NUCLEATION IN A SYSTEM OF *N*-PENTANOL–SULPHUR HEXAFLUORIDE AS AN EXAMPLE OF NONEQUILIBRIUM PHASE TRANSITION

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Received August 19, 1996

The paper presents some experimental results on the aerosol formation rate from the supersaturated n-pentanol vapor. The experiments performed allowed us to reveal that on receding of the system from the equilibrium state, the dependence of the nucleation rate on the vapor activity exhibits certain features of nonequilibrium phase transition, what enables one to suppose had the surface of nucleation rates is a multisheet surface.

INTRODUCTION

The process of atmospheric aerosol formation is very complicated and many factors are to be accounted for. When studying even relatively simple systems, for example, binary mixtures of vapor and gas-carrier, the experimental results do not agree with the classical approach. The influence of gas-carrier pressure on the vapor nucleation is among the above-mentioned factors.[1–3] In the framework of classical approach the effect of the environment, perhaps for binary mixture-gas-carrier, is considered as a mean field, which tends to destroy the fluctuations occurring in the system. However, we know that the increase of the fluctuation scale may result in the loss of stability and occurrence of coherent structures.[4] The fact of formation of the dissipative structures, when the system moves off from equilibrium or with the increase of the number of its degrees of freedom, lead to a conclusion that a relatively complicated system often occurs in a metastable state.[4]

This approach stimulates the investigation of atmospheric aerosol formation in model nonequilibrium systems.

Within the framework of the International experiment based on a comparison of data of the pentanol vapor nucleation rate, obtained using different methods implemented by different groups of researchers, we have discovered that the behavior of aerosol formation rate is not typical for standard models.

EXPERIMENT AND RESULTS

This paper presents an experimental setup allowing the determination of the dependence of nucleation rate on the activity of vapor of the substance studied.[2]

The main element of the experimental setup is the aerosol generator consisting of hot and cold thermostats.

The inertial gas-carrier flow enters the hot thermostat and is saturated with vapor of the substance studied. The vapor-gas flow, entering a cold part of a diffusion chamber, develops into a supersaturated state resulting in the formation of aerosol particles.

The aerosol concentration was measured using a photometric counter of aerosol particles. The experimental results were recalculated by numerical solution of heat mass equations in a laminar stationary axisymmetric vapor-gas flow.[2]

The vapor activity of the substance investigated was determined from calculations of the fields of temperature and vapor concentration in the diffusion chamber. In this case, by the vapor activity in the mixture we mean the ratio of partial vapor pressure at a given temperature of a mixture to the pure liquid vapor pressure at the same temperature (similar value for a one-component system is called supersaturation). In the experiment we determined the maximum of the vapor nucleation rate according to the algorithm from Ref. 5.

When conducting the experiment the gas temperature at the entrance to the diffusion chamber varied in the limits from 300 to 400 K at the rate of no more than 0.5 K/min.

The cold side temperature and total pressure in the diffusion chamber were kept constant. The gas volume flow rate was measured at the output of the system to the atmosphere and kept constant at all pressures, being equal to 3 $\mathrm{cm^3/s}$ within the limits of measurement error (not worse than 2 percent). The vapor partial pressure varied from 3 to 10 kPa in the experiment. The mean value of the aerosol particle concentration in the volume under study was shown in the curve of nucleation rate as one experimental point and determined using a data sample of 10^2 values at the initial portion of the curve of the nucleation rate J at $\log J = 0–2$ and up to 10^6 at $\log J = 6$ (J is expressed in $\mathrm{cm^{-3}{\cdot}s^{-1}}$).

Experimental dependences of J on the vapor activity (A) of *n*-pentanol in the atmosphere of sulphur hexafluoride in double logarithmic axes at nucleation temperatures $T = -5.5$°C; -9.5°C; -12.1°C and pressures $P = 0.1$; 0.2; 0.3 MPa are presented in Figs. 1–3. Figures 1 to 3 show that the increase of nucleation rate in the initial portion is linear.

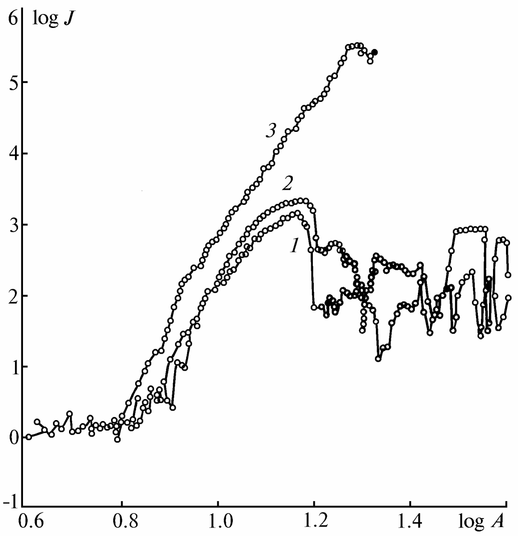

FIG. 1. The dependence of nucleation rate of the n-pentanol vapor activity in the atmosphere of sulphur hexafluoride at the nucleation temperature $t = -5.5$°C *and the system pressure*: 0.1 *(1)*, 0.2 *(2)*, *and* 0.3 MPa *(3)*.

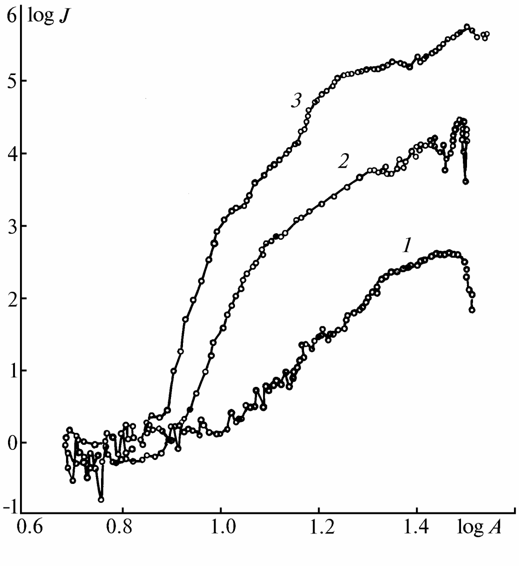

FIG. 2. The dependence of nucleation rate on the n-pentanol vapor activity in the atmosphere of sulphur hexafluoride at the nucleation temperature $t = -9.5$°C *and the system pressure*: 0.1 *(1)*, 0.2 *(2)*, and 0.3 MPa *(3)*.

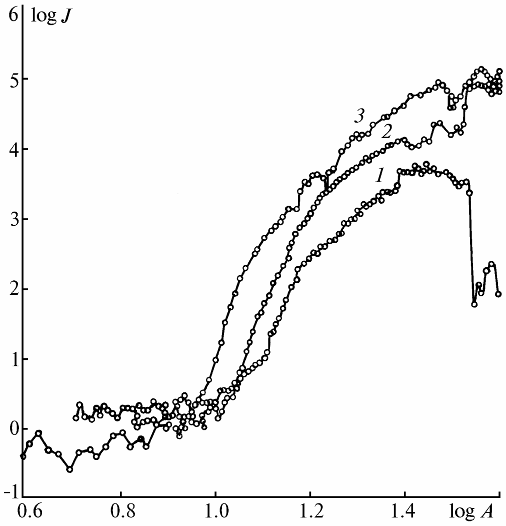

FIG. 3. The dependence of nucleation rate on the n-pentanol vapor activity in the atmosphere of sulphur hexafluoride at the nucleation temperature $t = -12.1$°C *and the system pressure*: 0.1 *(1)*, 0.2 *(2)*, and 0.3 MPa *(3)*.

With the increase of activity (supersaturation) of *n*-pentanol vapor the tangent of the slope angle in the coordinates presented varies stepwise and the nucleation rate reaches its maximum. Some new experiments have shown that the termination of the increase of nucleation rate and its decrease from a certain value of the activity are not caused by the depletion of *n*-pentanol vapor in the mixture at the input to the diffusion chamber.

Analysis for the experimental data (see Figs. 1–3) has shown that the increase of the mixture pressure resulted in the data shift to the region of lower values of the activity (as well as the increase of nucleation temperature) and in the increase of maximum values of the nucleation rate. The effect of total pressure in the system on the nucleation rate the given values of partial pressure of pentanol vapor and nucleation temperature has confirmed experimental results obtained earlier interpreted within the limits of binary nucleation.[1–3]

The special feature in the behavior of the nucleation rate curves is the stepwise change of the slope. The Table I presents the values of tangent of the slope angle of linear sections of the curves at the nucleation temperature -9.5°C and -12.1°C.

As is seen from the table, tangents of the slope angles vary within the limits from 2 to 24; as to an individual curve, the tangents of the slope angles vary by an integer factor. This fact with allowance for the fact that according to a kinetic model,[6] the value of tangent of the slope angle in the coordinates considered determines the number of vapor molecules in the critical nucleus, shows that the nucleation occurs in several channels (through critical nucleus of different type).

TABLE. I. Dependence of the values of tangent of the slope angle (tanα) *on the n-pentanol vapor activity* (log$A$) *at nucleation temperature* T = –9.5; –12.1 °C *and total pressure in the system* P = 0.1; 0.2; 0.3 MPa.

t,°C	P, MPa	tanα	log$A$	t,°C	P, MPa	tanα	log$A$
–9.5	0.1	6	1.0–1.35	–12.1	0.1	4	1.0–1.1
–9.5	0.1	3	1.35–1.45	–12.1	0.1	16	1.1–1.2
–9.5	0.2	16	0.95–1.05	–12.1	0.1	4	1.2–1.4
–9.5	0.2	8	1.05–1.1	–12.1	0.2	16	1.0–1.2
–9.5	0.2	4	1.1–1.3	–12.1	0.2	4	1.2–1.4
–9.5	0.3	24	0.9–1.0	–12.1	0.3	24	0.95–1.05
–9.5	0.3	8	1.0–1.25	–12.1	0.3	8	1.1–1.25
–9.5	0.3	2	1.25–1.55	–12.1	0.3	4	1.25–1.35

Another special feature in the behavior of the curves of nucleation rates are the pulsation of activity. The amplitude of pulsations greatly exceeds the measurement error. In this case, when the system off from the equilibrium (with the increase of vapor activity) the nucleation process of supersaturated vapor experience natural fluctuations and it may be referred to the nonequilibrium phase transitions, connected with the loss of stability of the initial state.

In Refs. 3 and 7 we study the initial state of a multicomponent system and determine it on the basis of their state diagrams. In this case, based on the topological analysis, a conclusion is drawn on the multisheet surface of aerosol formation rates of a given system. This explains the possibility of existence of several nonequilibrium states (stable simultaneously) and switches between them and it is represented by the experimental dependences of the pentanol nucleation rate in the atmosphere of sulfur hexafluoride presented here.

CONCLUSIONS

The dependence of the aerosol formation rate revealed of a binary system confirms the hypothesis on multisheet surface of nucleation rates. The investigation of model nonequilibrium systems is also of interest due to a possibility of formation of dissipative structures in open systems (as a result of the development of instabilities), such as, for example, cirrus clouds.

ACKNOWLEDGMENT

The authors are grateful to the Russian Foundation for Fundamental Research for the financial support of the work.

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