Equations determining the temperature of vibrations and dissociation constant of polyatomic molecules with consideration of fast exchange of vibrational quanta are formulated. The equations are simplified considerably if different groups of oscillators have similar temperatures of vibrations. In the case of practical interest, it is sufficient to know the vibrational relaxation time and monomolecular dissociation constant at high densities for solving the problem in a harmonic approximation. Quantitative results are obtained for carbon monoxide.

During thermal dissociation the ratio of the number of active \( n^* \), i.e., capable of spontaneous dissociation, and inactive \( n \) polyatomic molecules at high densities remains in equilibrium. In a sufficiently rarefied dissociating gas the ratio \( n^*/n \) is less than its own thermodynamic equilibrium value and depends on density.

These qualitative regularities, characteristic of any gas, are explained by all theories of monomolecular dissociation (see, for example, monographs [1, 2] and a paper [3]) in which the rate of translational-vibrational exchange of energy is considered in one or another approximation, but exchange of vibrational quanta is not taken into account.

Nevertheless, there are cases when exchange of vibrational quanta affects the kinetics of dissociation and it must be taken into account for a correct description of the process. This pertains first and foremost to one-component molecular gases. Upon collection of identical molecules there occurs a relatively rapid exchange of vibrational quanta which leads to the establishment of vibrational equilibrium (quasi-equilibrium) within the group of identical oscillators. Such quasi-equilibrium exists also during thermal dissociation of polyatomic molecules, since the dissociation rate for any densities does not exceed the rate of vibrational relaxation — a slower process than the exchange of vibrational quanta.

If the population of the vibrational levels of an active molecule is quasi-equilibrium, the nonequilibrium ratio \( n^*/n \) and the monomolecular dissociation constant proportional to it are expressed by the vibrational temperatures of the groups of oscillators. In this case, the more general relationship

\[
\frac{n^*}{n} = f(T, T_1, T_2, \ldots)
\]

(0.1)

determining the dependence of \( n^*/n \) on the temperatures of the oscillators \( T_i \) and on the temperature of translational motion is fulfilled instead of the usual thermodynamic relationship for \( T \).

Strictly speaking, the region of quasi-equilibrium distribution of the energy of each group of oscillators has an upper limit \( \varepsilon_i \) above which the condition of fast exchange of vibrational quanta is not fulfilled as a consequence of the strong anharmonicity of vibrations. (This problem in the case of diatomic molecules was examined in detail in [4].) The vibrational states of the active molecule can be located both below
(state I) and above (state II) the limits ε₁. For molecules in state I Eq. (0.1) is valid for any temperatures. For molecules in state II the true value of n*/n differs slightly from (0.1) owing to disturbance of the quasi-equilibrium distribution at oscillator energies greater than ε₁. However, for sufficiently high temperatures [5] such that

\[
\left( \frac{e}{kT} \right)^3 \tau \gg 1
\]

(0.2)

where τ is the vibrational relaxation time of the oscillators having a minimum vibration frequency, k is the dissociation constant, and ε is the energy of the bond being broken, the deviation of n*/n from equilibrium value is determined mainly by the marked decrease of the quasi-equilibrium populations of the vibrational levels in the neighborhood and below the limits ε₁. The aforementioned additional change of n*/n at temperatures satisfying inequality (0.2) is a relatively small correction.

The kinetics of monomolecular dissociation of a one-component gas at high temperatures satisfying inequality (0.2) is examined below and relationship (0.1) is presumed to be fulfilled. Inequality (0.2) is usually satisfied for kT/ε > (0.04-0.06)-1n 5, where δ is the ratio of the gas density to its normal density.

1. Equations Determining the Temperature of Vibrations

and Rate of Monomolecular Dissociation

Calculation of the monomolecular dissociation constant in the case of fulfilling relationship (0.1) and at a given temperature of translational motion T reduces to determination of the dependence of the dissociation constant on the vibrational temperatures and to a calculation of these temperatures with consideration of all positive and negative energy sources.

The dependence of the monomolecular dissociation constant on the vibrational temperatures in a harmonic approximation (k₁) and in an approximation of an ergodic active molecule (k₂) was determined in [6] and has, respectively, the form

\[
k₁ = A \exp \left( \frac{-ε₁ x₁^2}{k T} \right)
\]

(1.1)

\[
k₂ = A \exp \left( \frac{-ε₁ x η}{k T} \right)
\]

Here, ε₁ is the activation energy, A is determined by Slater's formula [2]

\[
2πA = \sqrt{2x₁ω₁^2 / x₁²}
\]

(1.2)

ω₁ is the angular frequency of oscillations, the x₁ are the coefficients of expansion of the reaction coordinate with respect to normal coordinates, Tm is the maximum temperature from the sequence T₁, T₂, ..., Tₙ.

If the reaction occurs without a change of spin, the activation energy figuring in (1.1) is equal to the energy of breaking the chemical bond ε. If the reaction is "spin-forbidden" and the limiting stage of the reaction is the change of spin at the point of intersection of terms, the activation energy ε₂ is equal to the value of the potential at the point of intersection, and can be both greater and less than the bond energy. The preexponential factor in such cases is considerably less than that determined by Eq. (1.2). For example, for reactions of monomolecular dissociation of singlet molecules of CO₂ (high temperatures) and N₂O into CO and N₂, respectively, with the formation of an oxygen atom in the triplet state, the experimentally found [7, 8] dissociation constants at high densities kₐ at which the ratio n*/n is equilibrium, and T = T₁, T₂, ... have the form

\[
kₐ = A \exp \left( \frac{-ε₂}{k T} \right)
\]

(1.3)

where A = 10¹¹⁻¹¹ sec⁻¹, ε₂ = 110 kcal/mole for CO₂, and A = 10¹¹⁻¹¹ sec⁻¹, ε₂ = 59.5 kcal/mole for N₂O. The corresponding values of the bond energy are equal to 126 and 38.3 kcal/mole.

The vibrational temperatures established during thermal dissociation are determined by equations of quasi-stationarity

\[
\frac{E₁(T) - E₁(T₀)}{τ₁} + \left( \frac{∂E}{∂t} \right) = k [Δε₁ - E₁(T)]
\]

(1.4)

\[
E₁(z) = k θ₁ / (exp θ₁ / z - 1), \quad θ₁ = k ω₁ / k
\]

Here, τ₁ and E₁ are the vibrational relaxation time and energy of the i-th oscillator, ∂E₁/∂t is the sum of the terms taking into account the change of the vibrational energy upon exchange of quanta, and Δ₁ is the contribution of the i-th vibration to the energy of the activated state of the active molecule [6]. In the case of a harmonic molecule