Physical Chemistry

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:

\[ \Delta G^0_T = A + BT \log T + CT \] (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 \( \Delta G^0_T \) 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 system:

\[
\begin{align*}
\text{SiO}_2 + \text{Mg} & = \text{MgO} + \text{SiO} \uparrow & \text{I} \\
\text{SiO}_2 + 2\text{Mg} & = 2\text{MgO} + \text{Si} & \text{II} \\
\text{SiO}_2 + 4\text{Mg} & = 2\text{MgO} + \text{Mg}_2\text{Si} & \text{III} \\
\text{SiO}_2 + \text{Si} & = 2\text{SiO} \uparrow & \text{IV} \\
\text{SiO}_2 + \text{MgO} & = \text{Mg}_2\text{SiO}_3 & \text{V} \\
\text{SiO}_2 + 2\text{MgO} & = \text{Mg}_2\text{SiO}_4 & \text{VI} \\
\end{align*}
\]

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

\[
\begin{align*}
\text{SiO}_2 + \text{Si} & = 2\text{SiO} \uparrow & \text{I} \\
\text{SiO}_2 + \text{MgO} & = \text{Mg}_2\text{SiO}_3 & \text{II} \\
\text{SiO}_2 + 2\text{MgO} & = \text{Mg}_2\text{SiO}_4 & \text{III} \\
\end{align*}
\]

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

\[
\begin{align*}
1^I. \text{Si}_(S) + \frac{1}{2}\text{O}_2(g) & = \text{SiO}_2(S) - /298-1688K/ - \Delta G^0_T (1^I) \\
1^II. \text{Si}_(L) + \frac{1}{2}\text{O}_2(g) & = \text{SiO}_2(S) - /1688-2000 K/ - \Delta G^0_T (1^II) \\
2^I. \text{Mg}_(S) + \frac{1}{2}\text{O}_2(g) & = \text{MgO}_(S) - /298-923 K/ - \Delta G^0_T (2^I) \\
2^II. \text{Mg}_(L) + \frac{1}{2}\text{O}_2(g) & = \text{MgO}_(S) - /923-1368 K/ - \Delta G^0_T (2^II) \\
2^III. \text{Mg}_(g) + \frac{1}{2}\text{O}_2(g) & = \text{MgO}_(S) - /1368-2000K/ - \Delta G^0_T (2^III) \\
3^I. \text{Si}_(S) + \frac{1}{2}\text{O}_2(g) & = \text{SiO} \uparrow - /298-1688 K/ - \Delta G^0_T (3^I) \\
\end{align*}
\]
Table 1
Initial thermodynamic data necessary for the analysis of processes expected in a reactive mix (SiO₂+ Mg) (1cal = 4.184 Joule)

<table>
<thead>
<tr>
<th>Element, compound</th>
<th>( \Delta H^{0,\text{mix}} ) kcal.mole(^{-1})</th>
<th>( S^{0,\text{mix}} ) cal.mole(^{-1}).K(^{-1})</th>
<th>T(_{\text{tr}})</th>
<th>T(_{\text{m}})</th>
<th>T(_{\text{b}})</th>
<th>Coefficients of equation ( C_p = a + bT + cT^2 ) (cal.mole(^{-1}).K(^{-1}))</th>
<th>Temperature Range</th>
<th>C(_{\text{pm}})</th>
<th>C(_{\text{pv}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>-</td>
<td>4.5±0.02</td>
<td>-</td>
<td>1688</td>
<td>-</td>
<td>11.9±0.2</td>
<td>-</td>
<td>5.72</td>
<td>0.59</td>
</tr>
<tr>
<td>Mg</td>
<td>-</td>
<td>7.81±0.02</td>
<td>-</td>
<td>923</td>
<td>1368</td>
<td>2.03±0.05</td>
<td>30.55</td>
<td>5.33</td>
<td>2.45</td>
</tr>
<tr>
<td>O(_2)</td>
<td>-</td>
<td>49.0±0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.16</td>
<td>1.00</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>217.72±0.34</td>
<td>10.0±0.10</td>
<td>-</td>
<td>2001</td>
<td>-</td>
<td>1.84</td>
<td>-</td>
<td>13.38</td>
<td>3.68</td>
</tr>
<tr>
<td>SiO</td>
<td>24.7</td>
<td>50.54±0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.14</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>143.76±0.07</td>
<td>6.47±0.05</td>
<td>-</td>
<td>3098</td>
<td>-</td>
<td>18.5±1.5</td>
<td>-</td>
<td>11.71</td>
<td>0.75</td>
</tr>
<tr>
<td>Mg(_2)Si</td>
<td>18.95</td>
<td>18.11±0.05</td>
<td>-</td>
<td>1358</td>
<td>-</td>
<td>20.5±2.5</td>
<td>-</td>
<td>16.5</td>
<td>4.02</td>
</tr>
<tr>
<td>MgSiO(_3)</td>
<td>370.2±0.4</td>
<td>16.22±0.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>22.0</td>
<td>7.9</td>
</tr>
<tr>
<td>Mg(_2)SiO(_4)</td>
<td>519.1±0.5</td>
<td>22.75±0.30</td>
<td>-</td>
<td>1923</td>
<td>-</td>
<td>18.00</td>
<td>-</td>
<td>35.0</td>
<td>-</td>
</tr>
<tr>
<td>Mg(_2)SiO(_3)</td>
<td>1519.1±0.5</td>
<td>22.75±0.30</td>
<td>-</td>
<td>2160</td>
<td>-</td>
<td>18.8±0.8</td>
<td>-</td>
<td>35.81</td>
<td>6.54</td>
</tr>
</tbody>
</table>

* - Calculated by the method offered in [5]
** - Coefficients \( C_p = f (T) \) calculated by the method offered in [6]
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\[ 3\text{II. } \text{Si(L)} + 1/2\text{O}_2(g) = \text{SiO}(g) \quad \Delta G^0_T(3\text{II}) \]

\[ 4\text{I. } \text{Si(S)} + 2\text{Mg(S)} = \text{Mg}_2\text{Si(S)} \quad \Delta G^0_T(4\text{I}) \]

\[ 4\text{II. } \text{Si(S)} + 2\text{Mg(L)} = \text{Mg}_2\text{Si(S)} \quad \Delta G^0_T(4\text{II}) \]

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:

\[ 5\text{I. } \text{Mg(S)} + \text{Si(S)} + 1.5\text{O}_2(g) = \text{MgSiO}_3(S) \quad \Delta G^0_T(5\text{I}) \]

\[ 5\text{II. } \text{Mg(L)} + \text{Si(S)} + 1.5\text{O}_2(g) = \text{MgSiO}_3(S) \quad \Delta G^0_T(5\text{II}) \]

\[ 5\text{III. } \text{Mg(g)} + \text{Si(S)} + 1.5\text{O}_2(g) = \text{MgSiO}_3(S) \quad \Delta G^0_T(5\text{III}) \]

\[ 5\text{IV. } \text{Mg(g)} + \text{Si(L)} + 1.5\text{O}_2(g) = \text{MgSiO}_3(S) \quad \Delta G^0_T(5\text{IV}) \]

\[ 6\text{I. } 2\text{Mg(S)} + \text{Si(S)} + 1.5\text{O}_2(g) = \text{Mg}_2\text{SiO}_4(S) \quad \Delta G^0_T(6\text{I}) \]

\[ 6\text{II. } 2\text{Mg(L)} + \text{Si(S)} + 1.5\text{O}_2(g) = \text{Mg}_2\text{SiO}_4(S) \quad \Delta G^0_T(6\text{II}) \]

\[ 6\text{III. } 2\text{Mg(g)} + \text{Si(S)} + 1.5\text{O}_2(g) = \text{Mg}_2\text{SiO}_4(S) \quad \Delta G^0_T(6\text{III}) \]

\[ 6\text{IV. } 2\text{Mg(g)} + \text{Si(L)} + 1.5\text{O}_2(g) = \text{Mg}_2\text{SiO}_4(S) \quad \Delta G^0_T(6\text{IV}) \]

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:

\[ \Delta G^0_T(1\text{I}) = -218670 - 4.62\cdot T\cdot \lg T + 58.12\cdot T \quad \text{cal.mole}^{-1} /298-1688 \text{ K} \]

\[ \Delta G^0_T(1\text{II}) = -234900 - 11.3\cdot T\cdot \lg T + 89.38\cdot T \quad \text{cal.mole}^{-1} /1688-2000 \text{ K} \]

\[ \Delta G^0_T(2\text{I}) = -144010 - 1.49\cdot T\cdot \lg T + 30.37\cdot T \quad \text{cal.mole}^{-1} /298-923 \text{ K} \]

\[ \Delta G^0_T(2\text{II}) = -155540 - 0.23\cdot T\cdot \lg T + 28.29\cdot T \quad \text{cal.mole}^{-1} /923-1368 \text{ K} \]

\[ \Delta G^0_T(3\text{I}) = -180720 - 8.0\cdot T\cdot \lg T + 78.36\cdot T \quad \text{cal.mole}^{-1} /1368-2000 \text{ K} \]

\[ \Delta G^0_T(3\text{II}) = -23640 + 6.73\cdot T\cdot \lg T - 41.75\cdot T \quad \text{cal.mole}^{-1} /298-1688 \text{ K} \]

\[ \Delta G^0_T(4\text{I}) = -34930 + 7.94\cdot T\cdot \lg T - 39.0\cdot T \quad \text{cal.mole}^{-1} /1688-2000 \text{ K} \]

\[ \Delta G^0_T(4\text{II}) = -18680 + 6.73\cdot T\cdot \lg T - 41.75\cdot T \quad \text{cal.mole}^{-1} /298-1688 \text{ K} \]

\[ \Delta G^0_T(5\text{I}) = -370400 - 4.41\cdot T\cdot \lg T + 81.16\cdot T \quad \text{cal.mole}^{-1} /923-1368 \text{ K} \]

\[ \Delta G^0_T(5\text{II}) = -404440 - 10.83\cdot T\cdot \lg T + 126.73\cdot T \quad \text{cal.mole}^{-1} /1368-1688 \text{ K} \]

As a result of algebraical summation of the corresponding equations \( \Delta G^0_T \) 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 \( \Delta G^0_T \) of these reactions is constructed (Fig. 1).

Data of Fig. 1 unequivocally show that in the investigated system of \((\text{SiO}_2 + \text{Mg})\) in the range of 1000-1300K energetically the most probable process is reaction III with formation of the silicide of magnesium. In
Reactions expected in mixtures of SiO2 - 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)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Coefficients of equations ( \Delta G^\circ_f = A + BT \lg T + CT )</th>
<th>Temperature Range K</th>
<th>Numerical values of Gibbs free energy (cal.mole(^{-1})) at critical temperatures, K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>I</td>
<td>51020 (±600)</td>
<td>9.86</td>
<td>11.12</td>
</tr>
<tr>
<td>II</td>
<td>-69350 (±240)</td>
<td>1.64</td>
<td>4.16</td>
</tr>
<tr>
<td>III</td>
<td>-88030 (±1120)</td>
<td>3.56</td>
<td>-4.7</td>
</tr>
<tr>
<td>IV</td>
<td>171390 (±1670)</td>
<td>18.08</td>
<td>-1.14</td>
</tr>
<tr>
<td>V</td>
<td>-7520 (±800)</td>
<td>3.17</td>
<td>-10.63</td>
</tr>
<tr>
<td>VI</td>
<td>-1040 (±1380)</td>
<td>8.37</td>
<td>10.31</td>
</tr>
<tr>
<td></td>
<td>-13370 (±880)</td>
<td>1.58</td>
<td>-5.03</td>
</tr>
<tr>
<td></td>
<td>-18090 (±1250)</td>
<td>-5.89</td>
<td>-4.65</td>
</tr>
</tbody>
</table>

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 SiO2 with silicon – is possible to occur only above 2000K.
Термодинамическое исследование процесса окиси кремния...

Металлическая фаза...

SiO₂ + Mg = MgO + SiO↑
SiO₂ + 2Mg = 2MgO + Si
SiO₂ + 4Mg = 2MgO + Mg₂Si

SiO₂ + Si = 2SiO↑
SiO₂ + MgO = Mg₂SiO₃
SiO₂ + 2MgO = Mg₄SiO₄

Цитируемы работы...


Received April, 2009