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Фундаментальные и прикладные исследования в области химии и экологии

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Фундаментальные и прикладные исследования в области химии и экологии: материалы международной научно-практической конференции студентов, аспирантов и молодых ученых / редкол.: Л.М. Миронович (отв. ред.) [и др.]; Юго-Зап. гос. ун-т., ЗАО "Университетская книга", Курск, 2015. 255 с.

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Представлены материалы международной научно-практической конференции «Фундаментальные и прикладные исследования в области химии и экологии», проходившей 23-26 сентября 2015 г. в Юго-Западном государственном университете. Отражены результаты научных исследований российских и зарубежных студентов, аспирантов и молодых ученых в области органического синтеза, теоретической и экспериментальной химии, химической технологии, экологии и ресурсосбережения.

Предназначен для широкого круга специалистов, работающих в области химии, химического материаловедения, экологии, химической технологии и инновационных разработок в химии.

Ответственность за содержание публикуемых материалов несут их авторы.

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THE POTENTIAL – pH DIAGRAM FOR Mn – H₂O SYSTEM

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Thermodynamic information on aqueous manganese species is systematized. The reactions between various species are discussed. The activity – pH diagram for Mn^{II} species and the revised potential – pH diagrams of Mn – H₂O system at 25°C, 1 bar and $a_{[Mn]} = 1 \text{ mol l}^{-1}$ and $a_{[Mn]} = 10^{-6} \text{ mol l}^{-1}$ are plotted.

Since Pourbaix diagrams were firstly introduced, several papers concerning potential – pH diagrams for pure elements were published. However, even the diagrams presented in the most recent books [1–3] aren't consistent with each other and contain various species. This paper aims to collect and analyze available data on Gibbs energies of formation of manganese species and revise the diagram.

Elemental manganese has the simple cubic lattice at standard conditions. Five manganese oxides with oxidation degrees ranging from II to VII are known: MnO, Mn₃O₄, Mn₂O₃, MnO₂ and Mn₂O₇ [4]. However, Mn₂O₇ is extremely unstable in water solution and decomposes spontaneously according to equation $\text{Mn}_2\text{O}_7 (\text{s}) + \text{H}_2\text{O} (\text{l}) \rightarrow 2\text{MnO}_4^- (\text{aq}) + 2\text{H}^+ (\text{aq})$ [3].

In aqueous solution manganese forms a variety of unhydrolyzed and hydrolyzed species with oxidation degrees II (Mn²⁺, MnOH⁺, HMnO₂[–]), III (Mn³⁺), VI (MnO₄^{2–}) and VII (MnO₄[–]). There is no available thermodynamic information on MnOH²⁺, Mn(OH)₃[–] and Mn(OH)₄^{2–}. Polymerized species like Mn₂(OH)₃⁺ and Mn₂OH³⁺ and oxyhydrate MnOOH aren't considered. The standard Gibbs energies of formation used in calculations are presented in Table 1. The value of $\Delta_f G_{298}^\circ (\text{HMnO}_2^-)$ was calculated according to data on standard electrode potentials collected from various reference textbooks [7 – 10]. However, since the data from the various sources weren't consistent with each other, the averaged value was calculated.

Таблица 1. Расчет точек кривой ликвидуса двухкомпонентных металлических систем сплавов Al-Ge ($a_{\text{Al}}^{\text{Al-Ge}} = -0,0056$; $b_{\text{Al}}^{\text{Al-Ge}} = 1,6338$;

$a_{\text{Ge}}^{\text{Al-Ge}} = -0,0016$; $b_{\text{Ge}}^{\text{Al-Ge}} = 0,5398$; $\hat{a}_{\text{Al}}^{\text{Al-Ge}} = -0,0005$; $\hat{b}_{\text{Al}}^{\text{Al-Ge}} = 1,0161$; $\hat{a}_{\text{Ge}}^{\text{Al-Ge}} = 0,0005$;

$\hat{b}_{\text{Ge}}^{\text{Al-Ge}} = 0,4917$)

% мол. Al	$T, ^\circ\text{C}$							
	Справ. данные [3]	Расчет по ур-ю Шредера-Лешателлье	Относит. погрешн., %	Расчет по уравнениям (2)-(3)		Относит. погрешн., %	Расчет по ур-ям (4)-(5)	Относит. погрешн., %
0,0	940	940,00	0,00	940,00	–	0,00	940,00	0,00
10,0	900	906,08	0,68	900,4	–	0,04	898,38	0,18
20,0	852	870,33	2,15	852,26	–	0,03	851,33	0,08
30,0	794	832,34	4,83	794,36	–	0,05	797,08	0,39
40,0	728	791,51	8,72	725,38	–	0,36	733,04	0,69
50,0	652	746,94	14,56	643,92	–	1,24	655,28	0,50
60,0	560	697,23	24,51	548,52	–	2,05	557,51	0,44
65,0	500	669,73	33,95	495,13	–	0,97	498,05	0,39
69,7	424	641,73	51,35	441,27	428,41	4,07/1,04	433,5	2,24
75,0	473	606,89	28,31	–	469,88	0,66	472,88	0,03
80,0	510	569,64	11,69	–	509,08	0,18	510,54	0,11
85,0	548	561,63	2,49	–	548,03	0,01	548,39	0,07
90,0	587	593,77	1,15	–	586,39	0,10	586,12	0,15
95,0	623	626,54	0,57	–	623,82	0,13	623,43	0,07
100,0	660	660,00	0,00	–	660,00	0,00	660,00	0,00
Средняя ошибка аппроксимации, A			14,23	–	–	0,98/0,30	–	0,55/0,33

Работа выполнена при финансовой поддержке Минобрнауки РФ в рамках базовой части государственного задания СамГТУ в сфере научной деятельности по проекту № 1778.

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Table 1. The standard Gibbs energies of formation of manganese species.

Compound	$\Delta_f G_{298}^\circ, \text{J mol}^{-1}$	Reference	Compound	$\Delta_f G_{298}^\circ, \text{J mol}^{-1}$	Reference
MnO (s)	-362 800	[5, 6]	Mn ³⁺ (aq)	-85 000	[3, 6]
Mn ₃ O ₄ (s)	-1 283 000	[5, 6]	MnOH ⁺ (aq)	-405 000	[6]
Mn ₂ O ₃ (s)	-878 900	[5, 6]	HMnO ₂ ⁻ (aq)	-506 000	[7 – 10]
MnO ₂ (s)	-465 000	[5, 6]	MnO ₄ ²⁻ (aq)	-503 700	[3, 6]
Mn ²⁺ (aq)	-228 400	[3, 6]	MnO ₄ ⁻ (aq)	-447 300	[3, 6]

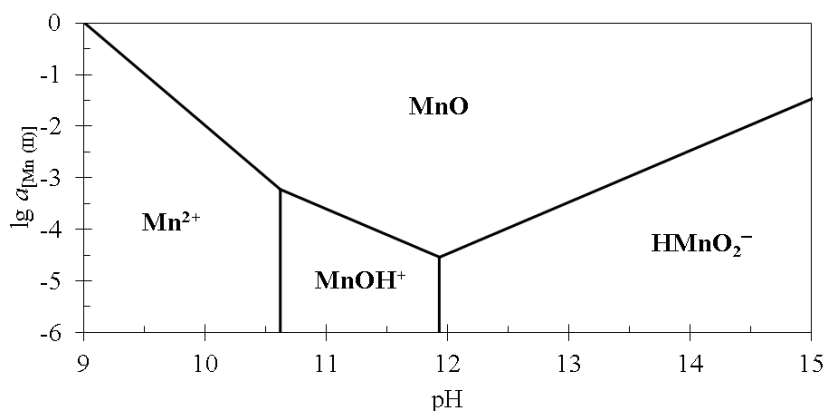
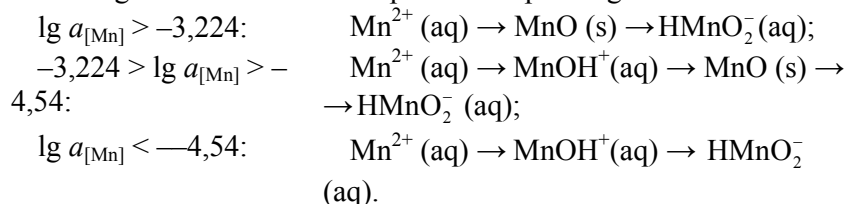


Figure 1. The activity – pH diagram for Mn^{II} species.

Figure 1 shows the predominance diagram of Mn^{II} species. The following order of oxidation is possible depending on ion activities:



Calculations show that in diluted media, when $a_{[\text{Mn}]} < 10^{-5} \text{ mol l}^{-1}$, the domain of stability of MnO vanishes and MnOH⁺ is oxidized directly to HMnO₂⁻.

The potential – pH diagrams of Mn – H₂O system plotted at 25°C, air pressure of 1 bar and activities of ions in solution, equal to 1 and $10^{-6} \text{ mol l}^{-1}$ are shown at Figures 2 and 3, respectively.

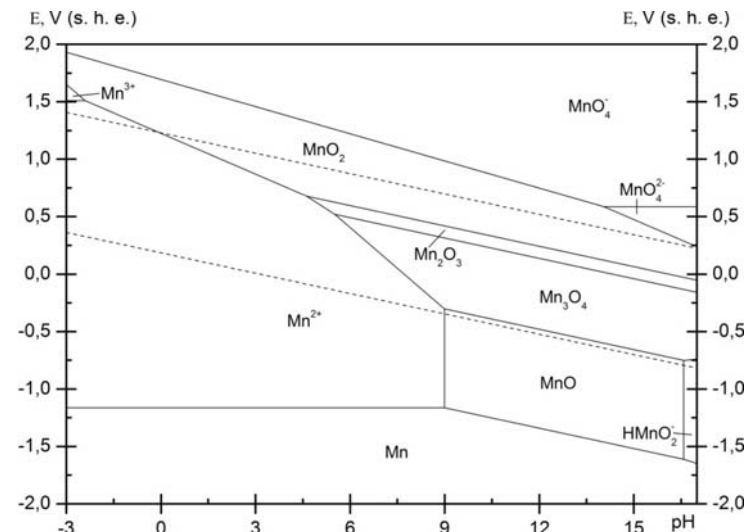


Figure 2 - The potential – pH diagram for Mn – H₂O system at $a_{[\text{Mn}]} = 1 \text{ mol l}^{-1}$

Figure 2 shows the diagram with the domain of thermodynamic stability of MnO, while Figure 3 presents a diagram without it.

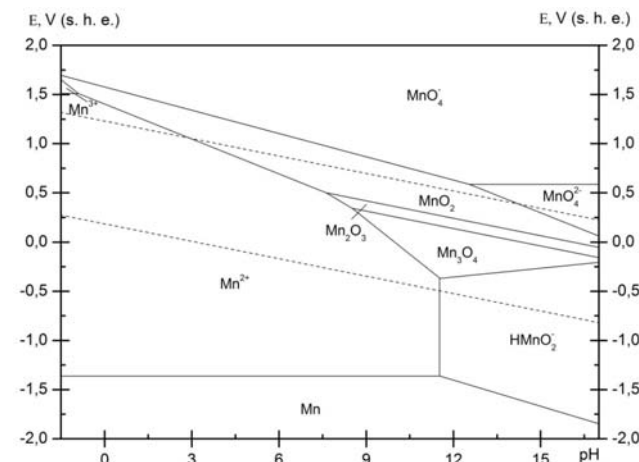


Figure 3 - The potential – pH diagram for Mn – H₂O system at $a_{[\text{Mn}]} = 10^{-6} \text{ mol l}^{-1}$.

Dashed lines represent the hydrogen and oxygen electrodes and border the domain of electrochemical stability of water at atmospheric conditions.

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СЕКЦИЯ 3

БЕЗОТХОДНЫЕ, РЕСУРСОСБЕРЕ- ГАЮЩИЕ ТЕХНОЛОГИИ И ЭКОЛОГИЧЕ- СКИЕ ПРОБЛЕМЫ СОВРЕМЕННОСТИ

УДК 544.653:544.016:544.313.2.031

THE POTENTIAL – pH DIAGRAM FOR Mn – H₂O SYSTEM

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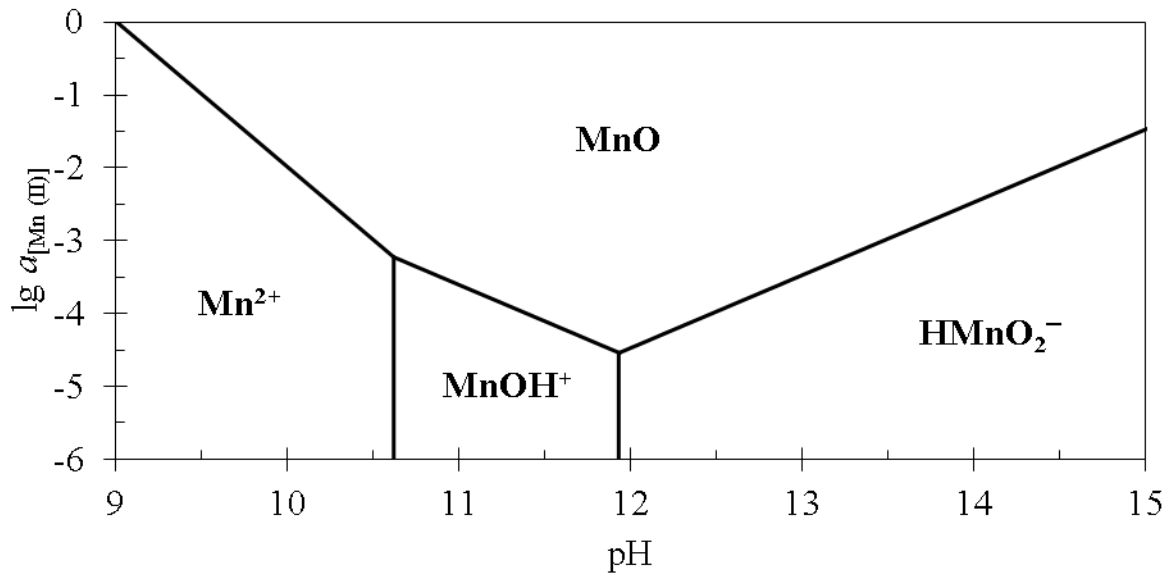


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Figure 1 shows the predominance diagram of Mn^{II} species. The following order of oxidation is possible depending on ion activities:

$\lg a_{[\text{Mn}]} > -3,224$: $\text{Mn}^{2+} (\text{aq}) \rightarrow \text{MnO} (\text{s}) \rightarrow \text{HMnO}_2^- (\text{aq})$;

$-3,224 > \lg a_{[\text{Mn}]} > -4,54$: $\text{Mn}^{2+} (\text{aq}) \rightarrow \text{MnOH}^+ (\text{aq}) \rightarrow \text{MnO} (\text{s}) \rightarrow \text{HMnO}_2^- (\text{aq})$;

$\lg a_{[\text{Mn}]} < -4,54$: $\text{Mn}^{2+} (\text{aq}) \rightarrow \text{MnOH}^+ (\text{aq}) \rightarrow \text{HMnO}_2^- (\text{aq})$.

Calculations show that in diluted media, when $a_{[\text{Mn}]} < 10^{-5} \text{ mol l}^{-1}$, the domain of stability of MnO vanishes and MnOH⁺ is oxidized directly to HMnO₂[–].

The potential – pH diagrams of Mn – H₂O system plotted at 25°C, air pressure of 1 bar and activities of ions in solution, equal to 1 and 10^{–6} mol l^{–1} are shown at Figures 2 and 3, respectively.

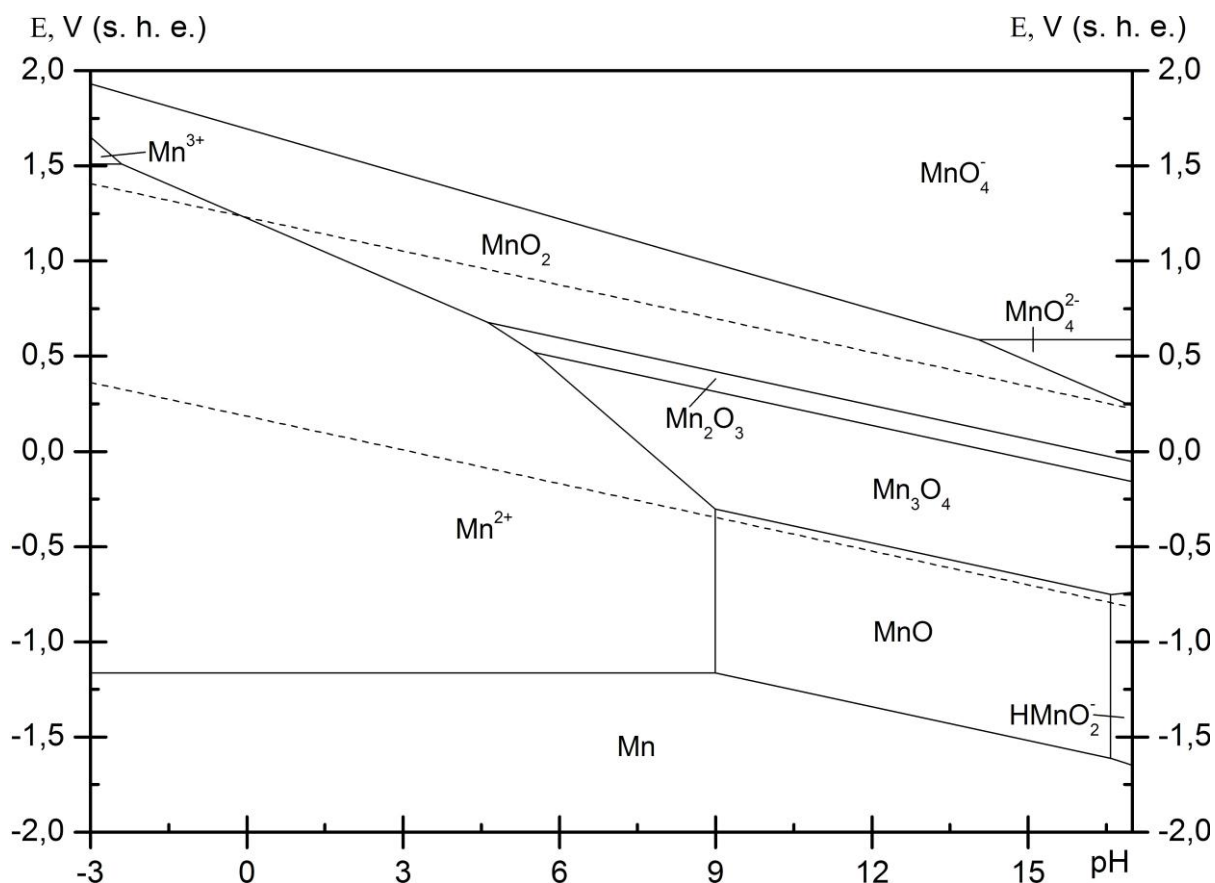


Figure 2. The potential – pH diagram for Mn – H₂O system at $a_{[\text{Mn}]} = 1 \text{ mol l}^{-1}$.

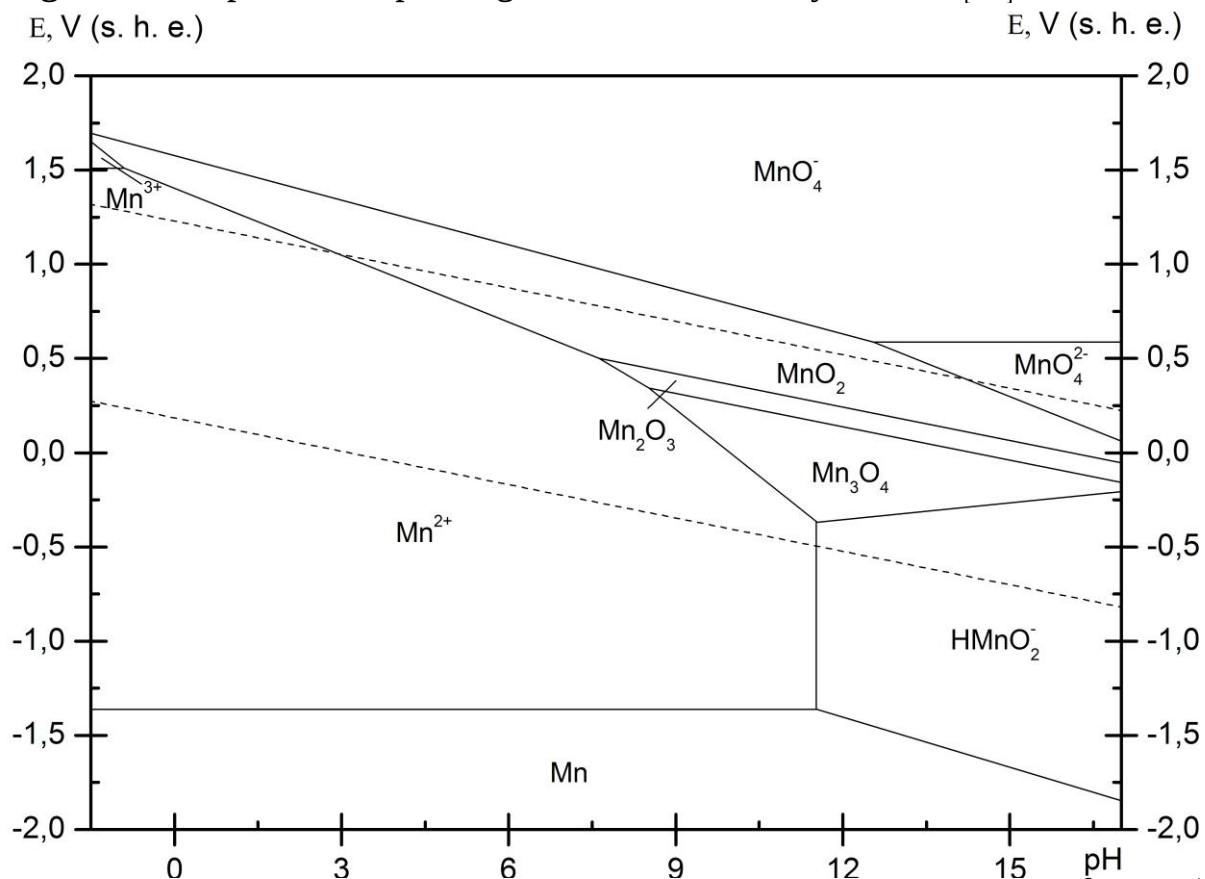


Figure 3. The potential – pH diagram for Mn – H₂O system at $a_{[\text{Mn}]} = 10^{-6} \text{ mol l}^{-1}$.

Figure 2 shows the diagram with the domain of thermodynamic stability of MnO, while Figure 3 presents a diagram without it.

Dashed lines represent the hydrogen and oxygen electrodes and border the domain of electrochemical stability of water at atmospheric conditions.

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