PROBLEMS OF THE THEORY OF MONOMOLECULAR DISSOCIATION OF A ONE-COMPONENT GAS AND DISSOCIATION CONSTANT OF CO_2 AT HIGH TEMPERATURES

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UDC 511.10

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

$$n^* / n = f(T, T_1, T_2, \ldots) \tag{0.1}$$

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 ε_1 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

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Moscow. Translated from Zhurnal Prikladnoi Mekhanika i Tekhnicheskaya Fiziki, No. 3, pp. 46–52, May-June, 1972. Original article submitted November 9, 1971.

(state I) and above (state II) the limits ε_1. 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 ε_1. However, for sufficiently high temperatures [5] such that

$$(\varepsilon / kT)^2 \tau_1 k \gg 1 \tag{0.2}$$

where τ_1 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 its 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 ε_1. 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 $kT/\varepsilon > (0.04-0.06) - \ln \delta$, 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 (k_1) and in an approximation of an ergodic active molecule (k_2) was determined in [6] and has, respectively, the form

$$\begin{gathered} k_1 = A \exp\left(-\varepsilon_a \Sigma \alpha_i^2 / k \Sigma \alpha_i^2 T_i\right) \\ k_2 = A \exp\left(-\varepsilon_a / kT_m\right) \end{gathered} \tag{1.1}$$

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

$$2\pi A = \sqrt{\Sigma \alpha_i \omega_i^2 / \Sigma \alpha_i^2} \tag{1.2}$$

ω_i is the angular frequency of oscillations, the α_i are the coefficients of expansion of the reaction coordinate with respect to normal coordinates, T_m is the maximum temperature from the sequence $T_1, T_2, \ldots$.

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 ε_a 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 CO_2 (high temperatures) and N_2O into CO and N_2, respectively, with the formation of an oxygen atom in the triplet state, the experimentally found [7, 8] dissociation constants at high densities k_a at which the ratio n*/n is equilibrium, and $T = T_1, T_2, \ldots$ have the form

$$k_\infty = A \exp\left(-\varepsilon_a / kT\right) \tag{1.3}$$

where $A = 10^{11.4}$ sec^{-1}, $\varepsilon_a = 110$ kcal/mole for CO_2, and $A = 10^{11.1}$ sec^{-1}, $\varepsilon_a = 59.5$ kcal/mole for N_2O. 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

$$\begin{gathered} \frac{E_i(T) - E_i(T_i)}{\tau_i} + \left(\frac{\partial E_i}{\partial t}\right) = k\left[\Delta_i \varepsilon_a - E_i(T_i)\right] \\ E_i(z) = k\,\theta_i / (\exp \theta_i / z - 1), \qquad \theta_i \equiv h\,\omega_i / k \end{gathered} \tag{1.4}$$

Here, τ_i and E_i are the vibrational relaxation time and energy of the i-th oscillator, $\partial E_i / \partial t$ is the sum of the terms taking into account the change of the vibrational energy upon exchange of quanta, and Δ_i 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

$$\Delta_i = \alpha_i{}^2 T_i{}^2 \sum_k \alpha_k{}^2 \Big/ \Big(\sum_e \alpha_e{}^2 T_e\Big)^2$$

In the case of an ergodic active molecule $\Delta_i = 1$ for oscillators having a maximum temperature and $\Delta_i = 0$ for all other oscillators. Equations (1.4) are a direct generalization of the equation describing the quasi-stationary stage of dissociation of diatomic gas [4, 5].

2. Simplification of Equations in the Case of Fast Exchange of Quanta between Different Oscillators. Isothermal Approximation

The complete set of data needed for an exact solution of Eqs. (1.4) is unknown even for the simplest polyatomic molecules. The basis of approximate solutions is the circumstance that the ratios of the times of relaxation and exchange of vibrational quanta in many cases differ in order of magnitude from unity. Such approximations are well known in the theory of vibrational relaxation. In particular, if the probability of a one-quantum exchange between different groups of oscillators is considerably greater than the probability of vibrational-translational transitions, the system of relaxation equations reduces to one differential equation for the total number of vibrational quanta ν and to simple algebraic relationships between T_i, T, and ν, expressed [9, 10] in the form

$$\theta_i / T_i - \theta_k / T_k = (\theta_i - \theta_k) / T$$

$$\nu = \sum_i (\exp \theta_i / T_i - 1)^{-1} \tag{2.1}$$

Approximation (2.1) is fulfilled best of all when "adjacent" values of θ_i satisfy the inequality

$$(|\theta_i - \theta_k|) / \theta_i \ll 1 \tag{2.2}$$

In the case of fast exchange of vibrational quanta, relationships (2.1) are valid also in a dissociating gas. The complete system of equations describing dissociation is obtained after adding to (2.1) the equation of quasi-stationarity of the number of vibrational quanta, which follows from (1.4) and in the case of one-quantum exchange, i.e., when $\sum_i \partial E_i / \partial t) / \theta_i = 0$, has the form

$$\sum_i [E_i(T) - E_i(T_k)] / \theta_i \tau_i = k \sum_i [\Delta_i \varepsilon_a - E_i(T_i)] / \theta_i \tag{2.3}$$

The following two possibilities of further simplification of the equations are typical.

1. It is known from experiment and the theory of vibrational relaxation of polyatomic molecules that the vibrational relaxation time τ_1 of oscillators having a minimum frequency is usually considerably less than all other τ_i. In such a case, it is sufficient to leave one term containing τ_1 instead of the first sum in Eq. (2.3).

2. If thermal dissociation of molecules is the only cause of disturbance of thermodynamic equilibrium, the deviation of all T_i from T is comparatively small. Hence follows when fulfilling inequality (2.2) that the relative differences of the two vibrational temperatures are quantities of the second order of smallness. This is seen directly from the following form of notation of relationship (2.1)

$$(T_i - T_k) / T_i = (\theta_i - \theta_k)(T_k - T) / \theta_i T$$

The more common two- or three-quantum exchange [11] in the case of almost multiple frequencies (Fermi resonance) leads to practical equalization of the vibrational temperatures.

These circumstances permit using an isothermal model of a polyatomic molecule in calculating the thermal dissociation rate. In the model it is assumed that all vibrational temperatures T_k are the same and nonequilibrium of the state is manifested only in the difference of T_k from T.

Within the framework of the isothermal model, retaining in the first sum of (2.3) only the one term $i = 1$ corresponding to the lowest-frequency oscillator and disregarding the difference of ratios θ_i/θ_1 from unity in the nonexponential part of (2.3), we have

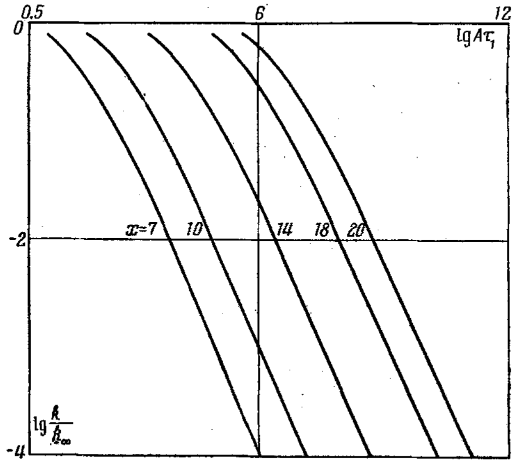

Fig. 1

$$[E_1(T) - E_1(T_k)] / \tau_1 = k(T_k)(\varepsilon_a - E) \qquad (2.4)$$

$$E \equiv \sum_i E_i(T_k), \quad k(T_k) \equiv A \exp(-\varepsilon_a / kT_k)$$

Here, it is taken into account that for equality of all vibrational temperatures

$$\sum_i \Delta_i = 1$$

Expression (2.4) for $k(T_k)$ follows from each Eq. (1.1).

Transcendental equation (2.4) determines the dependence of T_k and $k(T_k)$ on the temperature and density of the gas. For its solution, we must know the parameters A and ε_a figuring in the expression (2.4) for $k(T_k)$ and the vibrational relaxation time τ_1. Equation (2.4) can be regarded in a more general sense as a relation between $A\tau_1$, ε_a/kT and the ratio of the actual rate constant $k(T_k)$ into its equilibrium value $k_\infty \equiv k(T)$.

In the most interesting (in the sense of the interaction of the vibrational relaxation and dissociation processes) temperature region

$$E_i(T_i) \approx kT_i \ll \varepsilon_a$$

Here, at least for not too large molecules, the total vibrational energy is also considerably less than ε_a. After appropriate simplifications in the nonexponential parts of Eq. (2.4), we have

$$A\tau_1 x = y \exp[x / (1 - y)], \quad x = \varepsilon_a / kT, \quad y = 1 - T_k / T \qquad (2.5)$$

This equation differs substantially from the corresponding equation for diatomic gas [5] in that it contains as thermodynamic parameters not only the temperature but also the density (τ_1 is inversely proportional to density).

Let us consider at first the limiting cases of the solution of (2.5).

1. Small temperatures and large densities. In this case, as is easily seen, $y \ll 1$ and consequently, $k \approx k_\infty$.

2. Large temperatures and small densities. In this case, the deviation of T_k from T is large, i.e., y is of the order of unity, and changes little upon a change of temperature and density. Taking this change into account only in the exponential part of (2.5), we find

$$k \approx \text{const} / \tau_1 x$$

Thus, as could be expected, for small densities and high temperatures the monomolecular dissociation constant is proportional to the gas density.

In the remaining region of parameters Eq. (2.5) is solved numerically. The results of the solution are presented in Figs. 1 and 2.

The dependence of k/k_∞ on $A\tau_1$ and x solved explicitly relative to $\log(k/k_\infty)$ is expressed when $7 < x < 26$ also by the following interpolation formula:

$$\lg(k / k_\infty) = \begin{cases} t(1 + 4 \cdot 10^{-4} t^4)^{-1} - 4, & -1 \leqslant t < 5 \\ 0 & t \geqslant 5 \end{cases}$$

$$t = 0.337\, x - 0.87 \lg(A\tau_1) + 2.8$$

This formula reproduces the solution of Eq. (2.5) with an error of $\Delta k/k < 0.2$ upon a change of k/k_∞ from 1 to 10^{-5}.

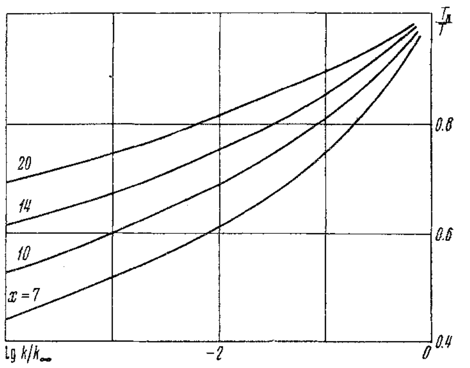

Fig. 2

TABLE 1

ε/kT	ε_a/kT	$\lg(k_\infty/k)$	k, sec^{-1}	k*, sec^{-1}	k/k*
10	8.73	1.51	$1.3\cdot10^6$	$5.4\cdot10^5$	2.4
12	10.5	1.10	$5.5\cdot10^5$	$2.0\cdot10^5$	2.8
14	12.2	0.77	$2.1\cdot10^5$	$6.2\cdot10^4$	3.4
16	14.0	0.45	$7.4\cdot10^4$	$1.8\cdot10^4$	4.1
18	15.7	0.20	$2.4\cdot10^4$	$4.5\cdot10^3$	5.3
20	17.5	0.04	$6.0\cdot10^3$	$1.1\cdot10^3$	5.4

3. Dissociation Constant of Carbon Dioxide

Carbon dioxide is one of the gases for the description of the thermal dissociation of which the isothermal model considered above is applicable. The symmetric stretching vibrations of the CO_2 molecules are in Fermi resonance with low-frequency, doubly degenerate flexural vibrations. Therefore, the temperatures of the three oscillators of the molecule in a quasi-stationary process

$$CO_2 \to CO + O$$

is maintained practically equal owing to exchange of vibrational quanta (two quanta of flexural vibrations to one quantum of symmetric stretching vibrations). It is known from experiment (see, for example, [12]) that the energy of asymmetric stretching vibrations relaxes also during a time close to the relaxation time τ_1 of flexural vibrations. The structure of the shock waves in carbon dioxide is characterized by the same vibrational relaxation time τ_1. The temperature dependence of τ_1 of carbon dioxide [13] is expressed by the formula

$$\lg(p\tau_1 \text{ atm}\cdot\text{sec}) = -8.56 + 25\,T^{-1/3} \tag{3.1}$$

In review [13] this dependence is presented graphically. Using (1.3) and (3.1), we can find the dissociation constant k as a function of the gas temperature and density. For this purpose, it is sufficient to substitute the numerical values of $A\tau_1$ and x into the solution of Eq. (2.5) found in the preceding section (see Fig. 1). The results obtained thereby are compared in Table 1 with the experimental data of S. A. Losev, N. A. Generalov, and V. A. Maksimenko [14] on the dissociation rate of carbon dioxide in shock waves.

The figures presented in the fifth column of Table 1 were calculated by the formula

$$k^* = 3\cdot10^7(\varepsilon/kT)^6\sqrt{T}\exp(-\varepsilon/kT)\,n\ \text{sec}^{-1}$$

obtained in [14] by treating measurement results. The concentration of molecules n corresponding to the table values of k and k* is $5\cdot10^{-6}$ cm^3/mole.

The agreement of the calculated and experimental values of k is satisfactory within the limits of error of measuring k_1 and τ_1. This agreement indicates a determining role of relaxation of the average vibrational energy in high-temperature kinetics of monomolecular dissociation. It is possible that the divergence between the calculations and experimental data upon a decrease of temperature is related with the relative increase of the role of the neglected disturbance of the Boltzmann distribution of energy with respect to the upper vibrational levels. This pertains in particular to the last two rows of Table 1 to which the limit of applicability of inequality (0.2) corresponds and where $k \approx k_\infty$ without consideration of disturbance of the Boltzmann distribution.

At present carbon dioxide is apparently the only one-component gas in which the monomolecular dissociation rate has been measured at high temperatures. Such measurements are very difficult. Nevertheless, they are very necessary for understanding the basic regularities of monomolecular dissociation of a one-component gas.

The author thanks S. A. Losev and N. A. Generalov for additional measurement data and I. S. Zaslonko for useful discussions.

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