Thermodynamic modeling of carbon nanoparticle C₃₂ heating in the nitrogen environment

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Abstract. Using computer thermodynamic modeling, the behavior of carbon nanoparticles was studied C₃₂ when heated in nitrogen atmosphere at pressure 10⁵ Pa. Modeling was carried out using a software package TERRA. Experiment temperature range – from 273 to 3373 K. A graph of the carbon balance in the system is constructed C₃₂-N₂, physical and chemical processes are described. The equilibrium constants of reactions with the allocation of temperature ranges are calculated and graphs of the dependence of the equilibrium constants of reactions on temperature are given.

1. Introduction
Knowledge of the temperature stability of carbon nanoparticles is necessary both for the development of technologies for the production and purification of carbon nanoparticles, and for their application [1].

Thermodynamic modeling consists in a thermodynamic analysis of the equilibrium state of the system as a whole [2].

2. Calculation Method
The calculations used the TERRA software package. Calculations of the phase composition and characteristics were carried out using the reference database [3-6].

In the calculation we used the thermodynamic parameters of condensed carbon nanoparticles C₃₂(c), vapors C, C₂, C₃, C₄, C₅, C₆, C₇, gases CN, CN₂, N₂C, NCN, C₂N, CNC, CCN, C₂N₂, C₄N, C₅N and solid solution of carbon nanoparticles C₁(s), C₂(s), C₃(s), C₄(s), C₅(s), C₆(s), C₇(s), C₂₈(s), C₃₂(s). Temperature ranged from 273 to 3373 K, pressure was 0.1 MPa. The ratio of carbon to nitrogen was 1:2.
3. Simulation results and discussion

Figure 1 shows the distribution of nanocarbon in the system \( \text{C}_{32}-\text{N}_2 \). The graph shows substances with a percentage of at least 2% over the entire temperature range.

![Graph showing distribution of nanocarbon in \( \text{C}_{32}-\text{N}_2 \).]

**Figure 1.** The distribution of carbon in the system \( \text{C}_{32}-\text{N}_2 \).

In the temperature range from 273 to 973 K the content of solid solution of carbon \( \text{C}_{32}(s) \) in the system \( \text{C}_{32}-\text{N}_2 \) is 100%. In the temperature range from 973 to 1773 K percentage \( \text{C}_{32}(s) \) decreases to 99.94% due to insignificant formation of \( \text{C}_2\text{N}_2 \) gases. Starting from 2073 K and higher, there is an increase in the following gases \( \text{C}_5\text{N} \), \( \text{C}_4\text{N} \), \( \text{C}_3 \), \( \text{C}_5 \), \( \text{CNC} \). Further increase in temperature in the system to 2673 K leads to a linear decrease in the content of solid solution of carbon \( \text{C}_{32}(s) \) to almost 0. At a temperature of 2673 K, \( \text{C}_{32}(s) \) is reset to zero, percentage of gases contained is as follows: 82% - \( \text{C}_5\text{N} \), 5% - \( \text{C}_5 \), 5% - \( \text{C}_2\text{N}_2 \), 3% - \( \text{C}_3 \), 3% - \( \text{C}_4\text{N} \), 2% - \( \text{CNC} \).

In the range of 2373-2673 K there is an increase in the amount of \( \text{C}_5\text{N} \) gases from 4% to 84%. At a temperature of 2673 K, an inflection point is observed. In the temperature range from 2673 to 3373 K, the \( \text{C}_5\text{N} \) content decreases and amounts to 28%. This is caused by a sharp increase in \( \text{C}_3 \), \( \text{CNC} \), \( \text{C}_5 \) gases.

At high temperatures, an increase in other gases and a solid solution containing \( \text{C}_{28} \) is observed in the system, but their content, in comparison with others, is small and does not exceed 4%.

In the system under consideration, physicochemical processes occur, which can be divided into three groups, shown in Table 1.

For the reaction equations given in Table 1, the equilibrium constants of the reactions of the \( \text{C}_{32}-\text{N}_2 \) system were calculated. The calculation was performed according to an analytical equation of the form

\[
\ln K_i = A_i + B_i \left(1/T\right)
\]

where \( K_i \) is the equilibrium constant of reactions occurring in the \( \text{C}_{32}-\text{N}_2 \) system, \( A_i \) is coefficient affecting the position (shift) of \( \ln K_i \) relative to the reciprocal temperature, \( B_i \) is coefficient influencing the angle of inclination \( \ln K_i \) relative to the reciprocal temperature.
The coefficients $A_i$ and $B_i$ of the reactions are calculated using the least squares method, coefficient of determination $R^2$ is determined and presented in Table 2.

### Table 1. Reactions occurring in the system C$_{32}$-N$_2$.

| No. | The name of the group | Reaction | Temperature range of the reaction (K) |
|-----|-----------------------|----------|---------------------------------------|
| 1   | Chemical reactions occurring between the condensed and gas phases | C$_{32}$(s)+16N$_2$→16C$_2$N$_2$ | 1773 – 2673 |
| 2   | Sublimation reactions with thermal dissociation | 5C$_{32}$(s)+16N$_2$→32C$_3$N | 2073 – 2673 |
| 3   | Chemical reaction in the gas phase | C$_{32}$(s)+4N$_2$→8C$_4$N | 2273 – 2673 |
| 4   | | C$_{32}$(s)+8N$_2$→16CNC | 2373 – 2673 |
| 5   | | 3C$_{32}$ (s)→32C$_3$ | 2373 – 2673 |
| 6   | | 5C$_{32}$ (s)→32C$_5$ | 2373 – 2673 |
| 7   | | C$_5$N→C$_3$ + CNC | 2373 – 3373 |

### Table 2. Coefficients of $A_i$ and $B_i$ reaction constants.

| No. | Reaction | $\Delta T$ (K) | $A_i$ | $B_i$ | $R^2$ |
|-----|----------|----------------|-------|-------|-------|
| 1   | C$_{32}$(s)+16N$_2$→16C$_2$N$_2$ | 473-3373 | -367092 | 72,4 | 0,8478 |
| 2   | 5C$_{32}$(s)+16N$_2$→32C$_3$N | 1573-3373 | -1823649,9 | 577,7 | 0,8113 |
| 3   | C$_{32}$(s)+4N$_2$→8C$_4$N | 273-3373 | -165717 | -49,6 | 0,915 |
| 4   | C$_{32}$(s)+8N$_2$→16CNC | 1073-3373 | -918645,9 | 230,2 | 0,8855 |
| 5   | 3C$_{32}$(s)→32C$_3$ | 1773-3373 | -2207021,1 | 647,96 | 0,9152 |
| 6   | 5C$_{32}$(s)→32C$_5$ | 1873-3373 | -2374175,3 | 686,3 | 0,8773 |
| 7   | C$_5$N→C$_3$ + CNC | 273-3373 | -19029,4 | -11,01 | 0,9417 |
Figure 2 (c) shows graphs of the dependences of the equilibrium constants of the reactions of the C\textsubscript{32}-N\textsubscript{2} system on 1/T in the temperature range of 1873-3373 K (reaction numbers are given in Table 2).

In Figure 2, the positions of the graphs show the magnitude and nature of the temperature dependence of the equilibrium constants of reactions. They are represented by analytical equation (1). In this equation, $A_i$ is the coefficient that affects the position of the straight line relative to the axis of the abscissas. The larger this coefficient, the higher the graph is in the figure and the reaction is more strongly shifted towards the formation of reaction products.

The $B_i$ coefficient indicates the angle of inclination between the reaction constant graph and the abscissas axis. The larger this coefficient, the stronger the reaction proceeds with increasing temperature.

The approximation values given in Table 2 indicate a deviation from a linear relationship. The percentage deviation for reactions 1 and 2 reaches 19%.

**Conclusions**

In this work, a computer experiment was conducted by the method of thermodynamic modeling to study the thermal properties of C\textsubscript{32} carbon nanoparticles. Simulation data show that in the temperature range from 273 to 973 K, the content of C\textsubscript{32}(s) carbon solid solution in the C\textsubscript{32}-N\textsubscript{2} system is 100%, with a temperature increase, its percentage decreases. Most reactions occur at a temperature of 2073 K and higher. An analysis of the processes shows that C\textsubscript{32} fullerene in a nitrogen atmosphere is thermally stable up to 2273 K. The main reaction products are gases C\textsubscript{5}N, C\textsubscript{4}N, C\textsubscript{3}, C\textsubscript{5}, CNC, and C\textsubscript{2}N\textsubscript{2}.

**References**

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