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Critical embryo phase transitions in the nucleated binary glycerin–carbon dioxide system

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In order to develop a consistent nucleation theory, the main assumptions of the theory should be revised. One of the questionable problems is the role of the carrier gas in nucleation and the surface tension for the critical embryo as a function of cluster size. Using a flow diffusion chamber, the vapor nucleation rates were measured with high precision and phase transitions in critical embryos containing two and more dozen molecules were detected. Phase transitions in critical embryos were used as markers to detect that the new phase critical embryos contain two components. Phase transitions of the first order related with critical point second-order phase transitions in the pure CO₂ carrier-gas were used as markers to demonstrate the presence of CO₂ in critical embryos of condensate. Results of this research, in our opinion, very clearly demonstrate that vapor nucleation in a gaseous atmosphere is a binary process and must be interpreted from the point of view of nucleation theory within a binary system. “Supercritical” nucleation is a virtual term born by interpretation of binary vapor–gas nucleation by using the nucleation model of a single component. A critical condition for the binary system could be a higher level for the single component critical pressure and/or temperature, which can produce the illusion of supercritical nucleation. One component interpretation can be used far from the critical condition. On the other hand, the Laplace pressure practically always is able to approach the nucleation condition to the critical pressure. This level of detail is a problem for future studies. The traditional application of classical nucleation theory for vapor–gas nucleation should be modified to consider the nucleation conditions in pressure-temperature-composition space. © 1998 American Institute of Physics.

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I. INTRODUCTION

Studies of vapor nucleation are of significant interest as this is a fundamentally important problem of the first-order phase formation kinetics description. Such information is necessary to create computational engineering methods which can be applied to modeling industrial new phase formation processes. The current technical level of research for the study of aerosol formation is of fairly high quality, but there is no theory that is suitable for quantitative prediction of experimental results.

The history of nucleation theory began about a hundred years ago. As a result of its rapid development, the classical theory of nucleation was created^{1,2} in the 1940's. However, it may hardly be considered as universal theory, because of its coincidence with experimental results within only a narrow range of temperatures and supersaturations for only some substances. In the common case, the theory of phase transitions cannot predict the phase transition pressure and temperature nowadays, and includes a number of assumptions to describe small clusters. Further, when the size dependencies of the surface tension and density of nuclei were taken into account^{3,4} and the inherent degrees of freedom were considered in the statistical sum for a nascent cluster,⁵ agreement between theoretical predictions and experimental results was worse.

In order to develop a consistent theory, the main assumptions of the theory should be reconsidered. One of the questionable problems is the role of the carrier gas in nucleation and the surface tension behavior of the critical embryo as a function of cluster size. From the standpoint of classical nucleation theory, a carrier gas does not participate in the formation of critical embryos, but only serves as a medium that maintains an isothermal condition for the nucleation processes. Users of classical theory employ the bulk liquid surface tension to calculate the nucleation rates.

II. EXPERIMENT

A. Basis for an experimental research

To create a more accurate theory and gain a better understanding of the aerosol formation processes, new qualitative experimental results are required. In 1989 the potentiality of the experimental detection of phase transitions inside the embryos of new phase was shown on the basis of critical embryo size measurements.⁶ It is well known that the equilibrium freezing–melting temperature in the bulk condensed phase is stable for a single component system. With fast cooling, one can detect supercooled liquid and a freezing point which is lower than the equilibrium temperature transition from the liquid to crystal state. Small pressures (up to

1 MPa) do not influence the freezing temperature, i.e., the liquid–solid line of an interphase equilibrium is practically vertical in the pressure–temperature axes for all compounds. The dT/dP values⁷ are around or less than 1.1 K/MPa (urethane). In the case of a binary system, the second component can shift the melting point more effectively. This means that the temperature of the phase transition in the condensed state could be used as a marker to identify that a system is binary. A system with a phase transition in the condensed state could be used to study the role of a carrier gas for vapor nucleation in a gaseous atmosphere.

It is well known that the chemical potential of a condensed phase has a singularity at the first-order phase transition temperature. The Gibbs' free energy of a critical embryo of a condensed phase, and therefore, the vapor nucleation rate, must respond to the nonmonotone temperature behavior of the chemical potential near the phase transition. That is, one can use the nonmonotone temperature nucleation rate behavior of the nucleation rate to detect the phase transition in a condensate.

Using this point, it is attractive to study glycerin vapor nucleation, because of the phase transition (freezing–melting) of glycerin, which occurs at a temperature $T_{\text{melt}} = 292.4$ K. If carbon dioxide is used as the carrier gas and enters a glycerin critical embryo, one should detect in the condensate the phase transition related to the carbon dioxide–glycerin critical line. Carbon dioxide (CO_2) has a low critical temperature $T_{cr} = 304.2$ K and critical pressure $P_{cr} = 7.39$ MPa, where a second-order phase transition occurs. A simplest estimation of the Laplace pressure, obtained from the bulk surface tension for the glycerin critical embryos, gives a pressure of more than 40 MPa. This pressure is supercritical for CO_2 , as well as (shown below) for the binary system of glycerin–carbon dioxide. One could find the phase transition, related with the critical line of the binary system, if the system under investigation is binary (components have at least partial solubility). Any glycerin phase transitions (except transition at critical point) higher than the glycerin melting point are unknown. Detection of a phase transition at a temperature higher than the glycerin melting point in condensate should guarantee that the carrier gas (CO_2) molecules enter into the critical embryos and, therefore, indicate that the nucleation of the carbon dioxide–glycerin system is a binary nucleation. If the carbon dioxide–glycerin system is a binary phenomenon, the surface tension for critical embryos should be analyzed as a surface tension of the binary system.

In the present work, nucleation of a carbon dioxide–glycerin system in the vicinity of the glycerin melting point and CO_2 critical temperatures is studied. It is necessary to note that the applied pressure interval 0.10–0.30 MPa for the system under investigation is much less than the critical pressures of the gas-carrier $P_{cr} = 7.39$ MPa. However, if the Laplace pressure is taken into account, the embryo of the new phase formation conditions should be near, but less than, the system critical pressure.

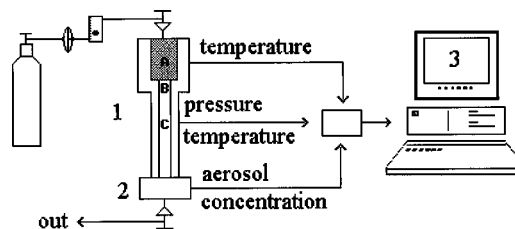


FIG. 1. Experimental setup scheme. 1-aerosol generator, containing hot thermostat with vapor saturation volume, A, laminator, B, and cooler, C; 2-laser aerosol counter; 3-system for computer collection of experimental parameters.

B. Experimental scheme

Aerosol formation was experimentally studied in a flow diffusion chamber, which is suitable to measure the dependence of the nucleation rate on the glycerin vapor activity at different pressures of the carrier gas.

The experimental setup (Fig. 1) contains an aerosol generator (1), which consists of hot (A,B) and cold thermostats (C). A high-pressure cylinder provided the inert carrier gas (with purity 99.99 vol. % or higher) which maintained the flow, via a pressure gas reducer, filter, flow meter, and pressure regulator, to the hot thermostat. Then, gas passed through a chromatographic carrier, alumina, (A) where vapor saturation of the substance under investigation occurred. Inside the second thermostat (B), a steady-state laminar flow was established. The vapor–gas mixture becomes supersaturated in the cooler (C), because of molecular diffusion and heat transfer. Aerosol particles are produced in the vicinity of the highest vapor supersaturation. The volume rate of gas flow was controlled to the level of $6.10 \text{ cm}^3/\text{s}$, which guaranteed laminar flow inside the aerosol particle generator. Temperature was measured with copper-constantan thermocouples, which were calibrated in the appropriate temperature range by using mercury thermometers with an accuracy of 0.1°C .

The aerosol concentration was measured by a laser photoelectric aerosol counter (2). Computer control of the aerosol concentration allowed the achievement of sufficient statistical data in the complete range of the experimental aerosol nucleation rates achievable in these experiments. The relative error in an aerosol concentration did not exceed 3% in these experiments. The sensor's signals were digitized and stored in buffer memory and then passed to a personal computer (3) for further processing.

C. A vapor nucleation rate evaluation

The vapor activity of the substance under investigation was evaluated by computer solution of heat and mass transfer equations for steady-state laminar axisymmetrical viscous vapor–gas flow. This steady-state vapor–gas flow may be described by a set of Navier–Stokes equations; in the cylindrical coordinate system, they can be represented as follows:⁸

$$P = \rho R_0 T / m, \quad (1)$$

$$2\pi \int_0^R r \rho u dr = Q, \quad (2)$$

$$\rho u \frac{\partial u}{\partial x} = -\frac{\partial P}{\partial x} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \eta \frac{\partial u}{\partial r} \right), \quad (3)$$

$$\rho u C_p \frac{\partial T}{\partial x} = u \frac{\partial P}{\partial x} + \eta \left(\frac{\partial u}{\partial r} \right)^2 + \frac{1}{r} \frac{\partial}{\partial r} \left(r \lambda \frac{\partial T}{\partial r} \right). \quad (4)$$

Here, x is the coordinate along the axis of a cylindrical tube; r is the coordinate along its radius, u is the velocity of the gas; T is the temperature; P is the pressure; ρ is the density of the gas; η and λ are its viscosity and heat conductivity, respectively; C_p is the heat capacity of the gas; R_o is the universal gas constant; m is the molecular weight of the gas; R is the radius of the tube; and Q is the mass flow rate of the gas.

The carrier gas flow was described by Eqs. (1)–(4) with the following boundary conditions:

$$\begin{aligned} \left. \frac{\partial u}{\partial r} \right|_{r=0} &= 0, \quad \left. \frac{\partial T}{\partial r} \right|_{r=0} = 0, \\ u(R, x) &= 0, \quad T(R, x) = T_c(x), \\ T(r, 0) &= T_o(r), \quad u(r, 0) = u_o(r), \end{aligned} \quad (5)$$

where $u(R, x)$ and $T_c(x)$ are the given gas flow velocity and temperature at the tube wall; and $T_o(r)$ and $u_o(r)$ are the initial gas flow uniform temperature and velocity distribution at the inlet of the tube, respectively. The effect of minor gaseous admixtures (vapor of the substance under investigation) on the density, heat capacity, viscosity, and heat conductivity of the carrier gas was neglected. The velocity and temperature space distribution for the carrier gas were found by numerical solution of the Navier–Stokes Eqs. (1)–(4) with the boundary conditions (5) by the finite-difference method.

Vapor diffusion in a steady-state laminar flow of a viscous gas within a cylindrical tube was described for the system under investigation by the molecular diffusion equation; in the cylindrical coordinate system, it assumes the form

$$\rho u \frac{\partial C}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \rho D \frac{\partial C}{\partial r} \right). \quad (6)$$

This equation was solved by the finite-difference method under the boundary conditions

$$\begin{aligned} C(R, x) &= C^0(T_c), \\ \left. \frac{\partial C}{\partial r} \right|_{r=0} &= 0, \quad C(r, 0) = C^*(r). \end{aligned}$$

Here, C is the mass concentration of the vapor of substance under investigation; D is the molecular diffusion coefficient; $C^0(P, T_c)$ is the concentration of saturated vapor at the tube wall (the walls of the tube are assumed to be covered with the glycerin film); and $C^*(r)$ is the initial uniform concentration profile for vapor at the inlet of the tube. The flow velocity distribution in the tube inlet cross section was assumed to be a Poiseuille's profile. The viscosity of carbon

dioxide η ($\text{Pa} \times \text{s}$) was calculated using an approximation equation, obtained on the basis of handbook data⁷

$$\eta = -5.0373 \times 10^{-7} + 5.687 \times 10^{-8} T - 1.729 \times 10^{-11} T^2.$$

The activity of glycerin vapors $a(r, x)$ was evaluated by using the temperature $T(r, x)$ and concentration $C(r, x)$ distribution as

$$a(r, x) = \frac{C(r, x)}{C^0(r, x)},$$

where $C^0(r, x)$ is the equilibrium concentration of saturated glycerin vapor at the temperature $T(r, x)$.

The pressure of saturated glycerin vapors,⁹ P (mm Hg), was approximated by the Clapeyron equation $\log(P) = A - B/T$, where $A = 11.44$ and $B = 4532$ for conditions of these experiments.

The diffusion coefficient D (cm^2/s) was calculated for the glycerin–carbon dioxide binary gas system by using the empirical correlation by Fuller, Schettler, and Giddings^{10(a)}

$$D = 3.3979 \cdot 10^{-6} \frac{T^{1.75}}{P},$$

where P is expressed in bar. The heat conductivity λ ($\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$) of carbon dioxide was approximated by an equation

$$\lambda = T^{1.75} (P \times e + k) + (P^2 \times l + Pm + n),$$

based on the published data,¹¹ where $e = -4.41995 \times 10^{-9}$, $k = 5.7498 \times 10^{-7}$, $l = 9.5477 \times 10^{-7}$, $m = 1.5510 \times 10^{-4}$, $n = 4.0693 \times 10^{-3}$, P is expressed in physical atmospheres. The maximum rate of aerosol particle formation was calculated by using the algorithm developed for the flow diffusion chamber by Wagner and Anisimov¹²

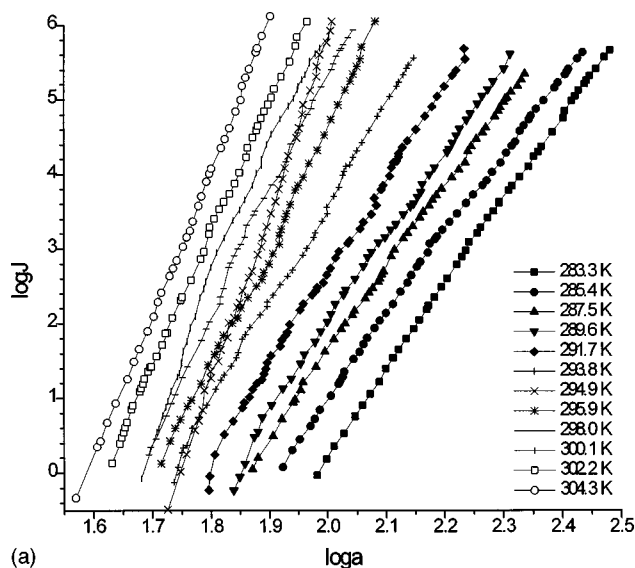
$$J_{\text{exp}}^{\text{max}} = \frac{N_{\text{exp}} J_{\text{theor}}^{\text{max}}}{\int J_{\text{theor}} dv},$$

where N_{exp} and $\int J_{\text{theor}} dv$ are the experimental and theoretical numbers of particles produced by the aerosol generator per unit time, respectively; $J_{\text{theor}}^{\text{max}}$ is the maximum of the theoretical nucleation rate in the experimental device. The theoretical nucleation rate was calculated by using the classical nucleation theory¹³

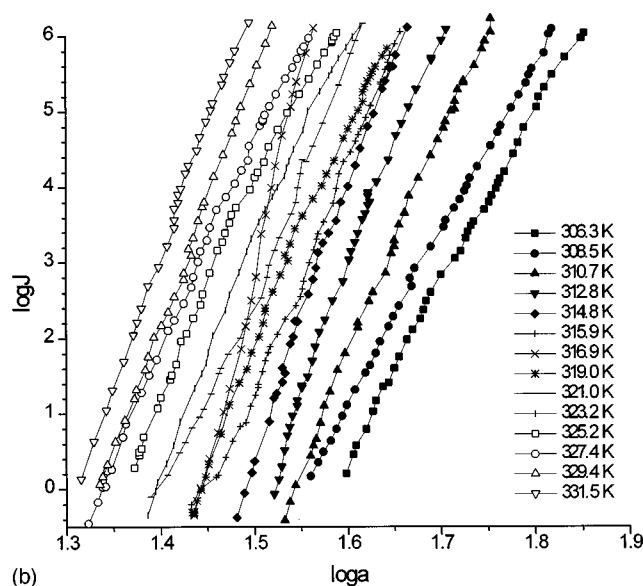
$$J_{\text{theor}} = \frac{V}{(kT)^2} \sqrt{\frac{2\sigma}{\pi \cdot m}} \cdot P^2 \cdot \exp \left(-\frac{16\pi \cdot \sigma^3 \cdot V^2}{3(kT)^3 \cdot (\ln S)^2} \right).$$

where σ is the surface tension; m , V are molecular mass and volume, and $\ln S$ is the vapor supersaturation (or vapor activity).

The relative error for vapor activity a and nucleation temperature T did not exceed 2% to 3%. By determining the nucleation rate with high relative accuracy, it is possible to detect the critical embryo phase transitions with confidence. The absolute error was some percents larger than the relative error due to inaccuracy of thermophysical constants. The total relative error for the nucleation rate J was about 25% or 0.1 decimal order.



(a)



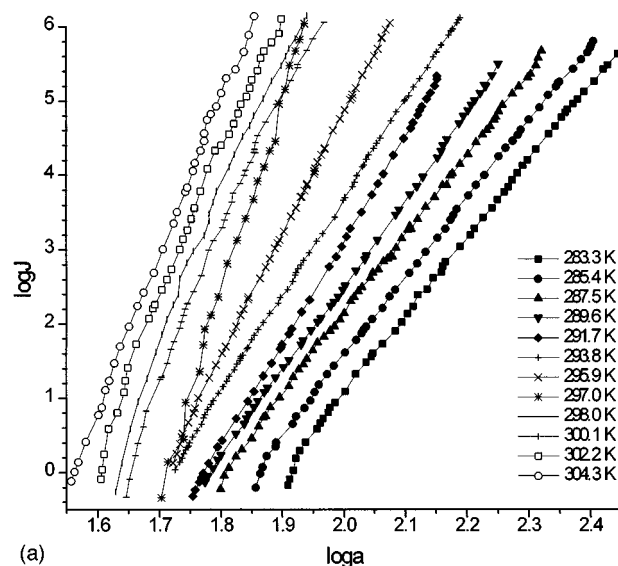
(b)

FIG. 2. (a) and (b) Glycerin nucleation rate, J , on the vapor activity, a , at total pressure $P=0.10$ MPa.

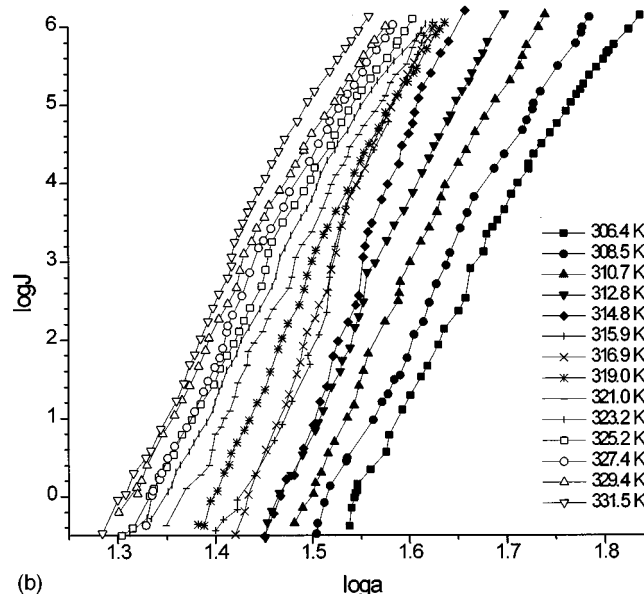
III. EXPERIMENTAL RESULTS AND DISCUSSION

Isothermal nucleation of supersaturated glycerin vapors in the carbon dioxide atmosphere was studied in the temperature interval of 283.2–331.4 K at the total pressures $P=0.10, 0.20$, and 0.30 MPa. Figures 2–4 display the experimental nucleation rates, $\log J$, versus activity of glycerin vapors, $\log a$, at different nucleation temperatures and total pressures.

The experimental glycerin vapor activity on nucleation temperature at fixed nucleation rates ($\log J=2.0; 4.0$) is shown in Figs. 5(a)–5(c). The singularity temperature behavior for vapor activity allows identification of two-phase transitions in the condensate. One of them is two degrees centigrade higher than the equilibrium bulk glycerin melting–freezing temperature in CO_2 atmosphere at the total pressure of 0.10 MPa. We suggest that this singularity identifies the phase transition with glycerin embryos freezing–melting. The narrow temperature interval (2–6 °C) of phase transi-



(a)



(b)

FIG. 3. (a) and (b) Glycerin nucleation rate, J , on the vapor activity, a , at total pressure $P=0.20$ MPa.

tions, shown by the shaded strips in Figs. 5(a)–5(c), illustrate the low ability of condensate embryos to be in metastable liquid and crystal states. By application of the equation¹⁴

$$\left(\frac{\partial \ln J}{\partial \ln a} \right)_{T,P} = n + 2,$$

the number of glycerin molecules (n^*) in critical embryos was evaluated. Results are presented at the same Figs. 5(a)–5(c) by diamond-shaped signs. It can be seen that in the vicinities of the phase-transition temperatures, there are anomalous jumps in the embryo sizes.

As mentioned above, a glycerin first-order phase-transition higher than the glycerin melting point is unknown. Phase transitions were found at temperatures higher than the glycerin melting point. The temperature of this second transition comes nearer to the carbon dioxide critical temperature when the carbon dioxide partial pressure is higher. For these two reasons, the second break on the $\log a(T)$ curve should

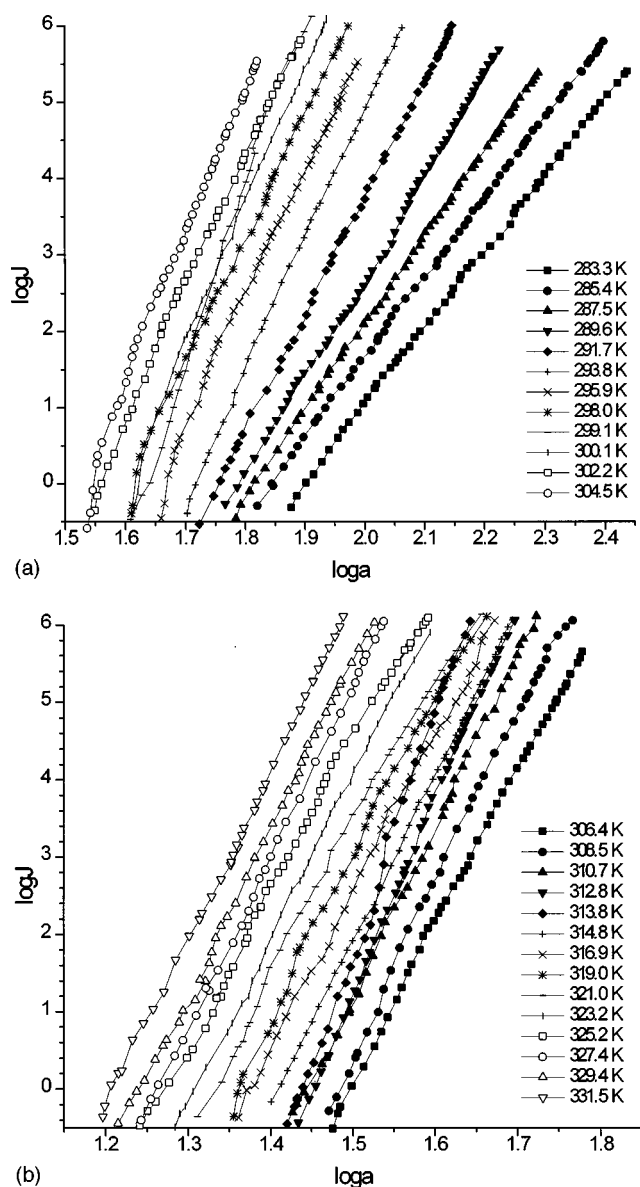


FIG. 4. (a) and (b) Glycerin nucleation rate, J , on the vapor activity, a , at total pressure $P = 0.30$ MPa.

be identified as the phase transition related with the critical point of carbon dioxide. This result indicates that carbon dioxide is incorporated inside the critical embryos of the system under investigation. Because the experiment shows that carbon dioxide exists inside embryos of the new phase, systems such as carbon dioxide–glycerin should be considered as being binary systems.

As shown in Figs. 5(a) and 5(b), the phase-transition temperatures for single CO_2 and glycerin phase transitions and the experimental values for the system under investigation increase to 7° when the CO_2 atmosphere pressure increased up to 0.30 MPa. The break related with the melting point shifts to higher temperatures when the total pressure increases (at the system pressure $P = 0.10$ MPa: 293.8–295.9 K; at the pressure $P = 0.20$ MPa: 295.9–298.0 K; under $P = 0.30$ MPa: 298.0–300.1 K). The temperature interval of the next phase transition has the opposite trend: With increasing pressure, the phase-transition temperature is low-

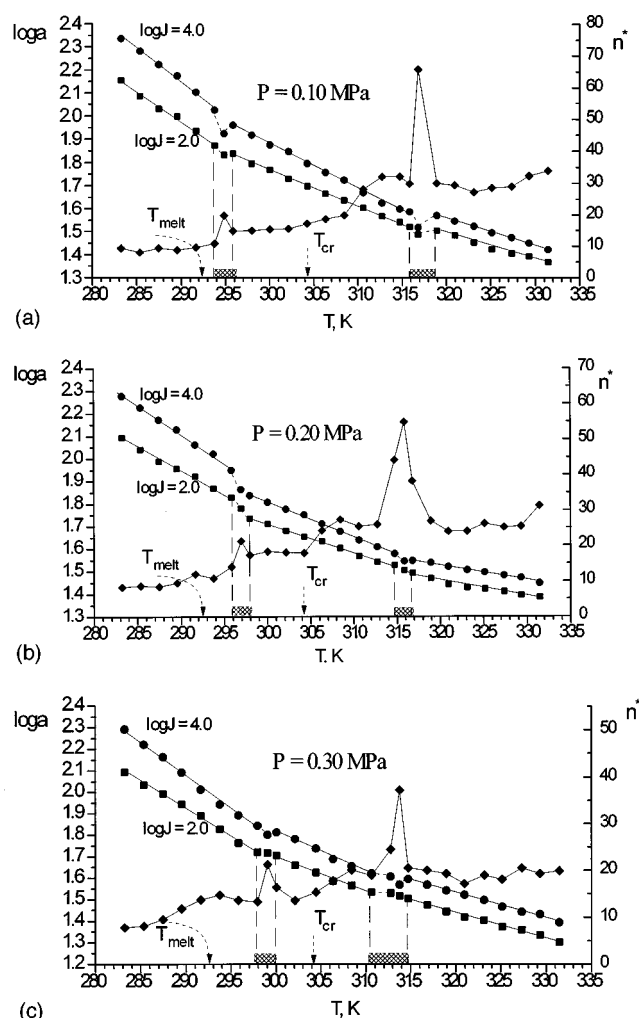


FIG. 5. (a)–(c) The experimental glycerol vapor activities, a , on nucleation temperatures, T , at fixed nucleation rate $\{lg J = 2.0$ (■); 4.0 (●) $\}$ and total pressures $P = 0.10, 0.20, 0.30$ MPa. The number of glycerin molecules, n^* , in critical embryos vs the nucleation temperature, T , at $lg J = 3.0$.

ered (at the system pressure $P = 0.10$ MPa: 315.9–319.0 K; at the pressure $P = 0.20$ MPa: 314.8–316.9 K; and at $P = 0.30$ MPa: 310.7–314.8 K).

The supercooled vapor could produce supercooled liquid glycerin. This should reduce the temperature for freezing of glycerin as in the case, for example, of freezing of $\text{C}_6\text{F}_5\text{OH}$ ¹⁵ and other compounds. The experimental results show the opposite trend for the glycerin–carbon dioxide system. The phase-transition latent heat cannot initiate the trend in these experiments. This heat is insufficient to increase the cluster temperature, because the CO_2 and glycerin partial pressure differ by four orders of magnitude. The correspondingly higher CO_2 collision frequency with growing clusters avoids superheating of the new phase embryos.

At critical conditions (critical point or critical line, for binary system), phase transitions of the second order take place. At the critical condition, the surface tension and nucleation rate drop to zero, because phase transitions of the second order have no different phases nor any interface surfaces. Nonzero nucleation rates correlated with the critical line of the carbon dioxide–glycerin system were measured in

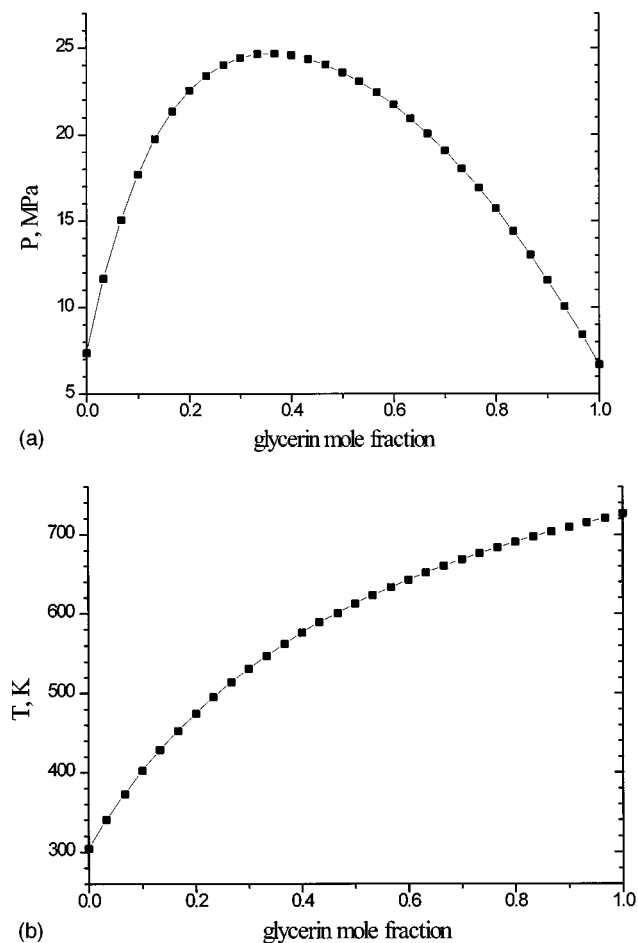


FIG. 6. (a) Carbon dioxide-glycerin system critical pressure, P , and (b) temperature, T , on glycerin mole fraction.

the given research. This means that the nucleation conditions for this phase transition are under critical. It is also obvious that the detected phase transition is of the first order, because the smallest deviation to lower temperature from a vapor-liquid critical condition temperature leads to phase transitions of the first order.

Critical points for single components in the case of a binary system produce the critical line from one to another critical point. The method offered by Li, Kreglewski, and Kay^{10(b)} was used to evaluate the critical line temperatures and pressures for the system glycerin-carbon dioxide versus composition are presented in Fig. 6. One can see that the system critical pressures do not exceed 25 MPa, which is much less than our estimation of critical embryo pressure, 40 MPa, in a droplet approximation with a surface tension of bulk glycerin. This means that the surface tension of critical embryos is smaller than the bulk glycerin surface tension. In approximation of the bulk liquid density, the critical embryo surface tension is smaller by 38% than the bulk glycerin surface tension.

As mentioned above, the Laplace pressure in critical embryos of glycerin is high enough to establish conditions of critical embryo formation near the critical pressure. Lowering of the second phase-transition temperature with increasing mole fraction of the carrier gas was observed. It can be

seen from Figs. 5 and 6 that lowering the phase-transition temperatures has good correlation with lowering of the critical line temperature with increasing gas-carrier pressure (or mole fraction). We should note here that phase-transition temperature can only have correlation with the critical temperature of the system under investigation. We have insufficient knowledge about the pressure and composition of new phase embryos for more careful analysis. On the other hand, the relationship of the second phase transition with the critical line of the glycerin-carbon dioxide system is very clearly shown in our experiments. Such system behavior has good qualitative agreement with the calculated trend for critical temperature of a binary system [Fig. 6(b)]. This conclusion is in agreement with preliminary results of the glycerin-sulfur hexafluoride system,^{16,17} where a phase transition of critical embryos was detected too.

During the last decade, there has been discussion of the role of the carrier or background gas and the effect of its pressure. For example, Katz *et al.*^{18,19} have observed a gas pressure effect on vapor critical supersaturation. With results given here, the validity of interpretation of glycerin vapor nucleation in helium, argon, and nitrogen atmospheres in the approximation of binary ideal solutions²⁰ increases. Heist *et al.*²¹ have reported strong effects of pressure and the nature of the carrier gas on vapor nucleation rates at pressures up to 40 bar. On the other hand, good quality measurements with expansion chambers have shown no effects of the nature of the background gas on nucleation rates.^{22,23} Wagner *et al.*²² conclude that there is no influence of the carrier gas on the vapor nucleation. All of the carrier gas effects on nucleation can be explained by the thermal effects of nucleation and the kinetic properties of a nucleated vapor gas mixture. To test this point a special analysis of heat-mass transfer in a cloud diffusion chamber was done.²⁴

Seemingly, the results of our research contain enough evidence for the point of view that vapor nucleation in a gas atmosphere is binary nucleation. In a common case of vapor-gas nucleation, the presence of the critical line for a binary vapor-gas system should be found. Ideas of the topology of the equilibrium interface surfaces for binary (or multicomponent) phase state diagrams described, for example, by Prausnitz *et al.*^{10(c)} should be involved for interpretation of a vapor-gas nucleation rate surfaces.

In Fig. 7 is shown comparison of the experimental nucleation rates with classical nucleation theory at four nucleation temperatures and a total pressure 0.10 MPa. It can be seen that experimental curves at 327 and 304 K could be theoretically described by fitting the theory parameters. For example, surface tension variations of 0.1%–0.3% can change the theoretical nucleation rate by some orders of magnitude. The next two experimental curves could be fit only with considerable change in the number of molecules in the new phase embryos. Using the surface tension of bulk liquid could lead to considerable contradictions of classical theory with experimental results on nucleation rates, when the critical line for the vapor-gas system limits the critical embryos nucleation conditions. The surface tension for critical embryos should be used in the approximation of a binary sys-

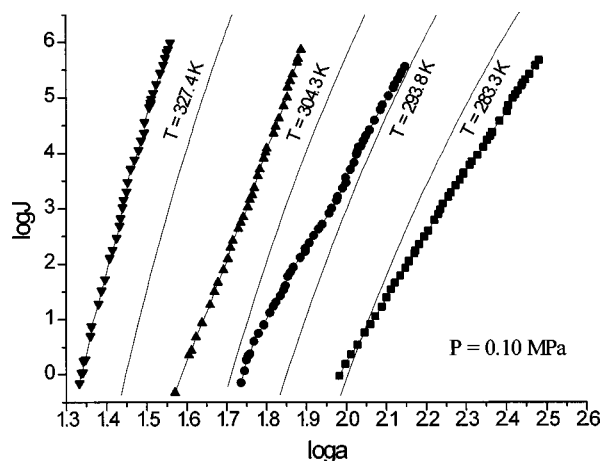


FIG. 7. Comparison of experimental nucleation rates, J , vs glycerin vapor activity, a , of carbon dioxide-glycerin system with classical nucleation theory (Ref. 13) at total pressure $P=0.1$ MPa.

tem. This will lead to considerable progress in classical theory application.

IV. CONCLUSION

Using a flow diffusion chamber, one can measure vapor nucleation rates with high precision and detect phase transitions in critical embryos containing two and more dozen molecules. Related with the glycerin- CO_2 critical line, a phase transition can be used as a marker to demonstrate that CO_2 exists in critical embryos of condensate. In our opinion, results of this research very clearly demonstrate that vapor nucleation in a gas atmosphere is binary nucleation and must be interpreted by using formalism of a binary system. Supercritical nucleation is a virtual term born by interpretation of binary vapor-gas nucleation in the approximation of a single component. It is well known that nucleation can take place only under the critical condition, because a supercritical fluid has no ability to be heterogeneous. The critical condition for the binary system could be higher than the single component critical pressure or/and temperature. This can produce the illusion of supercritical nucleation. One component interpretation for a vapor-gas nucleation could be used if one has evidence that a carrier gas influence on nucleation is small enough to use the one component nucleation theory for the description of experimental results. On the other hand, the Laplace pressure is practically always able to produce near critical pressure. This level of detail is a problem for future studies. The traditional application of classical nucleation theory for the vapor-gas nucleation will be modified by consideration of nucleation conditions in the pressure-temperature-composition space.²⁵

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