NEW MICROSCOPIC MODELS OF CLUSTERING KINETICS

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Successes in describing the kinetics of clustering in hypersonic jets and molecular beams [1], diffusion chambers and Wilson cloud chambers, during the growth of surface films [2-4], etc., have been due to the use of the Becker–Dering and Zel'dovich–Frenkel theories [4] and the quasichemical model [5, 6] as well as its different variants [7, 8]. A large number of studies devoted to different aspects of the problem have been done in these areas. Nevertheless, insufficient attention has been focused to date on the analysis of the kinetic equations, which take into account the numerous reactions and are important in the study of the nucleation kinetics in the supercritical region, processes of the coagulation and breakup of drops in the atmosphere, and in other problems [2, 7, 8]. This also pertains to the development of micromodels of clusters and their interactions, which allow equilibrium distribution functions to be calculated for particles of arbitrary size as well as the condensation and evaporation coefficients and the efficiency of inelastic impacts.

In this paper we consider some of these subjects. A system of kinetic equations of the general type is formulated and a diffusion version is derived with allowance for multiparticle interactions. A simple model is presented for the kinetics of nonisothermal nucleation. We analyze the problem of finding the equilibrium size distribution functions of clusters, using methods of statistical methods on the basis of a micromodel of a cluster. Models are proposed for calculating the condensation and evaporation coefficients and the efficiency of inelastic impacts.

1. General Kinetic Equation of Clustering Theory. A. We consider isothermal homogeneous clustering with allowance for numerous nonmolecular processes,

$$\begin{gathered}(\nu)+(\mathbf{k})\rightleftarrows(\nu+k-k')+(\mathbf{k}'),\\ (\mathbf{k})\equiv(k_1,\ k_2,\ \ldots),\ (\mathbf{k}')\equiv(k_1',\ k_2',\ \ldots),\\ k\equiv k_1+k_2+\ldots,\ k'\equiv k_1'+k_2'+\ldots,\ k_i,\ k_i'\geqslant 0.\end{gathered}\tag{1.1}$$

The symbol (ν) denotes a cluster consisting of ν molecules. At times much longer than the time of multiparticle interaction in (1.1) and shorter than size, the relaxation time of clusters the following system of nonlinear equations can be written for the distribution function n(ν, t) ≡ n(ν):

$$\begin{gathered}\partial_t n(\nu)=I(\nu)=\sum_{\substack{\mathbf{k},\mathbf{k}'\\ (\nu+k-k'\geqslant k_1')}}[n(\mathbf{k}')\,n(\nu+k-k')\,\omega(\nu+k-k',\mathbf{k}'|\mathbf{k})-\\ -n(\mathbf{k})\,n(\nu)\,\omega(\nu,\mathbf{k}|\mathbf{k}')]\,q(\nu,\mathbf{k}|\mathbf{k}'),\\ n(\mathbf{k})\equiv n(k_1)n(k_2)\ \ldots,\ n(\mathbf{k}')\equiv n(k_1')n(k_2')\ldots,\ n(0)\equiv 1,\\ q(\nu,\mathbf{k}|\mathbf{k}')=1+\sum_{i\geqslant 1}\left(\delta_{\nu k_i}-\delta_{\nu k_i'}\right).\end{gathered}\tag{1.2}$$

Here $\omega(\nu,\ \mathbf{k}|\mathbf{k}')$ is the rate constant of the direct reaction (1.1), which we naturally consider to be symmetrical with respect to permutations inside group ν, **k** and **k**′ ($\omega(\nu,\ \mathbf{k}|\mathbf{k}')=\omega(\mathscr{P}[\nu,\ \mathbf{k}]|\mathscr{P}'[\mathbf{k}'])$, $\mathscr{P}$, $\mathscr{P}'$ are arbitrary permutations). The summation in (1.2) with allowance for the symmetry property of ω is carried out over nondecreasing components of vectors **k** and **k**′, condition $\nu+k-k'\geqslant k_1$ is put on all these considerations. Function q takes into account the fact that if **k** has s components with $k_i=\nu$, and **k**′ has s′ components with $k_i'=\nu$ then the coefficient (1 + s − s′) must be placed in front of the corresponding term in the sum (1.2).

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System (1.2) is the most general mathematical form of the quasichemical model of clustering kinetics, including those used earlier [5, 7, 8]:

1) the Smoluchowski model $(\nu) + (k) \to (\nu + k)$, for which

$$I_1(\nu) = \frac{1}{2}\sum_{k=1}^{\nu-1} n(k)\, n(\nu - k)\, \beta(\nu - k, k) - \sum_{k \geqslant 1} n(k)\, n(\nu)\, \beta(\nu, k),\ \beta(\nu, k) = \omega(\nu, k \mid 0)(1 + \delta_{\nu k});$$

2) the Melzak model $(\nu) + (k) \to (\nu + k)$, $(\nu) \to (1) + (1_{\nu-1})$, for which

$$(1_\nu) \equiv \underbrace{(1) + (1) + \ldots + (1)}_{\nu},\ I_2(\nu) = I_1(\nu) + I_2^*(\nu),$$

$$I_2^*(\nu) = \delta_{\nu,1} \sum_{k \geqslant 1} n(k)\, P(k)\, k - n(\nu)\, P(\nu),\ P(\nu) = \omega(\nu, 0 \mid 1_\nu);$$

3) the Szilard–Farkas model $(\nu) + (k) \rightleftarrows (\nu + k)$, for which

$$I_3(\nu) = I_1(\nu) + I_3^*(\nu),\ I_3^*(\nu) = \sum_{k \geqslant 1} \alpha(\nu + k, k)\, n(\nu + k) - \frac{1}{2}\sum_{k=1}^{\nu-1} \alpha(\nu, k)\, n(\nu),\ \alpha(\nu + k, k) = \omega(\nu + k, 0 \mid k)(1 + \delta_{\nu k}); \tag{1.3}$$

4) the Zel'dovich monomolecular model is obtained from (1.3) for $k = 1$;

5) the generalized Szilard–Farkas model $(\nu + k) \rightleftarrows (\nu + k - k') + (k')$, for which

$$I_5(\nu) = \sum_{\substack{k, k' > 0 \\ (\nu + k \geqslant 2k')}} [n(k')\, n(\nu + k - k')\, \omega(\nu + k - k', k' \mid k) - n(k)\, n(\nu)\, \omega(\nu, k \mid k')]\,(1 + \delta_{\nu k}).$$

Models 1 and 2 were used in theory of coagulation [7, 8] and models 3 and 4 were used in the theory of condensation [4, 5], while model 5 has not previously been used.

B. The nonlinear system (1.2) is complicated for mathematical analysis because of its high dimension. The method of transition from (1.2) to a quasilinear parabolic (Fokker–Planck) equation, therefore, is effective for large clusters ($\nu \gg k$, k', $q = 1$, with the condition $\nu + k - k' \geq k'_1$ satisfied automatically). Previously such a transition was effected on the basis of the Zel'dovich monomolecular model [9]. Let us give the simplest derivation of the diffusion approximation, using (1.2). Introducing the notation $\omega(\nu, \mathbf{k} \mid \mathbf{k}') \equiv \omega_\nu(\mathbf{k} \mid \mathbf{k}')$, we recast $I(\nu)$ in (1.2) at $\nu \gg k$, k' in the form

$$I(\nu) = \sum_{\mathbf{k}, \mathbf{k}'} n(\mathbf{k})\, [\omega_{\nu + k' - k}(\mathbf{k} \mid \mathbf{k}')\, n(\nu + k' - k) - \omega_\nu(\mathbf{k} \mid \mathbf{k}')\, n(\nu)]. \tag{1.4}$$

When the first term in (1.4) behind the summation sign is expanded in a Taylor series in $(k' - k)$, we obtain

$$I(\nu) = \sum_{l \geqslant 1} \frac{\partial_\nu^{(l)}}{l!} \sum_{\mathbf{k}, \mathbf{k}'} n(\mathbf{k})\, n(\nu)\, \omega_\nu(\mathbf{k} \mid \mathbf{k}')\, (k' - k)^l. \tag{1.5}$$

For large clusters usually

$$|\partial_\nu \omega_\nu(\mathbf{k} \mid \mathbf{k}')| = \varepsilon_\omega(\nu)\, \omega_\nu(\mathbf{k} \mid \mathbf{k}'),\ |\partial_\nu n(\nu)| = \varepsilon_n(\nu)\, n(\nu), \tag{1.6}$$

where $\varepsilon_{\omega,n}(\nu)$ are small quantities at $\nu \gg 1$ (this has been demonstrated for the Zel'dovich model, e.g., in [9]). When in (1.5) we confine the discussion to quadratic terms in $|\mathbf{k}' - \mathbf{k}|\, \varepsilon_{\omega,n}(\nu)$, we find

$$\partial_t n(\nu) = -\partial_\nu J(\nu),\ J(\nu) = A(\nu)n(\nu) - B(\nu)\partial_\nu n(\nu); \tag{1.7}$$

$$A(\nu) = -\sum_{\mathbf{k},\mathbf{k}'} n(\mathbf{k})\left[\omega_\nu(\mathbf{k}\,|\,\mathbf{k}')(k'-k) + \partial_\nu\omega_\nu(\mathbf{k}\,|\,\mathbf{k}')\frac{(k'-k)^2}{2}\right],$$
$$B(\nu) = \sum_{\mathbf{k},\mathbf{k}'} n(\mathbf{k})\,\omega_\nu(\mathbf{k}\,|\,\mathbf{k}')\frac{(k'-k)^2}{2}. \tag{1.8}$$

It is important that the diffusion and drift coefficients, B(ν) and A(ν), take into account the integrated contribution of multiparticle processes and Eq. (1.7) is quasilinear. For monomolecular model 4 from (1.8) we get the well-known result [9]

$$A(\nu) = W^+_{\nu-1/2} - W^-_{\nu+1/2},\ B(\nu) = \frac{1}{2}\left(W^+_\nu + W^-_\nu\right),$$
$$W^+_\nu \equiv n(1)\,\omega_\nu(1\,|\,0),\ W^-_\nu \equiv \omega_\nu(0\,|\,1),\ W^\pm_{\nu\pm 1/2} \simeq W^\pm_\nu \pm \frac{\partial_\nu}{2} W^\pm_\nu.$$

For kinetics with the reverse reactions (1.1) (models 3-5 of this type, 1,2 of the other) we introduce the microscopic detailed balancing principle in each of the transition channels $(\nu) \rightleftarrows (\nu') = (\nu + k - k')$,

$$n^e(\mathbf{k})\,n^e(\nu)\,\omega_\nu(\mathbf{k}\,|\,\mathbf{k}') = n^e(\mathbf{k}')\,n^e(\nu + k - k')\,\omega_{\nu+k-k'}(\mathbf{k}'\,|\,\mathbf{k}) \tag{1.9}$$

[$n^e(\nu)$ is the equilibrium distribution function]. For smooth distributions [condition (1.6)] we expand (1.9) in a series in (k' − k) about the point ν and we also carry out the moment linearization (1.7), setting $n(\mathbf{k}) \simeq n^e(\mathbf{k})$. Introducing the normalized quantity $\tilde{n}(\nu) \equiv n(\nu)/n^e(\nu)$, $\tilde{\omega}_\nu(\mathbf{k}|\mathbf{k}') = n^e(\mathbf{k})n^e(\nu)\omega_\nu(\mathbf{k}|\mathbf{k}')$, after straightforward manipulations instead of (1.7) and (1.8) we have

$$\partial_t n(\nu) = \partial_\nu\left[\tilde{B}(\nu)\,\partial_\nu\tilde{n}(\nu)\right],\ \tilde{B}(\nu) = \sum_{\substack{\mathbf{k},\mathbf{k}'\\(k>k')}} (k-k')^2\,\tilde{\omega}_\nu(\mathbf{k}\,|\,\mathbf{k}'), \tag{1.10}$$

i.e., the drift coefficient can be eliminated when the detailed balancing principle is involved. Equation (1.10) was also derived by the methods of nonequilibrium thermodynamics [10]. In contrast to [10], the treatment here allows the kinetic coefficients, which make allowance for the multiple processes, to be expressed in terms of the elementary probabilities discussed below.

C. Let us consider the generalization of model 3 to the case including more detailed processes $(\nu,\ E_\nu) + (k,\ E_k) \rightleftarrows (\nu + k,\ E_{\nu+k})$ [E_ν is the internal energy of a cluster (ν)] that underlie nonisothermal clustering. The system of kinetic equations for the distribution functions $n_\nu(E_\nu)$ will be written as

$$\partial_t n_\nu(E_\nu) = I_\nu(E_\nu) - I_\nu^{H}(E_\nu), \tag{1.11}$$

where $I_\nu(E_\nu)$ is the collision integral for processes of combination and decay obtained from (1.3) by the substitution $\beta(\nu - k, k) \to \omega^{\nu,E_\nu}_{\nu-k,E_{\nu-k};k,E_k}$, $\alpha(\nu, k) \to \omega^{\nu-k,E_{\nu-k};k,E_k}_{\nu,E_\nu}$ and the introduction of summation over $E_{\nu-k}$, E_k, and $I_\nu^H(E_\nu)$ is the integral of the inelastic collisions of molecules with a cluster. We assume that $\tau_E \ll \tau_\nu$ (τ_E and τ_ν are the energy and size relaxation times) and write $n_\nu(E_\nu)$ as

$$n_\nu(E_\nu) = n(\nu)\,x_\nu(E_\nu),\ \sum_{E_\nu} x_\nu(E_\nu) = 1. \tag{1.12}$$

Substituting (1.12) into (1.11) and summing over E_ν, we arrive at (1.3) with nonequilibrium rate constants

$$\alpha(\nu, k) = \sum_{E_{\nu-k},E_k,E_\nu} x_\nu(E_\nu)\,\omega^{\nu-k,E_{\nu-k};k,E_k}_{\nu,E_\nu}\text{, etc.} \tag{1.13}$$

From (1.11) we easily obtain a system of equations for the internal-energy density of clusters of size ν $\left(U_\nu = \sum_{E_\nu} E_\nu n_\nu(E_\nu)\right)$.

$$\partial_t U_\nu = q_\nu - q_\nu^{\text{H}},\ q_\nu = \sum_{E_\nu} E_\nu I_\nu(E_\nu),\ q_\nu^{\text{H}} = \sum_{E_\nu} E_\nu' I_\nu^{\text{H}}(E_\nu)$$

(q_ν and q_ν^{H} are the energy fluxes per cluster of size ν from the processes of combination–decomposition and inelastic impacts). For the monomolecular model we have a system similar to that given in [11]:

$$\begin{aligned} \partial_t n_\nu &= W_{\nu-1}^{+} n_{\nu-1} - W_\nu^{-} n_\nu - W_\nu^{+} n_\nu + W_{\nu+1}^{-} n_{\nu+1}, \\ \partial_t U_\nu &= j_{\nu-1}^{+} n_{\nu-1} - j_\nu^{-} n_\nu - j_\nu^{+} n_\nu + j_{\nu+1}^{-} n_{\nu+1} + j_\nu^{\text{H}} n_\nu. \end{aligned} \tag{1.14}$$

Microscopic models for the calculation of the kinetic coefficients $W_\nu^{\pm}$, $j_\nu^{\pm}$, j_ν^{H} are discussed in Sec. 3.

2. Equilibrium Distributions. Within the framework of the Szilard–Farkas nonisothermal model $(\nu - k, E_{\nu-k}) + (k, E_k) \rightleftarrows (\nu, E_\nu)$ we consider the problem of finding $n_\nu^e(E_\nu)$. According to statistical thermodynamics clusters satisfy the relations [12]

$$n_\nu^e(E_\nu) = n^e(\nu)\, x_\nu^e(E_\nu),\quad x_\nu^e(E_\nu) = Q_\nu^{-1} g_\nu(E_\nu) \exp\left(-\frac{E_\nu}{k_{\text{B}}T}\right); \tag{2.1}$$

$$\mu_k + \mu_{\nu-k} = \mu_\nu,\quad n^e(\nu) = \Lambda_\nu^{-3} Q_\nu \exp\left(\frac{\mu_\nu}{k_{\text{B}}T}\right),\quad \Lambda_\nu = \left[\frac{2\pi\hbar^2}{m_\nu k_{\text{B}}T}\right]^{1/2}, \tag{2.2}$$

where $Q_\nu = \sum_{E_\nu} g_\nu(E_\nu) \exp\left(-\frac{E_\nu}{k_{\text{B}}T}\right)$; and g_ν, m_ν, μ_ν are the internal statistical sum, mass, and chemical potential of a cluster (ν). Distribution (2.1), (2.2) satisfies the microscopic detailed balancing principle

$$n_k^e(E_k)\, n_{\nu-k}^e(E_{\nu-k})\, \omega_{k,E_k;\nu-k,E_{\nu-k}}^{\nu,E_\nu} = n^e(E_\nu)\, \omega_{\nu,E_\nu}^{k,E_k;\nu-k,E_{\nu-k}}, \tag{2.3}$$

while the probabilites ω averaged over the energy with functions $x_\nu^e(E_\nu)$ satisfy the macroscopic detailed balancing principle (law of mass action)

$$\frac{\beta(\nu - k, k)}{\alpha(\nu, k)} = \frac{n^e(\nu)}{n^e(\nu - k)\, n^e(k)} = \left(\frac{\Lambda_k \Lambda_{\nu-k}}{\Lambda_\nu}\right)^3 \frac{Q_\nu}{Q_k Q_{\nu-k}} \equiv K_\nu(k). \tag{2.4}$$

For the monomolecular model it follows from (2.2)-(2.4) that

$$\mu_\nu = \nu\mu_1,\ n^e(\nu) = \left[n^e(1)\right]^\nu \prod_{l=2}^{\nu} K_\nu(1) = \Lambda_\nu^{-3} z^\nu Q_\nu,\ z \equiv \exp\left(-\frac{\mu_1}{k_{\text{B}}T}\right). \tag{2.5}$$

We note that for large clusters described thermodynamically Eq. (2.3) is not satisfied but (2.4) remains valid. This means that a microscopic kinetic equation for $m_\nu(E_\nu, t)$ reflecting evolution $n_\nu(E_\nu, 0) \to n_\nu^e(E_\nu)$, does not exist for them but there is a system of coupled equations of the preceding point for successive evolution $n_\nu(E_\nu, 0) \to n_\nu^q(E_\nu, t) \equiv n(\nu, t)\, x_\nu^q(E_\nu, t) \xrightarrow[t\to\infty]{} n_\nu^e(E_\nu)$ [$x_\nu^q(E_\nu, t)$ is a quasistationary energy distribution]. The simplest is the Boltzmann distribution $x_\nu^q = Q_\nu^{-1}(T_\nu)\, g_\nu(E_\nu) \times \exp(-E_\nu/(k_{\text{B}}T_\nu))$ (T_ν is the internal temperature of a cluster of size ν). This assumption is used, e.g., in [10, 11]. In the thermodynamic limit

$Q_\nu \simeq \exp(-\mathcal{F}_\nu/(k_B T))$ ($\mathcal{F}_\nu$ is the free energy of a cluster of size ν). The results of most studies on the approximation of $\mathcal{F}_\nu$ for a monomolecular model, following [13], can be written as [S_ν is the surface area of a cluster (ν)]

$$\mathcal{F}_\nu = \mathcal{F}\nu + \alpha S_\nu + U_\nu^0,\ U_\nu^0 = U_1^0\nu - \varepsilon^0\nu - \varepsilon_s^0 S_\nu, \tag{2.6}$$

where $\mathcal{F}$ and ε^0 physically denote the volume density of the free energy and the binding energy (per molecule), α and ε_s^0 are the surface density of the free energy and the binding energy, and U_1^0 is the internal energy of a molecule.

Using (2.5) and (2.6), we obtain

$$n^e(\nu) = \Lambda_1^{-3}\nu^{3/2}\exp\left(a\nu - b\nu^{2/3}\right),$$

$$a = \ln(1+\zeta), \zeta \equiv n_1^e/n_{1\text{H}}^e = 1, b \equiv \frac{4\pi\eta^2}{k_B T} n_{1s}^e \Delta_s; \tag{2.7}$$

$$n_{1\text{H}}^e = \Lambda_1^{-3}\exp\left(-\frac{\Delta_\nu}{k_B T}\right),\ \eta \equiv \left(\frac{3m_1}{4\pi\rho_l}\right)^{1/3},$$

$$\Delta_s = \left(n_{1s}^e\right)^{-1}\left(\alpha - \varepsilon_s^0\right),\ \Delta_\nu = \varepsilon^0 - \mathcal{F}. \tag{2.8}$$

Here n_{1H}^e and n_{1s}^e are the equilibrium densities of saturated vapor and adsorbed molecules (n_{1s}^e is found from the Langmuir isotherm), ζ is the supersaturation, Δ_ν and Δ_s are the heat of evaporation of a molecule from the bulk of the cluster and the activation energy of an adsorbed molecule, and ρ_ℓ is the density of the liquid. It is important to emphasize that the formula for n_{1H}^e coincides with the Clapeyron–Clausius law to within the prexponential factor [12] and instead of the thermodynamic parameters μ and σ (σ is the surface tension) Eqs. (2.7) and (2.8) contain transparent parameters of the cluster micromodel, which admits experimental verification (see [14] in relation to the properties of real clusters). Condition $b > 0$ indicates that adsorbed molecules are held on the surface by the barrier-type potential (see Fig. 1). As shown in [13], distribution (2.7) is free of divergence as $\nu \to \infty$ in the thermodynamic limit and correctly reflects the pattern of phase stratification. Corrections (2.7), resulting from more accurate methods of calculating $\mathcal{F}_\nu$ (Lothe–Pound, Rice, Kikuchi methods), are discussed in [13].

3. Theoretical Methods of Calculating Kinetic Constants. The problem of theoretical approaches to calculations of condensation–evaporation coefficients and the probabilities of inelastic transition in clustering kinetics has been developed the least and the experimental data pertaining to it often differ by orders of magnitude. Accordingly, we shall discuss this in greater detail. We start from the general expression (1.13) for the nonequilibrium constant decay-rate constant and consider some approximate variants of it.

1. According to the theory of absolute reaction rates [15], $x_\nu(E_\nu) \simeq x_\nu^e(E_\nu)$, decay is assumed to occur by the mechanism of an activated complex $(\nu) \rightleftarrows (\nu)^* \rightleftarrows (\nu - k) + (k)$. The symbol $(\nu)^*$ is taken to mean a sphere of radius $r_\nu(k)$ (see Fig. 1) and $E_\nu{}^*(k)$, $E_\nu{}^c(k)$, $E_\nu{}^a(k)$ denote the energy of the activated complex, the binding energy of fragments $(\nu - k)$ and (k), and the activation barrier of coagulation of fragments $(\nu - k)$ and (k), respectively, via one-dimensional reaction channel [at $E_\nu \simeq E_\nu{}^*(k)$] – the relative motion of fragments $(\nu - k)$ and (k) in a barrier-type spherical field $V_{\nu-k}(r)$ (which is consistent with the comment in Sec. 2) with energy ε ($\varepsilon \geqslant 0$, $E_\nu \geqslant E_\nu{}^*(k) = f(E_{\nu-k}, E_k)$). On the basis of these assumptions, we write ω as

$$\omega_{\nu,E_\nu}^{\nu-k,E_{\nu-k};k,E_k} = H\left(E_\nu - E_\nu^*(k)\right)\Omega_\nu(\varepsilon)P_\nu(\varepsilon),\ H(x) = \begin{cases}1, x \geqslant 0,\\ 0, x < 0,\end{cases} \tag{3.1}$$

where $\Omega_\nu(\varepsilon)$ is the frequency of one-dimensional oscillations of fragments $(\nu - k)$ and (k) in the potential well and $P_\nu(\varepsilon)$ is the penetration probability. We use (2.1) for $x_\nu{}^e(E_\nu)$ and the representation (3.1) in (1.13), thus isolating the statistical sums of a stable cluster $(\nu)Q_\nu$ and the activated complex $(\nu)^*\ Q_\nu{}^*$ at $E_\nu \geqslant E_\nu{}^*(k)$. Shifting the origin for the energies to Q_ν and $Q_\nu{}^*$ $\left(Q_\nu = \tilde{Q}_\nu\exp\left(-\frac{E_\nu^c(k)}{k_B T}\right),\ Q_\nu^* = \tilde{Q}_\nu^*\exp\left(-\frac{E_\nu^*(k)}{k_B T}\right)\right)$, and also isolating from $Q_\nu{}^*$ the one-dimensional oscillating sum of the activated complex Q_1^* $(Q_\nu^* = Q_1^* Q_\nu^{**})$, from (1.13) we have the rough approximation

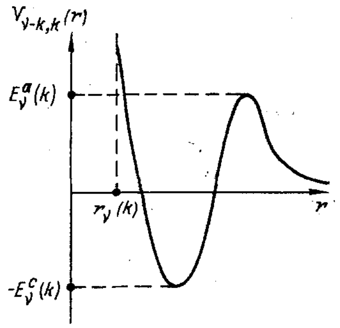

Fig. 1

$$\alpha(\nu,k)=D_\nu\left(Q_1^*\widetilde{Q}_\nu^{**}/\widetilde{Q}_\nu\right)\exp\left(-\frac{\Delta E_\nu^*(k)}{k_BT}\right),$$
$$Q_1^*=\sum_{\varepsilon_n\geqslant 0}\exp\left(-\frac{\varepsilon_n}{k_BT}\right),\ \Delta E_\nu^*(k)\equiv E_\nu^*(k)-E_\nu^c(k), \tag{3.2}$$
$$D_\nu=\sum_{\varepsilon_n\geqslant 0}P(\varepsilon_n)\Omega_\nu(\varepsilon_n)\exp\left(-\frac{\varepsilon_n}{k_BT}\right).$$

Equation (3.2) is a typical expression for a decay rate constant, where D_ν is the averaged barrier penetration factor. Let us now consider three cases: a) in the harmonic approximation $Q_1^*=\left[1-\exp\left(-\frac{h\Omega_\nu}{k_BT}\right)\right]^{-1}$, and at $h\Omega_\nu\ll k_BT$ Eq. (3.2) coincides with the expression for the evaporation coefficient given in [16]; b) at $h\Omega_\nu\gg k_BT$ we set $P_\nu(\varepsilon)=H(\varepsilon-E_\nu^a(k))$, $\widetilde{Q}_\nu^{**}\simeq\widetilde{Q}_\nu$, whereupon (3.2) goes over into the familiar Wigner–Polanyi formula [18]

$$\alpha(\nu,k)\simeq\Omega_\nu\exp\left(-\frac{\Delta E_\nu^a(k)}{k_BT}\right);\ \Delta E_\nu^a(k)=E_\nu^a(k)-E_\nu^c(k);$$

c) assuming the motion in the well to be quasiclassical $\left(\sum\limits_{\varepsilon_n\geqslant 0}\to\int\limits_0^\infty d\varepsilon\right)$, from (3.2) at $\widetilde{Q}_\nu^{**}\simeq\widetilde{Q}_\nu$ and $h\Omega_\nu\ll k_BT$ we find

$$\alpha(\nu,k)\simeq\frac{k_BT}{h}D_\nu(T)\exp\left(-\frac{\Delta E_\nu^*(k)}{k_BT}\right),\ D_\nu(T)=\int\limits_0^\infty d\varepsilon P_\nu(\varepsilon)\exp\left(-\frac{\varepsilon}{k_BT}\right).$$

A similar expression (but without an exponent) can be easily obtained from intuitive considerations for $\beta(\nu-k, k)$ while $\alpha(\nu, k)$ and $\beta(\nu-k, k)$ are related by the detailed balancing equation.

2. For the simple model of nonisothermal condensation ($T_\nu \neq T$) proposed in Sec. 1 we must take the nonequilibrium effects $(x_\nu(E_\nu)\neq x_\nu^e(E_\nu))$, and also calculate the rate constants of the condensation, evaporation, and elastic impacts of molecules on the surface of a cluster (ν). Let us investigate this, using the pattern of the dynamics of the gas-surface interaction. Suppose that $P_\nu^+(\varepsilon, \varepsilon'|T_\nu)$, $P_\nu^-(\varepsilon', \varepsilon|T_\nu)(\varepsilon>0, \varepsilon'<0)$ is the probability density of absorption–desorption processes and $P_\nu^{\text{н}}(\varepsilon, \varepsilon'|T_\nu)$ is the probability density of inelastic impacts (ε, $\varepsilon' > 0$) on the surface of a cluster (ν) with temperature T_ν. Assuming that $x_\nu(E_\nu)=x_\nu^q(E_\nu)$,

we arrived at an expression for all the kinetic coefficients of the nonisothermal model (1.14)

$$W_\nu^+(T, T_\nu) = k_B T n_1 S_\nu \frac{\bar{v}_1}{4} \langle P_\nu^+ \rangle,$$
$$W_\nu^-(T, T_\nu) = k_B T_\nu S_\nu \langle P_\nu^- \rangle; \tag{3.3}$$

$$j_\nu^+(T, T_\nu) = (k_B T)^2 S_\nu \frac{\bar{v}_1}{4} \langle (\tilde{\varepsilon} - \tilde{\varepsilon}') P_\nu^+ \rangle,$$
$$j_\nu^- = (k_B T_\nu)^2 S_\nu \langle (\bar{\varepsilon} - \bar{\varepsilon}') P_\nu^- \rangle; \tag{3.4}$$

$$j_\nu^{\text{н}}(T, T_\nu) = (k_B T)^2 \left(n_1 \frac{\bar{v}_1}{4} + n_g \frac{\bar{v}_g}{4} \right) S_\nu \langle (\tilde{\varepsilon} - \tilde{\varepsilon}') P_\nu^{\text{н}} \rangle \tag{3.5}$$

(the subscript g pertains to the characteristics of the passive gas). In Eqs. (3.3)-(3.5) $\tilde{\varepsilon} = \varepsilon / k_B T$, $\bar{\varepsilon} = \varepsilon / k_B T_\nu$, $v_{1,g} = \left(\frac{8 k_B T}{\pi m_{1,g}} \right)^{1/2}$, the symbol < > denotes averaging carried out as follows:

$$\langle P_\nu^+ \rangle = \int_{\tilde{E}_\nu^a}^{\infty} d\varepsilon e^{-\varepsilon} \int_{-\tilde{E}_\nu^c}^{\tilde{E}_\nu^a} d\varepsilon' P_\nu^+ (\varepsilon, \varepsilon' | T_\nu),$$
$$\langle P_\nu^- \rangle = \int_{-\bar{E}_\nu^c}^{\bar{E}_\nu^a} d\varepsilon' \Omega_\nu (\varepsilon') e^{-\varepsilon'} \int_{\bar{E}_\nu^a}^{\infty} d\varepsilon P_\nu^- (\varepsilon', \varepsilon | T_\nu) \text{, etc.}$$

when thermodynamic equilibrium exists between the gas and the clusters $j_\nu^{\text{н}} = 0$. If in the expressions for j_ν^+ and j_ν^- the average value, which is equal to $k_B(T - T_\nu)$, is carried out in front of the averaging sign for $(\varepsilon - \varepsilon')$, we obtain the approximation

$$j_\nu^+ \simeq k_B (T - T_\nu) W_\nu^+; \; j_\nu^- \simeq k_B (T - T_\nu) W_\nu^-. \tag{3.6}$$

Substituting (3.6) into (1.14) and expanding the terms in the neighborhood of the point ν, and also assuming for simplicity that $U_\nu = c_\nu n_\nu T_\nu$ (where c_ν is the heat capacity), we find a simple relaxation equation for T_ν:

$$c_\nu \partial_t (n_\nu T_\nu) = -\partial_\nu [\varkappa(\nu)(T_\nu - T)] + n_\nu j_\nu^{\text{н}}(T, T_\nu),$$
$$\varkappa(\nu) = k_B n_\nu (W_\nu^- - W_\nu^+).$$

In calculating W_ν^+ and W_ν^- we can use analytical formulas for the probabilities of inelastic impacts, given in studies on the interaction of gases from surfaces.

In summary, the proposed microscopic models are used for describing the kinetics of clusters of any size. They provide a possibility for calculating the condensation, evaporation, and inelastic-impact coefficients by the methods of the theory of chemical reactions in the interaction of a gas with surfaces. A more detailed study can be made by the interaction of a molecule with a cluster, the reciprocal influence of clustering and rotational and oscillatory kinetics, as well as other effects.

LITERATURE CITED

1. I. S. Kotake and I. I. Glass, "Flows with nucleation and condensation," Prog. Aerospace Sci., 19, No. 2-4 (1981).
2. Yu. F. Komnik, Physics of Thin Metallic Films [in Russian], Atomizdat, Moscow (1979).
3. V. I. Antsiferov, T. V. Bobrov, L. K. Druzhinin, et al., Powder Metallurgy and Evaporation Coatings [in Russian], Metallurgiya, Moscow (1987).
4. M. Fol'mer, Kinetics of the Formation of a New Phase [in Russian], Nauka, Moscow (1986).
5. A. A. Lushnikov and A. G. Sutugin, "Present state of the theory of homogeneous condensation," Usp. Khim., 5, No. 3 (1976).

6. F. F. Abraham, Homogeneous Nucleation Theory. The Pretransition Theory of Vapour Condensation, Academic Press, New York (1974).
7. V. M. Voloshchuk, Kinetic Theory of Coagulation [in Russian], Gidrometeoizdat, Leningrad (1984).
8. V. M. Voloshchuk and Yu. S. Sedunov, Coagulation Processes in Dispersed Media [in Russian], Gidrometeoizdat, Leningrad (1975).
9. F. M. Kuni and A. P. Grinin, "Small parameters of macroscopic condensation theory," Vestn. LGU, Fiz., Khim., No. 22(4) (1982).
10. A. P. Bashkirov and S. P. Fisenko, "Derivation of the equations of nonisothermal nucleation," Preprint No. 68 [in Russian], Inst. Prob. Mech. Acad. Sci. USSR, Moscow (1976).
11. A. V. Krestinin, Simple model of nonisothermal homogeneous condensation in gases," Khim. Fiz., 5, No. 2 (1986).
12. L. D. Landau and E. M. Lifshitz, Statistical Physics, Vol. 1, Pergamon Press, Oxford (1980).
13. A. V. Bogdanov, Yu. E. Gorbachev, G. V. Dubrovskiĭ, et al., "Equilibrium solutions of the quasichemical model of condensation," Preprint No. 1163 [in Russian], Physicotech., Inst. Acad. Sci. USSR, Leningrad (1987).
14. A. A. Vostrikov and D. Yu. Dubov, "Real properties of clusters and models of condensation," Preprint No. 112, Inst. Therm. Phys. Sib. Branch Acad. Sci. USSR, Novosibirsk (1984).
15. N. M. Kuznetsov, Kinetics of Monomolecular Decomposition [in Russian], Nauka, Moscow (1982).
16. E. Mortensen and H. Eyring, "Transmission coefficients for evaporation and condensation," J. Chem. Phys., 64, No. 7 (1960).
17. H. J. Kreuzer and H. W. Gortel, Physiosorption Kinetics, Springer-Verlag, Berlin (1985).