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KINETICS OF DIMER FORMATION IN RAREFIED WATER VAPOR STREAMS

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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 intepretation 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 $\xi_{2e}(T)$ 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:

$$M + M \rightleftarrows D^*; \tag{1}$$

$$M + M + M \rightleftarrows D + M. \tag{2}$$

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 $\varepsilon_K \gtrsim \varepsilon_D$ (ε_D is the dimer molecule dissociation

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TABLE 1

	I[15]	II[15]	III(EPEN model [14])
ε	6000	5000	5440
$I_A I_B I_C$	$4{,}32 \cdot 10^4$		$6{,}42 \cdot 10^4$
ν_{M-M}	399, 271, 205, 194, 103, 110		593, 496, 189, 168, 161, 98
ν_{W-M}	3746, 3732, 3646, 3579, 1616, 1599		
ν_{mon}	3756, 3657, 1595		

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

$$\frac{d\alpha_2}{dx} = -\frac{2(1-\alpha_2)}{(2-\alpha_2)}\left[K_d\alpha_2 - K_f\frac{4(1-\alpha_2)^2}{(2-\alpha_2)}\frac{p}{kT}\right]\frac{p}{vkT}, \tag{3}$$

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 α_2 in the general case. The reaction rate constants K_f and K_d depend on the temperature. Neglecting the thermal effect of the reaction, i.e., considering $\alpha_2\varepsilon_D \ll kT$, 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_d. 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 $P_f = 1$. The ratio between the forward and reverse reaction constants K_d/K_f equals, as is known, the equilibrium constant K_e. In [6] this ratio was expressed in terms of the dependence $\xi_{2e}(T)$ obtained from the SVC. To set the computed and experimental dependences in correspondence, the dissociation constant in [6] was assumed zero for $T^* < 0.58$ ($T^* = kT/\epsilon$ is the reduced temperature, and ϵ 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., by forming hydrogen bonds.

2. The use of the dependence $\xi_{2e}(T)$, 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.

We chose the following system of constants. The dissociation constant K_d and the equilibrium constant K_e, obtained on the basis of a statistical analysis of molecular data, were considered the main constants. It is clear from (3) that the recombination constant is defined by the ratio

$$K_f = \frac{K_d}{K_e} kT.$$

The dissociation constant can be written in the form [10]

$$K_d = Z_0 P_\sigma \frac{\rho(\varepsilon_0) kT}{Q_v(T)} e^{-\varepsilon_0/kT}, \tag{4}$$

where Z_0 is the collision frequency; $\rho(\varepsilon_0)$, density of states; Q_v, vibrational partition function; and P_σ, probability factor. The magnitude of the activation barrier ε_0 was equated to the dimer dissociation energy ε_D in the computations. The vibrational partition function and the density of states for a system of s harmonic oscillators have the form

$$Q_v(T) = \prod_{i=1}^{s} (1 - e^{-\varepsilon_i/kT})^{-1}; \tag{5}$$

$$\rho(\varepsilon) = \frac{(\varepsilon + \varepsilon_z)^{s-1}}{(s-1)! \prod\limits_{i=1}^{s} \varepsilon_i}, \tag{6}$$

where $\varepsilon_i = h\nu_i$ is the energy of a vibrational quantum; $\varepsilon_z = \frac{1}{2}\sum\limits_{i=1}^{s} h\nu_i$, zero energy; and s, number of active degrees of freedom. After substituting (5) and (6) into (4), the dissociation constant K_d can be calculated if the molecular constants of the water dimer are known. The number s can be taken equal to the number of (low-frequency) intramolecular vibrations in the water dimer molecule by considering that the internal rotation around the hydrogen bond can also be taken as a vibrational degree of freedom. The collision frequency is $Z_0 = 2d_{12}^2 \cdot (2\pi kT/m)^{1/2}$, where m is the reduced mass of the colliding molecules, d_{12} is the effective dimer $d_{12} = (1/2)(d_1 + d_2)$. Because only the product $d_{12}P_\sigma$ enters into the computation, the rough estimate d_{12} = 4 Å can be taken for d_{12}. The probability factor was here taken equal to one.

The equilibrium constants K_e for the water molecule dimerization reaction are estimated quite approximately in the literature up to now. This is related, firstly, to the absence of direct experimental and insufficiently accurate quantum-mechanical data about the structure, spectrum, and energetics of the water associates, and, secondly, to the absence of measurements of the dimer concentrations under equilibrium conditions. The temperature dependence of the increment in the Gibbs potential is displayed in Fig. 1 for the dimerization reaction (1 [14], 2 [11], 3 column II in Table 1, 4 [13], 5 [12], the data in [13] extrapolated from T = 400°K to the low-temperature domain, 11 from 220°K). It is seen that the literature data for ΔG°_f have a spread of about 1-2 kcal/mole. The spread in the magnitude of the equilibrium constant is especially significant in the low temperature domain since

$$K_e = \exp(\Delta G_f^0/RT).$$

An inaccuracy on the order of 0.5 kcal/mole (for $T \simeq 120$°K) in determining ΔG°_f will result in determining K_e to order-of-magnitude accuracy. For low concentrations $\xi_{2e} \simeq p/K_e$, i.e., even the equilibrium concentrations themselves can be calculated to within order of magnitude limits for the mentioned inaccuracy in determining ΔG°_f. Without having additional information available, at the present time it is apparently difficult to expect to achieve greater accuracy in computing low equilibrium concentrations of the water dimers. The accuracy in determining the nonequilibrium concentrations (without using adjustment parameters) cannot evidently be higher. It would be interesting to answer two questions in this connection: first, how well can the results of the experiment [6] be described by a statistical computation by using literature data on the molecular water dimer parameters (to the accuracy mentioned), and second, what is the sensitivity of a similar analysis to the inaccuracy of assigning the molecular constants themselves. Without intending to give an exhaustive critical survey of the literature data, we shall limit ourselves to using the three sets of molecular parameters presented in Table 1. The dimer was considered open in all the

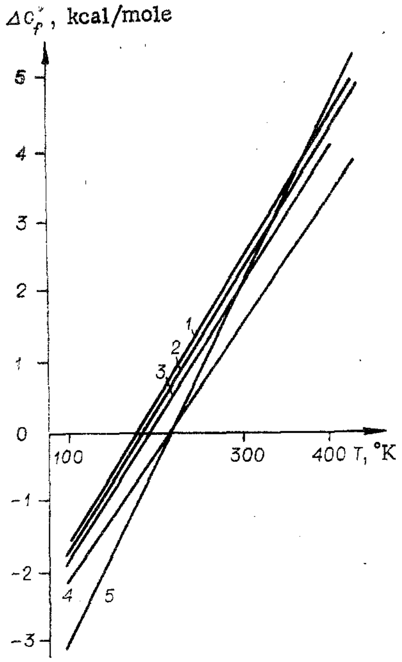

Fig. 1

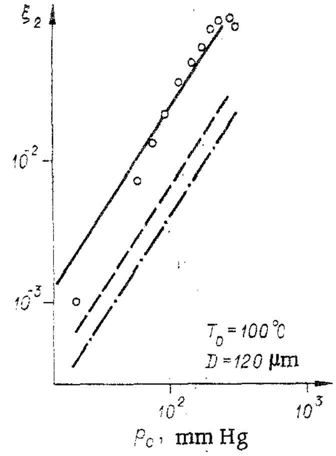

Fig. 2

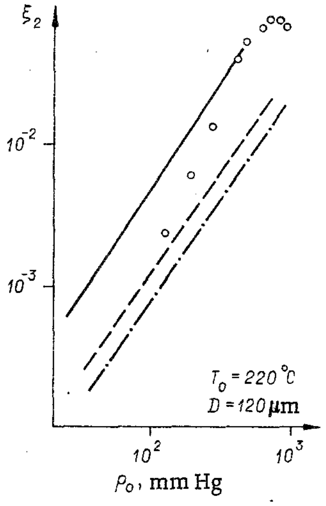

Fig. 3

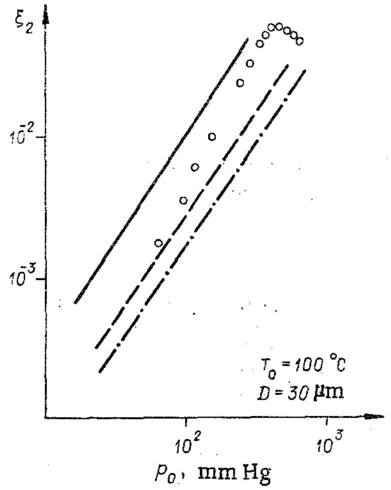

Fig. 4

versions, but the valence and deformation frequencies of the monomer ν_{MOH} and the dimer ν_{W-M} are borrowed from [15]. Equation (3) was solved on an electronic computer, where the calculations were truncated for $x/D \approx 8$ (D is the nozzle diameter), which corresponded to a quasistationary dimer concentration build-up [6]. The results of computing the nonequilibrium dimer concentrations for the experiment conditions [6] are shown in Figs. 2-4 (points are experiment [6], solid, dashed, and dash-dot lines are columns I-III in the table, respectively). Comparison with experiment shows:

1. A computation using literature molecular data yields satisfactory agreement with experiment in order of magnitude, without using adjustment constants.

2. The discrepancy between experimental and theoretical dependences can be compensated by selecting, e.g., the hydrogen bond energy (for a given set of frequencies) within known quantum-chemical estimates (see [16], for example) or by revising the probability factor which should actually differ from one because of the presence of molecule rotation and orientation effects.

3. The estimate of the equilibrium fraction of dimers under normal conditions ($T = 300°K$, $P_{H_2O} \approx 20$ mm Hg) by using the equilibrium constants calculated from data in Table 1 $\xi_{2e} \approx 10^{-3}-10^{-4}$ agrees with that taken in the literature (see [17], for instance).

In conclusion, we note that the correct solution of the inverse problem, i.e., the restoration of the molecular parameters from the measured dimer concentrations, or, e.g., the thermophysical properties of water vapor, is not possible at this time. However, direct statistical analyses using molecular data can now be recommended; however, the pretensions to high accuracy are not possible until new experimental results on the structure and spectra of the simplest associates of water will have been obtained.

APPENDIX

Let us first consider certain useful relationships between the useful component concentrations. Let $n_i = N_i/V$ be the number of particles of the i-th species per unit volume. Then the mass fraction of the particles is

$$\alpha_i = n_i\mu_i/\rho, \tag{A1}$$

where μ_i is the molecular weight and ρ is the gas density. Formula (A1) can be rewritten in the form

$$\alpha_i = N_i\mu_i/N\bar{\mu}, \tag{A2}$$

where $\bar{\mu}$ is the mean molecular weight and N is the total number of particles.

The molar fraction $\xi_i = N_i/N$ is related to α_i as follows:

$$\alpha_i = \xi_i\mu_i/\bar{\mu}.$$

In particular, for the dimerization reaction $\bar{\mu} = 2\mu_1/(2 - \alpha_2)$

$$\xi_1 = 2(1 - \alpha_2)/(2 - \alpha_2),\ \xi_2 = \alpha_2/(2 - \alpha_2). \tag{A3}$$

For low concentrations $\alpha_2 \approx 2\xi_2$, i.e., the mass fraction is twice the molar fraction.

The change in dimer concentration in the reaction (2) is written in a gasdynamic stream in the form [18]

$$\left(\frac{dn_2}{dt}\right)_p = \frac{dn_2}{dt} + \frac{n_2}{v}\frac{dv}{dt} = -K_d n_1 n_2 + K_f n_1^3. \tag{A4}$$

Let us examine the left side of (A4) after first dividing it by n

$$\frac{1}{n}\left(\frac{dn_2}{dt}\right)_p = \frac{1}{n}\frac{dn_2}{dt} + \frac{n_2}{n}\frac{dv}{dx}.$$

Because of the continuity equation $dv/dx = (1/V)(dV/dt)$, from which

$$\frac{1}{n}\left(\frac{dn_2}{dt}\right)_p = \frac{1}{n}\frac{dn_2}{dt} + \frac{n_2}{nV}\frac{dV}{dt} = \frac{1}{N}\frac{dN_2}{dt}.$$

Taking into account that $dN_2/dt = (\bar{\mu}N/\mu_2)d\alpha_2/dt$ according to (A2), we will have

$$\frac{1}{n}\left(\frac{dn_2}{dt}\right)_p = \frac{\bar{\mu}}{\mu_2}\frac{d\alpha_2}{dt}. \tag{A5}$$

The right side of (A4) is here written in the form

$$-K_d\xi_1\xi_2\left(\frac{p}{kT}\right) + K_f\xi_1^3\left(\frac{p}{kT}\right)^2. \tag{A6}$$

Using the normalization condition $\xi_1 + \xi_2 = 1$, and (A3), and equating (A6) and (A5), we arrive at (3).

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EXOTHERMIC GAS-PHASE REACTORS AS THE CAUSE OF MULTITEMPERATURE FLOWS OF POLYATOMIC GASES

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A multitemperature flow is usually understood as a flow of a polyatomic gas with different temperatures for the translational and vibrational degrees of freedom [1-3]. There can be differences in translational temperature in components of a mixture, which is one of the consequences of marked differences in molecular mass. The most familiar example of this kind is an ionized gas in an external electric or electromagnetic field [4, 5]. An example has been considered [6] of a multitemperature state for the translational degrees of freedom due to an endothermic reaction in a one-component light gas, which is in a thermostat composed of the heavy component that is neutral in relation to the reaction. The state of the diluent is not perturbed by the reaction, which is examined for times such that one can neglect the reverse reaction. A similar treatment is found in [7-10], where various cases of nonequilibrium velocity distributions were considered for components of a chemically reacting mixture.

A characteristic feature of an exothermic reaction in a mixture with substantial differences between the masses of the molecules is that the energy released by an elementary act is borne off almost completely by the lighter product. There is only slow energy exchange in collisions between particles differing considerably in mass, so the locally equilibrium energy distribution for the translational degrees of freedom of each of the components may occur before complete equilibrium. This situation is described by the equations of multitemperature gasdynamics, which are derived here.

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