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ХІМІЯ. ХІМТЕХНОЛОГІЯ

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THERMODYNAMIC OF OBTAINING OF MONODISPERSE PARTICLES SIO$_2$ BY TETRAETHOXYSILANE HYDROLYSIS IN THE SI-O-H-C-N SYSTEM

І.Г. Каюн, О.П. Мисов. **Термодинаміка отримання монодисперсних частинок SiO$_2$ гідролізом тетраетоксисилану в системі Si-O-H-C-N.** Висвітлено проблему синтезу монодисперсних частинок SiO$_2$ гідролізом (C$_2$H$_5$O)$_4$Si за методом Штобера. Метою дослідження є визначення умов проходження даної реакції у водно-аміачно-спиртовому середовищі при яких досягається максимальна концентрація твердої фази SiO$_2$ та мінімальна концентрація іонних сполук силіцію в розчині. Шляхом термодинамічного моделювання досліджений склад системи Si-O-H-C-N при термодинамічній рівновазі для різних заданих умов. Отримання максимальної кількості твердої фази SiO$_2$ при різних початкових концентраціях (C$_2$H$_5$O)$_4$Si досягається при початковій концентрації C$_2$H$_5$OH більше 1,2 моль/л, концентрація твердої фази SiO$_2$ пропорційна початковій концентрації (C$_2$H$_5$O)$_4$Si. Термодинамічні дослідження показують, що зміна температури реакції від 1 до 70 °C не впливає на концентрації іонних сполук силіцію в розчині та твердої фази SiO$_2$. Отримані результати зменшують область пошуку оптимальних умов отримання монодисперсних частинок SiO$_2$ та дають можливість більш глибоко зрозуміти процеси що протікають в системі Si-O-H-C-N.
Ключові слова: термодинаміка, метод Штобера, гідроліз тетраетоксисилану

I. Kayun, O. Musov. **Thermodynamic of obtaining of monodisperse particles SiO$_2$ by tetraethoxysilane hydrolysis in the Si-O-H-C-N system.** The problem of synthesizing of mono disperse SiO$_2$ particles with hydrolysis (C$_2$H$_5$O)$_4$Si by the Stober method is described. The purpose of the study is to determine the conditions for the passage of this reaction in a water-ammonia-alcohol medium, at which the maximum concentration of the solid phase of SiO$_2$ and the minimum concentration of silicon ion compounds in solution are reached. By thermodynamic modeling the composition of the Si-O-H-C-N system under thermodynamic equilibrium for various given conditions was studied. The maximum amount of solid phase SiO$_2$ at different initial concentrations (C$_2$H$_5$O)$_4$Si is achieved at an initial concentration of C$_2$H$_5$OH more than 1.2 mol/l, the concentration of the solid phase of SiO$_2$ is proportional to the initial concentration (C$_2$H$_5$O)$_4$Si. Thermodynamic studies show that a change in the reaction temperature from 1 to 70 °C does not affect the concentration of ionic silicon compounds in the solution and the solid phase of SiO$_2$. The obtained results reduce the search for optimal conditions for the production of monodisperse particles of SiO$_2$ and allow a deeper understanding of the processes taking place in the Si-O-H-C-N system.
Keywords: thermodynamics, Stober method, hydrolysis of tetraethoxysilane

Introduction. Actuality obtaining of mono-dispersed particles of SiO$_2$ due to their wide use in industry. This is the production of opals, photonic crystals, in the chemical industry as composite catalysts, etc.

Hydrolysis of tetraethoxysilane (TEOS) by the Stoeber method in a water-alcohol-ammonia medium allows for the obtaining of nano and submicron spherical particles of SiO$_2$ [1]. The size of SiO$_2$ particles synthesized by hydrolysis of TEOS largely depends on the concentration of TEOS, water, alcohol, ammonia and reaction temperature [2].

Due to the many components of the Si-O-H-C-N system, the development of technology for the synthesis of mono disperses spherical particles of SiO$_2$ requires numerous experiments. Thermodynamic studies will reduce their number, determine the conditions for which the maximum solid phase of SiO$_2$ will be obtained and determine 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 SiO_2. Restrict the search area of optimal conditions for the production of mono-dispersed SiO_2 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 thermo chemical parameters for 47 molecules in the Si-O-H system [6]. The thermo chemistry of compounds that can exist in the early stages of the high-temperature decomposition of TEOS in the preparation of amorphous silicon dioxide (α-SiO_2) 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 SiO_2 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 SiO_2 by hydrolysis of TEOS by the Stoeber method is carried out by reaction (1) in a water-alcohol-ammonia environment.

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH. \tag{1}$$

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: NH_4NO_3, SiC, Si, SiO_2;

Gas phase: NH_3, C_2H_4, CO_2, CO, H_2, CH_4, N_2, C_7H_8O, O_2, C_6H_6O, H_2O;

Aqua solution: H_4SiO_4, $H_2SiO_4^{-2}$, $H_3SiO_3^{+}$, $H_3SiO_4^{-}$, $CH_3CONH_2^{*}$, $C_2H_3O_2^{-}$, $C_2H_4O_2^{*}$, $C_4H_7O_2^{-}$, CO^{*}, CO_2^{*}, CO_3^{-2}, $C_2H_6^{*}$, $C_2H_5OH^{*}$, HCO_2^{-}, $H_2CO_2^{*}$, $C_2H_5NO_2^{*}$, $C_3H_3O_4^{-}$, $C_2HO_4^{-}$, H_2^{*}, HCO_3^{-}, $HSiO_3^{-}$, $C_3H_2O_4^{-2}$, $CH_3NH_2^{*}$, CH_3OH^{*}, N_2^{*}, NH_3^{*}, $NH_4CH_3COO^{*}$, $NH_4(CH_3COO)_2^{-}$, NH_4^{+}, OCN^{-}, $C_2O_4^{-2}$, $C_3H_8^{*}$, $C_3H_5O_2^{-}$, $C_3H_6O_2^{*}$, SiO_2^{*}, $H_2NCONH_2^{*}$, OH^{-}, H^{+}, H_2O.

The described thermodynamic model shows that the amount of solid phase SiO_2 depends on the concentration of C_2H_5ON. At the initial concentrations of H_2O=20 M, $(C_2H_5O)_4Si$=0.1 M, NH_4OH=1.5 M and at a temperature T=25 °C, the maximum solid phase of SiO_2 is formed at a concentration of C_2H_5ON greater than 0.9 M (Fig. 1). When the amount of alcohol from 0 M to 0.9 M changes, the concentration of $H_2SiO_4^{-2}$, $H_3SiO_4^{-}$, $HSiO_3^{-}$ decreases with exponential dependence. A further increase in C_2H_5OH 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 SiO_2 solid phase at different initial $(C_2H_5O)_4Si$ concentrations, we established the required concentration of C_2H_5OH (Fig. 2), which can be determined by equation (2). Thus under conditions of thermodynamic equilibrium for any initial concentrations $(C_2H_5O)_4Si$ the maximum amount of SiO_2 solid phase is reached at an initial concentration of C_2H_5OH of more than 1.2 mol/l.

$$y = 1,2 - 4*[Si(C_2H_5O)_4] \ . \tag{2}$$

In order to increase the SiO_2 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 H_2O=20 M, C_2H_5OH=9 M, NH_4OH=1.5 M. As can be seen from Fig. 3 concentrations of SiO_2 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 NH_4OH from 0 to 1.9 M leads to a decrease in the SiO_2 solid phase in the SiO-H-C-N system at $1e^{-5}$ M at a TEOS concentration of 0.2 M (Fig. 4). Subsequent studies have shown that the indicated change in the solid phase SiO_2 concentration does not depend on the concentration of TEOS.
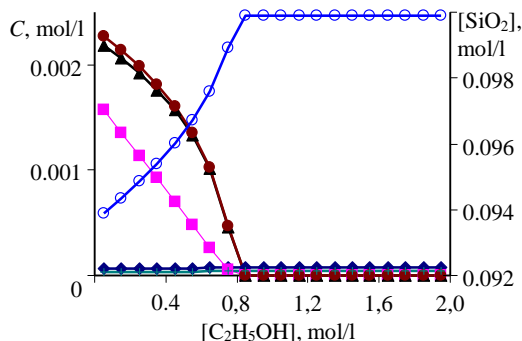

Fig. 1. Dependence of the concentration of silicon compounds (♦ - H_4SiO_4, ■ - $H_2SiO_4^{-2}$, ▲ - $H_3SiO_4^-$, ● - $HSiO_3^-$, + - SiO_2*, ○ - SiO_2) from the initial concentration of C_2H_5OH at the thermodynamic equilibrium of the Si-O-H-C-N system
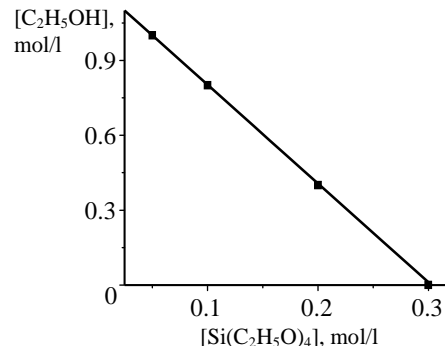

Fig. 2. The concentration of alcohol is required to obtain the maximum amount of SiO_2 solid phase at different initial concentrations $Si(C_2H_5O)_4$
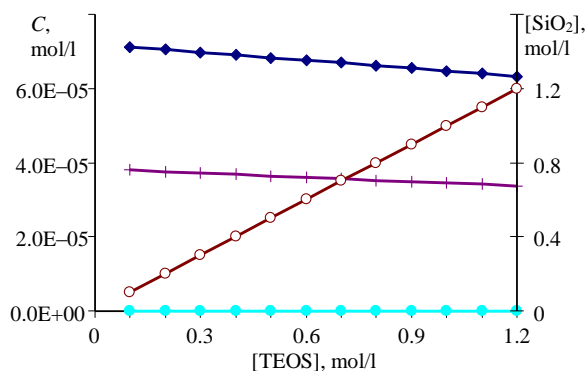

Fig. 3. The dependence of the concentration of silicon compounds (♦ - H_4SiO_4, ■ - $H_3SiO_3^+$, ▲ - $H_3SiO_4^-$, ● - $HSiO_3^-$, + - SiO_2*, ○ - SiO_2 from the initial concentration of TEOS at the thermodynamic equilibrium of the Si-O-H-C-N system

Fig. 4. The dependence of the concentration of silicon compounds (♦ - H_4SiO_4, ■ - $H_3SiO_3^+$, ▲ - $H_3SiO_4^-$, ● – $HSiO_3^-$, + - SiO_2*, ○ - SiO_2) from the initial concentration of NH_4OH at the thermodynamic equilibrium of the Si-O-H-C-N system
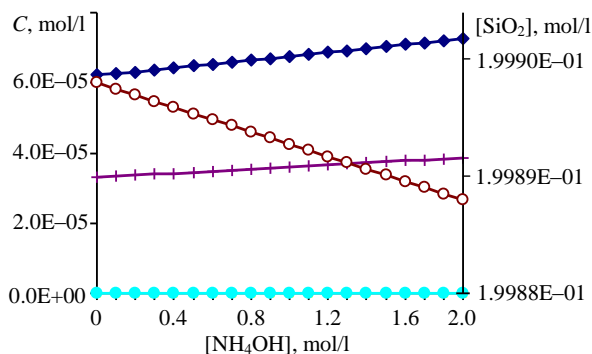
It is known that for the complete passage of reaction (1), the minimum concentration of H_2O should be twice as high as the concentration of $Si(OC_2H_5)_4$. Given the experimental data, the indicated ratio should be greater [8].

Thermodynamic studies of the influence of the initial concentration of H_2O are shown in Fig. 5 (initial modeling conditions: NH_4OH=1 M, C_2H_5OH=9 M, $(C_2H_5O)_4Si$=0.2 M, T=25 °C) show that SiO_2 can be obtained at an initial concentration of H_2O 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, H_2O in the system is formed with NH_4OH and C_2H_5ON and it is sufficient for the complete passage of the reaction (1). Taking into account the kinetic constraints on obtaining SiO_2 particles, it is expedient to provide an initial ratio of $H_2O/Si(OC_2H_5)_4$>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 H_2O=20 M,

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C_2H_5OH = 9 M, $(C_2H_5O)_4Si$ = 0.2 M, NH_4OH = 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 SiO_2 phase.

Table 1

Concentrations of compounds at the thermodynamic equilibrium of the Si-O-H-C-N system in the temperature range from 1 to 70 ℃

Compound	H_4SiO_4	$H_2SiO_4^{-2}$	$H_3SiO_3^+$	$H_3SiO_4^-$	$HSiO_3^-$	SiO_2^*	SiO_2
Concentration, mol/l	2.85E–05	1.28E–13	3.24E–10	8.80E–09	1.35E–08	9.52E–06	2.00E–01

The results of the thermodynamic calculations show that SiO_2 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

The ranges of variations of the parameters of the system S-O-H-C-N, in which a solid SiO_2 phase is formed

Parameter	Concentration $Si(OC_2H_5)_4$	Concentration H_2O	Concentration NH_4OH	Concentration C_2H_5OH	Temperature
Value range	0…1.2 M	0…19 M	0…1.9 M	0…10 M	1…70 °C

The experimental verification of theoretical studies was carried out at a temperature of T=25 °C and the concentrations of reagents H_2O=20 M, C_2H_5OH=10 M, $(C_2H_5O)_4Si$=0.2 M. Experimental studies show that the practical yield of SiO_2 is less than the theoretical by 10…15 %, depending on the initial concentration of NH_4OH (Fig. 6).
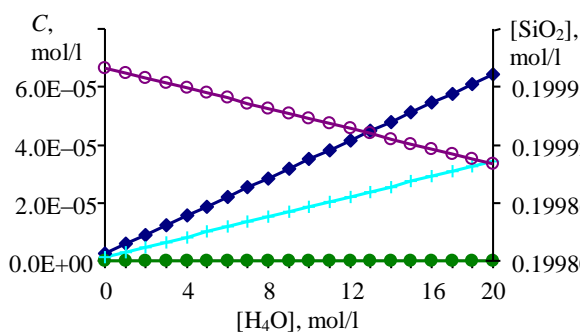

Fig. 5. Dependence of the concentration of silicon compounds (♦ - H_4SiO_4, ■ - $H_3SiO_4^-$, ● - $HSiO_3^-$, + - SiO_2^*, ○ - SiO_2) from the initial concentration of H_2O at the thermodynamic equilibrium of the Si-O-H-C-N system
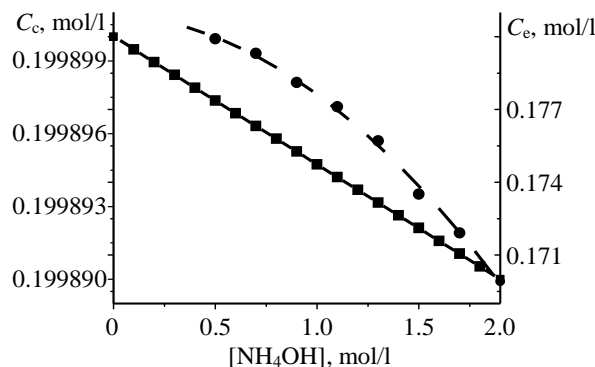
Fig 6. Comparison of thermodynamic calculations of SiO_2 (C_c) initial concentration at initial concentration change of NH4OH (■) and experimentally obtained concentration (C_e) (●)

In our opinion, the explanation for the difference in the results is the high concentration of NH_4OH (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 NH_4OH into N_2 and NH_3 and their removal from the solution in the form of gas.

Conclusions Under conditions of thermodynamic equilibrium, obtaining the maximum solids SiO_2 at different initial concentrations $(C_2H_5O)_4Si$ is achieved at an initial concentration of C_2H_5OH of more than 1 mol/l. The solid phase concentration of SiO_2 is proportional to the initial concentration of TEOS.

Thermodynamic studies show that SiO_2 can be obtained at an initial concentration of H_2O equal to 0 M. The increase in the initial concentration of NH_4OH from 0 to 1.9 M leads to a decrease in the SiO_2 solid phase in the SI-O-H-C-N system for $1e^{-5}$ M, regardless of the initial concentration of

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 SiO_2 phase.

Due to the kinetic constraints of the hydrolysis reaction of the TEOS, the practical yield of SiO_2 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 SiO_2 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.

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