Determination of Thermophysical Parameters of the system C\textsubscript{32}-Ar

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Abstract. In this paper, the thermophysical characteristics of the fullerene-argon (C\textsubscript{32}-Ar) system at atmospheric pressure are studied by thermodynamic modeling using the TERRA software system. Two groups of processes occurring in the system under consideration are determined: sublimation reactions with thermal dissociation and thermal dissociation reactions in the gas phase. The thermal physics of carbon vaporization in the gas phase is studied, the graphs of the dependence of the thermal characteristics of the C\textsubscript{32}-Ar system on temperature are constructed; the regularities in the inflection points of the graphs and changes in the compositions of the gas and condensed phases are revealed.

1. Introduction
Fullerenes have unique properties, such as diamagnetic properties, electrical conductivity, and high strength in combination with high values of elastic deformation [1]. These properties are determined by high strength of carbon-carbon bonds, the enormous strength of atomic packaging and rather low density of structural defects [2].

For economic reasons, multilayer carbon nanotubes and fullerenes are the most relevant carbon materials for use. Their total world production is currently about 1 million tons per year [3]. The growth of production volumes inevitably leads to the actualization of the issue of studying various properties, including fire-explosive [4]. In this regard, the problem of combustion and explosion of carbon materials, as well as their thermophysical parameters is particularly relevant.

2. Experimental
As an initial stage of their study, a computer experiment was chosen. It consists of modeling the heating of C\textsubscript{32} fullerenes in argon medium. The temperature range of the experiment is from 473 K to 4273 K at a pressure of 0.1 MPa. The molar ratio of argon to carbon is 4:1 mol.

In the case of heating of carbon fullerenes C\textsubscript{32} in an inert medium, a sublimation process takes place with thermal dissociation to vapors C, C\textsubscript{2}, C\textsubscript{3}, C\textsubscript{4} and C\textsubscript{5}, which can burn and explode under certain conditions. Modeling of the process will determine the thermal physics of the process of formation of carbon vapor in the gas phase.

One of the domestic programs that implement thermodynamic calculations is the TERRA software package. It is a stage of further development of the ASTRA software package. The theoretical foundations of the software package are presented in [5].
According to the second law of thermodynamics, the equilibrium of systems is characterized by the maximum entropy relative to the thermodynamic degrees of freedom, which include the concentration of the components of the equilibrium mixture, temperature and pressure.

\[
S = \sum_{g=1}^{G} S_g^0(T) - R \ln \frac{RT}{V} n_g + \sum_{c=1}^{C} S_c^0(T)n_c + \sum_{r=1}^{X} \left[ S_r^0(T) - R \ln w_{rx} \right] n_{rx} \Rightarrow S_{\text{max}},
\]

where \( n_g, n_c, n_{rx}, S_g^0, S_c^0, S_r^0 \) – the number of moles and standard entropy (at temperature T, K, and pressure 0.1 MPa) in gas (g), condensed (c), phases, and solution (rx);

\( G, C, X \) – the number of gaseous, condensed components and solutions in the thermodynamic system, respectively, mol;

\( w_{rx} \) – the molar fraction of the component in the solution, mole fraction;

\( R \) – the universal gas constant, 8,3144621 J/mol·K;

\( V \) – the specific volume, m³/kg.

The specific volume \( V \) and internal energy \( U \) remain constant variables, since the equilibrium conditions of the system with respect to the environment can be expressed by equations: \( dV=0 \) and \( dU=0 \) or \( V=\text{const} \) and \( U=\text{const} \).

The following additional restrictions are imposed on the range of permissible values of variables in establishing chemical and phase equilibrium by reaching the maximum entropy:
- constancy of the total internal energy of the system at equilibrium;
- preservation of the mass of all chemical elements;
- law of conservation of charge;
- equation of state for a mixture of ideal gases.

The equilibrium parameters of the thermodynamic system are determined by solving the mathematical problem of finding the extremum taking into account all constraints using the Lagrange function. The method of successive Newton approximations (Newton) is used for calculations, which provides high convergence of the results at the final stages of the iterative process. Terra software package is used to calculate the equilibrium conditions between the thermodynamic system and the environment for any pair of thermodynamic parameters: pressure, specific volume, temperature, entropy, enthalpy, internal energy. Also the complex allows to carry out calculations of the thermodynamic equilibrium of a system of an arbitrary elemental composition.

Thermodynamic modeling was successfully applied in [6, 7].

Calculations of the phase composition and equilibrium characteristics are carried out using a reference database on the properties of individual substances [8-11].

3. Results and Discussion

On figure 1 a graph of carbon distribution in the C32-Ar system is presented.

The content of condensed fullerene C32 in the system C32-Ar remains unchanged in the temperature range 473...2673 K and is 0,520 mol/kg. In the temperature range 2673...3873 K the content of C32 reduced practically to zero. The decrease in the content of condensed fullerene is accompanied by the beginning of the sublimation process of the condensed fullerene system and the appearance of gaseous C, C2, C3, C4, C5 in the system.

The content of gaseous C and C2 increases to a temperature of 4273 K; reaches 2,178 mol/kg and 1,391 mol/kg.

The content of gaseous C3 rises to a temperature of 3873 K; reaches 4,253 mol/kg. At a temperature of 3873 K, an inflection point is observed. In the temperature range 3873...4273 K content C3 decreases to 3,650 mol/kg.

The vapor content of C4 and C5 rises to a temperature of 3873 K and reaches 0,075 mol/kg and 0,332 mol/kg. In the temperature range 3873...4273 K content of C4 and C5 decreases linearly to 0,054 mol/kg and 0,105 mol/kg, respectively.

Description of reactions with temperature intervals was carried out on the basis of the graph (figure 1).
In the system under consideration there are physical and chemical processes that can be divided into 2 groups (table 1).

![Table 1. Reactions occurring in the C_{32}-Ar system.]

| №  | The name of the group                  | Reaction                  | Reaction temperature range, K |
|----|---------------------------------------|---------------------------|-------------------------------|
| 1  | Reaction sublimation thermal dissociation | C_{32}(s)→32C             | 773 – 3873                    |
|    |                                        | C_{32}(s)→16C_{2}         | 773 – 3873                    |
|    |                                        | 3C_{32}(s)→32C_{3}        | 773 – 3873                    |
|    |                                        | C_{32}(s)→8C_{4}         | 773 – 3873                    |
|    |                                        | 5C_{32}(s)→32C_{5}      | 773 – 3873                    |
| 2  | Thermal dissociation reactions in the vapor phase | 2C_{3}↔3C_{2}             | 3873 – 4273                   |
|    |                                        | C_{3}↔3C                  | 3873 – 4273                   |
|    |                                        | C_{2}↔2C_{2}              | 3873 – 4273                   |
|    |                                        | C_{4}↔4C                  | 3873 – 4273                   |
|    |                                        | 4C_{5}↔5C_{4}             | 3873 – 4273                   |
|    |                                        | 3C_{5}↔5C_{3}             | 3873 – 4273                   |
|    |                                        | 2C_{5}↔5C_{2}             | 3873 – 4073                   |
|    |                                        | C_{5}↔5C                  | 3873 – 4073                   |

The thermophysical parameters of the C_{32}-Ar system at a pressure of 0,1 MPa in the temperature range from 473 K to 4273 K calculated using the TERRA software are shown in figure 2-7.
Figure 2. The dependence of the specific volume of the C$_{32}$-Ar system on temperature.

Figure 3. The complete dependence of the enthalpy of the system C$_{32}$-Ar from temperature.

Figure 4. The dependence of the entropy of the system C$_{32}$-Ar from temperature.

Figure 5. The dependence of the total internal energy of the system C$_{32}$-Ar from temperature.

Figure 6. Dependence of the mass fraction of the condensed phase of the C$_{32}$-Ar system on temperature.

Figure 7. The dependence of equilibrium heat capacity of the system C$_{32}$-Ar from temperature.
Specific volume of the C_{32}-Ar system (figure 2) increases over the entire temperature range. In the temperature range 473 K – 4273 K – increases from 0.788 m^3/kg to 9.736 m^3/kg. At temperatures 3673 K and 3973 K observed inflection points.

The total enthalpy of the C_{32}-Ar system (figure 3) in the temperature range 473...4273 K increases from 1087 kJ/kg to 8878,870 kJ/kg. At 3673 K and 3973 K there are inflection points.

In the temperature range from 473 K to 4273 K, the entropy of the C_{32}-Ar system (figure 4) increases from 3,492 kJ/kg·K to 6,745 kJ/kg·K. At temperatures of 1873 K, 3673 K and 3973 K, inflection points are observed.

Total internal energy of the C_{32}-Ar system (figure 5) in the temperature range from 473 K to 4273 K increases linearly from 695,902 kJ/kg to 7973,210 kJ/kg. At temperatures of 3673 K, 3973 K observed inflection points.

Mass fraction of the condensed phase of the C_{32}-Ar system (figure 6) in the temperature range from 473 K to 2673 K is constant and is 0.200. In the temperature range from 2673 K to 3973 K – decreases; when the system reaches a temperature of 3973 K it is 0. At a temperature of 3673 K and 3973 K, inflection points are observed.

Specific equilibrium heat capacity of the C_{32}-Ar system (figure 7) in the temperature range from 473 K to 3773 K increases from 0.660 kJ/kg·K to 16,688 kJ/kg·K. In the range from 3773...3873 K, the parameter value decreases to 2,427 kJ/kg·K. When the temperature rises from 3873 K to 4273 K, the specific equilibrium heat capacity of the C_{32}-Ar System increases linearly to 4,207 kJ/kg·K. At temperatures of 3673 K, 3773 K and 3973 K, the inflection points are observed. Up to a temperature of 3973 K, the specific equilibrium heat capacity of the C_{32}-Ar system is determined by the heat capacity of the condensed phase C_{32}(s). From 3973 K the specific equilibrium heat capacity of the system is determined by the steam phase.

Conclusion
The analysis of high-temperature interactions during heating of C_{32} fullerenes in the argon atmosphere is performed. Two groups of physicochemical interactions are observed in the system under consideration: sublimation with thermal dissociation, thermal dissociation in the gas phase. With an increase in temperature to 3873 K, the transition of condensed fullerenes to the gas phase is observed. At temperatures above 3873 K the dissociation reactions of the gas phase components prevail.

Thermophysical characteristics of the system are determined primarily by the properties of carbon. In thermophysical parameters of the observed pattern of nonlinear change of the properties when the temperature rises above 3073 K. This high temperature interval corresponds to the beginning of the transition of the condensed graphite in a gaseous phase.

The appearance of inflection points on the graphs of thermal characteristics at 3673 K and 3773 K is explained by a decrease in the content of condensed C_{32} from 0.210 mol/kg to 0.001 mol/kg and an increase in the content of gaseous C, C_{2}, C_{3}, C_{4}, C_{5} from 0.160 mol/kg, 0.159 mol/kg, 1.122 mol/kg, 0.015 mol/kg and 0.067 mol/kg to 0.855 mol/kg, 0.824 mol/kg, 4.194 mol/kg, 0.071 mol/kg and 0.255 mol/kg respectively; at 3873 K – due to the process of molization in the vapor phase; at 3973 K – linear decrease in gaseous C_{3}, C_{4}, C_{5} to 3,650 mol/kg, 0,054 mol/kg and 0,105 mol/kg.

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