

RELAXATION EQUATION FOR THE VIBRATIONAL ENERGY OF THE MOLECULES IN THE GAS
BEHIND AN INTENSE SHOCK FRONT

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A sufficiently rigorous derivation of the vibrational-energy relaxation equation for a dissociating gas is possible only for the model of single-quantum transitions in a harmonic oscillator; in this case, it is not difficult to obtain [1, 2]

$$\frac{d\varepsilon}{dt} = \frac{\varepsilon^\circ - \varepsilon}{\tau} + E^* \frac{dn}{dt} \quad (1)$$

Here ε is the vibrational energy per unit volume of the gas, ε° is the equilibrium value of ε , τ is the relaxation time, E^* is the average vibrational energy lost during each molecular dissociation, and n is the number density of molecules. In a description of the relaxation processes in intense shock waves in a gas, the anharmonicity and thus multiquantum transitions and dissociation become important. To determine whether Eq. (1) can be used in this case, we must examine the system of kinetic equations for the number of molecules x_i at each vibrational level under the assumption that transitions $i \leftrightarrow j$ are possible between any two levels, and that transitions $i \leftrightarrow d$ are possible from any level to the dissociation continuum:

$$\frac{dx_i}{dt} = Z \sum_{j \neq i}^{d-1} P_{ji}(T) x_j - Z \sum_{j \neq i}^d P_{ij}(T) x_i + Z P_{di}(T) x_d^2, \quad i = 0, 1, 2, \dots, d-1 \quad (2)$$

$$\frac{1}{2} \frac{dx_d}{dt} = Z \sum_{j=0}^{d-1} P_{jd}(T) x_j - Z \sum_{j=0}^{d-1} P_{dj}(T) x_d^2 \quad (3)$$

Here x_d is the concentration of dissociated atoms, Z is the collision frequency, and $P_{ij}(T)$ and $P_{jd}(T)$ are the probabilities for the corresponding transitions. Solving system (2), (3) numerically, and calculating $\varepsilon = \sum E_i x_i(t)$ (E_i is the energy of the i -th level) and $n = \sum x_i(t)$, we see that Eq. (1) can be approximately satisfied in oxygen even at very high temperatures, up to $T = 20\,000^\circ \text{K}$. The probabilities $P_{ij}(T)$ and $P_{jd}(T)$ used in the solution were determined within the framework of classical mechanics by a variation of the initial collision conditions (different molecular orientations and different oscillation phases) for an O_2 -Ar mixture.

The intramolecular potential was calculated by the Rydberg-Klein-Rees method for the real molecule with an account of anharmonicity. The intermolecular potential used was a sum of exponential terms corresponding to the repulsive forces between the incident atoms and the atoms bound in the molecule, with the parameters obtained from the elastic scattering of molecular beams (some of the details of the dynamical-problem formulation are described in [3]).

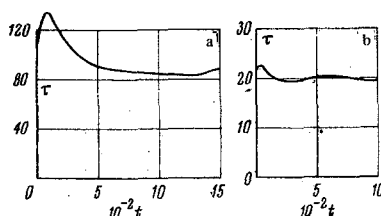


Fig. 1

The quantity E^* , given by

$$E^* = \frac{1}{dn/dt} (\sum P_{di} E_i x_d^2(t) - \sum P_{id} E_i x_i(t)) \quad (4)$$

is found from a solution of Eqs. (2) and (3) to be independent of the time and to be $E^* = D - 1.3kT$ (D is the dissociation energy); accordingly the difference $D - E^*$ is approximately equal to the average thermal energy of the system, regardless of the extent to which the system deviates from equilibrium. Since the quantity τ in Eq. (1) changes only very slightly (Fig. 1), Eq. (1) may be assumed satisfied. This result is closely associated with the fact that the deviations from a Boltzmann distribution of molecules among levels as the system approaches equilibrium are important only at those levels where there are relatively few molecules.

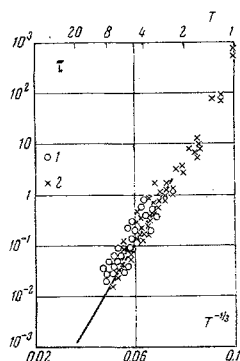


Fig. 2

The values of τ were found according to Eq. (1) at temperatures up to $10\,000^\circ\text{K}$ (Fig. 2), from shock-tube experiments in which the population changes in the lower levels of the oxygen molecule were studied (from the UV absorption spectrum of the gas behind the shock front). The agreement between experiment and calculation confirms the conclusions regarding the use of Eq. (1) to solve the corresponding high-temperature gas dynamic problems.

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