

Prigogine electrochemistry attractors for dissolution, protolysis, and reduction-oxidation of Mn compounds.

$\text{MnO}_2 + 4\text{OH}^- = \text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^-$; Expression of absolute potential has standard $E^\circ_{\text{classic}} = 0,595 \text{ V}$ [1],

water logarithm $-0,0591/3 \cdot \log(55,3^{\wedge}2) = -0,068663$ and sum $\Delta E^\circ = 0,10166 - 0,37239$:

$E^\circ_{\text{MnO}_2/\text{MnO}_4^-} = E^\circ_{\text{MnO}_2/\text{MnO}_4^-} - 0,0591/3 \cdot \log([\text{H}_2\text{O}]^2) + \Delta E^\circ = 0,595 - 0,0591/3 \cdot \log(55,3^{\wedge}2) + 0,10166 - 0,37239 = 0,25561 \text{ V}$

$\Delta G_{\text{eqMnO}_2/\text{MnO}_4^-} = E^\circ_{\text{MnO}_2/\text{MnO}_4^-} \cdot F \cdot 3 = -0,25561 \cdot 96485 \cdot 3 = 73,9876 \text{ kJ/mol}$,

$\Delta G_{\text{eqMnO}_2/\text{MnO}_4^-} = G_{\text{MnO}_4^-} + 2G_{\text{H}_2\text{O}} - (G_{\text{MnO}_2} + 4G_{\text{OH}^-}) = 476,95 + 2 \cdot 0 - (93,5224 + 4 \cdot 77,36) = 73,9876 \text{ kJ/mol}$,

$G_{\text{MnO}_2} = G_{\text{MnO}_4^-} + 2G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqMnO}_2/\text{MnO}_4^-} + 4G_{\text{OH}^-}) = 476,95 + 2 \cdot 0 - (73,9876 + 4 \cdot 77,36) = 93,5224 \text{ kJ/mol}$,

$\text{MnO}_2 + 6\text{H}_2\text{O} = \text{MnO}_4^- + 4\text{H}_3\text{O}^+ + 3\text{e}^-$; Expression of potential has standard $E^\circ_{\text{classic}} = 1,679 \text{ V}$ [1], water logarithm

$-0,0591/3 \cdot \log(1/55,3^{\wedge}6) = +0,20599$ and $\Delta E^\circ = 0,10166 - 0,37239$:

$E^\circ_{\text{MnO}_2/\text{MnO}_4^-} = E^\circ_{\text{MnO}_2/\text{H}^+} - 0,0591/3 \cdot \log(1/[\text{H}_2\text{O}]^6) + \Delta E^\circ = 1,679 - 0,0591/3 \cdot \log(1/55,3^{\wedge}6) + 0,10166 - 0,37239 = 1,61426 \text{ V}$

$\Delta G_{\text{eqMnO}_2/\text{H}^+} = E^\circ_{\text{MnO}_2/\text{H}^+} \cdot F \cdot 3 = 1,61426 \cdot 96485 \cdot 3 = 467,2556 \text{ kJ/mol}$,

$\Delta G_{\text{eqMnO}_2/\text{H}^+} = G_{\text{MnO}_4^-} + 4G_{\text{H}_3\text{O}^+} - (G_{\text{MnO}_2} + 6G_{\text{H}_2\text{O}}) = 476,95 + 4 \cdot 22,44 - (99,4544 + 6 \cdot 0) = 467,2556 \text{ kJ/mol}$,

$G_{\text{MnO}_2} = G_{\text{MnO}_4^-} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqMnO}_2/\text{H}^+} + 6G_{\text{H}_2\text{O}}) = 476,95 + 4 \cdot 22,44 - (467,2556 + 6 \cdot 0) = 99,4544 \text{ kJ/mol}$,

Substanc	$\Delta H^\circ_{\text{H}}$, kJ/mol	$\Delta S^\circ_{\text{H}}$, J/mol/K	$\Delta G^\circ_{\text{H}}$, kJ/mol
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
H₃O⁺	$G_{\text{AlbertyH}_3\text{O}^+}$	22,44	-257,46
H₃O⁺	-285,809	-168,8	-217,2345
$G_{\text{e-}}$ H₃O⁺	formation	-235,48	22,029
H₂gas	Alberty	pH=7,36	85,64
H₂(aq)	23,4	-130	99,13
H₂(aq)	-5,02	-363,92	103,24
H(Pt)aq	-	-	48,56
MnO₄⁻	-541,4	-191,2	-447,2
MnO₄⁻	formation	-447,2	391,572
MnO₄⁻	$E^\circ_{\text{Mn}^{2+}/\text{MnO}_4^-}$	1,483458V	714,133
MnO₄⁻	$\Delta E^\circ_{\text{H}^+/\text{MnO}_4^-}$	-1,754188	714,133
MnO₄²⁻	-653,0	59,0	-500,7
MnO₄²⁻	formation	-500,7	359,294
MnO₄²⁻	=0,25561	457,396	449,233
MnO	-385,2	59,7	-362,9
MnO	formation	-362,9	0
MnO₂	-520	53,1	-465,1
MnO₂	formation	-465,1	49,35
MnO₂	$G_{\text{MnO}_2} = 0$ kJ/mol [1,8]		$G_{\text{Mn}} = 162$
MnO₂	$E^\circ_{\text{MnO}_2/\text{OH}^-}$	0,25561 V	330,7054
MnO₂	$E^\circ_{\text{MnO}_2/\text{H}^+}$	1,61426	336,6374
MnOOH	$E^\circ_{\text{MnOOH}/\text{MnO}_2}$	1,072265V	255,62
MnOOH	Formation	1,072265V	256,042
Mn²⁺	-220,8	-73,6	-228,1
Mn²⁺	$E^\circ_{\text{Mn}(\text{H}_2\text{O})_6/\text{Mn}}$	-1,146745	227,684
Mn²⁺	$E^\circ_{\text{Mn}^{2+}/\text{Mn}}$	-1,404233	177,996
Mn²⁺	$E^\circ_{\text{H}^+} - E^\circ_{\text{MnO}_4^-}$	-1,754188	177,989
$G_{\text{e-}}$ Mn²⁺	formation	-228,1	21,44
MnH₂O²⁺	1,483458 V	-228,1	177,996
MnH₂O²⁺	formation	-228,1	415,181
Mn	$G_{\text{MnOOH}} =$	32,0 CRC	211,4
Mn	$G_{\text{Mn}^{2+}} =$	227,684	-1,146745
Mn	$G_{\text{MnMn}^{2+}} =$	177,996	-1,404233
O₂aqua	-11,7	-94,2	16,4

Formation $\text{Mn} + 2\text{O}_2^{\text{gas}} + \text{e}^- = \text{MnO}_4^-$;

$\Delta G^\circ_{\text{MnO}_4^-} = G_{\text{MnO}_4^-} - (G_{\text{Mn}} + 2G_{\text{O}_2} + G_{\text{e-}}) = 714,133 - (211,35 + 2 \cdot 303,1 + 21,222) = -447,2 \text{ kJ/mol}$;

$G_{\text{BioChemH}_2\text{O}} = 237,191 - 151,549 = 85,642 \text{ kJ/mol}$.

CRC Handbook of Chemistry and Physics, [1]

Biochem.Thermodyn., Massachusetts Technology Inst.[8] pH=7,36

$\Delta G^\circ_{\text{H}_3\text{O}^+ \text{ absolute}} = G_{\text{H}_3\text{O}^+} - (0,5G_{\text{H}_2}^{\text{gas}} + 1,5 \cdot G_{\text{O}_2}^{\text{gas}}) = -257,46 \text{ kJ/mol}$;

$\Delta G^\circ_{\text{H}_3\text{O}^+} = \Delta H - T \cdot \Delta S = -285,809 - 298,15 \cdot -168,8/1000 = -235,48 \text{ kJ/mol}$;

$G_{\text{e-}} = \Delta G^\circ - G_{\text{H}_3\text{O}^+} + (1,5 \cdot G_{\text{H}_2}^{\text{gas}} + 0,5 \cdot G_{\text{O}_2}^{\text{gas}}) = 22,029 \text{ kJ/mol}$; [1,8,26].

Biochem.Thermodyn., Massachusetts Technology Inst.[8] pH=7,36

$\Delta H^\circ_{\text{H}_3\text{O}^+} = -285,809 \text{ kJ/mol}$ [Mischenko](#) 1972, Himia, Leningrad [26,1]

Biochem.Thermodyn., Massachusetts Technology Inst.[8] pH=7,36

$\Delta G_{\text{eq}} = -847,7 \text{ kJ/mol}$; $\Delta G_{\text{Hess}} = -1044,2 \text{ kJ/mol}$

[1]

[1,8] $G_{\text{MnO}_4^-} = \Delta G^\circ_{\text{MnO}_4^-} + (G_{\text{Mn}} + 2G_{\text{O}_2} + G_{\text{e-}}) = 391,572 \text{ kJ/mol}$;

$G_{\text{MnO}_4^-} = \Delta G_{\text{eqMn}^{2+}/\text{MnO}_4^-} - 8G_{\text{H}_3\text{O}^+} + (G_{\text{Mn}^{2+}} + 12G_{\text{H}_2\text{O}}) = 714,133 \text{ kJ/mol}$;

$G_{\text{MnO}_4^-} = G_{\text{Mn}^{2+}} + 7G_{\text{H}_2\text{O}} - (\Delta G_{\text{HessPt}})_{\text{H}} + 3G_{\text{H}_3\text{O}^+} + 5G_{\text{H(Pt)}} = 714,133 \text{ kJ/mol}$;

[1]

[1,8] $G_{\text{MnO}_4^{2-}} = \Delta G^\circ_{\text{MnO}_4^{2-}} + (G_{\text{Mn}} + 2G_{\text{O}_2} + 2G_{\text{e-}}) = 359,294 \text{ kJ/mol}$;

$G_{\text{MnO}_4^{2-}} = \Delta G_{\text{eqMnO}_4^-/\text{MnO}_4^{2-}} + G_{\text{MnO}_4^-} = -27,717 + (714,13) = 449,23 \text{ kJ/mol}$;

$\Delta G^\circ = \Delta H - T \cdot \Delta S = -385,2 - 298,15 \cdot -0,0592 = -367,5495 \text{ kJ/mol}$; [1]

$G_{\text{MnO}} = \Delta G^\circ_{\text{MnO}} + (G_{\text{Mn}} + G_{\text{O}_2}^{\text{gas}}) = -362,9 + (211,35 + 0,5 \cdot 303,1) = 0 \text{ kJ/mol}$;

$\Delta G^\circ = \Delta H - T \cdot \Delta S = -520 - 298,15 \cdot -0,0531 = -504,168 \text{ kJ/mol}$; [1]

$G_{\text{MnO}_2} = \Delta G^\circ_{\text{MnO}_2} + (G_{\text{Mn}} + G_{\text{O}_2}^{\text{gas}}) = 465,1 + (211,35 + 303,1) = 49,35 \text{ kJ/mol}$;

$G_{\text{MnO}_2} = 0 = \Delta G^\circ_{\text{MnO}_2} + G_{\text{Mn}} + G_{\text{O}_2}^{\text{gas}} = -465,1 + G_{\text{Mn}} + 303 \text{ kJ/mol}$; [1,8]

OH- $G_{\text{MnO}_2} = G_{\text{MnO}_4^-} + 2G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqMnO}_2/\text{MnO}_4^-} + 4G_{\text{OH}^-}) = 330,7054 \text{ kJ/mol}$;

H+ $G_{\text{MnO}_2} = G_{\text{MnO}_4^-} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqMnO}_2/\text{H}^+} + 6G_{\text{H}_2\text{O}}) = 336,6374 \text{ kJ/mol}$;

$G_{\text{MnOOH}} = \Delta G_{\text{eqMnOOH}/\text{MnO}_2} + G_{\text{H}_2\text{O}} - (G_{\text{MnO}_2} + G_{\text{H}_3\text{O}^+}) = 255,62 \text{ kJ/mol}$;

$G_{\text{MnOOH}} = \Delta G^\circ_{\text{MnOOH}} + (G_{\text{Mn}} + G_{\text{O}_2}^{\text{gas}} + 0,5G_{\text{H}_2}) = 256,042 \text{ kJ/mol}$;

$\Delta G^\circ = \Delta H - T \cdot \Delta S = -220,8 - 298,15 \cdot -0,073 = -199,035 \text{ kJ/mol}$; [1]

$G_{\text{Mn}^{2+}} = \Delta G_{\text{Mn}^{2+}/\text{H}_2\text{O}/\text{Mn}} + G_{\text{Mn}} + G_{\text{H}_2\text{O}} = -221,287 + 448,97 = 227,684 \text{ kJ/mol}$;

$G_{\text{Mn}^{2+}} = \Delta G_{\text{Mn}^{2+}/\text{H}_2\text{O}/\text{Mn}} + (G_{\text{Mn}} + G_{\text{H}_2\text{O}}) = -270,97474 + 448,97 = 178 \text{ kJ/mol}$;

$G_{\text{Mn}^{2+}} = \Delta G_{\text{HessPt}}_{\text{H}} - 7G_{\text{H}_2\text{O}} + (G_{\text{MnO}_4^-} + 3G_{\text{H}_3\text{O}^+} + 5G_{\text{H(Pt)}}) = 177,989 \text{ kJ/mol}$;

$G_{\text{Mn}^{2+}} = 448,97$; $2G_{\text{e-}} = \Delta G^\circ_{\text{Mn}^{2+}} - G_{\text{Mn}^{2+}} + (G_{\text{Mn}}) = 2 \cdot 21,44 \text{ kJ/mol}$;

$G_{[\text{Mn}(\text{H}_2\text{O})_2]^{2+}} = \Delta G^\circ_{\text{Mn}^{2+}} - 2G_{\text{e-}} + (G_{\text{Mn}} + G_{\text{H}_2} + 0,5G_{\text{O}_2}/2) = 177,996 \text{ kJ/mol}$;

$G_{[\text{Mn}(\text{H}_2\text{O})_2]^{2+}} = \Delta G^\circ_{\text{Mn}^{2+}} - 2G_{\text{e-}} + (G_{\text{Mn}} + G_{\text{H}_2} + 0,5G_{\text{O}_2}/2) = 415,181 \text{ kJ/mol}$;

$G_{\text{Mn}} = -\Delta G^\circ_{\text{MnO}_2} - G_{\text{O}_2}^{\text{gas}} = 362,9 - 0,5 \cdot 303,1 = 211,35 \text{ kJ/mol}$. [1,8]

$G_{\text{Mn}} = G_{\text{Mn}^{2+}} - (\Delta G_{\text{eqMn}^{2+}/\text{Mn}} + G_{\text{H}_2\text{O}}) = 227,684 + 221,287 = 448,971 \text{ kJ/mol}$;

$G_{\text{Mn}} = G_{\text{Mn}^{2+}} - (\Delta G_{\text{eqMn}^{2+}/\text{Mn}} + G_{\text{H}_2\text{O}}) = 448,971 \text{ kJ/mol}$;

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$$\begin{aligned}
G_{MnO_4} &= \Delta G^\circ_{MnO_4} + (G_{Mn} + 2G_{O_2} + G_{e^-}) = -447,2 + (211,35 + 2 \cdot 303,1 + 21,222) = 714,133 \text{ kJ/mol}; \\
G_{e^-} &= G_{MnO_4} - (G_{Mn} + 2G_{O_2} + \Delta G^\circ_{MnO_4}) = 714,133 - (211,35 + 2 \cdot 303,1 - 447,2) = 21,222 \text{ kJ/mol}; \\
\Delta G^\circ_{MnO_4} &= G_{MnO_4} - (G_{Mn} + 2G_{O_2} + G_{e^-}) = 476,957 - (211,35 + 2 \cdot 303,1 + 21,222) = -447,2 \text{ kJ/mol}; \\
G_{MnO_4} &= \Delta G^\circ_{MnO_4} + (G_{Mn} + 2G_{O_2} + G_{e^-}) = -447,2 + (211,35 + 2 \cdot 303,1 + 21,222) = 476,957 \text{ kJ/mol}; \\
G_{e^-} &= G_{MnO_4} - (G_{Mn} + 2G_{O_2} + \Delta G^\circ_{MnO_4}) = 476,957 - (211,35 + 2 \cdot 303,1 - 447,2) = 21,222 \text{ kJ/mol}; \\
\text{Formation Mn} + 2O_2^{gas} + 2e^- &= MnO_4^{2-}; \\
\Delta G^\circ_{MnO_4^{2-}} &= G_{MnO_4^{2-}} - (G_{Mn} + 2G_{O_2} + 2G_{e^-}) = 359,294 - (211,35 + 2 \cdot 303,1 + 2 \cdot 21,222) = -500,7 \text{ kJ/mol}; \\
G_{MnO_4^{2-}} &= \Delta G^\circ_{MnO_4^{2-}} + (G_{Mn} + 2G_{O_2} + 2G_{e^-}) = -500,7 + (211,35 + 2 \cdot 303,1 + 2 \cdot 21,222) = 359,294 \text{ kJ/mol}; \\
2G_{e^-} &= G_{MnO_4^{2-}} - (G_{Mn} + 2G_{O_2} + \Delta G^\circ_{MnO_4^{2-}}) = 359,294 - (211,35 + 2 \cdot 303,1 - 500,7) = 2 \cdot 21,222 = 42,444 \text{ kJ/mol}; \\
\text{Formation } 1,5H_2^{gas} + 0,5O_2^{gas} &= H_3O^+ + e^-; \Delta G^\circ_{H_3O^+} = \Delta H - T \cdot \Delta S = -285,809 - 298,15 \cdot (-168,8/1000) = -235,48 \text{ kJ/mol}; \\
\Delta G^\circ &= G_{H_3O^+} + G_{e^-} - (1,5 \cdot G_{H_2}^{gas} + 0,5 \cdot G_{O_2}^{gas}) = 22,44 + G_{e^-} - (1,5 \cdot 85,6 + 0,5 \cdot 303,1) = -235,48 \text{ kJ/mol}; \\
G_{e^-} &= \Delta G^\circ - G_{H_3O^+} + (1,5 \cdot G_{H_2}^{gas} + 0,5 \cdot G_{O_2}^{gas}) = -235,48 - 22,44 + (1,5 \cdot 85,6 + 0,5 \cdot 303,1) = 22,029 \text{ kJ/mol}; \\
\text{Formation Mn} + O_2^{gas} &= MnO_2; \Delta G^\circ_{MnO_2} = G_{MnO_2} - (G_{Mn} + G_{O_2}^{gas}) = 49,35 - (211,35 + 303,1) = -465,1 \text{ kJ/mol}; \\
G_{MnO_2} &= \Delta G^\circ_{MnO_2} + (G_{Mn} + G_{O_2}^{gas}) = -465,1 + (211,35 + 303,1) = 49,35 \text{ kJ/mol}; \\
G_{Mn} &= G_{MnO_2} - (\Delta G^\circ_{MnO_2} + G_{O_2}^{gas}) = 49,35 - (-465,1 + 303,1) = 211,35 \text{ kJ/mol. [1,8]} \\
\text{Formation Mn} + 0,5O_2^{gas} &= MnO; \Delta G^\circ_{MnO} = G_{MnO} - (G_{Mn} + G_{O_2}^{gas}/2) = 0 - (211,35 + 0,5 \cdot 303,1) = -362,9 \text{ kJ/mol}; \\
G_{MnO} &= \Delta G^\circ_{MnO} + (G_{Mn} + G_{O_2}^{gas}/2) = -362,9 + (211,35 + 0,5 \cdot 303,1) = 0 \text{ kJ/mol}; \\
G_{Mn} &= G_{MnO} - (\Delta G^\circ_{MnO} + G_{O_2}^{gas}/2) = 0 - (-362,9 + 0,5 \cdot 303,1) = 211,35 \text{ kJ/mol}; \\
Mn^{2+} + 12H_2O &= MnO_4^{2-} + 8H_3O^+ + 5e^-; \text{Expression of potential has standard } E^\circ_{classic} = 1,507 \text{ V [1], water logarithm and} \\
\Delta E^\circ: E^\circ_{Mn^{2+}/MnO_4^{2-}} &= E^\circ - 0,0591/5 \cdot \log(1/[H_2O]^{12}) = 1,507 - 0,0591/5 \cdot \log(1/55,3^{12}) + 0,10166 - 0,37239 = 1,483458 \text{ V.} \\
\Delta G_{eqMn^{2+}/MnO_4^{2-}} &= E^\circ_{Mn^{2+}/MnO_4^{2-}} \cdot F \cdot 5 = 1,483458 \cdot 96485 \cdot 5 = 715,657 \text{ kJ/mol}, \\
\Delta G_{eqMn^{2+}/MnO_4^{2-}} &= G_{MnO_4^{2-}} + 8G_{H_3O^+} - (G_{Mn^{2+}} + 12G_{H_2O}) = 476,95 + 8 \cdot 22,44 - (-59,187 + 12 \cdot 0) = 715,657 \text{ kJ/mol}, \\
G_{MnO_4^{2-}} &= \Delta G_{eqMn^{2+}/MnO_4^{2-}} - 8G_{H_3O^+} + (G_{Mn^{2+}} + 12G_{H_2O}) = 715,657 - 8 \cdot 22,44 + (-59,187 + 12 \cdot 0) = 476,95 \text{ kJ/mol}, \\
G_{Mn^{2+}} &= G_{MnO_4^{2-}} + 8G_{H_3O^+} - (\Delta G_{eqMn^{2+}/MnO_4^{2-}} + 12G_{H_2O}) = 476,95 + 8 \cdot 22,44 - (715,657 + 12 \cdot 0) = -59,187 \text{ kJ/mol}, \\
\Delta G_{eqMn^{2+}/MnO_4^{2-}} &= G_{MnO_4^{2-}} + 8G_{H_3O^+} - (G_{Mn^{2+}} + 12G_{H_2O}) = 714,133 + 8 \cdot 22,44 - (177,989 + 12 \cdot 0) = 715,657 \text{ kJ/mol}, \\
G_{MnO_4^{2-}} &= \Delta G_{eqMn^{2+}/MnO_4^{2-}} - 8G_{H_3O^+} + (G_{Mn^{2+}} + 12G_{H_2O}) = 715,657 - 8 \cdot 22,44 + (177,989 + 12 \cdot 0) = 714,133 \text{ kJ/mol}, \\
G_{Mn^{2+}} &= G_{MnO_4^{2-}} + 8G_{H_3O^+} - (\Delta G_{eqMn^{2+}/MnO_4^{2-}} + 12G_{H_2O}) = 714,133 + 8 \cdot 22,44 - (715,657 + 12 \cdot 0) = 177,989 \text{ kJ/mol}, \\
\text{Formation Mn} + 6H_2^{gas} + 3O_2^{gas} &= [Mn(H_2O)_6]^{2+} + 2e^-; \\
\text{One coordinative bond has } 190,5255 \text{ kJ/mol} &= H_2O \Rightarrow \square \Delta Mn^{2+}; \\
\text{but six coordinative bonds have sum of six times } 6 \cdot 190,5255 &= 1143,153 \text{ kJ/mol } [Mn(H_2O)_6]^{2+}; \\
\Delta G^\circ_{Mn^{2+}/MnO_4^{2-}} &= G_{Mn^{2+}} + 2G_{e^-} - (G_{Mn} + 6G_{H_2} + 3G_{O_2}) = G_{Mn^{2+}} + 2 \cdot 21,222 - (448,971 + 6 \cdot 85,64 + 3 \cdot 303,1) = -228,1 \text{ kJ/mol}; \\
G_{Mn^{2+}} &= \Delta G^\circ_{Mn^{2+}/MnO_4^{2-}} + (G_{Mn} + 6G_{H_2} + 3G_{O_2}) = -228,1 - 2 \cdot 21,222 + (448,971 + 6 \cdot 85,64 + 3 \cdot 303,1) = 1601,567 \text{ kJ/mol}; \\
\text{Formation Mn} &= Mn^{2+} + 2e^-; \\
\Delta G^\circ_{Mn^{2+}} &= G_{Mn^{2+}} + 2G_{e^-} - (G_{Mn}) = 177,989 + 2 \cdot 21,44 - (448,971) = -228,1 \text{ kJ/mol}; \\
2G_{e^-} &= \Delta G^\circ_{Mn^{2+}} - G_{Mn^{2+}} + (G_{Mn}) = -228,1 - (177,989) + (448,971) = 42,44 = 2 \cdot 21,44 \text{ kJ/mol}; \\
\text{Formation Mn} + 0,5O_2^{gas} + H_2^{gas} &= [Mn(H_2O)]^{2+} + 2e^-; \\
\Delta G^\circ_{Mn^{2+}} &= G_{[Mn(H_2O)]^{2+}} + 2G_{e^-} - (G_{Mn} + G_{H_2} + 0,5G_{O_2}/2) = 415,181 + 2 \cdot 21,44 - (448,971 + 85,64 + 303,1/2) = -228,1 \text{ kJ/mol}; \\
G_{[Mn(H_2O)]^{2+}} &= \Delta G^\circ_{Mn^{2+}} - 2G_{e^-} + (G_{Mn} + G_{H_2} + 0,5G_{O_2}/2) = -228,1 - 2 \cdot 21,44 + (448,971 + 85,64 + 303,1/2) = 415,181 \text{ kJ/mol}; \\
Mn + 6H_2O &= [Mn(H_2O)_6]^{2+} + 2e^-; \text{Expression of potential has standard } E^\circ_{classic} = -1,185 \text{ V [1], water logarithm and} \\
\Delta E^\circ: E^\circ_{Mn^{2+}/Mn} &= E^\circ - 0,0591/2 \cdot \log(1/[H_2O]^6) = -1,185 - 0,0591/2 \cdot \log(1/55,3^6) + 0,10166 - 0,37239 = -1,146745 \text{ V.} \\
\Delta G_{Mn^{2+}/Mn} &= E^\circ_{Mn^{2+}/Mn} \cdot F \cdot 2 = -1,146745 \cdot 96485 \cdot 2 = -221,287 \text{ kJ/mol}, \\
\Delta G_{Mn^{2+}/Mn} &= G_{Mn^{2+}} - (G_{Mn} + G_{H_2O}) = -9,937 - (211,35 + 0) = -221,287 \text{ kJ/mol}, \\
G_{Mn^{2+}} &= \Delta G_{Mn^{2+}/Mn} + (G_{Mn} + G_{H_2O}) = -221,287 + (211,35 + 0) = -9,937 \text{ kJ/mol}, \\
G_{Mn} &= G_{Mn^{2+}} - (\Delta G_{eqMn^{2+}/Mn} + G_{H_2O}) = -9,937 - (-221,287 + 0) = 211,35 \text{ kJ/mol}, \\
\Delta G_{Mn^{2+}/Mn} &= E^\circ_{Mn^{2+}/Mn} \cdot F \cdot 2 = -1,146745 \cdot 96485 \cdot 2 = -221,287 \text{ kJ/mol}, \\
\Delta G_{Mn^{2+}/Mn} &= G_{Mn^{2+}} - (G_{Mn} + G_{H_2O}) = 177,996 - (399,283 + 0) = -221,287 \text{ kJ/mol}, \\
G_{Mn^{2+}} &= \Delta G_{Mn^{2+}/Mn} + (G_{Mn} + G_{H_2O}) = -221,287 + (399,283 + 0) = 177,996 \text{ kJ/mol}, \\
G_{Mn} &= G_{Mn^{2+}} - (\Delta G_{eqMn^{2+}/Mn} + G_{H_2O}) = 177,996 - (-221,287 + 0) = 399,283 \text{ kJ/mol}, \\
\Delta G_{Mn^{2+}/Mn} &= E^\circ_{Mn^{2+}/Mn} \cdot F \cdot 2 = -1,146745 \cdot 96485 \cdot 2 = -221,287 \text{ kJ/mol}, \\
\Delta G_{Mn^{2+}/Mn} &= G_{Mn^{2+}} - (G_{Mn} + G_{H_2O}) = 227,684 - (448,971 + 0) = -221,287 \text{ kJ/mol}, \\
G_{Mn^{2+}} &= \Delta G_{Mn^{2+}/Mn} + (G_{Mn} + G_{H_2O}) = -221,287 + (448,971 + 0) = 227,684 \text{ kJ/mol}, \\
G_{Mn} &= G_{Mn^{2+}} - (\Delta G_{eqMn^{2+}/Mn} + G_{H_2O}) = 227,684 - (-221,287 + 0) = 448,971 \text{ kJ/mol},
\end{aligned}$$

$\text{Mn} + \text{H}_2\text{O} = [\text{Mn}(\text{H}_2\text{O})]^{2+} + 2\text{e}^-$; Expression of potential has standard $E^\circ_{\text{classic}} = -1,185 \text{ V}$ [1], water logarithm and ΔE° : $E^\circ_{\text{Mn}2+\text{H}_2\text{O}/\text{Mn}} = E^\circ - 0,0591/2 \cdot \log(1/[\text{H}_2\text{O}]^6) = -1,185 - 0,0591/2 \cdot \log(1/55,3^6) + 0,10166 - 0,37239 = -1,4042325 \text{ V}$.
 $\Delta G_{\text{Mn}2+\text{H}_2\text{O}/\text{Mn}} = E^\circ_{\text{Mn}2+\text{H}_2\text{O}/\text{Mn}} \cdot F \cdot 2 = -1,40423247 \cdot 96485 \cdot 2 = -270,97474 \text{ kJ/mol}$,
 $\Delta G_{\text{Mn}2+\text{H}_2\text{O}/\text{Mn}} = G_{\text{Mn}2+} - (G_{\text{Mn}} + G_{\text{H}_2\text{O}}) = -59,6247 - (211,35 + 0) = -270,97474 \text{ kJ/mol}$,
 $G_{\text{Mn}2+} = \Delta G_{\text{Mn}2+\text{H}_2\text{O}/\text{Mn}} + (G_{\text{Mn}} + G_{\text{H}_2\text{O}}) = 270,97474 + (211,35 + 0) = 482,32474 \text{ kJ/mol}$,
 $G_{\text{Mn}} = G_{\text{Mn}2+} - (\Delta G_{\text{eqMn}2+/\text{Mn}} + G_{\text{H}_2\text{O}}) = 482,32474 - (-270,97474 + 0) = 753,3 \text{ kJ/mol}$,
 $\Delta G_{\text{Mn}2+\text{H}_2\text{O}/\text{Mn}} = E^\circ_{\text{Mn}2+/\text{Mn}} \cdot F \cdot 2 = -1,40423247 \cdot 96485 \cdot 2 = -270,97474 \text{ kJ/mol}$,
 $\Delta G_{\text{Mn}2+\text{H}_2\text{O}/\text{Mn}} = G_{\text{Mn}2+} - (G_{\text{Mn}} + G_{\text{H}_2\text{O}}) = 177,996 - (448,971 + 0) = -270,97474 \text{ kJ/mol}$,
 $G_{\text{Mn}2+} = \Delta G_{\text{Mn}2+\text{H}_2\text{O}/\text{Mn}} + (G_{\text{Mn}} + G_{\text{H}_2\text{O}}) = -270,97474 + (448,971 + 0) = 177,996 \text{ kJ/mol}$,
 $G_{\text{Mn}} = G_{\text{Mn}2+} - (\Delta G_{\text{eqMn}2+/\text{Mn}} + G_{\text{H}_2\text{O}}) = 177,996 - (-270,97474 + 0) = 448,971 \text{ kJ/mol}$,
 $\text{MnO}_4^{2-} = \text{MnO}_4^- + \text{e}^-$; Expression of potential has standard $E^\circ_{\text{classic}} = 0,558 \text{ V}$ [1], water logarithm +0,20599 and ΔE° :
 $E^\circ_{\text{MnO}_4/\text{MnO}_4^-} = E^\circ - 0,0591/1 \cdot \log([\text{H}_2\text{O}]^0) + 0,10166 - 0,37239 = 0,558 - 0,000 + 0,10166 - 0,37239 = 0,28727 \text{ V}$;
 $\text{MnO}_4^- + \text{e}^- = \text{MnO}_4^{2-}$; inverse $\Delta G_{\text{eqMnO}_4/\text{MnO}_4^{2-}} = E^\circ_{\text{eqMnO}_4/\text{MnO}_4^{2-}} \cdot F \cdot 1 = -0,28727 \cdot 96485 \cdot 1 = -27,717 \text{ kJ/mol}$,
 $\Delta G_{\text{eqMnO}_4/\text{MnO}_4^{2-}} = G_{\text{MnO}_4^{2-}} - G_{\text{MnO}_4^-} = 449,233 - (714,133) = -27,717 \text{ kJ/mol}$,
 $G_{\text{MnO}_4^{2-}} = \Delta G_{\text{eqMnO}_4/\text{MnO}_4^{2-}} + G_{\text{MnO}_4^-} = -27,717 + (714,133) = 686,416 \text{ kJ/mol}$,
 $\text{MnO}_2 + 4\text{OH}^- = \text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^-$; Expression of potential has standard $E^\circ_{\text{classic}} = 0,595 \text{ V}$ [1],
water logarithm -0,06866 V and ΔE° : $E^\circ_{\text{MnO}_2/\text{OH}^-} = 0,25561 \text{ V}$
 $E^\circ_{\text{MnO}_2/\text{OH}^-} = E^\circ_{\text{classic}} - 0,0591/3 \cdot \log([\text{H}_2\text{O}]^2) + 0,10166 - 0,37239 =$
 $= 0,595 - 0,0591/3 \cdot \log(55,3^2) + 0,10166 - 0,37239 = 0,25561 \text{ V}$
 $\Delta G_{\text{MnO}_2/\text{OH}^-} = E^\circ_{\text{MnO}_2/\text{OH}^-} \cdot F \cdot 3 = 0,25561 \cdot 96485 \cdot 3 = 73,9876 \text{ kJ/mol}$,
 $\Delta G_{\text{eqMnO}_2/\text{MnO}_4^-} = G_{\text{MnO}_4^-} + 2G_{\text{H}_2\text{O}} - (G_{\text{MnO}_2} + 4G_{\text{OH}^-}) = 714,133 + 2 \cdot 0 - (93,5224 + 4 \cdot 77,36) = 73,9876 \text{ kJ/mol}$,
 $G_{\text{MnO}_2} = G_{\text{MnO}_4^-} + 2G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqMnO}_2/\text{MnO}_4^-} + 4G_{\text{OH}^-}) = 714,133 + 2 \cdot 0 - (73,9876 + 4 \cdot 77,36) = 330,7054 \text{ kJ/mol}$,
 $\text{MnO}_2 + 6\text{H}_2\text{O} = \text{MnO}_4^- + 4\text{H}_3\text{O}^+ + 3\text{e}^-$; Expression of potential has standard $E^\circ_{\text{classic}} = 1,679 \text{ V}$ [1],
water logarithm -0,0591/3 * log(1/55,3^6) = +0,20599 and $\Delta E^\circ = 0,10166 - 0,37239 = 1,61426 \text{ V}$
 $E^\circ_{\text{MnO}_2/\text{H}^+} = E^\circ_{\text{MnO}_2/\text{H}^+} - 0,0591/3 \cdot \log(1/[\text{H}_2\text{O}]^6) + \Delta E^\circ = 1,679 - 0,0591/3 \cdot \log(1/55,3^6) + 0,10166 - 0,37239 = 1,61426 \text{ V}$
 $\Delta G_{\text{eqMnO}_2/\text{H}^+} = E^\circ_{\text{MnO}_2/\text{H}^+} \cdot F \cdot 3 = 1,61426 \cdot 96485 \cdot 3 = 467,2556 \text{ kJ/mol}$,
 $\Delta G_{\text{eqMnO}_2/\text{H}^+} = G_{\text{MnO}_4^-} + 4G_{\text{H}_3\text{O}^+} - (G_{\text{MnO}_2} + 6G_{\text{H}_2\text{O}}) = 714,133 + 4 \cdot 22,44 - (336,6374 + 6 \cdot 0) = 467,2556 \text{ kJ/mol}$,
 $G_{\text{MnO}_2} = G_{\text{MnO}_4^-} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqMnO}_2/\text{H}^+} + 6G_{\text{H}_2\text{O}}) = 714,133 + 4 \cdot 22,44 - (467,2556 + 6 \cdot 0) = 336,6374 \text{ kJ/mol}$,

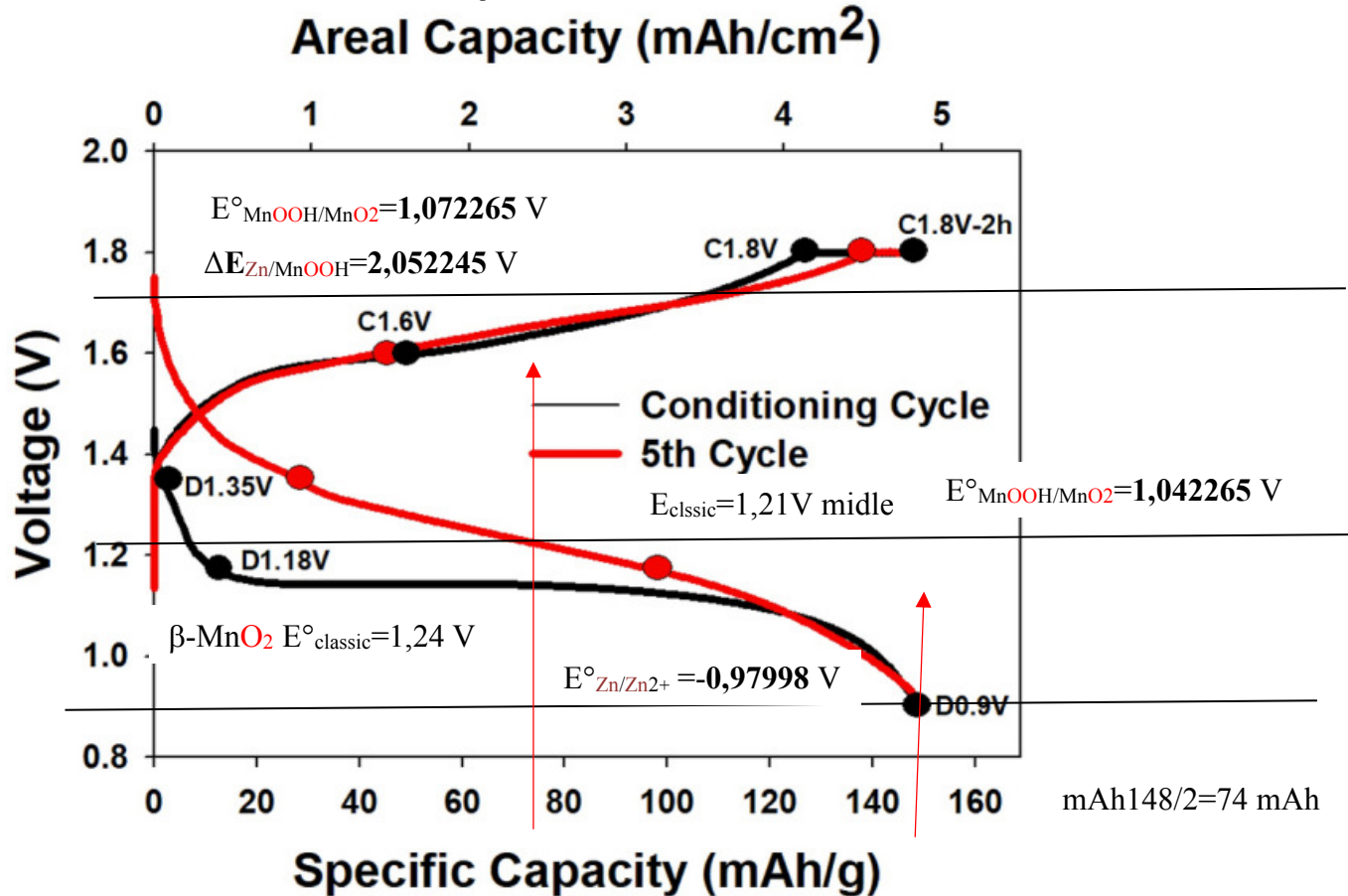


Figure 2. Discharge/charge voltage profiles for the first and fifth cycles of a Zn||EMD cell showing where electrodes were extracted for characterization. $\text{MnO}_2 + \text{H}_3\text{O}^+ + \text{e}^- = \text{MnOOH} + \text{H}_2\text{O}$; $\text{Zn} + \text{H}_2\text{O} = \text{Zn}^{2+} + 2\text{e}^-$;

Manganese(III) oxyhydroxide $\text{MnOOH} + \text{H}_2\text{O} = \beta\text{-MnO}_2 + \text{H}_3\text{O}^+ + \text{e}^-$; oxidation Nernst's half reaction Average standard potential has $E^\circ_{\text{classic}} = 1,24 \text{ V}$ [36], water logarithm and sum ΔE° :

$$E^\circ_{\text{MnOOH/MnO}_2} = E^\circ - 0,0591/1 \cdot \log(1/[\text{H}_2\text{O}]) + 0,10166 - 0,37239 = 1,24 + 0,103 + 0,10166 - 0,37239 = 1,072265 \text{ V};$$

$$\beta\text{-MnO}_2 + \text{H}_3\text{O}^+ + \text{e}^- = \text{MnOOH} + \text{H}_2\text{O}; \text{inverse } \Delta G_{\text{MnOOH/MnO}_2} = E^\circ_{\text{MnOOH/MnO}_2} \cdot F \cdot 1 = -1,072265 \cdot 96485 \cdot 1 = -103,4575 \text{ kJ/mol},$$

$$\Delta G_{\text{eqMnOOH/MnO}_2} = G_{\text{MnOOH}} + G_{\text{H}_2\text{O}} - (G_{\text{MnO}_2} + G_{\text{H}_3\text{O}^+}) = 255,62 + 0 - (336,6374 + 22,44) = -103,4575 \text{ kJ/mol},$$

$$G_{\text{MnOOH}} = \Delta G_{\text{eqMnOOH/MnO}_2} + G_{\text{H}_2\text{O}} - (G_{\text{MnO}_2} + G_{\text{H}_3\text{O}^+}) = -103,4575 - 0 + (336,6374 + 22,44) = 255,62 \text{ kJ/mol},$$

$$\text{Formation } \Delta G^\circ_{\text{MnOOH}} = G_{\text{MnOOH}} - (G_{\text{Mn}} + G_{\text{O}_2}^{\text{gas}} + 0,5 G_{\text{H}_2}) = 255,62 - (448,971 + 303,1 + 0,5 \cdot 85,64) = -538,849 \text{ kJ/mol}.$$

$$G_{\text{MnOOH}} = \Delta G^\circ_{\text{MnOOH}} + (G_{\text{Mn}} + G_{\text{O}_2}^{\text{gas}} + 0,5 G_{\text{H}_2}) = -538,849 + (448,971 + 303,1 + 0,5 \cdot 85,64) = 256,042 \text{ kJ/mol}.$$

$$K_{\text{eqMnOOH/MnO}_2} = [\text{MnOOH}] \cdot [\text{H}_2\text{O}] / [\text{MnO}_2] \cdot [\text{H}_3\text{O}^+] = ([\text{MnOOH}] / [\text{MnO}_2]) \cdot (55,3 / 10^{(-7,36)}) = 10^{18,125} = \exp(-\Delta G_{\text{eqMnOOH/MnO}_2} / R/T) = \exp(103457,5 / 8,3144 / 298,15) = 10^{18,125};$$

In water medium and pH=7,36 ratio is $([\text{MnOOH}] / [\text{MnO}_2]) = 10^{18,125} / (55,3 / 10^{(-7,36)}) = 1052627880$;
 $\epsilon\text{-MnO}_2$ $E^\circ = 1,322 \text{ V}$; $\beta\text{-MnO}_2$ $E^\circ = 1,238$ to $1,242 \text{ V}$; average $E^\circ_{\text{classic}} = 1,24 \text{ V}$; $\gamma\text{-MnO}_2$ $E^\circ = 1,322 \text{ V}$; [36]
 standard Gibbs energies of formation are calculated to $\beta\text{-MnO}_2$ be $-462,7 \text{ kJ/mol}$ and $\epsilon\text{-MnO}_2$ $-427,3 \text{ kJ/mol}$, and from CRC 2017 [1] $\Delta G^\circ_{\text{MnO}_2} = -465,1 \text{ kJ/mol}$ like $\beta\text{-MnO}_2$ be $-462,7 \text{ kJ/mol}$ respectively.

Formation shows more deep stability $\Delta G^\circ_{\text{MnOOH}} = -535,5297 \text{ kJ/mol}$ between manganese oxides, where one mol manganese invest free energy $G_{\text{Mn}} = 448,971 \text{ kJ/mol}$, as in formation of $\beta\text{-MnO}_2$ just $G_{\text{Mn}} = 162 \text{ kJ/mol}$.
 Since $\beta\text{-MnO}_2$ is the thermodynamically most stable in phase of MnO_2 , these formation energies indicate that the $\epsilon\text{-MnO}_2$ is less stable by $-35,4 \text{ kJ/mol}$, i. e., $\epsilon\text{-MnO}_2 \Rightarrow \beta\text{-MnO}_2$ ΔG° transform: $-35:4 \text{ kJ/mol}$;

$\text{Zn} + \text{H}_2\text{O} = \text{Zn}^{2+} + 2\text{e}^-$, $2\beta\text{-MnO}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^- = 2\text{MnOOH} + 2\text{H}_2\text{O}$; $\text{Zn} + 2\beta\text{-MnO}_2 + 2\text{H}_3\text{O}^+ = \text{Zn}^{2+} + 2\text{MnOOH} + 2\text{H}_2\text{O}$,
 Absolute potential has $E^\circ_{\text{Classic}} = -0,7618 \text{ V}$ [32], water logarithm $-0,0515$ and sum ΔE° summa

$$\Delta E^\circ: E^\circ_{\text{Zn/Zn}^{2+}} = E^\circ_{\text{classic}} - 0,0591/2 \cdot \log(1/[\text{H}_2\text{O}])) + \Delta E^\circ = -0,7618 + 0,051497 + 0,10166 - 0,371339 = -0,97998 \text{ V}.$$

$$\Delta G_{\text{eqZn}} = E^\circ_{\text{Zn}} \cdot F \cdot 2 = -0,97998 \cdot 96485 \cdot 2 = -189,10674 \text{ kJ/mol},$$

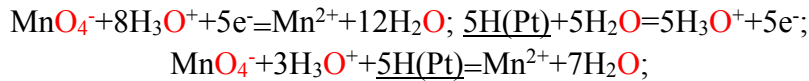
$$\Delta G_{\text{eqZn}} = G_{\text{Zn}^{2+}} - (G_{\text{Zn}} + G_{\text{H}_2\text{O}}) = 215,55 - (404,657 + 0) = -189,107 \text{ kJ/mol};$$

$$G_{\text{Zn}^{2+}} = \Delta G_{\text{eqZn}} + (G_{\text{Zn}} + G_{\text{H}_2\text{O}}) = -189,107 + (404,657 + 0) = 215,55 \text{ kJ/mol};$$

$$\Delta G_{\text{eqZn/MnOOH}} = (E^\circ_{\text{Zn/Zn}^{2+}} - E^\circ_{\text{MnOOH/MnO}_2}) \cdot F \cdot 1 \cdot 2 = (-0,97998 - 1,0723) \cdot 96485 \cdot 2 = -2,0523 \cdot 96485 \cdot 2 = -396,0217 \text{ kJ/mol}.$$

$$K_{\text{eq}} = \exp(-\Delta G_{\text{eqH/MnO}_4} / R/T) = \exp(396021,7 / 8,3144 / 298,15) = \exp(159,7546) = 10^{69,3805};$$

$$\text{Sum of standard potentials } \Delta E_{\text{Zn/MnOOH}} = (E^\circ_{\text{Zn/Zn}^{2+}} - E^\circ_{\text{MnOOH/MnO}_2}) = (-0,97998 - 1,072265) = -2,052245 \text{ V};$$



Balancing the Electrons $+ne^- = 5e^- = -ne^-$ gives the Red-Ox reaction: $\text{MnO}_4^- + 3\text{H}_3\text{O}^+ + \underline{5\text{H(Pt)}} = \text{Mn}^{2+} + 7\text{H}_2\text{O}$;

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

$$\Delta G_{\text{eqH/MnO}_4} = (E^\circ_{\text{H}} - E^\circ_{\text{MnO}_4}) \cdot F \cdot 1 \cdot 5 = (-0,27073 - 1,483458) \cdot 96485 \cdot 5 = -1,754188 \cdot 96485 \cdot 5 = -846,2641459 \text{ kJ/mol}$$

$$\Delta G_{\text{HessPtH}} = G_{\text{Mn}^{2+}} + 7G_{\text{H}_2\text{O}} - (G_{\text{MnO}_4} + 3G_{\text{H}_3\text{O}^+} + 5G_{\text{H(Pt)}}) = 177,989 + 7 \cdot 0 - (714,133 + 3 \cdot 22,44 + 5 \cdot 48,56) = -846,2642 \text{ kJ/mol};$$

$$G_{\text{MnO}_4} = G_{\text{Mn}^{2+}} + 7G_{\text{H}_2\text{O}} - (\Delta G_{\text{HessPtH}} + 3G_{\text{H}_3\text{O}^+} + 5G_{\text{H(Pt)}}) = 177,989 + 7 \cdot 0 - (-846,2642 + 3 \cdot 22,44 + 5 \cdot 48,56) = 714,133 \text{ kJ/mol};$$

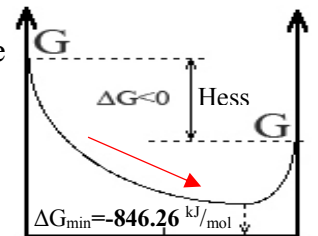
$$G_{\text{Mn}^{2+}} = \Delta G_{\text{HessPtH}} - 7G_{\text{H}_2\text{O}} + (G_{\text{MnO}_4} + 3G_{\text{H}_3\text{O}^+} + 5G_{\text{H(Pt)}}) = -846,2642 - 7 \cdot 0 + (714,133 + 3 \cdot 22,44 + 5 \cdot 48,56) = 177,989 \text{ kJ/mol};$$

$$E^\circ_{\text{H}} - E^\circ_{\text{MnO}_4} = -1,754188 \text{ V}$$

$K_{\text{eq}} = \exp(-\Delta G_{\text{eqH/MnO}_4} / R/T) = \exp(846264,1459 / 8,3144 / 298,15) = \exp(341,382) = 10^{148,26}$;
 Exothermic and exoergonic MnO_4^- reduction by $\underline{5\text{H(Pt)}}$ Hess free energy change negative and equilibrium state minimum $\Delta G_{\text{min}} = \Delta G_{\text{eqOxRed}} = -846,26 \text{ kJ/mol}$ reaching

$$\text{equilibrium mixture } 10^{148,5} = K_{\text{eq}} = \frac{[\text{H}_2\text{O}]^7 \cdot [\text{Mn}^{2+}]}{[(\text{Pt})\text{H}]^5 \cdot [\text{MnO}_4^-] \cdot [\text{H}_3\text{O}^+]^3};$$

Prigogine attractor is free energy change minimum ΔG_{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 $\underline{5\text{H(Pt)}} + \text{MnO}_4^- + 3\text{H}_3\text{O}^+$
 products $\text{Mn}^{2+} + 7\text{H}_2\text{O}$

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