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Experimental and Theoretical Determination of the Saturation Vapor Pressure of Silicon in a Wide Range of Temperatures

V. G. Sevast'yanov[a, *], P. Ya. Nosatenko[b], V. V. Gorskii[b], Yu. S. Ezhov[c], D. V. Sevast'yanov[a], E. P. Simonenko[a], and N. T. Kuznetsov[a]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia*

* *e-mail: v_sevastyanov@mail.ru*

[b] *OAO Military-Industrial Corporation NPO Mashinostroyenia, ul. Gagarina 33, Reutov, Moscow oblast, 143966 Russia*

[c] *Institute of Thermal Physics of Extreme States, Joint Institute for High Temperatures, Russian Academy of Sciences, ul. Izhorskaya 13/19, Moscow, 125412 Russia*

Abstract—Reference books and original studies devoted to the determination of the saturation vapor pressure of silicon in a wide range of temperatures have been analyzed. It has been established that no reliable experimental data in the range of high temperatures (above 2000 K) are available in the literature. It has been demonstrated that there is a need to perform additional theoretical and experimental investigations with the use of different methods. The total pressure and partial pressures of Si_n ($n = 1–6$) molecules over liquid silicon are calculated in the temperature range 1700–3400 K. The calculation of the composition of the gas phase over the "Si(l)–container" systems is performed. Materials of the crucibles intended for the use in experimental investigations of the temperature dependence of the saturation vapor pressure of silicon over the liquid phase are recommended.

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1. INTRODUCTION

The attainment of a stable content of silicon in the gas phase that corresponds to its pressure of higher than 1 Pa will make it possible to effectively solve a number of technological problems associated with the gas-phase processes of synthesis of high-temperature materials, including the problems of siliconizing, i.e., the surface or volume saturation of a material (for example, graphite) with silicon in the temperature range 1800–2200°C. Moreover, the silicon vapor pressure is one of the most important parameters used in the computer simulation required for the growth of pure silicon single crystals of large sizes by the Czochralski method. A preliminary analysis of the literature has demonstrated that reliable data on the silicon vapor pressure at technologically appropriate pressures that correspond to processes of vaporization of silicon (above 1420°C) are unavailable. Data on the behavior of "silicon(solid, gas, melt)–container" systems under specific experimental conditions are either insufficient or also unavailable.

The purpose of this work is to analyze studies on the determination of the saturation vapor pressure of silicon at different temperatures and to theoretically determine the composition of the gas phase over liquid silicon and "silicon–container" systems used in the gas-phase siliconizing technology.

2. PHYSICOCHEMICAL CONSTANTS OF SILICON

Over two decades (1961–1981), the Committee on Data for Science and Technology (CODATA) had been concerned with the proper choice of the constants characterizing the thermodynamic and thermochemical properties of silicon and included the quantity $\Delta_f H^0$(Si, g, 298.15) in the system of CODATA Key Values for Thermodynamics [1]. The quantities obtained according to the CODATA recommendations and the recommendations themselves entered into many fundamental reference books, including monographs [2–4].

The equilibria given below have been most frequently used in studies on the measurement of the silicon vapor pressure, because they allow one to calculate the key quantity for silicon compounds, i.e., the standard enthalpy of formation $\Delta_f H^0$(Si, g, 298.15):

$$\mathrm{Si(cr)} \longrightarrow \mathrm{Si(g)}, \quad (1)$$

$$\mathrm{Si(l)} \longrightarrow \mathrm{Si(g)}, \quad (2)$$

$$\mathrm{Si(cr)} \longrightarrow \mathrm{Si(g)} + \mathrm{C(graphite)}. \quad (3)$$

The enthalpies of reactions (1) and (2) correspond to the enthalpy of sublimation and the enthalpy of vaporization of silicon, respectively.

The results obtained by the authors of [5–14] using different methods and equilibria (1)–(3) are presented in Table 1. Different modifications (cubic, hexagonal)

Table 1. Results of the determination of the standard enthalpy of formation $\Delta_f H^0$(Si, g, 298.15) (kJ/mol) (designations: MS is mass spectrometry, Eff is the effusion method without mass spectrometric finish, VS is the vaporization from surface, FM is the flow method, Tors is the torsion method)

References	Method	Reaction	Temperature range, K	$\Delta_f H^0$(Si, g, 298.15), kJ/mol	
				Second law	Third law
[5]	MS	3	2149–2316	–	452.5 ± 12.6
[6]	VS	1	1473–1598	457 ± 50	456.2 ± 2.0
[7]	MS	2	1703–2160	451 ± 2.5	461.8 ± 6.5
[8]	Eff	2	1640–2054	459.3 ± 0.6	450.6 ± 0.2
[8]	FM	2	1854	–	444.3 ± 3.5
[8]	Eff	3, hex	1785–2068	445 ± 17	442.6 ± 2.8
[8]	Eff	3, cubic	1858–1973	444.9 ± 4.0	443.0 ± 2.4
[9]	Eff	1	1485–1593	361 ± 14	383.5 ± 1
[10]	Eff	1, 2	1848–2003	4711 ± 110	453.5 ± 12.6
[10]	Eff	3, cubic	2117–2171	631 ± 280	453.8 ± 4.0
[11]	Tors	2	1683–1873	367	427.7 ± 5.2
[12]	VS	1	1373–1623	439 ± 40	448.7 ± 2.5
[13]	MS	1	1547–1674	481 ± 11	460.6 ± 5.4
[14]	MS	1	1517–1674	468.6 ± 12.6	460.2 ± 12.6

of silicon carbide were used in reaction (3). The pressure over liquid silicon was measured in [5, 7, 8, 10, 11]. The CODATA group of experts (J.D. Cox, D.D. Wagman, and V.A. Medvedev) analyzed these results and recommended the value of $\Delta_f H^0$(Si, g, 298.15) = 450 ± 8 kJ/mol for use in practice.

The physicochemical constants used in this study for crystalline, liquid, and gaseous silicon (monoatomic) are listed in Table 2.

3. ANALYSIS OF THE EXPERIMENTAL STUDIES ON THE DETERMINATION OF THE SATURATION VAPOR PRESSURE OF SILICON

One of the first serious review papers on the vapor pressure of inorganic and organic compounds was published in 1947 by Stull [15]. The vapor pressures obtained for different inorganic and organic compounds by analyzing a large number of original studies were presented in the tabulated form in [15]. The Stull tables translated into Russian were published in the Soviet Union as a separate book in 1949 [16]. The temperatures corresponding to the saturation vapor pressures of 1, 5, 10, 20, 40, 60, 100, 200, 400, and 760 mmHg are given for each compound in the Stull tables. The data for silicon are summarized in Table 3.

The references to earlier studies of silicon vapor pressures [17–19] are presented in the works by Stull [15, 16]. It should be noted that, in the Russian-language variant of the Stull tables [16], we found a misprint in the ordinal number in the list of references for silicon (Alphabetical Index, p. 65): the number "259" is given instead of the number "359".

Kelley [17] used the experimental data reported in [18, 19] on the vapor pressures for calculating free energies of vaporization of inorganic compounds. As in the papers by Stull [15, 16], Kelley [17] also listed the temperatures corresponding to the saturation vapor pressures of 0.0001, 0.001, 0.01, 0.1, 0.25, 0.5, and 1.0 atm for each compound in the tables. The data for silicon are summarized in Table 4.

The reported data satisfy the following expression for the dependence of the vapor pressure over liquid silicon on temperature (K) in the range 1845–2560 K [17]:

$$\log P_{Si}[atm] = -27620/T - 1.27 \times \log T + 15.12. \quad (4)$$

This expression was derived by Kelley [17] from the results of the earlier studies [18, 19], in which the silicon vapor pressure was determined by measuring the weight loss.

Von Wartenberg [18] measured the silicon vapor pressure over the solid phase in the temperature range 1478–1588 K. The enthalpy of sublimation of silicon (184 kJ/mol) was determined from the temperature dependence of the vapor pressure.

Table 2. Physicochemical constants of silicon

Compound	Constant	Value	Dimensionality
Si, cr, cubic	$\Delta_f H^0(0)$	0*	kJ/mol
Si, cr, cubic	$\Delta_f H^0(298.15)$	0*	kJ/mol
Si, cr, cubic	$\Delta_f G^0(298.15)$	0*	kJ/mol
Si, cr, cubic	$\Delta H^0(298.15) - \Delta H^0(0)$	3213.312 ± 4.184	J/mol
Si, cr, cubic	$S^0(298.15)$	18.828 ± 0.083	J/(mol K)
Si, cr, cubic	$C_p^0(298.15)$	20.041 ± 0.041	J/(mol K)
Si, cr, cubic	T_{melt}	1688 ± 3	K
Si, l	T_{boil}	3522 ± 40	K
Si, amorph.	$\Delta_f H^0(298.15)$	4.184	kJ/mol
Si, l	$\Delta_f H^0(298.15)$	48.470 ± 0.4	kJ/mol
Si, l	$S^0(298.15)$	44.460 ± 0.4	J/(mol K)
Si, g	$\Delta_f H^0(0)$	447.688 ± 6.276	kJ/mol
Si, g	$\Delta_f H^0(298.15)$	450 ± 8*	kJ/mol
Si, g	$\Delta_f G^0(298.15)$	407.592	kJ/mol
Si, g	$\Delta H^0(298.15) - \Delta H^0(0)$	7552.12 ± 4.184	J/mol
Si, g	$S^0(298.15)$	167.866 ± 0.025	J/(mol K)
Si, g	$C_p^0(298.15)$	22.254 ± 0.004	J/(mol K)
Si, g	IP	786.512 ± 0.104	kJ

* CODATA recommendation (1984) [1].

Table 3. Silicon vapor pressures over Si(l) at different temperatures from the Stull tables [15, 16]

Temperature, K	1997	2108	2161	2215	2273	2309	2356	2424	2493	2560
Silicon vapor pressure, mmHg	1	5	10	20	40	60	100	200	400	760

The silicon vapor pressures determined in the temperature range 2163–2468 K by measuring the weight loss of silicon from a silicon carbide crucible in [19] are presented in Table 5. The dependence of the logarithm $\log P$ (mmHg) on the temperature (K), which was constructed using the above results, is shown in Fig. 1. The extrapolation of the curve allowed Ruff and Konschak [19] to estimate temperatures at which the silicon vapor pressure is equal to 1 mmHg (1960 ± 50 K) and 760 mmHg (2665 ± 50 K).

A comparison of Tables 3 and 4 shows that the silicon vapor pressures presented in the Stull tables [15, 16] are based on the data of Kelley [17], which, in turn, were obtained from the results taken from [18, 19]. The crystalline silicon samples used in [18] contained 4.1% (sample I) or 1.8% (sample II) SiO_2 and 0.1% Fe + Al (i.e., the activity of silicon in the solid phase in the course of sublimation was most likely smaller than unity). Moreover, as will be shown below, the determined enthalpy of sublimation of silicon (184 kJ/mol) is very strongly underestimated. This indicates that the data obtained in [18] are not reliable. In any case, the results obtained in [18] were not used by Stull [15, 16] and Kelley [17], because these data correspond to the

Table 4. Silicon vapor pressures over Si(l) at different temperatures from the Kelley tables [17]

Temperature, K	1845	1980	2140	2330	2420	2490	2560
Silicon vapor pressure, atm	0.0001	0.001	0.01	0.1	0.25	0.5	1.0
Silicon vapor pressure, mmHg	0.076	0.76	7.6	76	190	380	760

Table 5. Silicon vapor pressures over Si(l) according to the experimental data taken from [19]

Temperature, K	2163	2183	2258	2323	2248	2358
Silicon vapor pressure, mmHg	10.5	13	25	62	95?	110
Temperature, K	2428	2383	2388	2468	2428	2433
Silicon vapor pressure, mmHg	111	178	183	210	219	304?

silicon vapor pressure over the solid phase, whereas the reference tables by Stull and Kelley contain silicon vapor pressures over liquid silicon. As regards the data presented in [19], it seems likely that they were used by Kelley [17] to derive Eq. (4), which was extended through extrapolation outside the temperature range 2163–2468 K studied in [19]. Therefore, the silicon vapor pressures presented in the Stull tables [15, 16], in actual fact, are based on the results of only one study [19] and their processing performed by Kelley [17]. As was noted by Honig [20], the results obtained in [19] are characterized by a considerable scatter: the enthalpy of vaporization that is determined by processing only the high-temperature points (see Fig. 1) is equal to 406 kJ/mol, whereas the processing of all experimental points leads to a value of 469 kJ/mol. We evaluated the data obtained in [19] (see Table 5) with the use of the least-squares method. As a result, the equation for the dependence of the silicon vapor pressure over liquid silicon on the temperature (K) in the range 2163–2468 K has the form

$$\log P_{Si}[\text{Pa}] = (-2.35 \pm 0.31) \times 10^4/T + (14.12 \pm 1.35), \quad (5)$$

provided all points given in Table 5 should be processed. If the two points corresponding to temperatures of 2248 and 2433 K (which were called into question in [19]) are excluded from the analysis (see Table 5), the equation takes the form

$$\log P_{Si}\,[\text{Pa}] = (-2.48 \pm 0.22) \times 10^4/\text{T} + (14.61 \pm 0.96). \quad (6)$$

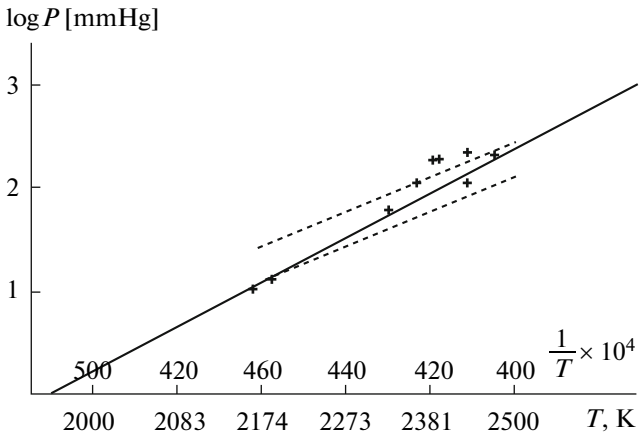

Fig. 1. Logarithmic dependence of the silicon vapor pressure over liquid silicon on the temperature [19].

Taking into account the aforesaid, we believe that the data on the silicon vapor pressures presented in the Stull tables [15, 16] are unreliable because they are based on the results of only one investigation [19] performed in the early twentieth century, which is characterized by a considerable scatter of the data. Therefore, it is surprising that, in the database of the National Institute of Standards and Technology (NIST, United States) [http://webbook.nist.gov/cgi/cbook.cgi?ID=C7440213&Units=SI], the dependence of the silicon vapor pressure on the temperature (K) in the range 1997–2560 K is described by the Antoine equation

$$\log P\,[\text{bar}] = A - B/(T + C), \quad (7)$$

in which the coefficients (A = 9.56436, B = 203308.848, C = −123.133) were calculated by researchers of the National Institute of Standards and Technology from the data taken from the Stull work [15].

The largest number of studies on the determination of the silicon vapor pressure were performed in the middle of the twentieth century. In [20], Honig summarized the results of the original investigations available to that time [19, 21]. The results obtained in [19] were discussed above. As regards the data obtained by Baur and Brunner [21], three experimental points for the silicon vapor pressure were determined in the temperature range 1980–2160 K in the study of vaporization of silicon from an alundum (Al_2O_3) crucible. We can agree with the conclusion drawn by Honig [20] that, since silicon at these temperatures should react with the crucible material with the formation of SiO in the gas phase, the data obtained by Baur and Brunner by measuring the weight loss of the crucible [21] seem to be strongly overestimated. The experiments performed by Honig [20] involved the mass spectrometric investigation of sublimation of silicon in the temperature range 1450–1650 K. The silicon samples were placed in a beryllium oxide crucible. The mass spectrum exhibited ions corresponding to molecules Si–Si_7 so that the content of monoatomic silicon was approximately two orders of magnitude higher than that of the other molecules. The obtained enthalpy of sublimation of silicon to monoatomic molecules at the temperature of the

Table 6. Partial pressures of different molecules (atm) over SiC [5]

T, K	Si	SiC	SiC_2	Si_2	Si_2C	Si_2C_2	Si_3
2149	2.1×10^{-5}		1.9×10^{-6}	3.8×10^{-8}	1.4×10^{-6}		
2168	2.7×10^{-5}		2.5×10^{-6}	4.8×10^{-8}	1.9×10^{-6}		
2181	3.3×10^{-5}	2.2×10^{-9}	4.2×10^{-6}	6.7×10^{-8}	2.6×10^{-6}		
2196	4.1×10^{-5}		4.4×10^{-6}	1.1×10^{-7}	3.9×10^{-6}	8.5×10^{-9}	
2230	6.5×10^{-5}		6.5×10^{-6}	1.6×10^{-7}	5.1×10^{-6}	1.6×10^{-8}	3.2×10^{-9}
2247	8.3×10^{-5}	6.3×10^{-9}	1.1×10^{-5}	2.1×10^{-7}	8.1×10^{-6}		
2316	2.0×10^{-4}	1.9×10^{-8}	3.1×10^{-5}	7.0×10^{-7}	2.2×10^{-5}	7.5×10^{-8}	1.6×10^{-8}

experiment is equal to 439 ± 50 kJ/mol. The large error in the results was explained by the possible interaction of silicon with the crucible material at experimental temperatures with the formation of SiO(g) and Be. Since the sublimation occurred under nonequilibrium conditions (from open surface), the results presented by Honig could not correspond to the saturation vapor pressure of silicon at the aforementioned temperatures.

Tseplyaeva et al. [9] determined the silicon vapor pressure by the effusion method. The material was vaporized from a molybdenum cup. According to [9], the standard enthalpy of formation $\Delta_f H^0$(Si, g, 298.15) is equal to 361 ± 14 kJ/mol (second law) or 383.5 ± 1.0 kJ/mol (third law). In the temperature range 1485–1593 K, the silicon vapor pressure over the solid phase is described by the equation

$$\log P_{Si}\,[\text{Pa}] = -18558/T + 11.73. \quad (8)$$

It should be noted that the data obtained in [9] are recommended by Nesmeyanov [22] as the most reliable at that time (1961), even though it is evident that, these results are strongly underestimated as compared to the value of $\Delta_f H^0$(Si, g, 298.15) recommended by CODATA [1] (see above).

Zemskov [11] determined the silicon vapor pressure from the torque force of an elastic fiber. Single-crystal silicon and graphite cell were used in the study. In the temperature range 1683–1873 K, the partial pressure of silicon over the liquid phase is described by the equation

$$\log P_{Si}\,[\text{Pa}] = -16260/T + 8.94. \quad (9)$$

The data on the vaporization rate of elements (predominantly, metals) are given in [23]. The conversion of the data on the vaporization rate to the silicon vapor pressure in the temperature range 1700–2200 K leads to the following equation:

$$\log P_{Si}\,[\text{Pa}] = -20512/T + 10.89. \quad (10)$$

Special attention should be focused on the works by Drowart et al. [5] and Davis et al. [10], in which the study of vaporization of silicon was performed together with the investigation of thermal dissociation of silicon carbide. Drowart et al. [5] presented the results of the mass spectrometric investigation of the composition of the gas phase that is in the thermodynamic equilibrium with solid SiC of the hexagonal modification in the temperature range 2149–2316 K. The SiC sample was placed in the graphite effusion cell. The experiments revealed that the gas phase in equilibrium with solid SiC predominantly consists of Si, SiC_2, and Si_2C molecules, even though there are more complex molecules. The partial pressures of molecules according to the data taken from [5] are listed in Table 6. The enthalpy of reaction (3), which was calculated from the third law of thermodynamics, is equal to 523 ± 13 kJ/mol at 298 K. In [5], the silicon vapor pressure over silicon was calculated from the equation

$$\Delta G_T^0(\text{SiC}) = RT\ln(P_{Si}/P'_{Si}), \quad (11)$$

where P'_{Si} is the saturation vapor pressure of silicon over silicon and P_{Si} is the partial pressure of silicon over SiC (i.e., the dissociation pressure of SiC).

The enthalpy of formation of atomic silicon in the gas phase, which was calculated from these data with the use of the third law, is presented in Tables 1 and 10.

The results on the determination of the silicon vapor pressure (by the Knudsen effusion method) with the control of the integrated weight loss and the dissociation pressure of silicon carbide are presented in the paper by Davis et al. [10]. The cracking of crucibles was observed when melting silicon in graphite crucibles. However, silicon mixed with silicon carbide can be heated in the crucibles that were previously used in experiments on the study of dissociation of silicon carbide. For this reason, a mixture of silicon carbide and silicon (from 0.22 to 0.45 mole of silicon per mole of silicon carbide) was placed in the graphite effusion cell in experiments on the measurement of the silicon vapor pressure. As a rule, these samples were mixed between the experiments. The silicon vapor pressures obtained by vaporizing liquid silicon in the graphite crucible coated from the inside with silicon carbide are summarized in Table 7. The silicon vapor pressures listed in Table 7 were preliminarily corrected (within 5%) taking into account the concentration of mole-

Table 7. Experimental data on the silicon vapor pressure over the liquid phase [10]

Temperature, K	Time, s × 10^{-3}	Weight loss, g × 10^3	P_{Si}, atm × 10^6	$-\Delta[(F - H_{298})/T]$	$\Delta_S H_{298}$, kJ/mol
1848	10.98	3.12	3.91	34.316	456.9
1855	10.09	4.21	5.75	34.289	452.2
1858	10.74	3.73	4.79	34.277	455.6
1861	11.58	5.74	7.04	34.265	450.6
1877	7.50	4.26	8.09	34.205	451.5
1881	6.78	2.69	5.48	34.189	456.6
1884	6.90	4.47	9.23	34.178	451.0
1932	5.52	5.69	14.8	33.993	453.6
1934	5.40	8.48	22.5	33.985	447.3
1956	10.20	9.37	13.2	33.903	460.2
2003	3.66	10.70	41.9	33.732	450.6

Table 8. Partial pressures in the boron–silicon–carbon system [24]

	$-\log P$ [atm]										
T, K	B	BC_2	B_2C	Si	BSi	BCSi	BSi_2	Si_2	SiC_2	Si_2C	SiC
2249	5.24	6.55	7.20	4.38	8.49	6.62	…	7.49	5.22	5.82	8.13
2305	4.92	6.25	6.92	4.27	8.25	6.34	8.96	7.55	4.89	5.74	7.92
2344	4.68	5.82	6.46	4.16	8.06	6.11	8.66	7.26	4.96	5.33	7.72
2301	5.00	6.23	7.17	4.34	8.70	6.77	…	…	5.09	6.25	…
2150	5.77	…	…	4.89	8.60	6.77	…	…	…	…	…
2166	5.54	…	…	4.49	…	6.46	8.41	7.46	5.42	5.62	…
2083	5.70	7.41	…	4.46	8.74	6.66	8.89	…	…	5.42	…

cules that should be contained in the gas phase according to the data obtained by Drowart et al. [5]. The enthalpy of sublimation of silicon, which was determined from direct measurements (see Table 7), is equal to 453.5 ± 12.6 kJ/mol (see also Tables 1 and 10). Unfortunately, the authors of [10] did not process data on the silicon vapor pressure in order to derive the equation describing the temperature dependence of the saturation vapor pressure of silicon. We evaluated the data obtained in [10] (see Table 7) with the use of the least-squares method. As a result, the equation for the dependence of the silicon vapor pressure over liquid silicon on the temperature (K) in the range 1848–2003 K is written in the form:

$$\log P_{Si}\,[\mathrm{Pa}] = (-2.16 \pm 0.26) \times 10^4/T + (11.36 \pm 1.38). \quad (12)$$

The paper by Verhaegen et al. [24] is worthy of notice. In that work, the vaporization processes in the boron–carbon and boron–silicon–carbon systems were investigated in the temperature range 1780–2500 K by the Knudsen effusion method with the mass spectrometric analysis of the composition of the gas phase. The partial pressures of molecules (determined in [24]) in the boron (B)–silicon (SiC)–carbon (graphite effusion cell) system are given in Table 8. In the opinion of the authors of [24], the partial pressures are correct within a factor of 2.

The last (according to the time of publication, 1999) study on the measurement of the silicon vapor pressure was performed by Tomooka et al. [25] with the use of the Knudsen effusion method with the mass spectrometric analysis of the composition of the gas phase. The vapor pressure was measured in the temperature range 1762–1998 K on a time-of-flight mass spectrometer equipped with a boron nitride Knudsen effusion cell. It was established that the gas phase over liquid silicon consists predominantly of Si and Si_2 molecules. The absolute pressure was determined by comparing the intensities of the ionic currents of Si(g) and Si_2(g) with the intensity of the ionic current of Ag(g) over pure silver. The ionization cross sections of

Table 9. Parameters of sublimation of silicon according to the data available in the literature

References (authors)	Method	Crucible (cell) material	Temperature range, K	$\Delta_f H^0_{298}$ (Si, g), $\Delta_s H^0_{298}$ (Si), kJ/mol		$P = f(T)$
				Second law	Third law	
[18] (Von Wartenberg)	Weight loss measurements	–	1478–1588	184	–	–
[20] (Honig)	Mass spectrometric method (non-equilibrium sublimation)	BeO crucible	1450–1650	–	440.5 ± 50.0	There is a plot of the dependence of P (mmHg) on $1/T$ (see also [28])
[6] (Batdorf and Smits)	Weight loss measurements (vaporization from the surface)	Tantalum cell	1473–1598	457 ± 50	456.2 ± 2.0	There is a plot of the dependence of P (mmHg) on $1/T$ (see also [28])
[9] (Tseplyaeva et al.)	Effusion method	Molybdenum crucible	1485–1593	361 ± 14	383.5 ± 1.0	$\log P$ [Pa] $= -18558/T + 11.73$
[12] (Gulbransen et al.)	Weight loss measurements (determination of the vaporization rate of silicon under vacuum)	–	1373–1623	439 ± 40	448.7 ± 2.5	There are experimental data on the silicon vapor pressure and the plot of the dependence of $\log P$ [atm] on $1/T$ (see also [25])
[13] (Zmbov et al.)	Knudsen effusion method with mass spectrometric finish	–	1547–1674	481 ± 11	460.6 ± 5.4	There are experimental data on the silicon vapor pressure at different temperatures
[14] (Zmbov et al.)	Knudsen effusion method with mass spectrometric finish	Graphite cell	1517–1674	468.6 ± 12.6	460.2 ± 12.6	There are experimental data on the silicon vapor pressure at different temperatures
[28] (Souchière et al.)	Weight loss measurements (determination of the vaporization rate of silicon under vacuum)	–	1500–1660	417.3	–	$\log P$ [Pa] $= -20800/T + 10.91$

Table 10. Parameters of vaporization of silicon according to the data available in the literature

References (authors)	Method	Crucible (cell) material	Temperature range, K	$\Delta_f H^0_{298}$ (Si, g), $\Delta_s H^0_{298}$ (Si), kJ/mol		$\Delta_v H^0_{298}$ (Si), kJ/mol		$P = f(T)$
				Second law	Third law	Second law	Third law	
[19] (Ruff and Konschak)	Weight loss measurements	SiC crucible (siliconizing of the graphite crucible)	2163–2468	–	–	406(only high-temperature points) [20]; 469 (all points) [20]	–	See above (Table 5, Fig. 1, Eqs. (5) and (6))
[5] (Drowart et al.)	Knudsen effusion method with mass spectrometric analysis of the composition of the gas phase over hexagonal SiC	Graphite effusion cell	2149–316	–	452.5 ± 12.6 calculation from the cycle according to the data taken from [25]	–	402.2 ± 12.6 according to the data taken from [25]	See above (Table 6)
[7] (Drowart et al.)	Knudsen effusion method with mass spectrometric finish	–	1703–2160	451.0 ± 2.5	461.8 ± 6.5	–	–	–
[8] (Grieveson and Alcock)	Knudsen effusion method	–	1640–2054	459.3 ± 0.6	450.6 ± 0.2	–	–	–
	Flow method	–	1854	–	444.3 ± 3.5	–	–	–
[10] (Davis et al.)	Knudsen effusion method	Graphite effusion cell with a mixture of Si and SiC	1848–2003	–	453.6 ± 12.6	–	–	See above (Table 7, Eq. (12))
[11] (Zemskov)	Torsion method	–	1683–1873	367	427.7 ± 5.2	–	–	See above (Eq. (9))
[27] (Schmude)	Knudsen effusion method with mass spectrometric finish	Boron nitride effusion cell	1362–1940	–	456 ± 4	–	403 ± 4	There is a plot of the dependence of $\log P$ [Pa] on $1/T$ (see also [25])
[25] (Tomooka et al.)	Knudsen effusion method with mass spectrometric finish	Boron nitride effusion cell	1762–1998	457.6 ± 19.1	459.4 ± 2.3	407.4 ± 19.1	409.2 ± 2.3	See above (Eq. (13))

Table 11. Relationships for the dependence of the silicon vapor pressure over liquid silicon

References (authors)	$P(\mathrm{Si}, \mathrm{Pa}) = f(T, K)$	Temperature range, K	Notes
[25] (Tomooka et al.)	$\log P = (-2.08 \pm 0.10) \times 10^4/T + (10.84 \pm 0.53)$	1762–1998	–
[10] (Davis et al.)	$\log P = (-2.16 \pm 0.26) \times 10^4/T + (11.36 \pm 1.38)$	1848–2003	Derived in our review with the use of the least-squares method from the data obtained by Davis et al. (see Table 7)
[11] (Zemskov)	$\log P = -16260/T + 8.94$	1683–1873	Derived in our review with the use of the least-squares method from the data obtained by Zemskov

Ag and Si atoms were taken from the Mann tables [26]. The ionization cross section of Si_2 was taken equal to a value that exceeds the ionization cross section of the silicon monomer by a factor of 1.5. The enthalpy of vaporization of silicon to Si(g) in the standard state according to the calculations from the third law (409.2 ± 2.3 kJ/mol) is in good agreement with that obtained from the second law (407.4 ± 19.1 kJ/mol). The relationships for the vapor pressures of Si(g) and Si_2(g) over Si(l) are written as follows [25]:

$$\log P_{\mathrm{Si}}\,[\mathrm{Pa}] = (-2.08 \pm 0.10) \times 10^4/T + (10.84 \pm 0.53), \quad (13)$$

$$\log P_{\mathrm{Si_2}}\,[\mathrm{Pa}] = (-2.46 \pm 0.09) \times 10^4/T + (10.93 \pm 0.47). \quad (14)$$

The enthalpies of formation of Si(g) and Si_2(g) were calculated using the standard enthalpies of vaporization of silicon to Si(g) and Si_2(g) from the second and third laws. The results obtained were analyzed in [25] with due regard for the data available in the literature [5, 6, 12, 20, 27–29]. Reasoning from good agreement between the enthalpies of vaporization of silicon according to the calculations from the second and third laws, Tomooka et al. [25] made the inference that their data on the vapor pressure are fairly reliable.

The available original data on the vaporization of silicon are presented in Tables 9 (sublimation) and 10 (vaporization).

It can be seen from Tables 9 and 10 that the studies on the determination of the silicon vapor pressure can be separated into two groups:

(1) studies with the use of the mass spectrometric analysis and

(2) studies with the use of different variants of weight loss measurements (in particular, the Knudsen effusion method without the mass spectrometric finish).

The relative concentrations of molecules in the gas phase cannot be determined in experiments on the measurement of the time dependence of the weight loss. However, when the relative concentrations of molecules in the gas phase are known, the experiments on the measurement of the weight loss can provide an accurate determination of the absolute pressure of the main component of the gas phase (in our case, atomic silicon) and silicon-containing species. It is believed that the mass spectrometric method makes it possible to determine the absolute pressures within a factor of two. Changes in the sample weight in experiments on the measurement of the weight loss are determined with an accuracy of 20%. Consequently, the experiments on the measurement of the weight loss and mass spectrometric experiments complement each other.

It follows from Table 9 that the sublimation process is most adequately described by Zmbov et al. [14], which is evidenced by the coincidence (within a relatively small experimental error) of the enthalpies of sublimation of silicon according to the calculations from the second and third laws. As regards the vaporization of silicon, five works [5, 7, 8, 10, 11, 25] (see Table 10) are of most interest. The work by Ruff and Konschak [19] was considered above. As was already noted, we believe that the data obtained in [19] are unreliable. Among the aforementioned six papers, only three papers contain expressions for the temperature dependences of the silicon vapor pressure over liquid silicon (see Table 11).

It can be seen from Table 11 that the relationship derived from the data reported by Zemskov [11] differs substantially from those obtained from the results of Tomooka et al. [25] and Davis et al. [10] in both the slope (determining the enthalpy of vaporization of silicon) and the value of the free term. However, the expressions based on the results obtained in [10] and [25] coincide with each other to within the errors in the coefficients A and B in the equation $\log P = A/T + B$ determined using the least-squares method. There-

Table 12. Approximation coefficients of the heat capacity $C_p(T)$ for silicon compounds: $C_p(X) = C1 + C2X^{-2} + C3X + C4X^2 + C5X3$, where $X = T/10000$ (T, K; C_p, J/(mol K))

Compound	$C1$	$C2$	$C3$	$C4$	$C5$	Temperature range, K
Si(cr, l)	2.3698E+1	−4.351E-3	3.305E+1	0.0	0.0	298–1690
	2.72E+1	0.0	0.0	0.0	0.0	1690–3500
Si(g)	2.0932E+1	1.2337E-3	−2.0424E+0	−1.7255E+1	2.9237E+2	298–1500
	1.5331E+1	1.8673E-2	4.6764E+1	−9.3475E+1	6.1173E+1	1500–6000
Si_2(g)	3.7669E+1	−8.9888E-4	−2.4022E+2	3.9272E+2	−1.0142E+3	298–1500
	3.5057E+1	1.1586E-2	1.5084E+1	8.3025E+1	−1.2231E+2	1500–6000
Si_3(g)	5.0416E+1	−5.3353E-3	2.8466E+2	−2.3805E+3	6.4939E+3	298–1500
	4.9149E+1	6.3301-2	7.4509E+1	−8.7747E+1	1.7851E+1	1500–6000
Si_4(g)	8.3331E+1	−8.4070E-3	−1.7856E+1	2.058E+2	−6.4694E+2	298–1500
	8.8995E+1	−3.9309E-2	−4.8698E+1	1.4669E+2	−1.5257E+2	1500–3500
Si_5(g)	9.3437E+1	−1.4188E-2	2.9599E+2	−2.1916E+3	5.6152E+3	298–1500
	1.0797E+2	−2.7340E-2	4.8173E-1	−5.6344E-1	1.1625E-1	1500–3500
Si_6(g)	1.3175E+2	−1.7196E-2	6.6699E+0	1.18321E+1	−5.4071E+1	298–1500
	1.3177E+2	−1.7283E-2	6.5156E+0	5.8813E-1	−6.9657E-2	1500–3500

fore, in our opinion, the results obtained by Tomooka et al. [25] and Davis et al. [10] are most reliable and promising from the viewpoint of further investigations. In this case, we propose to use relationship (13) for the vapor pressure from the paper by Tomooka et al. [25] as the basic relationship, because it determines the silicon vapor pressure over liquid silicon with the minimum error (as compared to the results of the other studies).

For practical purposes (in particular, for siliconizing), it is important to know the saturation vapor pressure of silicon over the liquid phase at high temperatures. However, it follows from the above data that the most reliable results were obtained at temperatures below 2000 K. The extrapolation of the Tomooka data to higher temperatures can lead to adequate results only in a narrow range. It is clear that the solution to this problem calls for additional experiments with the use of a combination of various methods.

4. CALCULATION OF THE COMPOSITION OF THE GAS PHASE OVER SILICON AND "SILICON–CONTAINER" SYSTEMS

It was shown in [5, 7, 13, 14, 20] that, apart from monoatomic silicon, the gas phase over Si(cr) and Si(l) contains a considerable number of polyatomic molecules Si_2, Si_3, Si_4, Si_5, and Si_6. In order to calculate equilibria, it is necessary to know the temperature dependences of the thermodynamic properties for all participants of the equilibrium. The thermodynamic properties of the main individual compounds according to the data available in the literature are given below.

Si(cr). Crystalline silicon (cubic modification, diamond structure) is assumed to be the standard state of the element, and, hence, we have $\Delta_f H^0(0) = \Delta_f H^0(298.15) = \Delta_f G^0(298.15) \equiv 0$ by definition. The dependence of the heat capacity at constant pressure on the temperature was most accurately measured almost to the melting temperature (298–1556 K) by Serebrennikov and Gel'd [29]. The approximation coefficients for this dependence according to the data obtained in [29] in the range 298.15–1690 K are presented in Table 12. These coefficients provide the basis for the calculations of all the other thermodynamic functions with the IVTANTERMO program package [4]. The errors in the calculations of the values of $\Phi^0(T)$ at 2000 and 3000 K are equal to 0.6 and 2.0 J/(mol K), respectively.

Si(l). The enthalpy of melting $\Delta_{melt}H^0$(Si, cr, 298.15) = 50.21 ± 0.8 kJ/mol is taken according to the results of the measurements performed by Olette [30], who also determined the melting temperature of silicon at atmospheric pressure (T_{melt} = 1688 ± 3K). The heat capacity of liquid silicon is taken equal to 27.2 J/(mol K) according to the data obtained in [30, 31]. The approximation coefficients of the heat capacity from the melting temperature to the boiling temperature are listed in Table 12. The enthalpy of formation of Si(l) was calculated from the chosen values of the enthalpy of melting and the difference $H(298.15) - H(0)$. The value of S^0(Si, l, 298.15) was calculated

Table 13. Thermodynamic properties of polyatomic silicon molecules

Compound	C_p(298.15), J/(mol K)	S^0(298.15), J/(mol K)	H(298.15)−H(0), kJ/mol	$\Delta_f H$(298.15), kJ/mol	$\Delta_f H$(0), kJ/mol
Si_2(g)	36.3 ± 2.1	238.0 ± 1.5	10.3 ± 1.5	583.9 ± 13.0	580.0 ± 19.0
Si_3(g)	51.0 ± 5.5	279.2 ± 5.6	12.5 ± 0.5	627.9 ± 15.0	625.0 ± 15.0
Si_4(g)	73.8 ± 6.7	308.3 ± 6.1	16.7 ± 0.9	643.5 ± 22.0	634.0 ± 23.0
Si_5(g)	85.4 ± 8.1	311.7 ± 7.9	17.2 ± 1.1	700.7 ± 24.0	681.3 ± 25.0
Si_6(g)	112.6 ± 9.5	351.0 ± 10.1	32.4 ± 2.1	733.0 ± 41.0	719.9 ± 42.0

Table 14. Partial pressures and total pressures $P(\Sigma)$ (MPa) over liquid silicon (equilibrium vaporization, $P = 0.1$ MPa = const)

T, K	$P(\Sigma)$	P(Si)	$P(Si_2)$	$P(Si_3)$	$P(Si_4)$	$P(Si_5)$	$P(Si_6)$
1700	6.96E-08	6.78E-08	9.92E-10	4.23E-10	3.59E-10	4.60E-12	7.51E-12
1800	3.28E-07	3.17E-07	6.12E-09	2.48E-09	1.80E-09	2.05E-11	3.08E-11
1900	1.31E-06	1.22E-06	3.10E-08	1.20E-08	7.52E-09	7.73E-11	1.08E-10
2000	4.56E-06	4.53E-06	1.33E-07	4.94E-08	2.71E-08	2.53E-10	3.34E-10
2100	1.41E-05	1.33E-05	4.96E-07	1.76E-07	8.56E-08	7.33E-10	9.17E-10
2200	3.92E-05	3.83E-05	1.63E-06	5.57E-07	2.42E+07	1.91E-09	2.28E-09
2300	1.00E-04	9.30E-05	4.82E-06	1.59E-06	6.22E-07	4.57E-09	5.18E-09
2400	2.36E-04	2.17E-04	1.30E-05	4.13E-06	1.47E-06	1.01E-08	1.09E-08
2500	5.20E-04	4.74E-04	3.23E-05	9.92E-06	3.22E-06	2.07E-08	2.16E-08
2600	1.08E-03	9.73E-04	7.45E-05	2.22E-05	6.62E-06	4.04E-08	4.02E-08
2700	2.11E-03	1.89E-03	1.62E-04	4.66E-05	1.28E-05	7.37E-08	7.16E-08
2800	3.95E-03	3.50E-03	3.31E-04	9.26E-05	2.37E-05	1.29E-07	1.21E-07
2900	7.08E-03	6.22E-03	6.44E-04	1.75E-04	4.16E-05	2.16E-07	1.97E-07
3000	1.22E-02	1.06E-02	1.20E-03	3.16E-04	7.02E-05	3.49E-07	3.08E-07
3100	2.03E-02	1.75E-02	2.13E-03	5.49E-04	1.14E-04	5.44E-07	4.68E-07
3200	3.27E-02	2.79E-02	3.66E-03	9.19E-04	1.80E-04	8.21E-07	6.90E-07
3300	5.11E-02	4.33E-02	6.08E-03	1.48E-03	2.74E-04	1.21E-06	9.98E-07
3400	7.81E-02	6.54E-02	9.79E-03	2.34E-03	4.07E-04	1.73E-06	1.38E-06

from the data taken from [30, 31]. The errors in the calculations of the values of $\Phi^0(T)$ at 2000 and 3000 K are equal to 0.5 and 2.0 J/(mol K), respectively.

Si(g). According to the CODATA recommendations [1], the standard enthalpy of formation is assumed to be $\Delta_f H^0$(Si, g, 298.15) = 450 ± 8 kJ/mol. The heat capacity at constant pressure was calculated from the molecular constants recommended in [32, 33]. The approximation coefficients of the heat capacity in the temperature range 298–6000 K are given in Table 12. The errors in the calculations of the values of $\Phi^0(T)$ at 2000 and 3000 K are equal to 0.2 and 0.3 J/(mol K), respectively.

Si_2(g). The standard enthalpy of formation of Si_2(g) was calculated from the dissociation energy $D_0 = 330 \pm 10$ kJ/mol [34]. The thermodynamic functions of a gaseous molecule Si_2 were calculated from the molecular constants obtained by the authors of [34, 35] in the study of electronic spectra. The approximation coefficients of the heat capacity in the temperature range 298–6000 K are presented in Table 12. The errors in the calculations of the values of $\Phi^0(T)$ at 2000 and 3000 K are equal to 0.9 and 2.0 J/(mol K), respectively.

Si_3(g), Si_4(g), Si_5(g), and Si_6(g). The enthalpies of formation of Si_3(g), Si_4(g), Si_5(g), and Si_6(g) (see Table 13) were estimated from the results of investigations of equilibria $Si_n \longrightarrow n$Si with the use of the mass spectrometric method by Drowart et al. [5] and Schmude et al. [36–38]. The temperature dependences of the thermodynamic functions were calculated using the statistic thermodynamics with the results of spectral investigations [39–41] and theoretical calculations [42–45]. The approximation coefficients of the heat capacity in the temperature range 298–3500 K are listed in Table 12. The thermodynamic properties of gaseous polyatomic silicon molecules, which were used in the calculations, are presented in Table 13. The errors in the calculations of the values of $\Phi^0(T)$ at 2000 and 3000 K can reach 7 and 8 J/(mol K), respectively.

Table 15. Ratios between the partial pressures

T, K	$P(\Sigma)/P(Si)$	$P(Si_2)/P(Si)$	$P(Si_3)/P(Si_2)$	$P(Si_4)/P(Si_3)$	$P(Si_5)/P(Si_4)$	$P(Si_6)P(Si_5)$
1700	1.0265E+00	1.46E-02	6.24E-03	5.29E-03	6.78E-05	1.11E-04
1800	1.0347E+00	1.93E-02	7.82E-03	5.68E-03	6.47E-05	9.72E-05
1900	1.0782E+00	2.55E-02	9.88E-03	6.19E-03	6.36E-05	8.89E-05
2000	1.0483E+00	3.06E-02	1.14E-02	6.23E-03	5.82E-05	7.68E-05
2100	1.0602E+00	3.73E-02	1.32E-02	6.44E-03	5.51E-05	6.89E-05
2200	1.0235E+00	4.26E-02	1.45E-02	6.32E-03	4.49E-05	5.95E-05
2300	1.0753E+00	5.18E-02	1.17E-02	6.69E-03	4.91E-05	5.57E-05
2400	1.0876E+00	5.99E-02	1.90E-02	6.77E-03	4.65E-05	5.02E-05
2500	1.0970E+00	6.81E-02	2.09E-02	6.79E-03	4.37E-05	4.56E-05
2600	1.1100E+00	7.66E-02	2.28E-02	6.80E-03	4.15E-05	4.13E-05
2700	1.1164E+00	8.57E-02	2.47E-02	6.77E-03	3.90E-05	3.79E-05
2800	1.1286E+00	9.46E-02	2.65E-02	6.77E-03	3.69E-05	3.46E-05
2900	1.1383E+00	1.04E-01	2.81E-02	6.69E-03	3.47E-05	3.17E-05
3000	1.1509E+00	1.13E-01	2.98E-02	6.62E-03	3.29E-05	2.91E-05
3100	1.1600E+00	1.22E-01	3.14E-02	6.51E-03	3.11E-05	2.67E-05
3200	1.1720E+00	1.31E-01	3.29E-02	6.45E-03	2.94E-05	2.47E-05
3300	1.1801E+00	1.40E-01	3.42E-02	6.33E-03	2.79E-05	2.28E-05
3400	1.1942E+00	1.50E-01	3.58E-02	6.22E-03	2.65E-05	2.11E-05

The equilibrium compositions were calculated with the program package and database IVTANTERMO [4]. All calculations were carried out for processes at the constant pressure ($P = 0.1$ MPa = const).

The results of the calculations of the partial pressures of the components of the gas phase over liquid silicon (equilibrium vaporization, process at the constant pressure $P = 0.1$ MPa) are given in Table 14.

It should be immediately noted that the pressures obtained correspond to equilibrium vaporization of liquid silicon contained in an "ideal" (i.e., inert) chamber. Consequently, these pressures can be considered as ***reference*** values.

In the use of the above pressures as reference values, it is necessary to take into account that they were calculated with the error dependent on the temperature due to the errors of the values used in the calculations. For example, the errors of the standard enthalpy of formation and standard entropy of monoatomic silicon lead to a change in the partial vapor pressure (main component (see Table 14)) P(Si) and the total pressure by a factor of 1.6 at 2000 K and by a factor of 1.3 at 3000 K. Therefore, the ratio between the partial pressures is a more informative characteristic of the vapor composition. Table 15 presents the ratios of the total pressure and the partial pressures of the components to the partial pressure of monoatomic silicon for the equilibrium vaporization of liquid silicon at the constant pressure (0.1 MPa).

The decimal logarithms of the total pressure and partial pressure of monoatomic silicon are adequately described by the linear relationships (15) and (16) in the temperature range 1700–3400 K:

$$\log P[(\Sigma)\ [\mathrm{MPa}]] = -20567/T + 10.94, \quad (15)$$

$$\log P[(\mathrm{Si})\ [\mathrm{MPa}]] = -20348/T + 10.81. \quad (16)$$

Similar results were obtained in [46], even though, in the calculation of P(Si), Desai [46] did not take into account the contribution of all polyatomic molecular species. It can be seen from relationships (13) and (16) that the results of the calculations of the saturation vapor pressure of silicon over the liquid phase are in good agreement with the data obtained by Tomooka et al. [25].

Silicon is one of the most active elements: it forms chemical compounds almost with all elements of the Periodic Table. Silicon and metals form silicides of different compositions; as a rule, lower silicides that are stable above 1500 K are the most stable under vacuum. Consequently, the measured (in particular, by the Knudsen effusion method with the mass spectrometric analysis of the composition of the gas phase) vapor pressure of monoatomic silicon corresponds to a heterogeneous system with the participation of a silicide and should not coincide with a reference value. However, this pressure can differ not very strongly from the reference pressure if the processes of silicide

Table 16. Vapor pressures over molybdenum disilicide and the "Si(l)–SiC(s)" system

T, K	Si(l)–SiC(s) system			$MoSi_2$(s)		
	$P(\Sigma)$, Pa	P(Si), Pa	$P(Si_2C)$, Pa	$P(\Sigma)$, Pa*	P(Si), Pa*	P(Mo), Pa*
1850	0.684	0.644	0.016	0.0018	0.0008	0.0004
1900	1.350	1.25	0.043	0.003	0.002	0.001
1950	2.59	2.38	0.016	0.008	0.0054	0.0027
2000	4.81	4.35	0.248	0.018	0.013	0.0064
2050	8.66	7.72	0.561	0.043	0.028	0.014
2100	15.32	13.3	1.22	0.094	0.062	0.031
2150	26.4	22.4	2.552	0.195	0.13	0.065
2200	44.5	36.8	5.16	0.392	0.26	0.13
2250	673.7	59.2	10.0	0.768	0.51	0.25
2300	109.9	93.05	19.1	1.45	0.97	0.48

* From $MoSi_2$(s).

Table 17. Vapor pressures over liquid silicon (references pressures) and the "4Si(l)–$MoSi_2$(s)" system

T, K	Si(l)			4Si(l)– $MoSi_2$(s) system		
	$P(\Sigma)$, Pa	P(Si), Pa	$P(Si_2C)$, Pa	$P(\Sigma)$, Pa*	P(Si), Pa*	P(Mo), Pa*
1850	0.667	0.643	0.014	0.667	0.643	0.014
1900	1.310	1.260	0.031	1.310	1.260	0.031
1950	2.484	2.379	0.066	2.484	2.379	0.066
2000	4.56	4.35	0.133	4.56	4.35	0.133
2050	8.186	7.72	0.261	8.186	7.72	0.261
2100	14.12	13.3	0.496	14.12	13.3	0.496
2150	23.8	22.4	0.952	23.8	22.4	0.952
2200	39.2	36.8	1.63	39.2	36.8	1.63
2250	63.3	59.2	2.84	63.3	59.2	2.84
2300	100.1	93.05	4.82	100.1	93.1	4.82

* 4Si(l)– $MoSi_2$(s) system.

formation on the container surface are completed and the pressure of monoatomic silicon over the silicide at the experimental temperature is considerably lower than the pressure over liquid silicon. The partial pressures of silicon over different silicides at temperatures up to 1500 K are given in the reference book [47].

The results of the calculations of the partial pressures of monoatomic silicon and the total pressure over liquid silicon (reference pressure), as well as the pressures over the "Si(l)–$MoSi_2$(s)" and "Si(l)–SiC(s)" systems and over $MoSi_2$(s), are presented in Tables 16 and 17. It can be seen from these tables that the partial pressure P(Si) over molybdenum disilicide (the most stable compound) is substantially lower than that over liquid silicon. Therefore, the compositions of the gas phases over liquid silicon and the Si(l)–$MoSi_2$(s) system (see Table 17) almost coincide with each other. At the same time, the partial pressures over the Si(l)–SiC(s) system (see Table 16) differ significantly from the reference values. For example, the fraction of SiC_2 molecules in the gas phase increases with an increase in the temperature and, at 2300 K (the pressure is approximately equal to 100 Pa), the ratio between the pressures of monoatomic silicon and the above molecules is approximately equal to 9 : 2, which corresponds to a concentration ratio of 9 : 4. This situation can substantially affect the processes of transfer of silicon-containing species at high temperatures.

The calculations for the "Si(l)–C(gr)" system lead to identical results, because the silicon carbide is initially formed in the system (there occurs siliconizing of the surface and bulk of the container, product, and Knudsen cell). This inference is confirmed by the results obtained by Zmbov et al. [14].

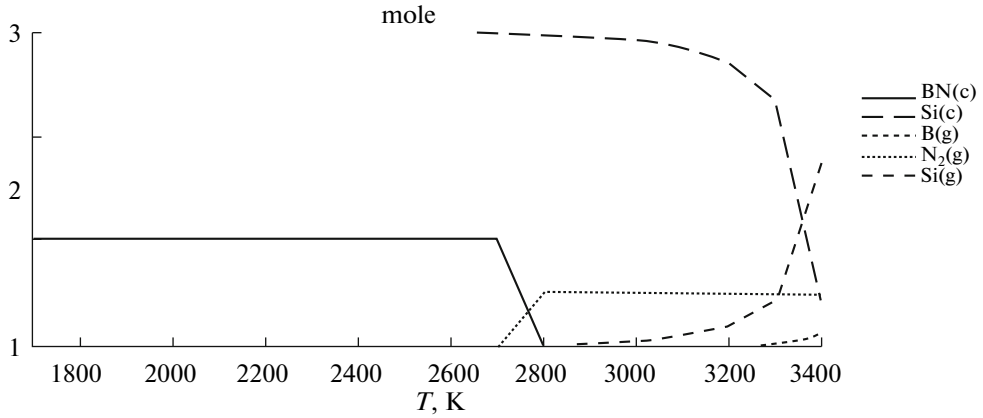

Fig. 2. Molar composition in the BN + Si(l) system.

According to the thermodynamic calculations (IVTANTERMO), the mole fraction of the gas phase formed upon vaporization of liquid silicon from boron nitride is very small; in this case, molecular nitrogen is the main component (see Fig. 2, Table 18). In particular, at a temperature of 2100 K, the gas phase contains 2.8×10^{-11} mol and the ratio between the mole fractions of the main components $n(N_2(g))/n(Si(g))$ is equal to 7680. Therefore, the presence of nitrogen in the gas phase can substantially suppress the silicon diffusion, i.e., reduce the efficiency of the siliconizing process. Consequently, the measurement of the silicon vapor pressure by the Knudsen method with the use of boron nitride cells should be limited by the low-temperature range.

Iridium is one of the most promising materials for use in fabricating crucibles. It is known that iridium silicides are unstable at temperatures above 1800 K.

Table 18. Results of the calculations of the composition in the "3Si(l)–BN(s)" system at $P = 0.1$ MPa (for $N_2(g)$ and Si(g), the partial pressures and mole fractions are given at temperatures up to $T = 2700$ K (inclusive) and above 2700 K, respectively)

T, K	Molar composition of the system				
	B(s)	BN(s)	Si(s)	$N_2(g)$	Si(g)
1700	0.00E+00	1.00E+00	3.00E+00	0.00E+00	0.00E+00
1800	0.00E+00	1.00E+00	3.00E+00	0.00E+00	0.00E+00
1900	0.00E+00	1.00E+00	3.00E+00	0.00E+00	0.00E+00
2000	0.00E+00	1.00E+00	3.00E+00	0.00E+00	0.00E+00
2100	0.00E+00	1.00E+00	3.00E+00	1.10E-11	1.47E-15
2200	0.00E+00	1.00E+00	3.00E+00	3.45E-11	1.27E-14
2300	0.00E+00	1.00E+00	3.00E+00	5.59E-11	5.12E-14
2400	0.00E+00	1.00E+00	3.00E+00	7.56E-11	1.65E-13
2500	0.00E+00	1.00E+00	3.00E+00	9.38E-11	4.47E-13
2600	0.00E+00	1.00E+00	3.00E+00	1.11E-10	1.09E-12
2700	0.00E+00	1.00E+00	3.00E+00	1.26E-10	2.44E-12
2800	1.00E+00	0.00E+00	2.98E+00	5.00E-01	1.83E-02
2900	9.99E+00	0.00E+00	2.95E+00	5.00E-01	3.36E-02
3000	9.98E+00	0.00E+00	2.92E+00	4.99E-01	6.08E-02
3100	9.95E+00	0.00E+00	2.85E+00	4.99E-01	1.11E-01
3200	9.90E+00	0.00E+00	2.70E+00	4.98E-01	2.12E-01
3300	9.75E+00	0.00E+00	2.33E+00	4.97E-01	4.68E-01
3400	8.90E+00	0.00E+00	3.64E+00	4.92E-01	1.83E+00

Nonetheless, reliable data on the use of iridium as a material of containers intended for the study of the vaporization of silicon are not available in the literature.

In closing this section, we note the following.

(1) The pressure of silicon-containing components (predominantly, monoatomic silicon) over a heterogeneous system containing silicides is measured *in all cases* in experimental investigations of the silicon vapor pressure.

(2) The calculations have demonstrated that the vapor with the "purest" composition is formed over liquid silicon when molybdenum (or tungsten) disilicide or silicon carbide is used as the crucible material. Moreover, it is necessary to investigate the possibility of using iridium for these purposes.

5. CONCLUSIONS

(1) Reference books and original studies devoted to the determination of the saturation vapor pressure of silicon in a wide range of temperatures have been analyzed. The results obtained by Tomooka et al. [25] have been recommended for use as the basic data. It has been established that reliable experimental data in the range of high temperatures (above 2000 K) are not available in the literature. It has been demonstrated that there is a need to perform additional theoretical and experimental investigations with the use of hybrid methods.

(2) The total pressure and partial pressures of Si_n ($n = 1$–6) molecules over liquid silicon were calculated in the temperature range 1700–3400 K. The calculation of the composition of the gas phase over "Si(l)–container" systems was performed. The results of the calculation of the vapor pressure of Si(g) over the liquid phase are in good agreement with the data obtained by Tomooka et al. [25].

(3) Molybdenum (or tungsten) disilicide and silicon carbide have been recommended as materials for crucibles used in experimental investigations of the temperature dependence of the saturation vapor pressure of silicon over the liquid phase.

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