The concentration of the solid phase of SiO requires numerous experiments. Thermodynamic studies will reduce the search for the composition of the Si-O-H-C-N system, which greatly affects the characteristics of the synthesized particles [3].

Analysis of recent research and publications. The influence of water, ammonia and TEOS concentrations on the particle diameter and their uniformity in size was considered repeatedly [4]. The possibility to obtain homogeneous particle sizes at high concentrations of TEOS [5] was investigated.

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The described work only partially investigated the problem of synthesis of monodisperse particles SiO₂. Restrict the search area of optimal conditions for the production of mono-dispersed SiO₂ particles is possible by thermodynamic studies. The thermodynamic study of tetraethoxysilane hydrolysis by the stoeber method has been given insufficient attention. There are studies that only partially describe the properties of the multi-component system Si-O-H-C-N. Calculated and experimentally confirmed data of thermochemical parameters for 47 molecules in the Si-O-H system [6]. The thermochemistry of compounds that can exist in the early stages of the high-temperature decomposition of TEOS in the preparation of amorphous silicon dioxide (α-SiO₂) nano particles [7] is investigated.

Thus, the Si-O-H-C-N system, represented by tetraethoxysilane in a water-alcohol-ammonia environment, is not investigated from thermodynamic positions. However, there is information on the thermodynamic parameters of the compounds that make up the investigated system and can be formed as a result of the reaction.

**The purpose** of the study is to determine the conditions for the hydrophilic reaction of the TEOS in aqueous ammonia-alcoholic medium, in which the maximum concentration of SiO₂ solid phase and the minimum concentration of ionic compounds of silicon in the solution is reached.

**Presentation of the main material.** Synthesis of monodisperse particles of SiO₂ by hydrolysis of TEOS by the Stoeber method is carried out by reaction (1) in a water-alcohol-ammonia environment.

\[
\text{Si(OC}_4\text{H}_4\text{O})_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_6\text{O} \text{H}.
\] (1)

The reaction components (1) form a system of Si-O-H-C-N, the thermodynamic studies of which are well described by a mathematical model created on the basis of the “Selector” software complex. The principle embodied in the program is based on minimizing the isobaric-isothermal potential of Gibbs.

In thermodynamic calculations, the following assumptions were adopted: the Si-O-H-C-N system is at constant temperature and atmospheric pressure. In the thermodynamic model, the standard “Selector” databases are used: Yokokawa, sprons98, sprons07, dump. The model includes the following components:

- **Solid phase:** NH₄NO₃, SiC, Si, SiO₂;
- **Gas phase:** NH₃, C₂H₄, CO₂, CO₂, H₂, CH₄, N₂, C₂H₅OH, O₂, C₆H₆O, H₂O;
- **Aqua solution:** H₂SiO₄, H₃SiO₄²⁻, H₃SiO₄³⁻, H₃SiO₄⁺, CH₃CONH₂*, C₂H₅OH*, C₂H₅OH*, CO₂*, CO₂*, CO₂*, C₂H₂*, C₂H₂OH*, HCO₂*, H₂CO₂*, C₂H₂NO₂*, C₂H₅O₄*, C₂H₅OH*, H₂*, HCO₂*, H₂O*, HCO₃⁻, CH₃OH*, CH₃OH*, N₂*, N₂*, NH₄*, NH₄*, CH₃COO*, NH₄(CH₃COO)₂, NH₄⁺, OCN⁻, C₂O₄²⁻, C₂H₂*, C₂H₅O₂*, C₂H₅O₂*, SiO₂*, H₂NCONH₂*, OH⁻, H⁺, H₂O.

The described thermodynamic model shows that the amount of solid phase SiO₂ depends on the concentration of C₂H₅OH. At the initial concentrations of H₂O=20 M, (C₂H₅OH)Si=0.1 M, NH₄OH=1.5 M and at a temperature T=25 °C, the maximum solid phase of SiO₂ is formed at a concentration of C₂H₅OH greater than 0.9 M (Fig. 1). When the amount of alcohol from 0 M to 0.9 M changes, the concentration of H₂SiO₄²⁻, H₃SiO₄⁺, HSiO₃⁻ decreases with exponential dependence. A further increase in C₂H₅OH has little effect on their number. The concentrations of other compounds of silicon C are lower than those described above, so it is possible to assume that they will not affect the characteristics of the synthesized particles.

In order to obtain the maximum SiO₂ solid phase at different initial (C₂H₅OH)Si concentrations, we established the required concentration of C₂H₅OH (Fig. 2), which can be determined by equation (2). Thus under conditions of thermodynamic equilibrium for any initial concentrations (C₂H₅OH)Si the maximum amount of SiO₂ solid phase is reached at an initial concentration of C₂H₅OH of more than 1.2 mol/l.

\[
y = 1.2 - 4 \times [\text{Si(C}_2\text{H}_5\text{O})_4] .
\] (2)

In order to increase the SiO₂ solid phase, it is expedient to increase the initial number of TEOS. Fig. 3 shows the simulation results of the system Si-O-H-C-N at a temperature T=25 °C, which consisted of H₂O=20 M, C₂H₅OH=9 M, NH₄OH=1.5 M. As can be seen from Fig. 3 concentrations of SiO₂ and TEOS are proportional.
Concentrations of other compounds of silicon are practically unchanged. Simulation is limited by the maximum number of TEOS at which it is possible to obtain uniform spherical particles of size [3]. An increase in the initial concentration of NH₄OH from 0 to 1.9 M leads to a decrease in the SiO₂ solid phase in the SiO-H-C-N system at 10⁻⁵ M at a TEOS concentration of 0.2 M (Fig. 4). Subsequent studies have shown that the indicated change in the solid phase SiO₂ concentration does not depend on the concentration of TEOS.

It is known that for the complete passage of reaction (1), the minimum concentration of H₂O should be twice as high as the concentration of Si (OC₂H₅)₄. Given the experimental data, the indicated ratio should be greater [8].

Thermodynamic studies of the influence of the initial concentration of H₂O are shown in Fig. 5 (initial modeling conditions: NH₄OH=1 M, C₂H₅OH=9 M, (C₂H₅O)₄Si=0.2 M, T=25 °C) show that SiO₂ can be obtained at an initial concentration of H₂O equal to 0 M. Since the model shows the thermodynamic equilibrium of the system Si-O-H-C-N, which is not limited in time, H₂O in the system is formed with NH₄OH and C₂H₅ON and it is sufficient for the complete passage of the reaction (1). Taking into account the kinetic constraints on obtaining SiO₂ particles, it is expedient to provide an initial ratio of H₂O/Si (OC₂H₅)₄>2 concentrations.

Investigated temperature range is due to boiling of the reaction mixture and its freezing is from 1 to 70 °C. Table 1 shows the simulation results of the system Si-O-H-C-N consisting of H₂O=20 M,
C₃H₇OH = 9 M, (C₅H₅O)₂Si = 0.2 M, NH₂OH = 1.5 M. Thus, under thermodynamic equilibrium conditions, the temperature change of the system is not affects the concentration of compounds of silicon in the solution and solid SiO₂ phase.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H₅SiO₄⁺</th>
<th>H₅SiO₄⁻²</th>
<th>H₅SiO₄⁰⁺</th>
<th>H₅SiO₄⁰⁻</th>
<th>H₅SiO₄⁻³</th>
<th>SiO₂⁺</th>
<th>SiO₂⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration, mol/l</td>
<td>2.85E–05</td>
<td>1.28E–13</td>
<td>3.24E–10</td>
<td>8.80E–09</td>
<td>1.35E–08</td>
<td>9.52E–06</td>
<td>2.00E–01</td>
</tr>
</tbody>
</table>

**The results** of the thermodynamic calculations show that SiO₂ solids in the Si-O-H-C-N system are formed at a wide variation of the reaction temperature and the concentrations of reagents (Table 2).

**Table 2**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration (\text{Si(OC₃H₅)}₃)</th>
<th>Concentration (\text{H}_2\text{O})</th>
<th>Concentration (\text{NH}_2\text{OH})</th>
<th>Concentration (\text{C}_2\text{H}_6\text{OH})</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value range</td>
<td>0…1.2 M</td>
<td>0…19 M</td>
<td>0…1.9 M</td>
<td>0…10 M</td>
<td>1…70 °C</td>
</tr>
</tbody>
</table>

The experimental verification of theoretical studies was carried out at a temperature of \(T=25 \, ^\circ\text{C}\) and the concentrations of reagents \(\text{H}_2\text{O}=20 \, \text{M}, \text{C}_2\text{H}_6\text{OH}=10 \, \text{M}, \text{(C}_2\text{H}_5\text{O})_2\text{Si}=0.2 \, \text{M}.\) Experimental studies show that the practical yield of SiO₂ is less than the theoretical by 10…15 %, depending on the initial concentration of NH₂OH (Fig. 6).

![Fig. 5. Dependence of the concentration of silicon compounds (● - \(\text{H}_5\text{SiO}_4^+\), ● - \(\text{H}_5\text{SiO}_4^\circ\), ● - \(\text{HSiO}_3^\circ\), ○ - \(\text{SiO}_2^\circ\)) from the initial concentration of \(\text{H}_2\text{O}\) at the thermodynamic equilibrium of the Si-O-H-C-N system](image)

![Fig. 6. Comparison of thermodynamic calculations of \(\text{SiO}_2\) (\(C_c\)) initial concentration at initial concentration change of \(\text{NH}_4\text{OH}\) (●) and experimentally obtained concentration (\(C_c\))](image)

In our opinion, the explanation for the difference in the results is the high concentration of NH₂OH (a weak base) in the solution at the completion of the reaction. And as a consequence, the pH value is 10.8 and above, which leads to a higher concentration of water-dissolved silicon ions compared to the theoretically calculated value. In thermodynamic calculations, the pH ranges from 6 to 7, which is explained by the partial conversion of NH₂OH into N₂ and NH₃ and their removal from the solution in the form of gas.

**Conclusions** Under conditions of thermodynamic equilibrium, obtaining the maximum solids SiO₂ at different initial concentrations (\(\text{C}_2\text{H}_6\text{OH}\))Si is achieved at an initial concentration of \(\text{C}_2\text{H}_6\text{OH}\) of more than 1 mol/l. The solid phase concentration of SiO₂ is proportional to the initial concentration of TEOS.

Thermodynamic studies show that SiO₂ can be obtained at an initial concentration of H₂O equal to 0 M. The increase in the initial concentration of NH₂OH from 0 to 1.9 M leads to a decrease in the SiO₂ solid phase in the SI-O-H-C-N system for \(1\times 10^{-3}\) M, regardless of the initial concentration of H₂O.
TEOS. The change in reaction temperature from 1 to 70 °C does not affect the concentration of ionic silicon compounds in the solution and solid SiO2 phase.

Due to the kinetic constraints of the hydrolysis reaction of the TEOS, the practical yield of SiO2 is less than the theoretical by 10…15 %, depending on the initial concentrations of reagents.

Further study of the problem of obtaining mono-dispersed particles SiO2 should be directed to the experimental study of the Si-O-H-C-N system in order to detect the influence of technological parameters on the shape, average size and dispersion of the sizes of synthesized particles.

References


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