26. Ya. S. Uflyand, "Some new integral transforms and their application to mathematical physics problems," in: Questions in Mathematical Physics [in Russian], Nauka, Leningrad (1976).
27. G. Beitman and A. Érdein, Higher Transcendental Functions [in Russian], Vol. 1, Nauka, Moscow (1973).
28. N. N. Lebedev and I. P. Skal'skaya, "One expansion of an arbitrary function in an integral of spherical functions," Prikl. Mat. Mekh., 30, No. 2 (1966).
29. A. I. Moshinskii, "Some integral expansions of an arbitrary function in Legendre functions," Differents. Uravn., 26, No. 9 (1990).
30. V. V. Kafarov and I. N. Dorokhov, Systematic Analysis of Chemical Technology Problems. Fundamental Strategies [in Russian], Nauka, Moscow (1976).
31. N. I. Gel'perin, V. L. Pebalk, and A. E. Kostanyan, Flow Structure and Efficiency of Column Apparatus in the Chemical Industry [in Russian], Khimiya, Moscow (1977).

EFFECT OF EXCITATION OF INTERNAL DEGREES OF FREEDOM IN CLUSTERS ON CONDENSATION KINETICS

A. L. Itkin and E. G. Kolesnichenko

UDC 536.423.4

At present a number of experimental results have been presented on condensation of vapors of various substances, which cannot be explained by classical theory (see the review [1]). One of the factors not considered in such a theory is the effect of disruption of equilibrium cluster distribution over internal degrees of freedom due to the condensation affecting the kinetics of the process. A method for considering this effect has been proposed in a multimolecular model of condensation kinetics. The presence of internal degrees of freedom in a monomer can lead to an entire series of new condensation regimes. The present study will briefly evaluate such regimes.

The first question which arises upon consideration of internal degrees of freedom in a monomer is related to the method used for defining various types of cluster internal energy. It is clear that even small complexes (trimers, tetramers, etc.) may have a quite large number of oscillatory modes, which can conveniently be divided into two groups. In the first group we have oscillations of molecules entering into the composition of clusters – intermolecular oscillations, while in the second we have oscillations of atoms forming the molecule (monomer) – intramolecular oscillations. Intermolecular oscillations usually are of low energy. Thus, for Van der Waals complexes their characteristic frequencies lie in the range 50-200 cm^{-1}. As for intramolecular oscillations, various situations are possible.

1. If these oscillations are of low frequency, they effectively exchange energy with the intermolecular oscillations, which makes it possible to introduce the total oscillatory energy of the cluster $E_j(k)$ (where j is the number of molecules in the cluster and k is the energy level number). The existence of various types of intermolecular oscillations is not then considered.

2. If the monomers have high frequency oscillation modes, then their interaction with intermolecular oscillations is ineffective. The internal energy of the cluster can then be specified by quantum numbers k and ℓ, characterizing the total internal energy of low frequency intermolecular oscillations $E_j(k)$ and high frequency intramolecular oscillations $\mathscr{E}_j(\ell)$, as well as a quantum number characterizing the distribution of the latter over cluster monomers [the quantum number related to degeneration of the level (k, ℓ)]. Consideration of interaction leads to removal of the degeneration with respect to this number and development of a multiplet of closely spaced levels, while radiationless intracluster transitions [4] rapidly lead to a microcanonical distribution for a given $\mathscr{E}_j$. Here we will lim-

---

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 4, pp. 120-122, July-August, 1991. Original article submitted February 24, 1989; revision submitted March 28, 1990.

0021-8944/91/3204-0578$12.50

it our consideration to the case where the state of the cluster is defined by the energy $E_j(k)$. This is always possible in the first case, and in the second when excitation of high frequency oscillations is neglected.

Condensation regimes can be classified further by comparing the rates of condensation and oscillatory VV- and VT-relaxation of the monomers.

Using a quasisteady state method analogous to that developed in [2], we can obtain a closed system of equations for the slow variables.

1. For frozen oscillations and for an equilibrium distribution of monomer populations, which is realized if the times of VV-exchange (τ_{VV}) and VT-relaxation (τ_{VT}) are significantly less than the characteristic time of dimer dissociation (τ_d), these equations have a similar structure. Their coefficients depend on the temperature T, however in the latter case this dependence is more complex in form. In both situations, by using the quasisteady state method, it is possible to obtain a closed system of equations for the cluster concentration n_j.

2. A closed system of equations describing evolution of the concentrations n_j can also be obtained in the case where the characteristic times are related as $\tau_{VV} \ll \tau_{VT} \approx \tau_d$. In this case the structure of the equations again coincides with that considered above, although the constants which appear in them become two-temperature ones.

3. The most complex case is that in which $\tau_d \ll \tau_{VV} \approx \tau_{VT}$. It is then impossible to obtain a closed system of equations for the concentrations n_j, and it is necessary to solve simultaneously the equations for the concentrations n_j ($j = 1, \ldots, N$) and the populations $x_1(k)$ ($k = 1, \ldots, M$). The constants in the equations for n_j ($j = 2, \ldots, N$) then depend in a complex manner on $x_1(k)$ ($k = 1, \ldots, M$) and n_1.

In all the situations listed above, the equations for the concentrations n_j ($j > r + 1$) have the form used in the Szillard model of [1]. Here r is a parameter of the theory, introduced in [2] and characterizing the size of the cluster, for which the condensation rate is comparable to the oscillatory relaxation rate at upper levels. However, if in that model the constants for attachment (or breakoff) of a monomer to or from a cluster K_j^+ and K_j^- depend on the temperature T, then in our case they are nonequilibrium rate constants dependent on the populations $x_1(k)$ ($k = 1, \ldots, M$) (Sec. 3) of on the oscillatory temperature T_V (Sec. 2), and coincide with those used in the Szillard model only for a Boltzmann monomer distribution (Sec. 1).

However, for $j \leq r + 1$ the equations for the concentrations n_j differ significantly for those of the Szillard model. Effects related to this difference were discussed in [3].

LITERATURE CITED

1. Yu. I. Petrov, Clusters and Small Particles [in Russian], Nauka, Moscow (1986).
2. A. L. Itkin and E. G. Kolesnichenko, "Role of nonequilibrium in condensation kinetics," Dokl. Akad. Nauk SSSR, 311, No. 3 (1990).
3. A. L. Itkin and E. G. Kolesnichenko, "Causes of carrier gas effect on condensation kinetics," Pis'ma Zh. Tekh. Fiz., 12, No. 7 (1989).
4. E. G. Kolesnichenko and A. L. Itkin, "Kinetic description of intramolecular processes in rarified gases," in: Nonequilibrium Gas Flows with Physicochemical Conversions [in Russian], Mosk. Gos. Univ. (1989).