EQUATION FOR THE NUMBER OF QUANTA

AND THE DISSOCIATION RATE IN A DIATOMIC GAS

M. B. Zheleznyak and A. Kh. Mnatsakanyan

We examine vibrational relaxation in a one-component diatomic gas, the molecules of which are described by a Morse potential. An expression is obtained for the mean number of quanta of a molecule assuming there exists a sharp boundary which separates vibrational levels into two groups. In each group there dominates either vibrational-quantum exchange processes or energy-exchange processes between the vibrational and translational degrees of freedom. By solving numerically the system of equations for the number of quanta and for the dissociation rate for times larger than the vibrational relaxation time, the dependence of the dissociation constant on the number of quanta is obtained.

It is possible, when considering thermal dissociation in a one-component diatomic gas, to distinguish several characteristic times [1]. First of all, there is the formation time for the distribution over vibrational levels, τ^*; then, there is the relaxation time for the vibrational energy (or for the number of quanta), τ_{VT}, and the dissociation time, τ_D. In the presence of strong exchange of quanta at the lower vibrational levels, which occurs at fairly low gas temperatures, there exists among the characteristic times the relation $\tau^* \gg \tau_{VT} \ll \tau_D$. In this case over the time τ^* there is in the system of molecules a quasistationary distribution over the vibrational levels [1], which is determined by the number of vibrational quanta, slowly varying in time, and by the dissociation rate and gas temperature.

To determine the number of quanta in a system of anharmonic oscillators, the system of equations for the equilibrium of particles at vibrational levels has been solved numerically [2, 3] or the equation for a harmonic oscillator has been used [4, 5]. The applicability of the energy equation in the harmonic approximation to a system of anharmonic oscillators was not discussed in [4, 5].

For times $t > \tau_{VT}$ the number of quanta of the system, and also the quasistationary distribution, are determined by only the dissociation rate. Dissociation causes a deviation of the distribution from the equilibrium distribution corresponding to the gas temperature, which then affects the magnitude of the dissociation constant. A number of papers [4-8] have been devoted to the study of this phenomenon. Treanore and Marrone [6, 7] give general expressions for the kinetics of vibrational relaxation and dissociation, and in the harmonic approximation they obtain equations for the vibrational energy and dissociation constant. Kuznetsov [8] also shows in the harmonic approximation that dissociation leads to an appreciable lowering of the vibrational temperature and to a reduction in the dissociation rate.

An analogous treatment of a system of harmonic oscillators is given by Kuznetsov [5]. He assumed that at the lower vibrational levels, where quantum-exchange processes dominate, the distribution of Treanore [9] is realized. At the upper levels, where energy exchange occurs between the translational and vibrational degrees of freedom, a Boltzmann distribution with the gas temperature is achieved. Kuznetsov [5] failed to take into account the distorting influence of dissociation on the distribution and used the equation for the vibrational energy in the harmonic approximation.

In the present paper we give an expression for the rate of change of the number of quanta in the quasistationary regime ($t \gg \tau^*$) for a system of anharmonic oscillators. The obtained expression is trans-

formed to a simple form under the condition that there exist a sufficiently sharp boundary separating the vibrational levels into two groups, in each of which there dominates either quantum-exchange processes or energy-exchange processes between the vibrational and translational degrees of freedom. By solving numerically the system of equations for the number of vibrational quanta and the dissociation rate for times $t > \tau_{VT}$ we obtain the dependence of the dissociation constant on the number of quanta in the system. It is shown that the use of the harmonic-oscillator equation leads to a considerable exaggeration of the effect of dissociation on the store of vibrational quanta in the system and, hence, on the dissociation constant.

To describe the nonequilibrium dissociation of diatomic molecules, we use a kinetic equation representing the dissociation process as the motion of molecules in energy space. In the kinetics of transitions between vibrational levels we take into account only single-quantum transitions. The population of the vibrational levels and the decay rate of the molecules are determined by the probabilities for vibrational−translational exchange $P_{K+1,K}$ (V−T processes) and for exchange of vibrational quanta $Q_{K+1,K}^{m,m+1}$ (V−V processes).

It is assumed that dissociation can occur only from the top vibrational level N with probability P_{NC}. Let us consider the initial stage of dissociation on suddenly raising the translational temperature of the gas T. In this case the number of quanta in a single molecule q is less than the equilibrium number q^0 at the gas temperature. In addition, recombination of atoms can be ignored.

The system of equations determining the population of the vibrational levels n_K has the form

$$\frac{1}{n_M}\frac{dn_K}{dt} = \Delta j_K^{(VT)} + \Delta j_K^{(VV)}; \quad \frac{1}{n_M}\frac{dn_N}{dt} = j_{N-1}^{(VT)} + j_{N-1}^{(VV)} - \lambda, \tag{1}$$

where $j_K^{(VT,VV)}$ is the flux of particles between levels K-1 and K due to V−T and V−V processes; $\Delta j_K = j_K - j_{K+1}$; n_M is the concentration of the molecules; and $\lambda n_M = -dn_M/dt$ is the dissociation rate of the molecules.

We can write the expression for the fluxes in the form

$$j_K^{(VT)} = P_{K-1,K}\, x_{K-1} - P_{K,K-1}\, x_K;$$

$$j_K^{(VV)} = x_{K-1}\sum_0^{N-1} n_{m+1} Q_{K-1,K}^{m+1,m} - x_K \sum_0^{N-1} n_m Q_{K,K-1}^{m,m+1};$$

$$x_K = n_K/n_M; \quad \sum_0^N x_K = 1. \tag{2}$$

Since we are considering conditions under which $q < q^0$, the sums in (2) are linearized, and the solution to the system (1) for times $t > \tau^*$ is obtained in the form [1, 10]

$$x_K = x_K^0(1 + \lambda\chi_K); \tag{3}$$

$$x_K^0 = x_0 \exp\left[-\frac{E_1}{T_1}(K+1) + \frac{(K+1)E_1 - E_{K+1}}{T}\right]\cdot\prod_0^K \varphi_{i+1};$$

$$\varphi_{i+1} = \left[\beta Q_{i+1,i}^{01} + P_{i+1,i}\exp\left(\frac{E_1}{T_1} - \frac{E_1}{T}\right)\right]\Big/(\beta Q_{i+1,i}^{01} + P_{i+1,i});$$

$$\chi_K = \chi_0 - \sum_0^{K-1} \frac{\sum_0^m x_i^0}{x_{m+1}^0(\beta Q_{m+1,m}^{01} + P_{m+1,m})},$$

where x_K^0 is the quasistationary distribution in the absence of dissociation; E_K is the energy of the K-th level; T_1 is the population temperature of the first excited state; β is a factor effectively taking into account the contribution to the transition probability from all excited states (the explicit form of β is given in [10]); the quantity χ_0 is found from the normalization condition.

We see that the distribution (3) depends on the parameter T_1 or on the store of quanta in a single molecule q, which is uniquely related to T_1. The relation between q and T_1 is determined by

$$q = \sum_0^N K x_K \tag{4}$$

Let us write an equation for the number of quanta. Multiplying each equation in (1) by K and summing, we obtain

$$\frac{dq}{dt} = \sum_{0}^{N-1} j_{K}^{(VT)} - \lambda (N - q). \tag{5}$$

Putting (3) into (5), we get an expression for the rate of change of the number of quanta in the quasistationary regime:

$$\frac{dq}{dt} = \sum_{0}^{N} \left\{ P_{K+1,K} x_{K+1}^{0} \left[\frac{\exp\left(\frac{E_1}{T_1} - \frac{E_1}{T}\right)}{\varphi_{K+1}} - 1 \right] \right\} - \lambda \left\{ N - q \div \sum_{0}^{N} P_{K+1,K} x_{K+1}^{0} \left[\frac{\exp\left(\frac{E_1}{T_1} - \frac{E_1}{T}\right)}{\varphi_{K+1}} \chi_K - \chi_{K+1} \right] \right\}. \tag{6}$$

The system of equations (4) and (6) determines T_1 as a function of time. The condition that (4) and (6) be applicable for time $t > \tau^*$ is $\tau^*/\tau_D \ll 1$.

Equation (6) simplifies considerably if there is a sufficiently well-defined boundary n* dividing the vibrational spectrum into two parts. In the region of the lower vibrational levels $K < n^*$ the V−V processes dominate; in the upper region $K > n^*$ the V−T processes are most important.

In this approximation we have

$$\frac{\exp\left(\frac{E_1}{T_1} - \frac{E_1}{T}\right)}{\varphi_{K+1}} = \begin{cases} \exp\left(\frac{E_1}{T_1} - \frac{E_1}{T}\right), & K < n^* \\ 1, & K > n^*. \end{cases} \tag{7}$$

A consequence of (7) is the fact that Eq. (6) depends weakly on the form of the probabilities at the upper levels even for fairly high temperatures, when multiple-quantum transitions are possible.

When (7) is taken into account, Eq. (6) is transformed up to terms of order $P_{K+1,K}/Q_{K+1,K}^{m,m+1}$ ($K < n^*$) to the form

$$\frac{dq}{dt} \frac{\tilde{q}(T) - \tilde{q}(T_1)}{\tau_{anh}} - \lambda(n^* - q);$$

$$\tau_{anh}^{-1} = \sum_{0}^{n^*} P_{K+1,K} x_{K+1} \tilde{q}(T_1) Q(T).$$

Here $\tilde{q}(T) = (e^{E_1/T} - 1)^{-1}$ is the number of quanta, and $Q(T) = (1 - e^{-E_1/T})^{-1}$ is the harmonic-oscillator partition function.

In the general form (4) the dependence of $q(T_1, T)$ is fairly complicated. However, if we consider the condition of preferential excitation of the vibrational degrees of freedom ($T_1 < T$), the quantities q calculated for the harmonic and anharmonic oscillators are similar to one another [1]. In this case we find

$$\frac{dq}{dt} \approx \frac{q^0 - q}{\tau_{anh}} - \lambda(n^* - q). \tag{8}$$

Let us consider further as a molecular model the Morse oscillator, which is characterized by the relations $D = E_1 N/2$ and $N = 1/2x_e$, where D and x_e are the dissociation potential and the anharmonicity parameter. We take the transition probabilities in the form [1, 11]

$$P_{K+1,K} = \frac{K+1}{1 - K/2N} P_{10} \exp\left(\frac{K\delta}{N}\right) \cdot \frac{3 - \exp[-\delta(1 - K/N)]}{3 - \exp(-\delta)}; \tag{9}$$

$$Q_{K+1,K}^{01} = \frac{K+1}{1 - K/2N} Q_{10}^{01} \exp\left(-\frac{K\delta}{N} - \frac{E_1 K}{TN}\right) \cdot \frac{3 - \exp\left(-\frac{K\delta}{N}\right)}{2};$$

$$\delta = 2\sqrt{\gamma D/T}; \quad \gamma = \frac{M}{m}\left(\frac{\pi}{3}\alpha L\right)^2,$$
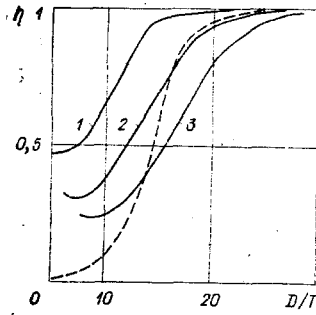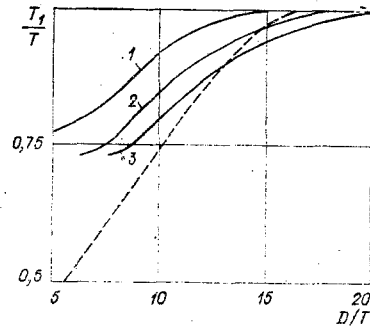
Fig. 1   Fig. 2

where M and m are the reduced masses of the colliding particles and the oscillator; α is the parameter of the Morse potential; L is a characteristic length of the interaction potential of the colliding particles.

Using (9) we find the level n* from the condition $P_{K+1,K} = \beta Q_{K+1,K}^{01}$,

$$n^* = \frac{N}{2}\left[1 + \frac{\ln\left(\beta Y_{10}^2\right)}{\delta}\right],\tag{10}$$

where Y_{10}^2 is the square of the matrix element for the transition $1 \to 0$.

Multiplying Eq. (8) by E_1 and substituting Eq. (10) into Eq. (8), we obtain

$$\frac{d\varepsilon(T_1)}{dt} = \frac{\varepsilon(T) - \varepsilon(T_1)}{\tau_{anh}} + \frac{dn_M}{dt}[D - \varepsilon(T_1) + E^*]; \quad E^* = D\frac{\ln\beta Y_{10}^2}{\delta},\tag{11}$$

where $\varepsilon = E_1 q$. For τ_{anh} we can take the approximate expression from [9].

Equation (11) is analogous to the equation of the vibrational energy for a harmonic oscillator. The difference consists of the magnitude of the relaxation time and the additional term E^* in the coefficient of dn_m/dt. The quantity E^* is negative, which leads to a decrease in the effect of dissociation on the distribution of the lower vibrational levels for the Morse oscillator. This reflects the weak exchange of vibrational quanta of the lower levels with the upper ones, where the distortion of the distribution due to the dissociation flux is most important.

The dissociation rate of the molecules is determined by the equation

$$\frac{1}{n_M}\frac{dn_M}{dt} = -\eta(T_1, T)\,\kappa_D(T),\tag{12}$$

where $K_D(T)$ is the dissociation constant of the molecules in an inactive gas, obtained for the same transition probabilities between the levels as in the actual gas [10].

The factor $n(T_1, T)$ allows for the change in the dissociation rate due to the deviation of T_1 from T, which is a consequence of the action of the V−V processes. The temperature T_1 has to be found from the simultaneous solution of Eq. (12) with Eq. (6) or Eq. (11). The quantity η can be represented approximately in the form

$$\eta(T_1, T) \approx \frac{Q(T)}{Q(T_1)}\prod_{K=0}^{N-1}\left[\varphi_{K+1}\exp\left(\frac{E_1}{T} - \frac{E_1}{T_1}\right)\right].\tag{13}$$

We take the expression for K_D from [11],

$$\kappa_D = ze^{-D/T}\left(1 - e^{-E_1/T}\right)\left(2NT/\pi E_1\right)^{1/2}G;$$

$$G = \frac{M}{m}\frac{1 - \sqrt{\gamma T/D}}{1 + \sqrt{\gamma T/D}}\frac{3 - \exp(-2\gamma)}{\mathrm{erf}\left(\sqrt{2\gamma}\right)}e^{-\gamma},\tag{14}$$

where z is the number of collisions per unit time.

Let us consider the solution to Eqs. (6) and (12) for times $t \gg \tau_{VT}$, when $dq/dt \approx 0$. Putting (12)-(14) into (6) and using the transition probabilities (9), we find T_1 and η numerically for the given gas tem-

perature. The curves of $\eta(T)$ and $T_1(T)$ for quasistationary conditions are shown in Figs. 1 and 2 for $\gamma = 1, 2, 3$ and $N = 50$. Varying N from 25 to 100 does not affect the results in an essential way. For comparison we also present in Figs. 1 and 2 the results of Kuznetsov [5] (dashed curves). Comparison of the curves shows that the use of the vibrational-energy equation in the harmonic approximation [5] exaggerates the effect of dissociation on the population temperature of the lower levels T_1 and accordingly leads to an appreciable decrease in η. We note that in the limit of sufficiently high temperatures, when the $V-T$ processes are decisive, η should go to unity. However, the calculation at these temperatures is not possible because the quasistationary distribution is inapplicable.

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