

Thermodynamic Probability of Realization of the Process of Silicon Dioxide Reduction by Magnesium at High Temperatures

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ABSTRACT. The thermodynamic analysis of processes expected in SiO₂-Mg system at high temperatures has been conducted. The opinion has been expressed that energetically the most probable is reduction of silica by the reaction SiO₂ + 4Mg = 2MgO + Mg₂Si in the temperature range 1000-1300K. © 2009 Bull. Georg. Natl. Acad. Sci.

Key words: reduction, temperature, process, Gibbs free energy.

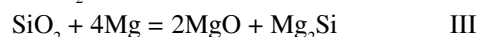
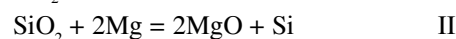
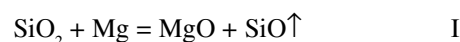
The high level of necessity of high-clean silicon causes the growth of intensity of researches in this direction. In this connection, a task is set to establish limits of thermodynamic probability of reactions of reduction of silicon dioxide (SiO₂) by magnesium (Mg) in a wide range of temperatures. To this end the method [1], formulation of trinomial equations of temperature dependence on Gibbs free energy have been used:

$$\Delta G_T^0 = A + BT \lg T + CT \quad (1)$$

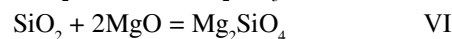
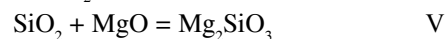
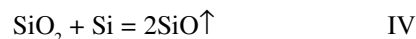
Necessary data for calculations [2-4] of the thermodynamic functions of the components of extending the investigated system of SiO₂-Mg are presented in Table 1. With the purpose of a range of action of the required equations ΔG_T^0 , for liquid magnesium and Mg₂Si their heat capacities are calculated [5, 6] respectively for the range 923-1368 K and 298-1358 K; these data are presented also in Table 1.

At the beginning it is necessary to determine the kind, quantity and limits of reactions expected in the SiO₂-Mg system. We consider that depending on degrees of reduction of silicon, the course of the following reactions must be expected in the investigated sys-

tem:



Besides there is the possibility of interaction of products of the reactions with the initial components under the scheme:



It is possible to present reactions I-IV as an algebraical sum of simple reactions proceeding in a certain temperature range:

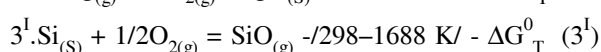
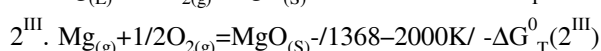
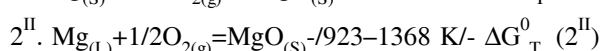
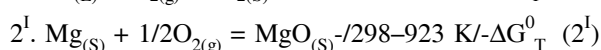
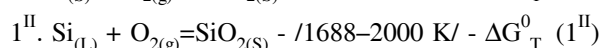
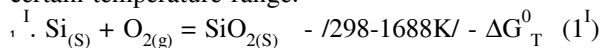
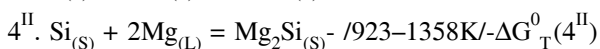
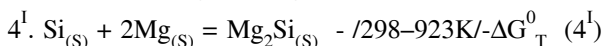
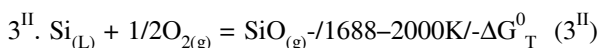


Table 1
Initial thermodynamic data necessary for the analysis of processes expected in a reactionary* mix (SiO₂+Mg) (1cal = 4.184 Joule)

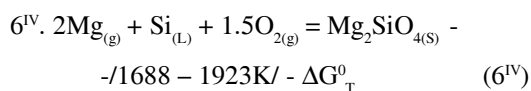
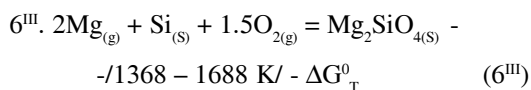
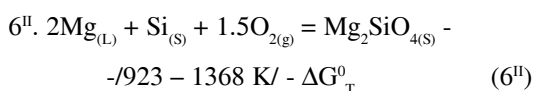
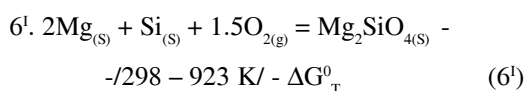
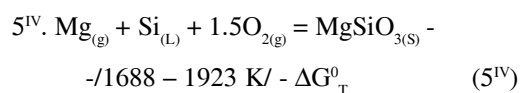
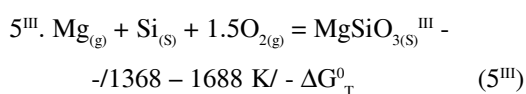
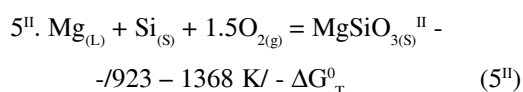
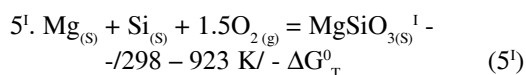
Element, compound	$-\Delta H_{298}^0$ kcal.mole ⁻¹	S_{298}^0 cal.mole ⁻¹ .K ⁻¹	T _{tr}		T _m	T _b	λ_{tr}	λ_m	λ_b	Coefficients of equation $C_p = a + bT + cT^2$ (cal.mole ⁻¹ .K ⁻¹)			Temperature Range	C _{pr,m}	C _{pv}
			K	K						a	b·10 ⁻³	-c·10 ⁵			
Si	-	4.5±0.02	-	1688	-	-	11.9±0.2	-	-	5.72	0.59	0.99	298-1688	6.12 (T _m -2873K)	cal.mole ⁻¹ .K ⁻¹
Mg	-	7.81±0.02	-	923	1368	-	2.03±0.05	30.55	-	5.33	2.45	0.103	298-923	8.11* (T _m -T _b)	4.98 (T _b -2000K)
O ₂	-	49.0±0.01	-	-	-	-	-	-	-	7.16	1.00	0.4	298-3000	-	-
SiO ₂	217.72±0.34	10.0±0.10	-	2001	-	-	1.84	-	-	13.38	3.68	3.45	298-2000	-	-
SiO	24.7	50.54±0.02	-	-	-	-	-	-	-	7.14	-	-	-	-	-
MgO	143.76±0.07	6.47±0.05	-	3098	-	-	18.5±1.5	-	-	11.71	0.75	2.80	298-3098	-	-
Mg ₂ Si	18.95	18.11±0.05	-	1358	-	-	20.5±2.5	-	-	16.5	4.02	1.48	(298-1358)**	-	-
MgSiO ₃	370.2±0.4	16.22±0.25	-	-	-	-	-	-	-	22.0	7.9	4.25	298-903	-	-
			903	-	-	0.16	-	-	-	28.75	-	-	903-1258	-	-
			1258	-	-	0.39	-	-	-	29.26	-	-	1258-1923	-	-
Mg ₂ SiO ₄	519.1±0.5	22.75±0.30	-	1923	-	-	18.00	-	-	35.0	-	-	T _m -2300	49.0	-
			-	2160	-	-	18.8±0.8	-	-	35.81	6.54	8.52	298-T _m	T _m -2300	-

*- Calculated by the method offered in [5]

**-. Coefficients C_p = f (T) calculated by the method offered in [6]



For reactions V and VI in a respective temperature range it is necessary to determine in advance Gibbs free energy for the formation of magnesium silicate from simple substances:



On the basis of data of Table 1 and the calculation scheme, presented in [1] for the above-stated simple reactions, equations of temperature change of Gibbs free energy are derived:

$$\Delta G_T^0(1^I) = -218670 - 4.62 \cdot T \cdot \lg T + 58.12 \cdot T \text{ cal.mole}^{-1} /298-1688 K/,$$

$$\Delta G_T^0(1^{II}) = -234900 - 11.3 \cdot T \cdot \lg T + 89.38 \cdot T \text{ cal.mole}^{-1} /1688-2000 K/,$$

$$\Delta G_T^0(2^I) = -144010 - 1.49 \cdot T \cdot \lg T + 30.37 \cdot T \text{ cal.mole}^{-1} /298-923 K/,$$

$$\Delta G_T^0(2^{II}) = -145540 - 0.23 \cdot T \cdot \lg T + 28.29 \cdot T \text{ cal.mole}^{-1} /923-1368 K/,$$

$$\Delta G_T^0(2^{III}) = -180720 - 8.0 \cdot T \cdot \lg T + 78.36 \cdot T \text{ cal.mole}^{-1} /1368-2000 K/,$$

$$\Delta G_T^0(3^I) = -23640 + 6.73 \cdot T \cdot \lg T - 41.75 \cdot T \text{ cal.mole}^{-1} /298-1688 K/,$$

$$\Delta G_T^0(3^{II}) = -34930 + 7.94 \cdot T \cdot \lg T - 39.0 \cdot T \text{ cal.mole}^{-1} /1688-2000 K/,$$

$$\Delta G_T^0(4^I) = -18680 + 1.92 \cdot T \cdot \lg T - 3.65 \cdot T \text{ cal.mole}^{-1} /298-923 K/,$$

$$\Delta G_T^0(4^{II}) = -22150 + 3.63 \cdot T \cdot \lg T - 5.0 \cdot T \text{ cal.mole}^{-1} /298-1358 K/,$$

$$\Delta G_T^0(5^I) = -370200 - 2.94 \cdot T \cdot \lg T + 77.86 \cdot T \text{ cal.mole}^{-1} /298-923 K/,$$

$$\Delta G_T^0(5^{II}) = -370400 - 4.41 \cdot T \cdot \lg T + 81.16 \cdot T \text{ cal.mole}^{-1} /923-1368 K/,$$

$$\Delta G_T^0(5^{III}) = -404440 - 10.83 \cdot T \cdot \lg T + 126.73 \cdot T \text{ cal.mole}^{-1} /1368-1688 K/,$$

$$\Delta G_T^0(5^{IV}) = -416660 - 10.93 \cdot T \cdot \lg T + 133.9 \cdot T \text{ cal.mole}^{-1} /1688-1923 K/,$$

$$\Delta G_T^0(6^I) = -520160 - 6.02 \cdot T \cdot \lg T + 113.83 \cdot T \text{ cal.mole}^{-1} /298-923 K/,$$

$$\Delta G_T^0(6^{II}) = -523930 - 8.12 \cdot T \cdot \lg T + 125.01 \cdot T \text{ cal.mole}^{-1} /923-1368 K/,$$

$$\Delta G_T^0(6^{III}) = -56020 - 26.51 \cdot T \cdot \lg T + 210.19 \cdot T \text{ cal.mole}^{-1} /1368-1688 K/,$$

$$\Delta G_T^0(6^{IV}) = -577220 - 31.07 \cdot T \cdot \lg T + 233.9 \cdot T \text{ cal.mole}^{-1} /1688-2000 K/.$$

As a result of algebraical summation of the corresponding equations ΔG_T^0 received above, it is possible to form equations of temperature dependence of Gibbs free energy for the expected processes I-VI. In Table 2 for the indicated reactions numerical values of coefficients of the required equations are presented. In the same Table the numerical values of Gibbs free energy I-VI of reactions calculated by the derived equations are presented at the critical temperatures. On the basis of these data, a graph of the temperature change of ΔG_T^0 of these reactions is constructed (Fig. 1).

Data of Fig.1 unequivocally show that in the investigated system of (SiO₂ + Mg) in the range of 1000-1300K energetically the most probable process is reaction III with formation of the silicide of magnesium. In

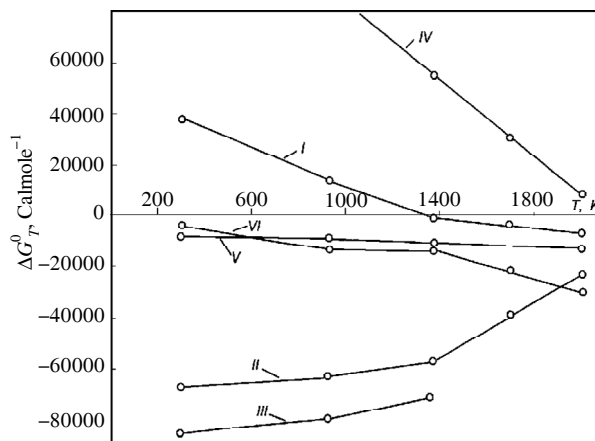


Fig. 1. Dependence of Gibbs free energy on the temperature for reactions I-VI.

Table 2

Reactions expected in mixtures of SiO_2 -Mg, corresponding to them equations of temperature changing of Gibbs free energy and numerical values of function at critical temperatures (1 cal = 4.184 Joule)

Reaction	Coefficients of equations $\Delta G_T^0 = A + BT \lg T + CT$			Temperature Range K	Numerical values of Gibbs free energy (cal.mole ⁻¹) at critical temperatures, K					
	-A	B	C		298	923	1358	1368	1688	2000
1	2	3	4		6	7	8	9	10	11
I										
$\text{SiO}_{2(\text{s})} + \text{Mg}_{(\text{s})} = \text{MgO}_{(\text{s})} + \text{SiO}_{(\text{g})}$	51020 (±600)	9.86	-69.50 (±0.96)	298-923	37580 (±890)	13860 (±1490)				
$\text{SiO}_{2(\text{s})} + \text{Mg}_{(\text{l})} = \text{MgO}_{(\text{s})} + \text{SiO}_{(\text{g})}$	49490 (±650)	11.12	-71.58 (±0.91)	923-1368		13850 (±1490)	-	-720 (±1900)		
$\text{SiO}_{2(\text{s})} + \text{Mg}_{(\text{g})} = \text{MgO}_{(\text{s})} + \text{SiO}_{(\text{g})}$	14310 (±650)	3.35	-21.51 (±0.86)	1368-1688				-750 (±1800)	-3750 (±2100)	
$\text{SiO}_{2(\text{s})} + \text{Mg}_{(\text{g})} = \text{MgO}_{(\text{s})} + \text{SiO}_{(\text{g})}$	19250 (±800)	11.24	-50.08 (±0.62)	1688-2000					-4020 (±1930)	-6700 (±2150)
II										
$\text{SiO}_{2(\text{s})} + 2\text{Mg}_{(\text{s})} = 2\text{MgO}_{(\text{s})} + \text{Si}_{(\text{s})}$	-69350 (±240)	1.64	2.62 (±1.19)	298-923	-67360 (±590)	-62450 (±1340)				
$\text{SiO}_{2(\text{s})} + 2\text{Mg}_{(\text{l})} = 2\text{MgO}_{(\text{s})} + \text{Si}_{(\text{s})}$	-72410 (±300)	4.16	-1.54 (±1.04)	923-1368		-62440 (±1260)	-	-56670 (±1720)		
$\text{SiO}_{2(\text{s})} + 2\text{Mg}_{(\text{g})} = 2\text{MgO}_{(\text{s})} + \text{Si}_{(\text{s})}$	-142670 (±300)	-11.38	98.60 (±0.90)	1368-1688				-56610 (±1530)	-38230 (±1820)	
$\text{SiO}_{2(\text{s})} + 2\text{Mg}_{(\text{g})} = 2\text{MgO}_{(\text{s})} + \text{Si}_{(\text{l})}$	-126540 (±400)	-4.7	67.34 (±0.70)	1688-2000					-38470 (±1480)	-22890 (±1800)
III										
$\text{SiO}_{2(\text{s})} + 4\text{Mg}_{(\text{s})} = 2\text{MgO}_{(\text{s})} + \text{Mg}_2\text{Si}_{(\text{s})}$	-88030 (±1120)	3.56	-1.03 (±0.96)	298-923	-85720 (±1410)	-79240 (±2010)				
$\text{SiO}_{2(\text{s})} + 4\text{Mg}_{(\text{l})} = 2\text{MgO}_{(\text{s})} + \text{Mg}_2\text{Si}_{(\text{s})}$	-94560 (±1300)	7.79	-6.54 (±1.12)	923-1358		-79280 (±2330)	-70300 (±2820)			
IV										
$\text{SiO}_{2(\text{s})} + \text{Si}_{(\text{s})} = 2\text{SiO}_{(\text{g})}$	171390 (±1670)	18.08	-141.62 (±1.70)	298-1688	142520 (±2180)	-	-	-	30840 (±2850)	
$\text{SiO}_{2(\text{s})} + \text{Si}_{(\text{l})} = 2\text{SiO}_{(\text{g})}$	165040 (±2000)	27.18	-167.38 (±1.42)	1688-2000					30570 (±4400)	8720 (±4840)
V										
$\text{MgO}_{(\text{s})} + \text{SiO}_{2(\text{s})} = \text{MgSiO}_{3(\text{s})\text{I}}$	-7520 (±800)	3.17	-10.63 (±0.71)	298-923	-8350 (±1000)	-8650 (±1450)				
$\text{MgO}_{(\text{s})} + \text{SiO}_{2(\text{s})} = \text{MgSiO}_{3(\text{s})\text{II}}$	-6190 (±900)	0.44	-5.25 (±0.91)	923-1368		-9640 (±1730)	-	-11480 (±2130)		
$\text{MgO}_{(\text{s})} + \text{SiO}_{2(\text{s})} = \text{MgSiO}_{3(\text{s})\text{III}}$	-5050 (±1000)	1.79	-9.75 (±1.03)	1368-1688				-10710 (±2420)	-11760 (±2740)	
$\text{MgO}_{(\text{s})} + \text{SiO}_{2(\text{s})} = \text{MgSiO}_{3(\text{s})\text{III}}$	-1040 (±1380)	8.37	-33.84 (±0.94)	1688-1923					-12560 (±2870)	-13250 (±3260)
VI										
$2\text{MgO}_{(\text{s})} + \text{SiO}_{2(\text{s})} = \text{Mg}_2\text{SiO}_{4(\text{s})}$	-13370 (±880)	1.58	-5.03 (±1.45)	298-923	-3700 (±1310)	-13690 (±2220)				
$2\text{MgO}_{(\text{s})} + \text{SiO}_{2(\text{s})} = \text{Mg}_2\text{SiO}_{4(\text{s})}$	-14180 (±1100)	-3.04	10.31 (±0.96)	923-1368		12980 (±1990)	-	-13120 (±2410)		
$2\text{MgO}_{(\text{s})} + \text{SiO}_{2(\text{s})} = \text{Mg}_2\text{SiO}_{4(\text{s})}$	18090 (±1250)	-5.89	-4.65 (±0.91)	1368-1688				-13540 (±2490)	-20850 (±2790)	
$2\text{MgO}_{(\text{s})} + \text{SiO}_{2(\text{s})} = \text{Mg}_2\text{SiO}_{4(\text{s})}$	19120 (±1650)	-3.77	-12.19 (±0.81)	1688-2000					-22000 (±3020)	-30120 (±3270)

the same temperature range of a certain reaction II with formation of elementary silicon is less favourable.

It is necessary to note that in the investigated temperature range of 298-2000K, though energetically the course of reaction 1 is improbable, however, considering the fact that one of the products of reactions (SiO)

is gaseous, it is not excluded that above 1400K, at observing certain kinetic conditions, there is a possibility of its realization. Formation of silicates of magnesium is realizable at high temperatures of the order of 1400-2000K. Reaction IV – interaction of SiO_2 with silicon – is possible to occur only above 2000K.

ფიზიური ქიმია

მაღალ ტემპერატურებზე მანგანუმით სილიციუმის დიოქსიდის აღდგენის პროცესის თერმოდინამიკური ალბათობის გამოკვლევა

ა. ნადირაძე*, ი. ბარათაშვილი**, ი. ფულარიანი*, ქ. უკლება*

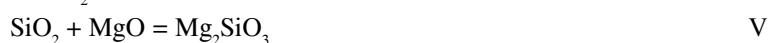
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** აკადემიის წევრი, ფ. თავაძის მეტალურგიისა და მასალათმცოდნეობის ინსტიტუტი, თბილისი

მაღალ ტემპერატურებზე $\text{SiO}_2 + \text{Mg}$ სარეაქციო ნარევეში მოსალოდნელი აღდგენითი პროცესები შეიძლება წარმართოს შემდეგი სქემით:



გარდა ამისა შეიძლება მოხდეს ურთიერთქმედება საწყის ნივთიერებებსა და რეაქციის პროდუქტებს შორის:



მოყვანილი რეაქციების განხორციელების თერმოდინამიკური ალბათობის განსაზღვრის მიზნით სათანადო ტემპერატურულ ინტერვალებში ამ რეაქციებისათვის შედგენილია გიბსის თავისუფალი ენერჯის (ΔG^0_T) განტოლებები, რომელთა საფუძველზე ცალსახად შეგვიძლია დაგადგინოთ, რომ აღდგენის პროცესი უნდა წარმართოს III სქემის მიხედვით.

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