EPJ Web of Conferences **318**, 06009 (2025) https://doi.org/10.1051/epjconf/202531806009
AAPM-III 2025

Changes in the thermal characteristics of fullerenes in a nitrogen atmosphere

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Abstract. In order to study the thermal stability of C_n fullerenes (n = 28, 32, 44, 50, 56, 60, 70, 84, 90, 94) in a nitrogen environment during the transition from the condensed phase to the gas phase, the method of thermodynamic modeling is used. This method consists in the analysis of the system using the TERRA software package. In this work, a comparative study of the thermal stability intervals of C_n fullerenes in the condensed and gas phases was carried out. Thermodynamic characteristics of sublimation reactions were determined: entropy and enthalpy indices, values of coefficients of determination.

1 Introduction

Fullerenes are molecular compounds belonging to the class of allotropic forms of carbon. At present, many types of fullerenes have been discovered, which are usually denoted as follows – C_{28}, C_{32}, C_{44}, … C_n, etc., where the index n is the number of carbon atoms. The spectrum of new properties, functional and operational characteristics of fullerene allows the introduction of these nanoparticles into various fields of activity. Fullerenes have high thermal stability, which is why they are used as additives for fire protection in paints and varnishes capable of forming coatings that turn into a thick layer of non-combustible foam with low thermal conductivity during a fire. They are called intumescent, or bloating. These coatings are able to slow down the process of heating building structures to a critical temperature for it. The high degree of resistance to fire due to the nanocomposite structure of coatings, in contact with fire is swelling, expanding paint material, which prevents the penetration of heat to the base layer below.

The question of thermal stability of nanoparticles is one of the main aspects of their study [1].

When the thermal effect on the system is a change in the structure of the chemical and physical composition of substances, which entails a complication of the calculation of the content of systems, but an alternative is to use the mathematical apparatus of equilibrium thermodynamics, namely, the method of thermodynamic modeling [2].

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2 Calculation methodology

The study was conducted using the TERRA software package, which determines the composition and properties of arbitrary systems [3]. Calculations of the list of elements included in the elementary composition of the carbon-nitrogen system, as well as their characteristics, are performed on the basis of the reference literature database in systematic form [4].

The work considers the use of the thermodynamic modeling method to study the heating process of fullerenes C_n (n=28, 32, 44, 50, 56, 60, 70, 76, 84, 90, 94) in a carbon-nitrogen system at a ratio of 1:2 and a pressure of 10 MPa. Not all reactions occurring in the C_n-N_2 system are of interest, but only the interaction of $C_{n(c)}$ with C_n and their thermostability.

In the C_n-N_2 system (n=28, 32, 44, 50, 56, 60, 70, 76, 84, 90, 94), the condensed phase contains: condensed fullerene $C_{n(c)}$ (n=28, 32, 44, 50, 56, 60, 70, 76, 84, 90, 94), couples C_k, k=1, 2, 3, 4, 5, 6, 7, 28, 32, 44, 50, 56, 60, 70, 76, 84, 90, 94 (depending on the fullerene under study, with a large number of atoms are prohibited) and N_2 gas.

3 Research results

Figures 1 and 2 show the interval thermal stability intervals for fullerenes C_n (n=28, 32, 44, 50, 56, 60, 70, 76, 84, 90, 94) in the condensed and gas phases, respectively. Values for plotting were obtained on the basis of calculated data.

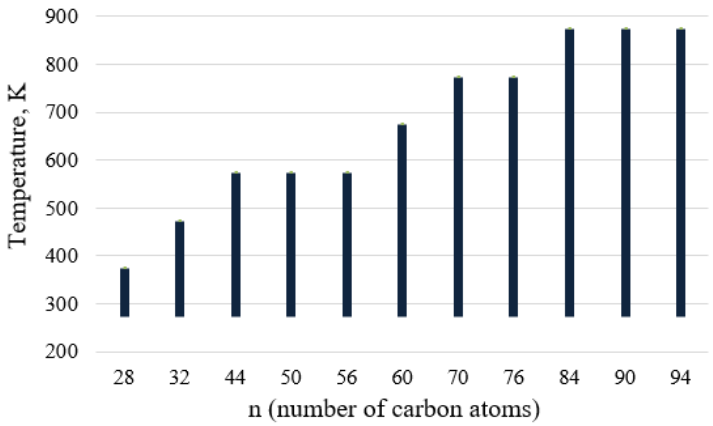

Fig. 1. Interval intervals of C_n stability in the condensed phase.

According to the data of the study and based on the graphs of Figures 1 and 2, the following conclusions can be drawn: in the condensed phase, with an increase in the number of carbon atoms, there is an increase in the thermal stability intervals of the nanoparticles under study, and in the gas phase, on the contrary, with an increase in the number of atoms, a decrease in the intervals of thermal stability is noticeable, and starting with C_{60} or more fullerenes show thermal instability.

In C_n-N_2 systems (n=28, 32, 44, 50, 56, 60, 70, 76, 84, 90, 94), the sublimation reactions occurring are presented in Table 1, the thermodynamic characteristics of these reactions and the value of approximation reliability are also shown there.

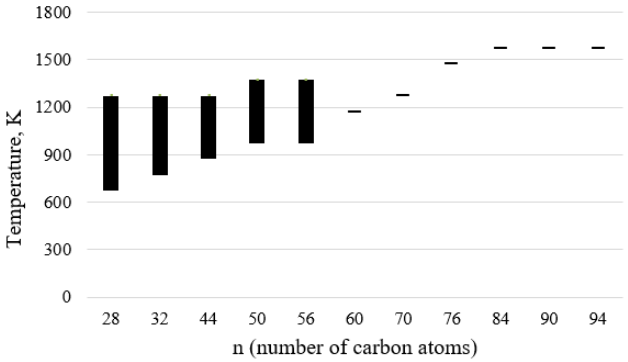

Fig. 2. Interval intervals of C_n stability in the gas phase.

Table 1. Thermodynamic characteristics of C_n in the C_n-N_2 system during the transition from the condensed phase to the gas phase.

No.	Reaction	Temperature range, [K]	ΔH, [kJ/mol]	ΔS, [J/mol*K]	R^2
1	$C_{28(c)} \rightarrow C_{28}$	373-673	95.22	118.18	0.9973
2	$C_{32(c)} \rightarrow C_{32}$	473-773	108.37	129.55	1
3	$C_{44(c)} \rightarrow C_{44}$	573-873	128.03	130.49	0.9895
4	$C_{50(c)} \rightarrow C_{50}$	573-873	145.61	136.18	1
5	$C_{56(c)} \rightarrow C_{56}$	573-973	150.75	167.58	0.9999
6	$C_{60(c)} \rightarrow C_{60}$	673-1173	171.04	114.86	0.9996
7	$C_{70(c)} \rightarrow C_{70}$	773-1273	179.84	109.75	0.9987
8	$C_{84(c)} \rightarrow C_{84}$	773-1573	185.54	97.94	0.9984
9	$C_{90(c)} \rightarrow C_{90}$	773-1573	193.53	94.19	0.9993
10	$C_{94(c)} \rightarrow C_{94}$	773-1573	195.62	90.65	0.9989

The formulas for calculating the enthalpy and entropy values of the reactions presented in Table 1 are derived using two equations (1) and (2), which express the change in Gibbs free energy. This quantity shows the change in energy during a chemical reaction and gives an answer to the question of the fundamental possibility of a given reaction to proceed.

$$\Delta G = \Delta H - T \cdot \Delta S \quad (1)$$

$$\Delta G = -R \cdot T \cdot \ln K \quad (2)$$

where ΔG is the change in Gibbs free energy [kJ/mol], ΔH is the change in enthalpy [kJ/mol], T is the thermodynamic temperature [K] , ΔS is the change in entropy [J/mol·K], R is the universal gas constant [J/mol·K], K is the equilibrium constant.

The enthalpic factor, associated with a decrease in enthalpy of the system, and the entropic factor, caused by an increase in disorder in the system due to an increase in its entropy, determine the spontaneous course of the thermal process [5].

By equating the right-hand sides of equations (1) and (2) and expressing lnK, we obtain equation (3), which shows the dependence of the equilibrium constant on enthalpic and entropic factors:

$$ln\,K = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} \quad (3)$$

The equilibrium constant can be calculated using the linear function equation (4):

$$ln\,K = A_i \cdot \frac{1}{T} + B_i \quad (4)$$

where Ai and Bi are coefficients describing the equilibrium constant of the reaction.

Comparing equations (3) and (4) we obtain formulas (5) for calculating the enthalpy and entropy for ongoing reactions

$$\Delta H = -A_i \cdot R\,, \quad \Delta S = B_i \cdot R \quad (5)$$

Analyzing the thermodynamic characteristics of the reactions obtained as a result of the calculations, it is noticeable that with an increase in the number of carbon atoms, the enthalpy indicators increase, which indicates an increase in the level of energy stored in the molecular structure. The entropy indices also increase up to a certain value, namely, up to the content of carbon atoms equal to 56, which is one of the formulations of the second law of thermodynamics, further, with increasing number of atoms there is a decrease in these indices, which indicates a possible non-isolated state of the system.

Temperature intervals of transition from the condensed phase to the gas phase increase with increasing number of atoms, but as noted earlier, starting from C_{56} when the condensed phase disappears, these nanoparticles show thermal instability, entering into reactions with new elements.

The values of the coefficients of determination (R^2) presented in Table 1 are close to or equal to 1, which is interpreted as a very high qualitative characteristic of the strength of the relationship.

4 Conclusion

Summing up the comparative study of the thermal stability and thermodynamic characteristics of reactions occurring in the C_n-N_2 system (n=28, 32, 44, 50, 56, 60, 70, 76, 84, 90, 94) relative to C_n in the condensed and gas phases, there are a number of features:

- in the condensed phase with an increase in the number of carbon atoms, the thermal stability intervals of the studied nanoparticles increase, for example, the thermal stability interval for fullerene C_{28} is 100K, and for C_{94} - 600K;
- in the gas phase, the thermal stability intervals of the nanoparticles under study decrease as the number of atoms increases; for example, the thermal stability interval for fullerene C_{28} is 600K, while for C_{94} it is 0K;
- the enthalpy values in sublimation reactions increase as the number of carbon atoms increases;
- the entropy indices in the reactions of transition from the condensed phase to the gaseous phase, in contrast to the enthalpy, behave ambiguously, increase to n=56, and then, with an increase in the number of carbon atoms, a decrease in these indices is noticeable.

This study continues the series of works on the thermal properties and thermodynamic characteristics of nanoparticles in the carbon-nitrogen system. The obtained data can be used to create carbon fillers for the purpose of introduction into compositions and increase the service life of flame retardant bloating coatings.

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