Processes of the formation of small associates, and in particular, of water molecule dimerization continue to attract the attention of specialists in different areas of science and its applications. Such processes are examined, e.g., in the construction of kinetic models of vapor condensation [1]; the representation of water molecule dimerization aids in the interpretation of the passage of IR radiation in the transparency windows of the atmosphere [2]. Preliminary estimates are made in [3] of the possibility of producing a gasdynamic condense-laser that uses the energy of vibrational excitation of dimers formed during the escape of low-density water vapor from a nozzle. A study of different aspects of the spectral and physicochemical phenomena of molecule associations under equilibrium and nonequilibrium conditions requires further refinement of the molecular parameters of associates, perfection of methods to determine these parameters, and construction of kinetic models of associate formation.

A number of papers have recently appeared on studying associates in molecular and gasdynamic beams of different gases [4-6], including water vapor [4, 6]. Results of mass spectral measurements of nonequilibrium concentrations of water dimers during the escape of rarefied vapor into a vacuum are presented in [6]. The dimer-formation model proposed in [6] permitted the author to describe the experimental results he obtained about dimer concentrations in a stream with sufficiently high accuracy. The principal statement in the construction of the kinetic model [6] is the use of the temperature dependence of the equilibrium dimer concentration $\xi(T)$ obtained earlier [7] by a computation of part of the second virial coefficient (SVC) of the vapor that corresponds to the bound and metastable states of the molecules. An attempt is made in this paper to relate nonequilibrium dimer concentrations directly to molecular parameters, whereupon the range of applicability of the kinetic model might be extended significantly.

Considerable cooling is achieved in the supersonic escape of a rarefied gas into an evacuated space; the translational temperature in the stream can be several tens of degrees Kelvin, for instance. Intensive molecule dimerization occurs in the initial stage of the cooling because of two- and three-particle monomer collisions:

\[ M + M \rightleftharpoons D^*; \]
\[ M + M + M \rightleftharpoons D + M. \]

The reactions (1) and (2) are reversible and each is characterized by its own rate of direct (formation) $K_F$ and reverse (dissociation) $K_D$ processes. Only vibrationally excited molecules with a complete store of vibrational energy $\varepsilon_K \geq \varepsilon_D$ ($\varepsilon_D$ is the dimer molecule dissociation energy) are involved in these reactions.
energy can be formed in reaction (1). For the water molecule, e.g., dimers whose intramolecular modes are excited by 1-1.5 quanta on the average are formed in reaction (1). At sufficiently low pressures, the spontaneous dissociation of molecules $D^*$ occurs more rapidly than does the deactivation $D^*$ during collision with a monomer. Therefore, dimers in the ground or near-ground excited state are formed principally because of the reaction (2). We limit ourselves here to an examination of mechanism (2), by considering that the molecule internal degrees of freedom are in equilibrium with the translational degrees. It is shown in the Appendix that a change in the dimer mass fraction along a one-dimensional gasdynamic stream is described by the equation

$$\frac{d\alpha_2}{dx} = -\frac{2(1-\alpha_2)}{(2-\alpha_2)} \left[ K_f \alpha_2 - K_r \frac{(1-\alpha_2)^2}{2} \right] \frac{p}{\rho kT}$$

where $T$, $p$, and $v$ are, respectively, the stream temperature, pressure, and velocity, which are functions of the streamwise coordinate $x$, and the dimer concentration $\alpha_2$ in the general case. The reaction rate constants $K_f$ and $K_r$ depend on the temperature. Neglecting the thermal effect of the reaction, i.e., considering $\alpha_2 \ll kT$, we will solve (3) in a given field of the stream temperature, density, and velocity. For a one-dimensional isentropic flow, the ratios $T/T_0$, $p/p_0$, and $v/v_0$ are known functions of the Mach number $M$ [8]. The dependence $M(x)$ used in [6] is used in our computation.

The key question in the solution of (3) is the selection of the constants $K_f$ and $K_r$. The quantity $K_f$ was computed as the frequency of three-particle collisions of monomers in [6], where it was considered that the probability factor is $F_f = 1$. The ratio between the forward and reverse reaction constants $K_f/K_r$ equals, as is known, the equilibrium constant $K_e$. In [6] this ratio was expressed in terms of the dependence $\xi_{se}(T)$ obtained from the SVC. To set the computed and experimental dependences in correspondence, the dissociation constant in [6] was assumed zero for $T^* < 0.58$ ($T^* = kT/\xi$ is the reduced temperature, and $\xi$ is the Stockmayer potential parameter). The need for this was given a foundation by a sharp diminution in the dissociation constant at low temperatures. Despite the good agreement with experiment obtained in [6], on the whole the author's approach raises a number of objections:

1. The frequency of the three particle collisions is determined insufficiently accurately, particularly for molecules intersecting mutually in a complex manner, e.g., forming hydrogen bonds.

2. The use of the dependence $\xi_{se}(T)$, obtained from the SVC computation, does not permit utilization of real physical parameters of the molecules and leaves slight possibilities for taking account of more complex associates together with the dimers.

3. The artificial change in the dissociation constant for $T^* < 0.58$ reflects the unsuitability of the method at low temperatures, and introduces additional arbitrariness into the computation.

4. Use of the temperature dependence of the gas-kinetic monomer section, obtained from data on the viscosity of the vapor in [9], hardly results in any substantial improvement in the model.

### Table 1

<table>
<thead>
<tr>
<th>$\xi (\text{[15]})$</th>
<th>$\eta (\text{[15]})$</th>
<th>$\eta (\text{EPEN model [14]})$</th>
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<tr>
<td>$e$</td>
<td>6000</td>
<td>5440</td>
</tr>
<tr>
<td>$I_A I_B I_C$</td>
<td>$4.32 \times 10^4$</td>
<td>$6.42 \times 10^4$</td>
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<td>$\nu W$</td>
<td>3746, 3732, 3646, 3579, 1616, 1599</td>
<td>3600, 496, 389, 168, 161, 85</td>
</tr>
<tr>
<td>$\nu_{\text{mon}}$</td>
<td>3756, 3657, 1595</td>
<td></td>
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</tbody>
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