KINETIC MODEL OF THE CONDENSATION OF A SUPERSATURATED GAS

V. K. Konyukhov and V. N. Faizulaev

UDC 539.196.198

In recent years there has been increased interest in the investigation of the microscopic picture of phase transitions in a supersaturated gas [1-3]. The reason for this is that in a number of cases (condensation of gas in supersonic nozzles of rocket engines and gasdynamic lasers, in wind tunnels) the role of the initial stage of nucleation is decisive for the process of condensation of the supersaturated gas. The theoretical kinetics of this stage of nucleation have not been extensively studied. The formulation and solution of problems related to the investigation of condensation kinetics have not gone essentially beyond the limits of the classical drop–liquid theory of nucleation [4], the foundations of which were laid in [5-7]. Thus, in [8-11], in the analysis of the nonstationary condensation process, use was made of a macroscopic description of the kinetics of nucleus formation and disintegration, which is not suitable for particles of small dimensions. The method most fully developed today is the statistical method of calculation of equilibrium concentrations of nuclei in a supersaturated gas [12-14]. However, within the limits of the classical theory [4] it cannot be used for analyzing the initial stage of nucleation.

The purpose of the present paper is to develop a kinetic model of nucleation that takes account of the characteristics of the process of association and dissociation of complexes of small dimensions [15].

§1. The classical theory is based on the assumption that it is possible to give a thermodynamic description of the state of a heterogeneous system consisting of molecules of supersaturated gas and nuclei of a liquid phase. It is assumed that the nuclei, present in a small concentration in the gas, are in thermal equilibrium with it, and the rates of the processes

$$A_{g-1}+A_1\xrightarrow{R_g}A_g,\quad A_g\xrightarrow{K_g}A_{g-1}+A_1 \tag{1.1}$$

of nucleus formation R_g and nucleus disintegration K_g satisfy the relation

$$N_{g-1}R_g=N_gK_g,\quad N_g=N_1^0\exp\left(-\Delta\Phi(g)/T\right), \tag{1.2}$$

which reflects the principle of detailed equilibrium for a stable heterogeneous system, where N_g, $\Delta\Phi(g)$ are the equilibrium concentration and free energy of the formation of a nucleus A_g from g molecules of A_1 at a degree of supersaturation of the gas $S=N_1/N_1^0$; N_1^0 is the concentration of molecules of saturated gas at temperature T. The reciprocal conversions of nuclei in the processes (1.1) are accompanied by a change in their internal energy ε, which is determined by the value of the binding energy (association energy) U_g of one molecule in the complex A_g. Thermodynamic equilibrium in the heterogeneous gas–nucleus system will exist only in the case when the processes (1.1) take place slowly in comparison with the process of heat exchange of the nuclei with the gas thermostat $R_g, K_g \ll Z_g^V$, where $Z_g^V=\alpha_V Z_g$; Z_g is the frequency of collisions of a nucleus with molecules of gas; α_V is the accommodation coefficient characterizing the effectiveness of the energy exchange between them.

This circumstance is usually overlooked when it is assumed [8-11] that the growth of nuclei in the association takes place as rapidly as the growth of macroscopic particles in the condensation of gas molecules on their surfaces $R_g=\alpha_a Z_g$, where α_a is the coefficient of adhesion of the molecules to the surface of the macroscopic liquid or solid body [16]. Such a definition of the growth rate R_g in the general case contradicts the assumption of the theory [4] that the nuclei are in thermal equilibrium with the gas. To see this, we note that from the relation (1.2) for a nucleus simulated by a spherical drop of liquid with a surface-tension energy $\mu g^{2/3}$ and $\Delta\Phi(g)=gT\ln S+\mu g^{2/3}$ it follows that the rate of vaporization of small particles A_g of subcritical

---

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 3, pp. 41-47, May-June, 1977. Original article submitted May 25, 1976.

dimensions [4], $K_g = R_g \exp[(g^{-1/3} - g_*^{-1/3})2\mu/3T]$, can be substantially greater than their growth rate, $K_g \gg R_g$, where $g_* = (2\mu/3T \ln S)^3$ is the critical nucleus dimension corresponding to the maximum free energy. If we take $\alpha_a \sim \alpha_v \sim 1$, we find that all the particles with such dimensions should vaporize faster than they collide with the gas molecules, and consequently they cannot be in thermal equilibrium with the gas. This erroneous conclusion resulted from the use for particles of all dimensions of the model of [4], in which it is assumed that with respect to the vaporization or condensation of molecules, a nucleus behaves like a thermostat of macroscopic dimensions. For particles of small dimensions, which do not have a large equilibrium reserve of internal energy, such an approach is unsuitable; for these the role of a thermostat is played by the gas molecules. The kinetics of the formation and disintegration of particles of small dimensions is determined by the course of the elementary processes in the gas and may be substantially different from what is considered in the classical theory.

§2. Let us consider a kinetic model of the initial stage of complex-formation in a supersaturated gas. We shall treat the processes (1.1) as chemical reactions taking place by way of an intermediate unstable complex (a complex with a tendency to spontaneous disintegration) A_g^*. In the case of an association reaction, it is formed as a result of the adhesion of the molecules to a stable complex (with no tendency to spontaneous disintegration) A_{g-1}:

$$A_{g-1} + A_1 \rightarrow A_g^*, \tag{2.1}$$

when the thermal energy E and the association energy U_g of the condensing molecule are completely converted into the energy ε of the internal degrees of freedom of the complex A_g^*; and the latter is therefore in a superexcited state, $\varepsilon \geq U_g$. If after a lifetime τ_g^* in the superexcited state, which is determined by the probability of the breakdown of some intermolecular bond, the unstable complex undergoes a deactivating collision with a gas molecule

$$A_g^* + A_1 \rightarrow A_g + A_1,$$

then it is converted to a stable complex A_g which is the final product of the association reaction (1.1). The reaction of dissociation of stable complexes (1.1) takes place in a similar manner. Initially in the process of activating collisions with gas molecules

$$A_g + A_1 \rightarrow A_g^* + A_1 \tag{2.2}$$

there is an excitation of the stable complex A_g to the state A_g^* with energy $\varepsilon \geq U_g$, and afterward there is spontaneous disintegration

$$A_g^* \rightarrow A_{g-1} + A_1$$

with the formation of the end product of the reaction, A_{g-1}. In this model the rate of association of stable complexes corresponds to the growth rate of nuclei of small dimensions, and the rate of their collision dissociation corresponds to the rate of vaporization.

§3. The calculation of the association and dissociation rates of stable complexes can be carried out most simply by using an approximation to the mechanism of strong collisions that is known from the theory of monomolecular reactions [17]. We denote by $k_g(\varepsilon)$ the rate of spontaneous disintegration of the unstable complex A_g^* with an energy of excitation of intermolecular oscillations $\varepsilon \geq U_g$ [when $\varepsilon < U_g$, $k_g(\varepsilon) = 0$], and we denote by $f_g'(\varepsilon)$, $f_g''(\varepsilon)$ the nonequilibrium energy distribution functions for the unstable complexes formed in the processes of collision activation (2.2) and adhesion (2.1), respectively. The possibility of subdividing the unstable particles into groups, each of which is characterized by its distribution function, is due to the fact that the excited complexes generated in the gas thermostat do not interact with one another.

For the statistical model of the disintegration of unstable complexes simulated by the system s_g of harmonic oscillators of identical frequency ν_g, the expression for $k_g(\varepsilon)$ has the form [17]

$$k_g(n) = \nu_g \Omega_g(n - n_U)/\Omega_g(n), \quad \Omega_g(n) = (n + s_g - 1)!/n!(s_g - 1)!,$$
$$n_U = U_g/h\nu_g,$$

where $\Omega_g(n)$ is the multiplicity of degeneration of the energy level $\varepsilon = nh\nu_g$ of the oscillatory system. The spontaneous-disintegration constant $k_g(n)$ is obtained on the assumption of randomness for the redistribution of energy over the oscillatory degrees of freedom of the complex. It is interpreted as the probability of fluctuation at which an energy greater than the association energy is concentrated at the oscillator simulating the dissociating bond. For a quasistationary description of the reactions (1.1) the rates of collision dissociation K_g and association R_g of the stable complexes A_g are defined as follows:

$$K_g = \sum_{n=n_U}^{\infty} f'_g(n)\, k_g(n), \quad R_g = \sum_{n=n_U}^{\infty} f''_g(n)\, Z_g^{\mathrm{V}}. \tag{3.1}$$

In the approximation for the mechanism of strong collisions

$$f'_g(n) = f_g^0(n)\, Z_g^{\mathrm{V}} / \left(Z_g^{\mathrm{V}} + k_g(n)\right), \tag{3.2}$$

where Z_g^{V} is the frequency of deactivating collisions; $f_g^0(n)$ is the equilibrium distribution function of the complexes with respect to energy. From the principle of detailed equilibrium it follows that

$$N_{g-1} f''_g(n)\, Z_g^{\mathrm{V}} = N_g f'_g(n)\, k_g(n). \tag{3.3}$$

Taking account of (3.2), (3.3), by substituting the expressions for $k_g(n)$ and the equilibrium distribution function

$$f_g^0(n) = \Omega_g(n) \exp(-\theta n)/F_g, \quad F_g = (1 - \exp(-\theta))^{-s_g}, \quad \theta = h\nu_g/T$$

into (3.1), we obtain a formula for the reduced reaction rate [17]:

$$\varphi_g = \frac{1}{F_g} \sum_{n=0}^{\infty} \Omega_g(n) \exp(-\theta n) \left[1 + \nu_g \Omega_g(n) / Z_g^{\mathrm{V}} \Omega_g(n + n_U)\right]^{-1}. \tag{3.4}$$

To the limiting values of the dissociation rate $K_g = K_g^{\infty} \varphi_g$ and the association rate $R_g = R_g^{\infty} \varphi_g$ of the stable complexes there correspond the quantities $K_g^{\infty} = \nu_g \exp(-\theta n_U)$, $R_g^{\infty} = \alpha_{g-1}^{a} Z_{g-1}$, which are realized in the case $\langle \tau_g^* \rangle Z_g^{\mathrm{V}} \gg 1$, where $\langle \tau_g^* \rangle = \delta_g^0 / K_g^{\infty}$ is the average lifetime; $\delta_g^0 = \sum_{n=n_U}^{\infty} f_g^0(n)$ is the equilibrium fraction of unstable particles in the gas. Under conditions of thermal equilibrium between the value of the coefficient of adhesion of the molecules to the complexes α_{g-1}^{a} and the frequency factor ν_g there exists a relation defined by formula (1.2). If $\langle \tau_g^* \rangle Z_g^{\mathrm{V}} \ll 1$, then the reaction rates, according to (3.4), are considerably less than their limiting values $\varphi_g = \langle \tau_g^* \rangle Z_g^{\mathrm{V}}$ and depend substantially on the particle dimensions. For $Z_g^{\mathrm{V}} / K_g^{\infty} \gg 1$ this case is possible only for particles of small dimensions $g \leq g_0$, $s_{g0} \simeq n_U(\exp(\theta) - 1)/3$, which do not have a large equilibrium reserve of oscillatory energy. The dissociation of such complexes follows the kinetic law for a second-order reaction and the association, that of a third-order reaction.

§4. Let us consider how the characteristics of the reactions (1.1) affect the kinetics of the condensation process and the energy distribution of the particles in the heterogeneous system of a supersaturated gas. We shall confine ourselves to analyzing the equations for concentrations c_g of particles of subcritical ($g < g_*$) and supercritical ($g > g_*$) dimensions

$$dc_g/dt = I_g - I_{g+1}, \; I_g = c_{g-1} R_g - c_g K_g, \; 2 \leqslant g \leqslant G$$

in the stationary approximation. We assume that the particles of supercritical dimensions beyond some value G are removed from the heterogeneous system $c_{G+1} = 0$ and are replaced by an equivalent number of gas molecules. The critical dimension g_* will be taken to be the minimum dimension of nuclei capable of systematic growth, $g > g_*$, $R_g > K_g$, in the supersaturated gas. In the region $g < g_*$, where $R_g < K_g$, the stationary distribution of nucleus concentrations with respect to dimensions is close to the equilibrium distribution $c_g \simeq N_g$, since it is determined preferentially by the balance of particles in the association and dissociation reactions, $A_{g-1} \rightleftharpoons A_g$, whose velocities in the thermal-equilibrium gas are related to each other by the principle of detailed equilibrium (1.2). Making use of the relation $I_g = I_{g+1} = I_0$, we can represent this distribution in the form

$$c_g = N_g - \sum_{m=1}^{g-1} C_m \prod_{j=m+1}^{g} R_j/K_j, \quad N_g = N_1 \prod_{j=2}^{g} R_j/K_j, \quad C_m = I_0/R_{m+1},$$

where $I_0 = r_G = \left(\sum_{j=1}^{G} 1/N_j R_{j+1} \right)^{-1}$ is the stationary rate of condensation of the supersaturated gas, or the rate of formation of condensation nuclei A_G [6].

The kinetics of the initial stage of complex-formation is essential for the process of condensation only during the period of time until a stationary distribution of nuclei with respect to dimensions is established. The length of this period $\tau_L = \sum_{g=2}^{g_*} c_g / r_{g-1}$ determines the delay of the process of condensation of the supersaturated gas $I(t) \approx I_0 \exp(-\tau_L/t)$ [8]. Since reactions involving subcritical particles of small dimensions ($g \leq g_0$)

take place slowly, the delay of the condensation process at the initial stage of complex-formation may be quite significant.

An estimate shows that for supersaturated water vapors S=60, T=240°K ($g_0=4$, $g_*=8$), the delay time due solely to the establishment of a stationary concentration of stable dimers ($U_2=2500$°K, $s_2=6$, $\nu_2=6\cdot 10^{12}$ sec^{-1}, $K_2=10^5$ sec^{-1}) is 10^{-5} sec. If these conditions are realized, for example, for the flow of a gas through a supersonic nozzle, then the length of the zone corresponding to the induction period of the condensation process is found to be more than 1 cm. In the region $g > g_*$, where $R_g > K_g$, the stationary distribution of particles with respect to dimensions is determined preferentially by the balance of the particles in the processes of stepwise association, $A_{g-1} \rightarrow A_g \rightarrow A_{g+1}$, and therefore it is a nonequilibrium distribution:

$$c_g = C_g + \sum_{m=1}^{G-g} C_{g+m} \prod_{j=1}^{m} K_{g+j}/R_{g+j}.$$

The nonequilibrium nature of the distribution of supersonic particles with respect to dimensions results in a nonequilibrium distribution of particles with respect to energy as well. We shall characterize the distribution of particles with respect to energy by the relative occupancy of the unstable states, δ_g^*:

$$\delta_g^* = \delta'_g + \delta''_g, \quad \delta'_g = \sum_{n=n_U}^{\infty} f'_g(n), \quad \delta''_g = \sum_{n=n_U}^{\infty} f''_g(n)\, c_{g-1}/c_g.$$

Then from (3.1), (4.1) it follows that the fraction of unstable particles of subcritical dimensions, $\delta_g^* \simeq \delta'_g + K_g/Z_g^{V}$, is close to the thermal-equilibrium fraction δ_g^0, and for $g \leq g_0$ this is known to be small, $\delta_g^* \ll 1$. For supercritical particles of small dimensions, for strong supersaturation of the gas ($S \gg 1$), when $R_g \gg K_g$, this can be substantially greater than the thermal-equilibrium value $\delta_g^* \simeq \delta'_g + R_{g+1}/Z_g^{V} \gg \delta_g^0$. The appearance in the supersaturated gas of a large number of nonequilibrium excited complexes makes it possible, in principle, to use their energy for generating laser radiation on the oscillatory transitions of intermolecular types of oscillations [18]. From this point of view, it is of interest to investigate the regime of extremely strong supersaturations of the gas, at which the nonequilibrium nature of the energy distribution may be manifested for supercritical complexes of small dimensions of the dimer and trimer types, which in the unstable state have the highest level of excitation of intermolecular oscillations.

§5. Let us consider the question of the mechanism of association of the excited molecules and the effect of the nonequilibrium distribution of the molecules with respect to different degrees of freedom upon the kinetics of condensation of the supersaturated gas. It should be borne in mind that the process of association of a molecule of a complex takes place in two phases which have different time scales: The first phase includes the capture (adhesion) of the molecule as a result of an inelastic collision of the molecule with the complex, where a portion $\Delta E'_0$ of the kinetic energy of motion of the molecule E_0 in the gravitational field U, $E'_0 = E_0 + U$, is converted into the energy of intermolecular oscillations of the complex. The capture of the molecule is possible [16] if the energy of relative motion of the participating entities after the collision is less than the gravitational energy. After this there is a relatively lengthy phase in which the newly formed complex remains in an unstable state. The lifetime of this complex depends on the energy of the translational (E_0) and rotational (E_R) degrees of freedom of the associated molecule which is converted into intermolecular oscillations. With increasing excitation energy ε, the lifetime τ_g^* of the unstable particles of small dimensions is sharply reduced, and therefore the presence of a nonequilibrium reserve of rotational energy of the molecules may have a substantial effect on the reduced rate of association in the initial stage of complex formation.

The resulting reduction in the rate of association of stable particles of small dimensions may lead, in accordance with (4.1), to a reduction (in comparison with equilibrium conditions) of the concentration of nuclei of critical dimensions and of the rate of condensation of the supersaturated gas. A reduction in the rate of association in a thermal-equilibrium gas may also be brought about by a reduction (owing to an excess of excited molecules) of the adhesion coefficient α_g^a. The reason for this is that the probability of capture of a rotationally excited molecule, $\alpha_a(E)$, is less than the probability, $\alpha_a(E_0)$, for an unexcited molecule, $\alpha_a(E) \approx \alpha_a(E_0)(1 - P(E, \Delta E_R))$, where $P(E, \Delta E_R)$, ΔE_R, are the probability of deactivation of a molecule and the value of the excitation energy. Here account has been taken of the fact that the generation of the energy $\Delta E_R \geq \Delta E'_0$ of the excited molecule at the moment of collision with the complex interferes with its capture by the gravitational potential. A similar definition applies to the probability of capture of oscillatorily excited molecules.

As was shown in [19], the probability of oscillatory deactivation of a molecule upon collision with a complex which has a deep gravitational potential may be quite high, $P \sim 10^{-2} - 1$. If upon collision the excited molecule is not deactivated, then the probability of its capture by the gravitational potential of the complex is $\alpha_a(E_0)$.

As a result of the weak interaction between the intramolecular and intermolecular oscillations, the energy of oscillatory excitation of the molecule may, after a time τ^*, be localized in the bond which has held it in the complex. Since the attenuation of the intramolecular oscillations is slow in comparison with the spontaneous disintegration of the unstable complexes of small dimensions, $\tau^* \gg \tau_g^*$, the oscillatory deactivation of the excited molecule in the bound state will not have any substantial effect on the process of association. However, if it is accompanied by the generation of energy $\Delta E_V > U_g$, it may cause a noncollision dissociation of stable complexes. In this case the dissociation of the complex takes place with rupture of the bond uniting it with the excited molecule, not of any other bond, as happens in the case of spontaneous disintegration of unstable complexes. The above facts may be utilized for heterogeneous separation of selectively excited isotopically displaced molecules [20].

LITERATURE CITED

1. D. Colomb, R. E. Good, and R. F. Brown, "Dimers and clusters in free jets of argon and nitric oxide," J. Chem. Phys., 52, No. 3, 1545 (1970).
2. T. A. Milne, A. E. Vandergrift, and F. T. Green, "Mass-spectrometric observations of argon clusters in nozzle beams. Kinetics of dimer growth," J. Chem. Phys., 52, No. 3, 1552 (1970).
3. W. G. Dorfeld and J. B. Hudson, "Condensation in CO_2 free jet expansion. Dimer formation. Growth of small clusters," J. Chem. Phys., 59, No. 3, 1235-1255 (1973).
4. Ya. I. Frenkel', Kinetic Theory of Liquids [in Russian], Izd. Akad. Nauk SSSR, Moscow (1945).
5. M. Volmer and A. Weber, "Keimbildung in übersättigten Gebilden," Z. Phys. Chem., 119, 277 (1926).
6. R. Becker and W. Döring, "Kinetische Behandlung der Keimbildung in übersättigten Dämpfen," Ann. Phys., 24, 719 (1935).
7. Ya. B. Zel'dovich, "On the theory of formation of a new phase. Cavitation," Zh. Éksp. Teor. Fiz., 12, No. 11-12, 525 (1942).
8. A. Kantrovits, "Nucleation in very rapid vapor expansions," J. Chem. Phys., 19, No. 9, 1097 (1951).
9. H. L. Frisch, "Time lag in nucleation," J. Chem. Phys., 27, No. 1 (1957).
10. W. G. Courtney, "Non-steady-state nucleation," J. Chem. Phys., 36, No. 8, 2009 (1962).
11. R. P. Andres and M. Boudart, "Time lag in multistate kinetics: nucleation," J. Chem. Phys., 42, No. 6, 2057 (1965).
12. J. Lothe and G. M. Pound, "Reconsiderations of nucleation theory," J. Chem. Phys., 36, No. 8, 2080 (1962).
13. H. Reiss, J. L. Katz, and E. R. Cohen, "Translation–rotation paradox in the theory of nucleation," J. Chem. Phys., 48, No. 12, 5553 (1968).
14. B. N. Hale and P. L. Plummer, "Molecular model for ice clusters in a supersaturated vapor," J. Chem. Phys., 61, No. 10, 4012 (1974).
15. V. K. Konyukhov and V. N. Faizulaev, A Kinetic Model of the Condensation of a Supersaturated Gas [in Russian], Preprint No. 32, Fiz. Inst. Akad. Nauk SSSR (1976).
16. Ya. I. Frenkel', "On the theory of the phenomena of accommodation and condensation," Usp. Fiz. Nauk, 20, No. 1, 84 (1938).
17. E. E. Nikitin, Theory of Elementary Atomic-Molecular Processes in Gases [in Russian], Khimiya, Moscow (1970).
18. V. K. Konyukhov, A. M. Prokhorov, V. I. Tikhonov, and V. N. Faizulaev, "A gasdynamic condensation laser using water vapors," Kvant. Élektron., 2, No. 9, 2106 (1975).
19. V. K. Konyukhov and V. N. Faizulaev, "The effect of the condensation of a gas on the rate of relaxation processes in gasdynamic lasers," Kvant. Élektron., 1, 12, 2623 (1974).
20. V. K. Konyukhov and V. N. Faizulaev, "Adsorption separation of gases and isotopically displaced molecules by an aerosol jet," Zh. Tekh. Fiz., Pis'ma Red., 1, No. 15, 719 (1975).