{,}55}$ $^{kJ}/_{mol}$;

$\Delta\mathbf{G}_{\mathbf{eq}\,Zn/MnOOH}=(E°_{Zn/Zn2+}-E°_{MnOOH/MnO2})\cdot F\cdot 1\cdot 2=(\mathbf{-0{,}97998-1{,}0723})*96485*2=\mathbf{-2{,}0523}*96485*2=\mathbf{-396{,}0217}$ $^{kJ}/_{mol}$.

$\mathbf{K_{eq}=exp(-\Delta G_{eq\,H/MnO4}/R/T)}=\exp(\mathbf{396021{,}7}/8{,}3144/298{,}15)=\exp(159{,}7546)=10^{\wedge 69{,}3805}$ ;

Sum of standard potentials $\Delta\mathbf{E}_{Zn/MnOOH}=(E°_{Zn/Zn2+}-E°_{MnOOH/MnO2})=(\mathbf{-0{,}97998-1{,}072265})=\mathbf{-2{,}052245}$ V;

$MnO_4^-+8H_3O^++5e^-=Mn^{2+}+12H_2O$; $\underline{5H(Pt)}+5H_2O=5H_3O^++5e^-$;

$MnO_4^-+3H_3O^++\underline{5H(Pt)}=Mn^{2+}+7H_2O$;

Balancing the Electrons $+ne^-=5e^-=-ne^-$ gives the Red-Ox reaction: $MnO_4^-+3H_3O^++\underline{5H(Pt)}=Mn^{2+}+7H_2O$;

Absolute scale Biochemistry Thermodynamic, Massachusetts Technology Inst. [8] pH=7,36

$\Delta\mathbf{G}_{\mathbf{eq}H/MnO4}=(E°_H-E°_{MnO4-})\cdot F\cdot 1\cdot 5=(-0{,}27073-\mathbf{1{,}483458})*96485*5=\mathbf{-1{,}754188}*96485*5=\mathbf{-846{,}2641459}$ $^{kJ}/_{mol}$

$\Delta G_{HessPt)H}=G_{Mn2+}+7G_{H2O}-(G_{MnO4}+3G_{H3O}+5G_{H(Pt)})=\mathbf{177{,}989}+7*0-(\mathbf{714{,}133}+3*\mathbf{22{,}44}+5*\mathbf{48{,}56})=\mathbf{-846{,}2642}$ $^{kJ}/_{mol}$;

$G_{MnO4-}=G_{Mn2+}+7G_{H2O}-(\Delta G_{HessPt)H}+3G_{H3O}+5G_{H(Pt)})=\mathbf{177{,}989}+7*0-(\mathbf{-846{,}2642}+3*\mathbf{22{,}44}+5*\mathbf{48{,}56})=\mathbf{714{,}133}$ $^{kJ}/_{mol}$;

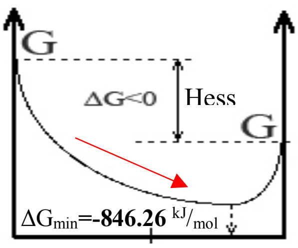
$G_{Mn2+}=\Delta G_{HessPt)H}-7G_{H2O}+(G_{MnO4}+3G_{H3O}+5G_{H(Pt)})=\mathbf{-846{,}2642}-7*0+(\mathbf{714{,}133}+3*\mathbf{22{,}44}+5*\mathbf{48{,}56})=\mathbf{177{,}989}$ $^{kJ}/_{mol}$;

$E°_H-E°_{MnO4-}=\mathbf{-1{,}754188}$ V

$\mathbf{K_{eq}=exp(-\Delta G_{eq\,H/MnO4}/R/T)}=\exp(\mathbf{846264{,}1459}/8{,}3144/298{,}15)=\exp(341{,}382)=10^{\wedge 148{,}26}$;

Exothermic and exoergonic $MnO_4^-$ reduction by $\underline{5H(Pt)}$ Hess free energy change negative and equilibrium state minimum $\Delta\mathbf{G}_{\mathbf{min}}=\Delta\mathbf{G}_{\mathbf{eqOxRed}}=\mathbf{-846{,}26}$ $^{kJ}/_{mol}$ reaching

equilibrium mixture $10^{148{,}5}=\mathbf{K_{eq}}=\dfrac{[H_2O]^7\cdot[Mn^{2+}]}{[(Pt)H]^5\cdot[MnO_4^-]\cdot[H_3O^+]^3}$;




Prigogine attractor is free energy change minimum $\Delta G_{min}$. Free energy change minimum reaching establishes equilibrium. Equilibrium state is attractor for all infinite non-equilibrium states.

5A+B+3C 50% D+8E

reactants_ $\underline{5H(Pt)}+MnO_4^-+3H_3O^+$

products $Mn^{2+}+7H_2O$

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