

## EMPIRICAL DETERMINATION OF THE CRITICAL NUCLEI COMPOSITION IN THE VICINITY OF GLYCERIN MELTING POINT

M.P. Anisimov, A.G. Nasibulin, and L.V. Timoshina

*Institute of Atmospheric Optics,  
Siberian Branch of the Russian Academy of Sciences, Tomsk  
Received July 17, 1996*

*The paper presents some results of determination of the critical nuclei size and composition based on the experimental data on the nucleation rate of glycerin vapor. The measurements have been performed in different gas media inside a diffusion chamber. The influence of phase transition of the first kind is revealed in the condensate on the process of aerosol formation in supersaturated vapor and on the size of a critical nucleus of a new phase. Analysis of the experimental data revealed the influence of the gas-medium concentration on the phase transition temperature. The composition of critical nuclei is shown to differ significantly from the system microscopic composition under given conditions. The results obtained enable us to draw the conclusions that the nucleation under study may be treated as a binary nucleation of the "vapor of the substance condensed – carrier gas system."*

### INTRODUCTION

Despite of a large number of experimental investigations, devoted to the study of nucleation of supersaturated vapor available, we have no clear understanding of the processes occurring in the aerosol formation. Experimental investigations enable us to determine only the dependences of nucleation rate on the activity (supersaturation) of vapor of a substance studied. The interpretation of experimental results often amounts to a comparison of the data obtained with the results of predictions of one of modifications of a classical nucleation theory. As a rule, such comparisons result in the fact that most of experimenters accept the inability of the nucleation theory to describe the experiment both quantitatively and qualitatively.

To gain a better understanding of the processes, occurring during aerosol formation, there is a need to obtain qualitatively new results. The useful data may be obtained if we try at a molecular level to study the processes occurring while forming a new phase in the vicinity of temperature point of the phase transition in the condensate.

The aim of this paper is to determine the composition and size of a critical nucleus formed under conditions of binary nucleation in the vicinity of temperature point of melting of the substance under study. It should be noted that the atmospheric nucleation often takes place close to the conditions of water or water solutions freezing, and the investigations of model systems in the vicinity of the phase transition of the first kind at the condensed state have been very promising for improvement and development of the theory of heteromolecular and, in particular, atmospheric nucleation.

The method of empirical determination of the size of critical nuclei was first proposed in Refs. 1 and 2 and was further developed in Refs. 3 and 4, when determining the composition of critical nuclei of a new phase in the case of nucleation of multicomponent vapor that was stimulated by the need for a quantitative description of the kinetics of formation of thermocondensation aerosols including the solution of atmospheric problems.

### RESULTS OF DETERMINATION OF THE SIZE AND COMPOSITION OF CRITICAL NUCLEI AND DISCUSSION

The number of molecules of the substance  $g_a^*$  under study and the gas-carrier  $g_b^*$  in a critical nucleus in the vicinity of melting temperature of glycerin was determined using the method proposed in Ref. 3, where

$$g_a^* = \frac{d \ln J}{d \ln A} - 2, \quad (1)$$

$$g_b^* = \frac{d \ln J}{d \ln P} - 2, \quad (2)$$

where  $J$  is the nucleation rate,  $P$  is the pressure of gas-carrier in the system, and  $A$  is the vapor activity of the substance under study, determined as the ratio of the vapor partial pressure to the equilibrium pressure at a given temperature.

Experimental investigations of nucleation of supersaturated glycerin vapor in the atmosphere of helium, argon and sulphur hexafluoride were performed in the flow-type diffusion chamber. A detailed description of this chamber and the algorithm for processing the experimental data, when

the nucleation rate depends on the activity of the substance under study, are given in Ref. 5. The results of the experimental investigation of nucleation in the vicinity of glycerin melting temperature point are published in Ref. 6.

Figures 1 and 2 present the obtained, based on the experimental data, dependences of the number of molecules in a critical nucleus on the nucleation temperature in the atmosphere of argon and sulphur hexafluoride at pressures of gas-carrier in the system of 1, 2 and 3 bar.

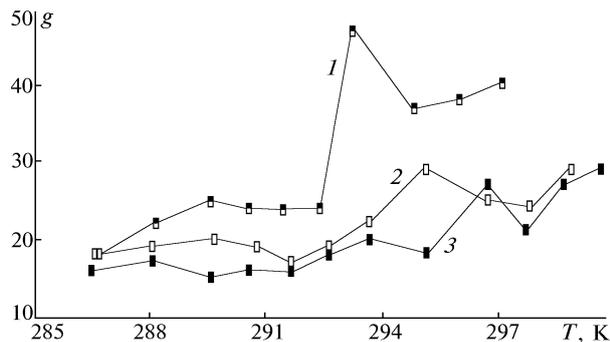


FIG 1. Dependence of the number of molecules in a critical nucleus on the nucleation temperature in the glycerin-argon system at a pressure of 1 (1), 2 (2), and 3 bar (3).

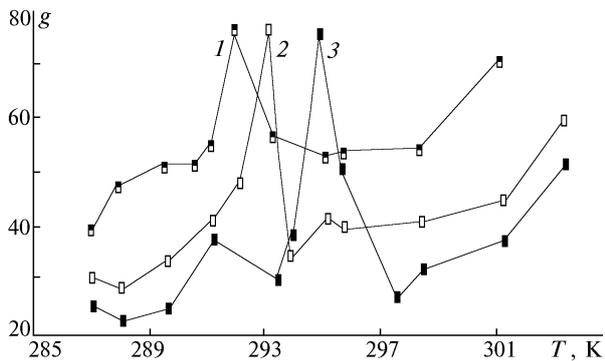


FIG 2. Dependence of the number of molecules in a critical nucleus on the nucleation temperature in the glycerin-sulphur hexafluoride at a pressure of 1 (1), 2 (2), and 3 bar (3).

The fact has attracted our attention that in the vicinity of the phase transition temperature we observe a large number of molecules in a critical nucleus. In this case the phase transition temperature with the pressure increase in the system is shifted to the range of higher temperatures when the glycerin-vapor nucleation occurs both in the argon atmosphere and in the atmosphere of sulphur hexafluoride. Similar dependence of the first kind phase transition temperature in the condensate on the pressure in the system is followed up when considering the experimental dependence of the glycerin vapor activity on the nucleation temperature<sup>7</sup> and when investigating the glycerin vapor isobaric nucleation at melting temperature.<sup>8</sup>

Based on the experimental data, the temperature shift of phase transition with the increase of the gas-carrier pressure in the system is undoubtful, but it cannot be explained from the viewpoint of the classical nucleation theory.

Similar influence of the pressure on the melting temperature variation is explained only for macroscopic bodies, whose volume variation  $\Delta V$  in the transition from a crystal phase to a liquid one is accompanied by its increase. Then, according to the Clausius-Clapeyron equation, the derivative of  $dP/dT > 0$ , and hence, the pressure increase in the system results in the increase of melting temperature

$$\frac{dP}{dT} = \frac{H}{T\Delta V}, \tag{3}$$

where  $T$  is the temperature of phase transition,  $H$  is the heat of phase transition, and  $P$  is the pressure. In the reference literature<sup>9</sup> the above cited data on the derivatives  $dT_{\text{mel}}/dP$  for a wide range of organic compounds do not exceed  $114.6 \cdot 10^{-2} \text{ K/MPa}$  (urethane) that corresponds to 1 K rise of melting temperature with the pressure increase of more than 10 bar in the system. Thus, the pressure effect on the melting temperature of macroscopic bodies turns out to be very insignificant.

When considering the effect of pressure on the temperature of phase transition in aerosol particles the effect of external pressure is insignificant since from the viewpoint of the volume variation since the Laplacian pressure in a critical glycerin nucleus about 30 or 40 molecules in size, is of the order of 800-1000 bar and the 1-2 bar increase of external pressure only slightly affects the nucleus volume.

Therefore the temperature shift of the phase transition in the direction of the increase of pressure (concentration) of gas-carrier in the system we explain, first of all, by the fact that the nucleation of substance in gaseous atmosphere should be considered as a binary nucleation of the "condensed substance vapor-gas-carrier" system. The melting temperature, determined when conducting thermal analysis<sup>6</sup> of pure glycerin (292.45 K), turned out to be lower than the temperature determined from the experimental results when introducing inert gases, argon and sulphur hexafluoride, into the system. It should be noted that the increase of these components content in the system resulted in the melting temperature shift in the direction of its increase (at the argon pressure in the system  $P = 1 \text{ bar}$  the temperature of phase transition  $T = 293.55 \text{ K}$ , at  $P = 2 \text{ bar}$   $T = 295.45 \text{ K}$ , at  $P = 3 \text{ bar}$   $T = 296.05 \text{ K}$ ; at a pressure in the system of sulphur hexafluoride  $P = 1 \text{ bar}$   $T = 292.55 \text{ K}$ , at  $P = 2 \text{ bar}$   $T = 293.75 \text{ K}$ , at  $P = 3 \text{ bar}$   $T = 295.55 \text{ K}$ ). Similar phase transition temperature shift is typical for the behavior of binary systems.

For a comparison, Fig. 3 shows the dependence of the size of a critical nucleus on the nucleation temperature in different gases at a pressure of 1 bar in the system. Figure 3 shows that both the size of the

critical nucleus and the phase transition temperature depend nonuniquely on the type of gas in which the nucleation occurs.

The size of the critical nucleus formed as a result of the glycerin vapor nucleation in the atmosphere of SF<sub>6</sub>, far exceed the size of nuclei formed in the helium and argon atmosphere. It is evident that this dependence of the size of the critical nucleus on the gas-carrier is the result of intermolecular interaction, which is most essential for molecules of glycerin and SF<sub>6</sub>.

Tables I–III give the experimental results of investigation of the critical nuclei composition in the vicinity of the first-kind phase transition in different gases and at different pressures.

Close analysis of table data shows that the mole fraction of a gas-carrier in critical nuclei may be as large as 0.36. At the first sight, this result seems to be extraordinary because solubility of gases in liquids in the absence of chemical interaction is negligibly small (from 10<sup>-3</sup> to 10<sup>-5</sup> mole fractions). It is evident that

such a comparison is not correct as regards the characteristic of macroscopic bodies and clusters of such a small size, as the critical nucleus (20–70 molecules).

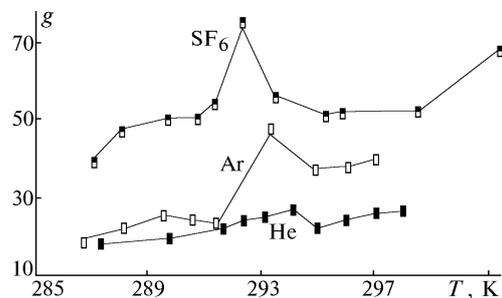


FIG. 3. Dependence of the number of molecules in the critical nucleus on the temperature of glycerin vapor in helium, argon and sulphur hexafluoride at a pressure of 1 bar.

TABLE I. Composition of critical nuclei at nucleation of glycerin vapor in the atmosphere of argon.

Nucleation temperature, K	Argon pressure, bar	Activity of glycerin vapor, log A	The number of molecules		Total number of molecules
			glycerin	argon	
286.85	1	2.36	14	4	18
288.35	1	2.33	18	4	22
289.75	1	2.31	19	6	25
290.75	1	2.29	17	7	24
291.65	1	2.26	19	5	24
292.65	1	2.22	20	4	24
293.55	1	2.21	40	7	47
295.15	1	2.15	29	8	37
296.35	1	2.13	30	8	38
297.45	1	2.11	31	9	40
286.75	2	2.32	14	4	18
288.25	2	2.30	15	4	19
289.85	2	2.24	15	5	20
290.95	2	2.24	14	5	19
291.85	2	2.19	13	4	17
292.85	2	2.16	14	5	19
293.95	2	2.14	15	7	22
295.25	2	2.09	23	6	29
297.05	2	2.05	18	7	25
298.15	2	2.03	17	7	24
299.25	2	2.04	20	8	28
286.65	3	2.28	12	4	16
288.25	3	2.23	13	4	17
289.75	3	2.18	12	3	15
290.75	3	2.15	14	2	16
291.85	3	2.13	13	3	16
292.85	3	2.10	13	5	18
293.95	3	2.05	13	7	20
295.45	3	2.02	14	4	18
296.05	3	1.97	20	7	27
298.05	3	1.96	16	5	21
299.05	3	1.94	19	8	27
300.05	3	1.92	21	9	30

TABLE II. Composition of critical nuclei at nucleation of glycerin vapor in the atmosphere of sulphur hexafluoride.

Nucleation temperature, K	Pressure of SF <sub>6</sub> , bar	Activity of glycerin vapor, log <i>A</i>	The number of molecules		Total number of molecules
			glycerin	SF <sub>6</sub>	
287.25	1	2.44	25	14	39
288.25	1	2.38	33	14	47
289.95	1	2.34	36	14	50
290.95	1	2.27	40	10	50
291.55	1	2.23	48	6	54
292.55	1	2.22	66	9	75
293.75	1	2.21	44	11	55
295.55	1	2.18	42	9	51
296.15	1	2.16	40	12	52
298.85	1	2.10	39	13	52
301.75	1	2.07	57	11	68
287.25	2	2.24	24	6	30
288.25	2	2.21	22	6	28
289.95	2	2.21	26	7	33
291.55	2	2.20	31	9	40
292.55	2	2.15	39	8	47
293.75	2	2.12	68	7	75
294.25	2	2.11	25	8	33
295.55	2	2.10	31	9	40
296.15	2	2.04	30	8	38
298.85	2	1.99	32	7	39
301.75	2	1.98	34	8	42
303.95	2	2.08	49	8	57
287.25	3	2.19	24	1	25
288.25	3	2.16	21	1	22
289.95	3	2.13	22	2	24
291.55	3	2.09	27	9	36
293.75	3	2.06	25	4	29
294.35	3	2.05	31	6	37
295.55	3	2.04	65	9	74
296.15	3	2.00	45	4	49
297.25	3	1.98	22	3	25
298.85	3	1.96	28	2	30
301.75	3	1.92	30	5	35
303.95	3	1.89	44	5	49

TABLE III. Composition of critical nuclei at nucleation of glycerin vapor in the helium atmosphere.

Nucleation temperature, K	Helium pressure, bar	Activity of glycerin vapor, log <i>A</i>	The number of molecules		Total number of molecules
			glycerin	helium	
287.45	1	2.68	18	1	19
289.95	1	2.57	19	1	20
292.85	1	2.53	22	1	23
293.35	1	2.46	24	2	26
294.35	1	2.43	26	2	28
295.25	1	2.41	21	2	23
296.25	1	2.38	22	3	25
297.35	1	2.40	23	3	26
298.35	1	2.35	25	3	28

As follows from the literature available (e.g., Ref. 10) the results are known on the investigation mutual solubility of silver and copper for the

particles 0.05–0.13 μm in size. In the above paper the author pointed out that at a decrease of a particle size the metal solubility increases within a wide

range and far exceeds the solubility for the samples of ordinary size. It is evident that similar dependence of mutual solubility on the size of reacting objects is the rule we managed to discover. At present no experimental data are available on the dependence of gas solubility in such small objects as aerosol particles (especially in critical nuclei of a new phase). This is explained, first of all, by the complexity of the experiment. We can only use a possibility, justified in the thermodynamic approximation, of determining the number of molecules of various types in a new phase critical nucleus and their relative content obtained from experimental data on the nucleation rate. Such an approach, as any other theory, has a series of shortcomings due to various approximations but this approach is very convenient for use in order to determine the size and composition of critical nuclei and allows the determination of quantitative characteristics of a new phase nuclei without additional expensive experimental methods.

The theory of solutions was developed for the processes occurring in a test tube and beyond any reasonable doubt, this theory is also valid for such a small cluster of molecules as a critical nucleus but only after taking into account of the conditions determining the characteristics of macro- and microobjects. Thus, taking into account, for example, the Laplacian pressure in the critical nuclei, one can explain the anomalous high solubility of the gas-carrier, i.e., the pressure increase, as a rule, results in an increase of the gas solubility.

The interaction between the liquids and gases the change in the liquid structure with the formation of gas hydrates (clathrate compounds) is possible, in addition to the formation of simple solutions.<sup>11</sup> In such compounds the gas mole fraction exceeds the solubility by some orders of magnitude typical for the macroscopic bodies and reaches 0.25. It is possible that in small clusters the analogous structures can be formed.

When forming the critical cluster the process of gas-carrier molecules capture by a nucleus cannot be considered to be a mere solution. It is quite possible that the molecules of gas-carrier are only adsorbed on a nucleus surface. The critical nucleus consists almost completely of surface molecules, therefore the value of surface adsorption for one nucleus molecule is much larger than this value for microscopic objects under usual or ordinary conditions.

Thus, at present it is almost impossible to determine correctly and properly the nature of interaction of molecules of a condensing substance and a gas-carrier when forming a nucleus of a new phase, namely, a critical nucleus. Agreement between different theoretical and experimental concepts on the necessity of considering the gas-carrier not only as a thermostated medium but as a participant of nucleation is the first essential step on

the road to an understanding of the processes of aerosol formation.

## CONCLUSIONS

The results of determination of the size of critical nuclei based on the experimental data show the influence of the first kind phase transition in a condensate on the nucleation process of supersaturated vapor. When interpreting the experimental results the influence of the gas-medium pressure (concentration) on the phase transition temperature was determined. It was found that the composition of critical nuclei differed greatly from the system macroscopic composition under given conditions. The results presented in this paper make it possible to conclude that the nucleation of the substance under study in the atmosphere of gas-medium should be considered to be a binary nucleation of the "condensed substance vapor-gas-medium" system.

## REFERENCES

1. M.P. Anisimov, V.G. Kostrovskii, and M.S. Shtein, *Kolloidnyi Zh.* **40**, 317–321 (1978).
2. D. Kashchiev, *J. Chem. Phys.* **76**, No. 10, 5098–5102 (1982).
3. M.P. Anisimov, S.N. Vershinin, A.A. Aksenov, and A.M. Semin, *Kolloidnyi Zh.* **49**, No. 5, 842–846 (1987).
4. V.M. Belanov, V.S. Vaganov, G.V. Gadiyak et al, *Fizich. Khimiya* **7**, No. 4, 555–563 (1988).
5. M.P. Anisimov, A.G. Nasibulin, and S.D. Shandakov, *Atmos. Oceanic Opt.* **9**, No. 6, 548–554 (1996).
6. M.P. Anisimov, A.G. Nasibulin, S.V. Timoshina, and N.I. Gordienok, *Investigation of nucleation of glycerin vapor in the vicinity of melting point in a medium of various gases-carriers* (Kemerovo State University, Kemerovo, 1996) 29 pp. Dep. v VINITI 9.04.96, No. 1132–B–96.
7. M.P. Anisimov, A.G. Nasibulin, and S.V. Timoshina, in: *Abstracts of Reports at the Third Interrepublic Symposium on Atmospheric and Oceanic Optics*, Tomsk (1996), pp. 102–103.
8. M.P. Anisimov, A.G. Nasibulin, Yu.I. Polygalov, and I.V. Samokhvalov, in: *Abstracts of Reports at the Third Interrepublic Symposium on Atmospheric and Oceanic Optics*, Tomsk (1996), pp. 97–98.
9. A.P. Babichev, N.A. Babushkina, A.M. Bratkovskii et al., I.S. Grigoriev, E.Z. Meylikhov eds., *Physical values: Reference Book* (Energoatomizdat, Moscow, 1991), 1232 pp.
10. M.Ya. Gen, E.A. Velichenkova, I.V. Eremina, and M.S. Ziskin, *Fiz. Tverdogo Tela* **6**, 1622–1626 (1964).
11. S.Sh. Byk, V.I. Makagon, and V.I. Fomina, *Gas Hydrates* (Chemistry, Moscow, 1980), 296 pp.