ON THE THEORY OF VIBRATIONAL RELAXATION

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Equilibrium with respect to vibrational degrees of freedom in gases (vibrational relaxation) is established as a result of energy transfer between the translational and vibrational degrees of freedom of the molecules upon collision. At temperatures below or of the order of the characteristic temperatures (for the vibrational degrees of freedom) the process of energy transfer between the translational motion of the molecules and their vibrations is of a one-quantum nature. This means that as a result of inelastic collisions the molecules can make transitions only to neighboring vibrational levels. At temperatures much higher than the characteristic temperatures the vibrational transitions are not limited by the selection rule $\Delta V = \pm 1$, i.e., they are of a multi-quantum nature. In the case of diatomic gases the boundary between the regions of one-quantum and multi-quantum transitions is the interval of temperatures determined from the condition

$$\frac{\omega}{2\pi} \tau_c \sim 1,$$

where $\omega$ is the circular frequency of vibrational motion (harmonic oscillator model), and $\tau_c$ is the collision time. The physical significance of condition (1) is obvious. At temperatures lower than the characteristic temperatures the collision time is large compared with the period of the vibrations, therefore the perturbations introduced by collisions are adiabatic in character. Under these conditions the transition probabilities are small and virtually only transitions to neighboring levels are allowed. At high temperatures the collision time is small as compared with the period of the vibrations. The perturbations due to collisions are nonadiabatic and sudden in nature. In this case the transition probabilities are large even for multi-quantum transitions.

Condition (1) can be rewritten in the form

$$\frac{\omega}{2\pi} \frac{2}{\sigma v} = \frac{m}{\pi a} \sqrt{\frac{m}{3kT}} \sim 1,$$

where $a^{-1}$ is the range of the intermolecular forces of repulsion ($a = 2 \times 10^{-8}$ cm$^{-3}$), $v$ is the thermal velocity of the molecules, and $m$ is the reduced mass of the colliding particles. For the binary mixture O$_2$-Ar or the one-component system O$_2$ the limiting temperature $T^*$ is determined from conditions (2) and is found to be approximately 4000–5000$^\circ$ K. With decrease in the frequency of the vibrations or with decrease in the reduced mass of the colliding particles (for a binary gas mixture) the values of $T^*$ decrease.

Vibrational relaxation of diatomic gases has now been quite thoroughly studied in the temperature interval from room temperatures to $T^*$. The Landau-Teller [1] theory (and its subsequent modifications [2]) satisfactorily describes the majority of the existing experimental data [3]. In accordance with [1] the relaxation of the vibrational energy $E$ of unit volume is described by the equation

$$\frac{dE}{dt} = -\frac{E - E_0}{\tau},$$

where

$$\tau = \left[Z P_{10} \left(1 - e^{-\frac{kT}{kT}} \right)\right]^{-1}.$$

Here $\tau$ is the relaxation time, $N$ is the number density of the molecules, $P_{10}$ is the probability of transition of a molecule from the first excited state to the ground state, referred to a single collision, $Z$ is the number of collisions experienced by a molecule in one second, and

$$E_0 = \frac{Nh vw}{1 - e^{-\frac{kT}{kT}}}$$

is the equilibrium value of the vibrational energy.

Vibrational relaxation at temperatures $T > T^*$ has not been investigated theoretically. Recently, however, experiments have been reported in which vibrational relaxation has been studied in precisely this temperature range [4–6].

In order to interpret the results obtained it is necessary to examine the process of vibrational relaxation at high temperature theoretically. This is the aim of the present paper.

For simplicity, we shall consider a binary mixture consisting of a monatomic gas and a small number of relaxing diatomic molecules. Under ordinary conditions (excluding the case of very high temperatures) the vibrational relaxation time is much greater than the translational and rotational relaxation times. Moreover, vibrational relaxation does not seriously interfere with the equilibrium distribution of energy with respect to the other degrees of freedom. Therefore, the process of vibra-

* $h$ should be read as $\hbar$. 
tional relaxation can be examined in isolation, assuming an equilibrium distribution of energy over the remaining degrees of freedom. At very high temperatures (for oxygen above 10,000 K) the vibrational relaxation time is comparable with the time required to establish a Maxwellian distribution and chemical equilibrium. Therefore the argument that follows will be confined to the region of not too high temperatures.

The study of vibrational relaxation at high temperatures can be much simplified if two factors are taken into account. In the region of temperatures in question

\[ h \omega \ll kT , \]

\[ \Delta \varepsilon \ll \frac{mv^2}{2} . \]

Here \( \Delta \varepsilon \) is the vibrational energy transferred to the molecule in a single collision with an atom. Condition (5) makes it possible to treat the problem in terms of classical mechanics, while condition (6) permits the use of the Fokker-Planck formalism.

In the space of vibrational energies \( \varepsilon \) the Fokker-Planck equation has the form

\[ \frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon} \left[ B \left( \frac{\partial f}{\partial \varepsilon} + \frac{f}{kT} \right) \right] , \]

where \( f(\varepsilon, t) \) is the probability density of the molecules in \( \varepsilon \) space at time \( t \). It is assumed that \( f \) does not depend on the coordinates of the configurational space. The quantity \( B \) is defined as follows:

\[ B = \frac{1}{2} \int (\Delta \varepsilon)^2 W(\varepsilon, \Delta \varepsilon) d(\Delta \varepsilon) , \tag{8} \]

where \( W(\varepsilon, \Delta \varepsilon) \) is the number of collisions experienced by the molecule in unit time, each of which transports the molecule from point \( \varepsilon \) to a neighborhood \( d(\Delta \varepsilon) \) of the point \( \varepsilon + \Delta \varepsilon \). Equation (7) may be obtained from the usual Fokker-Planck equation [7] if we require that as \( t \to \infty \), \( f \) tends to its equilibrium value. A direct derivation of (7) can also be found in [8].

To determine the coefficient \( B \), it is necessary to consider the dynamic problem of the collision of an oscillator with an atom. This problem was solved for one-dimensional collisions in [2], where the following expression was obtained for \( \Delta \varepsilon \):

\[ \Delta \varepsilon = \frac{1}{2} \int \int F(t) e^{\mu \sigma t} dt \]

\[ = \mu \sigma \cos \delta \int \int F(t) e^{\mu \sigma t} dt , \tag{9} \]

where \( \varepsilon = \mu \omega^2 x^2 / 2 \) is the initial vibrational energy of the oscillator, \( \mu \) is the reduced mass of the oscillator, and \( \delta \) is the initial phase of the oscillator.

Expression (8) was obtained on the assumption that inelastic scattering has only a weak effect on the trajectory of the centers of mass of the colliding particles. This condition is satisfied if (6) holds true. In this case the effect of an atom impinging on a molecule can be represented as the action of the external force \( F(t) \). The coefficient \( B \) in the Fokker-Planck equation (7) can be written, if we confine ourselves to one-dimensional collisions, in the form

\[ B = \frac{1}{2} \int \int \left[ \Delta \varepsilon (\varepsilon) \right]^2 \exp \left( -\frac{mv^2}{2kT} \right) \nu d\varepsilon . \tag{10} \]

From equations (9) and (10), after averaging over all the initial phases of the oscillator, we obtain

\[ B = \frac{1}{2} \int \int \Phi (\varepsilon) \exp \left( -\frac{mv^2}{2kT} \right) \nu d\varepsilon , \tag{11} \]

with account for (11) equation (7) assumes the form

\[ \frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon} \left[ (A + B) \left( \frac{\partial f}{\partial \varepsilon} + \frac{f}{kT} \right) \right] , \tag{12} \]

where

\[ A = \frac{1}{2} \int \int \Phi (\varepsilon) \exp \left( -\frac{mv^2}{2kT} \right) \nu d\varepsilon , \]

\[ B = \int \int \Phi (\varepsilon) \exp \left( -\frac{mv^2}{2kT} \right) \nu d\varepsilon , \]

With account for (11) equation (7) assumes the form

\[ \frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon} \left[ (A + B) \left( \frac{\partial f}{\partial \varepsilon} + \frac{f}{kT} \right) \right] , \tag{12} \]

We shall confine ourselves to an examination of the case when it is possible to neglect the quantity \( A \) as compared with \( B \), i.e., we shall consider those energies \( \varepsilon \) at which

\[ A \ll B \varepsilon . \tag{13} \]

Estimates show that over a quite broad interval of temperatures \( A \ll B \varepsilon \); therefore condition (13) is satisfied if the average energy per molecule \( \overline{\varepsilon} \sim kT \). It can be shown that the latter condition limits the applicability of the results obtained in relation to the analysis of the states of a gas behind a strong shock front. Immediately behind a strong shock front \( \overline{\varepsilon} \ll kT \), where \( T \) is the temperature of the translational degrees of freedom. Therefore, in this region condition (13) may not be satisfied. However, this is not important, since the overwhelming majority of experimental measurements of the rate of vibrational relaxation are not conducted in the region immediately adjacent to the shock front, where the results are least accurate, but relate to a certain central section of the relaxation zone where \( \overline{\varepsilon} \sim kT \). Therefore, in practice, condition (13) does not introduce additional constraints as compared with (8) and (6). With account for (13) equation (12) can be written in the form

\[ \frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon} \left( B \varepsilon \left( \frac{\partial f}{\partial \varepsilon} + \frac{f}{kT} \right) \right) . \tag{14} \]