Thermal behavior of $C_{32}$ carbon nanoparticles in a nitrogen atmosphere

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Abstract. Using the method of computer thermodynamic modeling, the behavior of carbon nanoparticles is studied $C_{32}$ when heated in nitrogen atmosphere at pressure $10^5$ Pa. The modeling consisted in a complete thermodynamic analysis of the system using the TERRA software package. Experiment temperature range – from 273 to 3373 K. A graph of the carbon balance in the system is built $C_{32}$-$N_2$, the ongoing physical and chemical processes are described, divided into four classes. 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
Nanoparticles different materials are finding ever more widespread use - from paint and varnish to food industry. The most "popular" carbon nanoparticles are nanotubes, fullerenes and graphene.

The special structure of fullerenes determines their unique physical and chemical properties. In combination with other substances, they make it possible to obtain materials with fundamentally new properties.

The most fully studied representative of the fullerene family is fullerene $C_{60}$, fullerene $C_{70}$ is the next most common. Higher fullerenes containing a larger number of carbon atoms are formed in much smaller amounts and often have a rather complex isomeric composition. Among the best studied higher fullerenes are $C_{84}$, $C_{90}$, $C_{94}$. 
Materials with the use of fullerenes have increased strength, wear resistance, thermal and chemical stability and reduced abrasion. Carbon nanoparticles, in particular, carbon nanotubes, have unique electrical, thermal, and mechanical properties, they are widely used in electronics, are part of composite materials, and are used for a variety of purposes.

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 [3-9].

In the calculation we used the thermodynamic parameters of condensed carbon nanoparticles $C_{32}(c)$, vapors C, C$_2$, C$_3$, C$_4$, C$_5$, C$_6$, C$_7$, C$_{28}$, C$_{32}$ and gases CN, CN$_2$, N$_2$, NC, C$_2$N, CNC, CCN, C$_2$N$_2$, CN, C$_3$N. 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 carbon nanoparticles in the system $C_{32}$-N$_2$.

![Figure 1. Distribution of carbon nanoparticles in the $C_{32}$-N$_2$ system in the temperature ranges of 273-2373 K (a) and 2373-3373 K (b).](image)

In the temperature range from 273 to 473 K the content of condensed carbon nanoparticles $C_{32}$ in the $C_{32}$-N$_2$ system is 100 %. In the temperature range from 473 to 773 K the condensed phase disappears with the appearance of $C_{32}$ vapors. Starting from 773 K all nanocarbon is in the gaseous phase. In the range 773-873 K the amount of $C_{32}$ vapor increases from 50 % to 100 % and remains unchanged with an increase in temperature from 873 to 1783 K. In the temperature range from 1783 to 2673 K the $C_{32}$ vapor content decreases and is 93 %. This is caused by the appearance of vapors C$_{28}$, C$_3$N, C$_2$N$_2$. The content of $C_{32}$ vapor in the temperature range 2673-3073 K decreases sharply and by the end of this temperature range is 15 %. With an increase in temperature to 2873 K and higher, the gas phase contains: C$_3$, C$_5$, C$_{32}$, CN, C$_3$N, CNC, C$_2$N$_2$, C$_3$N, C$_4$N. A further increase in temperature leads to a linear decrease in the content of vapors $C_{32}$. At a temperature of 3223 K, $C_{32}$ vapors are extremely small, the percentage
of vapors present is as follows: 47% - C5N, 19% - C3, 13% - C5, 8% - CNC, 5% - C4N, 3% - C2N2, 3% - CN, 2% - C2N.

At a temperature of 2873 K and higher, a small amount of C, C4, C6, C7, NCN, and CCN vapors is observed in the system.

The description of the reactions was carried out on the basis of the graphs in Figure 1 and the calculated data with the selection of temperature intervals for the course of reactions.

In the system under consideration, there are processes that can be divided into four groups, shown in Table 1.

| No. | The name of the group                   | Reaction                  | Temperature range of the reaction (K) |
|-----|----------------------------------------|---------------------------|---------------------------------------|
| 1   | Sublimation                            | C32(c) → C32              | 273 – 673                             |
| 2   |                                        | 7 C32 → 8 C28             | 1273 – 3273                           |
| 3   |                                        | 3 C32 → 32 C3             | 2073 – 3273                           |
| 4   | Dissociation in the gas phase           | 5 C32 → 32 C5             | 2273 – 3273                           |
| 5   |                                        | C32 → 16 C2               | 2373 – 3273                           |
| 6   |                                        | C32 → 8 C4                | 2673 – 3273                           |
| 7   |                                        | C32 + 16 N2 → 16C2N2      | 1273 – 3273                           |
| 8   | Chemical reactions in the gas phase     | 5C32 + 16 N2 → 32C3N      | 1973 – 3273                           |
| 9   |                                        | C32 + 8N2 → 16CNC         | 2073 – 3273                           |
| 10  |                                        | C32 + 4N2 → 8C4N          | 2273 – 3273                           |
| 11  | Dissociation and molization in the gas phase | C3N → C3 + CNC       | 3173 – 3373                           |

For the reaction equations given in Table 1, the equilibrium constants of the reactions of the C32-N2 system were calculated. The calculation was performed using the analytical equation (1):

$$\ln K = A_i (1/T) + B_i,$$

where K is the equilibrium constant of reactions occurring in the C32-N2 system, $A_i$ is a coefficient affecting the angle of inclination of lnK relative to the reciprocal temperature, $B_i$ is a constant affecting the position (displacement) of lnK relative to the reciprocal temperature.

The values of $A_i$ and $B_i$ reactions were calculated by the least squares method by drawing up the normal system of equations (2) and are presented in Table 2.
\[
\begin{align*}
B_i \cdot n + A_i \sum \frac{1}{T} &= \sum \ln K \\
B_i \left( \sum \frac{1}{T} \right)^2 A_i \left( \sum \frac{1}{T} \right)^2 = \sum \frac{1}{T} \cdot \ln K
\end{align*}
\]

(2)

**Table 2. Coefficients of A_i and B_i reaction constants**

| No. | Reaction           | ΔT (K)   | A_i       | B_i       |
|-----|--------------------|----------|-----------|-----------|
| 1   | \( \text{C}_{32}(\text{c}) \rightarrow \text{C}_{32} \) | 273 – 673 | -13122,3  | 15,74     |
| 2   | \( 7 \text{C}_{32} \rightarrow 8 \text{C}_{28} \) | 1273 – 3273 | -158317    | 33,49     |
| 3   | \( 3 \text{C}_{32} \rightarrow 32 \text{C}_{3} \) | 2073 – 3273 | -2382282   | 692,52    |
| 4   | \( 5 \text{C}_{32} \rightarrow 32 \text{C}_{5} \) | 2273 – 3273 | -2813825   | 814,29    |
| 5   | \( \text{C}_{32} \rightarrow 16 \text{C}_{2} \) | 2373 – 3273 | -1353200   | 337,71    |
| 6   | \( \text{C}_{32} \rightarrow 8 \text{C}_{4} \) | 2673 – 3273 | -725841    | 183,89    |
| 7   | \( \text{C}_{32}+16 \text{N}_{2} \rightarrow 16\text{C}_{2}\text{N}_{2} \) | 1273 – 3273 | -359603    | 60,66     |
| 8   | \( 5\text{C}_{32}+16 \text{N}_{2} \rightarrow 32\text{C}_{3}\text{N} \) | 1973 – 3273 | -1996568   | 606,61    |
| 9   | \( \text{C}_{32}+8\text{N}_{2} \rightarrow 16\text{CNC} \) | 2073 – 3273 | -1067221   | 300,09    |
| 10  | \( \text{C}_{32}+4\text{N}_{2} \rightarrow 8\text{C}_{4}\text{N} \) | 2273 – 3273 | -511139    | 135,65    |
| 11  | \( \text{C}_{3}\text{N} \rightarrow \text{C}_{3}+\text{CNC} \) | 3173 – 3373 | -36480,1   | 8,52      |

Using the calculated data, the dependence of the equilibrium constants of the reactions of the \( \text{C}_{32}-\text{N}_{2} \) system on the reciprocal temperature at different temperature intervals was determined in accordance with the ongoing processes. The weak course of reactions with increasing temperature is evidenced by negative \( A_i \) coefficients, which indicate the slope between the graph of the reaction constant and the abscissa axis.

For all dependencies, the coefficient of determination \( R^2 \) was calculated, which is equal to 1, this corresponds to an ideal model when all observation points lie exactly on the regression line, i.e. the sum of the squares of their deviations is 0.

Figure 2 (a) shows graphs of the dependences of the equilibrium constants of the reactions of the \( \text{C}_{32}-\text{N}_{2} \) system on \( 1/T \) in the temperature range of 273-673 K (reaction numbers are given in Table 2).

Figure 2 (b) shows graphs of the dependences of the equilibrium constants of the reactions of the \( \text{C}_{32}-\text{N}_{2} \) system on \( 1/T \) in the temperature range of 1273-3273 K (reaction numbers are given in Table 2).

Figure 2 (c) shows graphs of the dependences of the equilibrium constants of the reactions of the \( \text{C}_{32}-\text{N}_{2} \) system on \( 1/T \) in the temperature range of 1973-3373 K (reaction numbers are given in Table 2).

Figure 2 (d) shows graphs of the dependences of the equilibrium constants of the reactions of the \( \text{C}_{32}-\text{N}_{2} \) system on \( 1/T \) in the temperature range of 2273-3373 K (reaction numbers are given in Table 2).
Figure 2 (e) shows graphs of the dependences of the equilibrium constants of the reactions of the C_{32}-N_{2} system on 1/T in the temperature range of 3173-3373 K (reaction numbers are given in Table 2).

Figure 2. Graphs of the dependences of the equilibrium constants of reactions of the C_{32}-N_{2} system on 1/T.

4. Conclusion
A computer experiment was carried out using the method of thermodynamic modeling to study the thermal properties of C_{32} carbon nanoparticles. Simulation data show that in the temperature range from 273 to 473 K the content of condensed carbon nanocarbon C_{32} in the C_{32}-N_{2} system is 100%, with an increase in temperature its percentage decreases and starting from 773 K carbon is in the gaseous phase. The C_{32} vapor is thermally stable in the range 873-1783 K. Most of the reactions take place at temperatures of 1973 K and above. The main reaction products are the gases C_{3}, C_{5}, C_{28}, C_{32}, C_{3}N, C_{4}N, CNC and C_{2}N_{2}.

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