NON-EQUILIBRIUM ENERGY DISTRIBUTIONS OVER THE VIBRATIONAL DEGREES OF FREEDOM IN GASES

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CONTENTS

1. INTRODUCTION

Eの VERY process in a gaseous system proceeding with finite velocity involves a perturbation of the equilibrium distribution functions. This perturbation can affect to varying degrees the translational, rotational, vibrational, and other degrees of freedom.

This review will try to throw light on a set of problems involving distortions of the equilibrium energy distribution in the vibrational degrees of freedom. Until recently, these problems had been taken up only in studying ultrasonic dispersion. However, the situation has already changed considerably.

First of all, advances in high-velocity aerodynamics have aroused practical interest in the study of the structure of shock waves; in many respects, this structure depends on processes of vibrational relaxation. The development of experimental methods to study the state of a gas following a shock-wave front permits us to study the process of vibrational relaxation under conditions far different from those in ultrasonic fields. On the other hand, it has been found in chemical kinetics that a number of reactions produce vibrationally-excited molecules, or proceed by way of intermediate vibrationally-excited states. An example of the latter reaction is the thermal dissociation of molecules. Non-

equilibrium distributions in the vibrational energy arise in such reactions; under conditions found in practice, they can have an appreciable effect on the kinetics of process. Finally, various external influences, such as electric discharges or photolysis, also involve the appearance of vibrationally-excited molecules having non-equilibrium distributions.

In the theoretical study of such phenomena, two types of problems arise: first, the problem of the probability of the various elementary processes in the system, which may be solved by methods of quantum or classical mechanics; and second, the problem of the statistical characteristics of the system, which amounts to solving the appropriate gas-kinetic equations.

This article will be fundamentally concerned with statistical distributions and their interrelation with the kinetics of the macroprocesses.

Of course, in this field of phenomena the systems of practical interest will naturally be those in which finite perturbations appear in the equilibrium distribution functions. This is the principal difference between the problems discussed here and the analogous problems in the theory of dissipative processes, as are taken into account in the equations of hydrodynamics by using transfer coefficients (viscosity, heat con-

ductivity, etc.). The molecular-kinetic basis of these dissipative processes is in the infinitesimally small perturbations of the equilibrium distribution which completely determine the values of the transfer coefficients. In phenomena such as thermal dissociation, small deviations from the Boltzmann distribution would have only a slight influence on the kinetics of the process. To a considerable extent, this determines the method of solving the problems. The method must give a correct description of the finite deviations from statistical equilibrium.

The non-equilibrium systems studied here and the problems they involve are naturally divided into two groups. The first consists of systems having an initial non-equilibrium distribution, in which a process establishing the equilibrium takes place. The second consists of systems with a steady-state or quasi-steady-state (but not equilibrium) distribution established under the influence of perturbing factors that are constant or slowly varying in time. Such perturbations can formally be considered to be quasi-steady-state particle sources, either positive or negative. Section 2 treats the processes of establishment of vibrational equilibrium in a system having an initial non-equilibrium distribution. Section 3 will discuss the distribution of vibrational energy in systems containing particle sources.

2. VIBRATIONAL RELAXATION

2.1. Introduction. The process of establishment of equilibrium in the vibrational degrees of freedom (vibrational relaxation) is of interest in many fields of physics. In particular, we must take it into account in determining the thickness of shock waves in diatomic gases, in studying the absorption spectra of the products of flash photolysis, in the theory of dispersion of ultrasonic waves, in analyzing chemiluminescence spectra, in combustion theory, etc. In addition, vibrational relaxation occurs as an independent stage in such complex processes as the thermal dissociation of diatomic molecules or the establishment of a quasi-steady-state energy distribution in systems containing positive particle sources. In these examples, vibrational relaxation is a rapid process. Consequently, a quasi-steady-state distribution in the vibrational energy is established, and is determined at each given instant of time by the values of the slowly-varying parameters, such as the (non-equilibrium) composition of mixtures or the strength of sources, etc. In this sense, we can refer to the distribution as being synchronized with these parameters.

The given examples show the convenience of discussing separately the processes of vibrational relaxation in systems under non-equilibrium initial conditions.

2.2. Gas-kinetic equations. We begin with the simplest case, that of vibrational relaxation in a system of diatomic molecules present in small concentration in an inert monatomic gas. The process of vibrational relaxation in such a system is brought about by the interaction of the diatomic molecules with the molecules of the monatomic gas. We can neglect the interaction of the diatomic molecules with each other.

This interaction results in an energy exchange between the vibrational and translational degrees of freedom of the colliding molecules. The system of equations describing the vibrational relaxation is a system of balance equations for the number of molecules in each vibrational level. If we denote as $x_n(t)$ the concentration of molecules in the n-th vibrational level, this system of equations has the form

$$\frac{dx_n}{dt} = Z \Big(\sum_{m \neq n} P_{mn} x_m - x_n \sum_{m \neq n} P_{nm} \Big), \quad n = 0, 1, 2..., \quad (2.1)$$

where P_{ij} is the probability of transition of a molecule from the i-th to the j-th vibrational level on colliding with an atom, and Z is the number of collisions which the molecule undergoes per second. It is assumed that Z is independent of the vibrational state of the molecule. This latter condition is not strictly satisfied, but we may assume it, since in most practical cases, the amplitude of the vibrations of the atoms in a molecule is small in comparison with the mean distance between the atoms in the molecule. In deriving the system (2.1), the relative translational motion was considered classically. This is no limitation, since in cases of practical interest, the density and temperature of the system have values such that we can neglect the quantum corrections involving the finite wavelength of the de Broglie waves. It is assumed in deriving Eqs. (2.1) that the vibrational motion can be considered independently of the other types of internal motion: rotational, electronic, etc. Thus we avoid the question of strict derivation of the gas-kinetic equations for particles having internal degrees of freedom.

2.3. Transition probabilities. Before we solve system (2.1), we must express the transition probabilities P_{nm} in more concrete form. The probabilities P_{nm} are determined by the following equation:

$$P_{nm} = 2 \left(\frac{\mu}{2kT} \right)^2 \int_0^\infty v^3 p_{nm}(v) \exp\left(-\frac{\mu v^2}{2kT} \right) dv, \quad (2.2)$$

where μ is the reduced mass of the colliding molecules, and $p_{nm}(v)$ is the probability of transition of the molecule from the n-th to the m-th vibrational state on collision with an atom moving with a relative velocity v. The value of $p_{nm}(v)$ can be calculated quantum-mechanically by solving the Schrödinger equation describing the collision process. In line with what has been said above, the relative motion of the colliding molecules is considered classically in this problem. Such a calculation of p_{nm} by this method has been performed in [1-3]. In this review, we merely portray the conclusions qualitatively, touching

only those points which will be essential to the following argument.

The process of transformation of translational into vibrational energy on collision takes place for most molecules without change in their electronic states. This latter fact permits us to neglect the electronic degrees of freedom and consider the molecule as an oscillator. As a first approximation, the effect of rotation on the probabilities p_{nm} is commonly neglected. However, we must take it into account in discussing a number of problems: thermal dissociation, vibrational relaxation in diatomic gases, etc. The time for establishment of equilibrium over the rotational degrees of freedom is of the order of several free-flight times. Hence, in discussing vibrational relaxation, the question practically does not arise of the perturbation of rotational equilibrium. The fact that we can treat the problem of the vibrational-relaxation process separately is based on the large difference in relaxation times for the rotational, vibrational, and electronic degrees of freedom.

Since we consider the relative motion of the colliding particles from the classical viewpoint, we can describe the process of collision of an oscillator with an atom as the effect of an external force on the oscillator. For most of the molecules studied, the time of action of the force on the oscillator, or the collision time τ, is considerably longer than the period ω^{-1} of the characteristic vibrations of the oscillator.

According to the general theory of adiabatic invariants, the probability of transition of an oscillator from one quantum state to another owing to such a collision will be small. Hence, we can use perturbation theory to determine $p_{nm}(v)$.

In the simplest one-dimensional case, the Schrödinger equation describing the collision process has the form

$$ih\frac{da_k}{dt} = \sum_m a_m(t)\, V_{km}(r(t))\exp i\omega_{km}t,$$
$$a_m(-\infty) = \delta_{nm}. \tag{2.3}$$

Equation (2.3) is a representation in terms of the eigenfunctions of the unperturbed Hamiltonian of the molecule. $V_{km}(r(t))$ is the matrix element of the potential of the intermolecular interaction, and $r(t)$ is the classical trajectory for the relative motion of the centers of gravity of the colliding particles.

In the first-order approximation of the perturbation theory, the probability $p_{nm}(v)$ is given by the expression

$$p_{nn}(v) = |a_m(\infty)|^2 = \left| \frac{1}{h}\int_{-\infty}^{\infty} V_{nm}(r(t))\exp i\omega_{nn}t\, dt \right|^2. \tag{2.4}$$

We can simplify Eq. (2.4). The vibration amplitude of the atoms in the molecule in the lower vibrational levels is small in comparison with the radius of intermolecular interaction. Hence, we can expand $V(r,x)$ in a power series in $(x - x_{equil})$, where x is the in-

tramolecular coordinate, and retain only the linear term. In such a case,

$$V_{nm}(r) \equiv (n|V(r,\,x)|m) = \left(n\left|V(r,\,0) + x\frac{\partial V}{\partial x}\right|m\right) = x_{nm}\frac{\partial V}{\partial x}. \tag{2.5}$$

We can neglect the constant term $V(r,0)$, since it does not affect the probability of the transition. We can estimate the value of the integral in (2.4) by the method suggested in [2]. We shall treat the time t as a complex variable, and move the path of integration upward from the real axis into the upper half-plane. We shall shift the path of integration upward so as to by-pass any singular point in the integrand. Here, a singular point corresponds to a value t_1 such that

$$V_{nm}(r(t_1)) = \infty. \tag{2.6}$$

The major part of the integral arises from the immediate neighborhood of the singular point. Hence,

$$p_{nm}(v) \sim e^{2i\omega_{nm}t_1} = e^{-\omega_{nm}\tau}, \tag{2.7}$$

where

$$\tau = -2it_1.$$

The value of τ or t_1 is given by the condition (2.6). The value of τ can be estimated approximately from the following considerations, and is the characteristic time constant for the problem discussed. Using the two characteristic quantities entering into the theory of collision, the velocity v prior to collision and the radius a of intermolecular interaction, we can create only one combination having the dimensions of time, i.e., $\tau \sim (a/v)$. An exact calculation of the time τ for an exponential interaction potential $V = V_0 e^{-\alpha r}$ gives a value $\tau = 2\pi/\alpha v$.

The average over the thermal velocities [see Eq. (2.2)] has been calculated in [3,4], where an analytical expression for P_{nm} was derived. We must note the following essential fact. The integrand of (2.2), as we can easily see, has a sharp maximum, whose position is determined by the condition that the argument $(\omega\tau + \mu v^2/2kT)$ of the exponential be a minimum. From this condition, we can find the value of the velocity $(v*)$ corresponding to the maximum of the integrand:

$$v* = \left(\frac{2\pi kT\omega_{nm}}{\mu\alpha}\right)^{\frac{1}{3}}. \tag{2.8}$$

The major contribution to the integral in (2.2) comes from the region of the variables in the neighborhood of $v*$. Hence,

$$P_{nm} \sim |x_{nm}|^2\exp\left(-\omega_{nm}\frac{2\pi}{\alpha v*} - \frac{\mu v*}{2kT}\right) = |x_{nm}|^2\exp(-3\chi), \tag{2.9}$$

where

$$\chi = \frac{\mu v*^2}{2kT} = \left(\frac{\pi^2\mu\omega_{nm}^2}{2\alpha^2 kT}\right)^{\frac{1}{3}} = \frac{1}{2}\omega\tau*, \quad \tau* = \frac{2\pi}{\alpha v*}. \tag{2.10}$$

In the temperature range of practical interest, χ

= 5—10 for various gases. [4] Thus, the only collisions which are important in determining the transition probability P_{nm}, and hence, in transforming translational into vibrational energy, are those of particles whose velocities are on the tail of the Maxwell distribution. Consequently, the relaxation characteristics at ordinary temperatures give information on high-energy collisions, i.e., the collisions which are typical of a gas at a temperature χT.

We can draw the following conclusions from Eq. (2.9). Since the probability depends exponentially on the energy transferred, the only transitions practically allowed are those between adjacent levels; this rule holds independently of the model of the molecule. For a harmonic-oscillator model in the present approximation, it is exact, since for a harmonic oscillator, the x_{nm} differ from zero only when m = n ± 1. We see from Eq. (2.9) that $\ln P_{nm} \sim -T^{-1/3}$. This fact is the basis of the experimental verification of the theory of vibrational relaxation. All of the above considerations have been based on the semi-classical method of calculating transition probabilities given in [1]. A quantum-mechanical calculation of the transition probabilities is given in [4,5,6]. The equivalence of the expressions for the transition probability obtained by using the semi-classical and the consistently quantum methods has been shown in [7,4]. It is interesting to note that one can also derive a correct expression for the average energy taken up by an oscillator in a single collision with an atom from purely classical considerations [8,9-11]. Up to now, we have considered only the case $\omega\tau \gg 1$. However, in fast collisions with heavy molecules or molecules in upper vibrational levels, the opposite condition is satisfied: $\omega\tau \ll 1$. In particular, $\omega\tau \ll 1$ for collision of I_2 and He molecules in the gaseous state at room temperature. The transition probability P_{nm} for $\omega\tau \ll 1$ can be calculated by using Eq. (2.3). [12] When $\omega\tau \ll 1$, the exponential in Eqs. (2.3) can be replaced by unity. Then, the system of equations (2.3) can be solved exactly; here the transition probability p_{nm} is written in the form

$$p_{nm}(v) = |a_m(\infty)|^2 = \left| \int_{-\infty}^{\infty} \psi_m^*(x) \exp\left(-2ik_n\lambda x\right) \psi_n(x) \, dx \right|^2,$$

(2.11)

where $\psi_p(x)$ is the wave function of a molecule in the p-th vibrational state, and $k_n = \mu v/\hbar$. Equation (2.11) can also be derived in a consistently quantum-mechanical manner. [13,14]

An analysis of Eq. (2.11) shows that in collisions under strongly non-adiabatic conditions ($\omega\tau \ll 1$), not only the adjacent vibrational levels, but also the following levels can be excited. We can simplify Eq. (2.11). In particular, when $k_n x_{mean} \ll 1$, where x_{mean} is the mean amplitude of vibration of the atoms in the molecule, the exponential in (2.11) can be expanded in series. Keeping only the first non-zero term, we have

$$p_{nn}(v) = |k_n x_{nm}|^2.$$

(2.12)

This case occurs, e.g., in the collision of I_2 with He in the gas mixture at temperatures no higher than 1000°K.

For a harmonic oscillator, x_{nm} differs from zero only when m = n ± 1. Hence, under the conditions considered here, the only practically allowed transitions are those between adjacent levels, even in non-adiabatic collisions. The physical interpretation of this conclusion is obvious. The condition $k_n x_{mean} \ll 1$ limits the energy of relative motion to values permitting the excitation of only one vibrational quantum. When averaged over the Maxwell distribution, Eq. (2.12) takes the form

$$P_{n+1,n} = (n+1)P_{10},$$

(2.13)

where

$$P_{10} = \frac{2kT}{\hbar\omega}\frac{\mu}{M};$$

(2.14)

Here μ is the reduced mass of the colliding particles, and M is the reduced mass of the molecule.

Thus, the transition probabilities for collision of atoms with molecules have been calculated only in the two limiting cases ($\omega\tau \gg 1$, and $\omega\tau \ll 1$). Calculations of the probabilities $p_{nm}(v)$ for arbitrary values of $\omega\tau$ would require the use of numerical methods, and have not been carried out thus far.

2.4. Vibrational relaxation in an isothermal system. Relaxation equations. If we consider only one-quantum transitions, we can write the system of equations describing the process of vibrational relaxation of diatomic molecules occurring as a minor constituent in a monatomic gas, according to Secs. 2.2 and 2.3, in the form

$$\frac{dx_n}{dt} = Z\left(P_{n+1,n}x_{n+1} - P_{n,n+1}x_n\right.$$

$$\left. + P_{n-1,n}x_{n-1} - P_{n,n-1}x_n\right) \quad (n = 0, 1, 2, \ldots),$$

$$x_n|_{t=0} = x_n(0).$$

(2.15)

Here (2.15) is a linear system with constant coefficients. The coefficients P_{nm}, which are functions of the temperature, may be considered constant, since under these conditions the process of vibrational relaxation takes place isothermally.

The solution of the system (2.15) determines the functions $x_n(t)$, and permits us to follow the behavior of the molecules in each of the vibrational levels. This formulation of the problem is rational, and will be discussed in detail in Sec. 2.5.

However, in many practical problems, we are not interested in the distribution function, but in the behavior of certain macroscopic characteristics, in particular the vibrational energy. Such a formulation of the problem is characteristic of relaxation hydrodynamics.

The relaxation equation for the vibrational energy may be derived from system (2.15) without solving the latter.[2] Let us consider the model of a harmonic oscillator. In this case

$$|x_{n+1, n}|^2 = (n+1)|x_{10}|^2, \quad \text{and} \quad \omega_{n+1, n} = \omega$$

independently of the number n. The transition probability may be written in the form of Eq. (2.13):

$$P_{n+1, n} = (n+1) P_{10}, \quad \text{where} \quad P_{01} = P_{10} e^{-\theta}, \tag{2.16}$$

and $\theta = \hbar\omega/kT$. The latter condition involves the Maxwellian distribution of velocities of the colliding molecules, and is based on the principle of microscopic equilibrium.

By taking Eq. (2.16) into account, we can write the system (2.15) as follows:

$$\frac{dx_n}{dt} = ZP_{10} \{(n+1) x_{n+1} - [(n+1) e^{-\theta} + n] x_n$$

$$+ ne^{-\theta} x_{n-1}\} \quad (n = 0, 1, 2, \ldots). \tag{2.17}$$

We now multiply Eq. (2.17) by $\hbar\omega n$, and sum over all values of n. After some simple transformations, we obtain the following equation:

$$\frac{dE}{dt} = -ZP_{10}(1 - e^{-\theta}) \left\{E - \frac{\hbar\omega e^{-\theta}}{1 - e^{-\theta}}\right\},$$

where $E = \hbar\omega \Sigma n x_n(t)$ is the vibrational energy, and

$$\hbar\omega \frac{e^{-\theta}}{1 - e^{-\theta}} \equiv \hbar\omega (1 - e^{-\theta}) \sum n e^{-\theta}$$

is the equilibrium value of the vibrational energy $E_0(T)$.

Thus, the relaxation equation for the vibrational energy has the form

$$\frac{dE}{dt} = -\frac{1}{\tau} (E - E_0(T)), \tag{2.18}$$

where

$$\tau = [ZP_{10}(1 - e^{-\theta})]^{-1}. \tag{2.19}$$

This is the general form of the relaxation equation for any physical quantity in a state not deviating far from equilibrium. In the case of the harmonic-oscillator model, this equation is correct for all deviations from the equilibrium state.

Equation (2.19) determines the vibrational relaxation time. This characteristic of the relaxation process is one of the most important characteristics in the theory of the phenomena associated with the establishment of equilibrium over the vibrational degrees of freedom.

From the mathematical viewpoint, the total vibrational energy is one of the normal coordinates of system (2.17).[15] The other normal coordinates do not have such an obvious physical meaning, and as is shown in [15], they relax considerably more rapidly.

The solution of Eq. (2.18) is exponential in form:

$$E(t) - E_0 = [E(0) - E_0] e^{-\frac{t}{\tau}} \tag{2.20}$$

and depends only on the total vibrational energy at the initial instant of time. The way in which the molecules are distributed among the vibrational levels for a given value of the total vibrational energy has no effect on the relaxation process.

This latter fact is a characteristic of the harmonic-oscillator model.[16] For an anharmonic oscillator, the process of vibrational relaxation depends both on the way in which the molecules are distributed among the vibrational levels, and on the initial value of the vibrational energy.[17] When subject to such a dependence, the relaxation of the vibrational energy will generally no longer obey Eq. (2.18). However, in most practical cases (vibrational relaxation in shock waves and in the propagation of ultrasonic vibrations), the process of relaxation of the vibrational energy is quite accurately described by Eq. (2.18). This is true of all processes in which molecules in the lowest vibrational levels play the predominant role, since the role of anharmonicity then is insignificant.

The relaxation time determined by Eq. (2.19) is a quantity which can be directly measured experimentally. At present, there are some tens of experimental studies in which the temperature-dependence of τ has been studied for various gases. A very large mass of data on the behavior of τ at high temperatures has been obtained by studying vibrational relaxation in shock tubes. A detailed bibliography of these studies has been given in [18]. We shall cite the results on oxygen. Vibrational relaxation in this gas has been studied over a wide temperature range. In particular, in [19] the temperature range was 1200—7000°K.

Figure 1, taken from [19], shows the relation of $\tau(1 - e^{-\theta})$ to $T^{-1/3}$. When plotted logarithmically, this relation becomes linear, in agreement with the conclu-
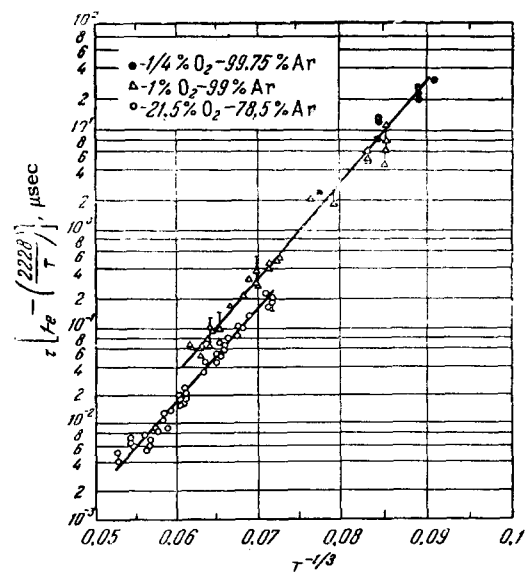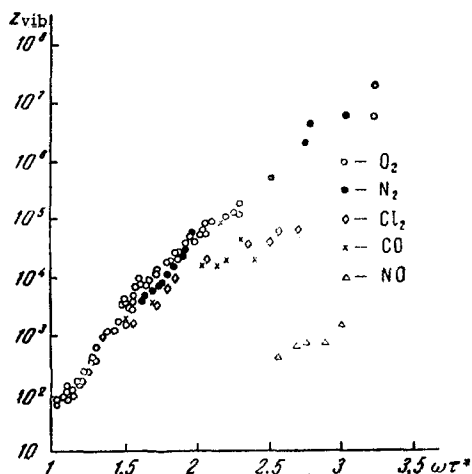

FIG. 1.

FIG. 2

sions of Sec. 2.3. Lest we give the impression of chance agreement between the theoretical and experimental results, we present here as a summarized diagram Fig. 2, in which $Z_{vib} = 1/P_{10}$ is plotted as a function of $\omega\tau^*$ for various gases. We see from Fig. 2 that the relation of Z_{vib} to $\omega\tau^*$ on a logarithmic scale is basically linear; the small deviations from linearity can be explained, e.g., by taking into account the temperature-dependence of the pre-exponential factor in P_{10},[26] or by assuming a dependence of the parameters of the intermolecular interaction potential (which approximate the true molecular interaction) on the energy of the colliding particles.

The existence of a linear relation between ln Z_{vib} and $\omega\tau^*$ confirms the hypothesis that the mechanism of excitation of vibrations for most of the molecules studied is adiabatic. An exception to this rule is apparently NO (in its ground electronic state) and other radicals. For NO, the experimentally-observed vibrational relaxation time turns out to be considerably less than those of N_2 and O_2.[20]

Two different explanations have been given for this difference. In [10,20] the anomalously short vibrational relaxation time of NO is ascribed to the attractive forces manifested in the formation of dimers. Calculations on this basis give good agreement with the experimental data. This difference is attributed in [21] to the participation of the electron cloud of NO in the transformation of translational into vibrational energy. In particular, it was shown that with non-adiabatic excitation (in the sense of a change in the electronic state of the colliding pair of NO molecules during the collision process), electronic transitions can occur between the states that develop from the initial state, which is degenerate at infinite distance. When the frequencies of the electronic transition and of the nuclear vibrations are equal, a peculiar resonance appears, which gives rise to rather large cross-sections for excitation of vibrations. A calculation on this basis also gives good agreement with the experimental data.

However, there is one principal distinction between these theories: they predict different temperature-dependences of the vibrational relaxation time τ. Thus, in the former case, the temperature dependence is fundamentally given by Eq. (2.9), i.e.,

$$\ln \tau (1 - e^{-\theta}) \sim T^{-\frac{1}{3}},$$

while in the latter case, $\ln \tau (1 - e^{-\theta}) \sim \epsilon_0/kT$, where $\epsilon_0 \sim 1000-2000°K$. This fact can be used to test the cited theories experimentally. However, the existing experimental data[20,22] are almost exclusively for two particular temperatures. There exists as yet no measurement of the vibrational relaxation time of NO (in the ground electronic state) over a broad temperature range.*

The case of vibrational relaxation of I_2 in an I_2-He mixture is also of interest. As has been noted in Sec. 2.3, although I_2-He collisions at temperatures above room temperature take place under highly non-adiabatic conditions ($\omega\tau \ll 1$), the only transitions practically allowed are those between adjacent vibrational levels. By using the method developed in this section, and applying Eq. (2.14), we can derive the following expression for the vibrational relaxation time of I_2 in I_2-He mixtures:[23]

$$\tau = \left[Z \frac{2kT}{\hbar\omega} \frac{\mu}{M} (1 - e^{-\theta}) \right]^{-1}$$

The value of τ found is valid approximately from room temperature to 1000°K. Under these conditions, $1 - e^{-\theta} \sim \theta = \hbar\omega/kT$. Hence, $\tau Z \sim 2(\mu/M)$. That is, it is practically independent of temperature. However, there are as yet no experimental data on vibrational relaxation of I_2 in I_2-He mixtures under conditions in which the derived formula can be applied.

Figures 1 and 2 compare only the trend with varying temperature of the experimental and theoretical curves for $\tau = \tau(T)$. However, the numerical theoretical results differ from the experimental by about an order of magnitude. We can hardly expect a better agreement of results at present. In fact, the existing theoretical calculations are subject to a practical difficulty involving the lack of exact information on the intermolecular-interaction potential, and in particular, on the value of α, in addition to the general defects (neglect of anharmonicity, approximate means of taking into account the rotational excitation in calculating P_{10} in the three-dimensional case, etc.). The existing data permit us to determine α with an accuracy of 200−300%.[24] This accuracy is inadequate, since a 10% change in α can under certain conditions alter the value of τ by an order of magnitude.[4] This sensitivity of τ to the value of α permits us to formulate the converse problem, and determine the value of α from known experi-

*Recently-performed experiments [65] have confirmed the existence of a non-adiabatic mechanism of interaction on NO molecules in the vibrational-relaxation process.

mental values of τ. This problem is of great importance, since it formulates a method permitting us to determine the characteristics of the intermolecular-interaction potential in an energy range which has been poorly studied up to now. In fact, the intermolecular-interaction potential is rather well known in the energy range up to 1000°K, where there are numerous data on transfer coefficients, and in the energy range corresponding to several thousand degrees, where there are data obtained by the molecular-beam method. [25]

The intermediate energy range, which is important in calculating the transfer properties of high-temperature gases, has remained unfilled. The study of vibrational relaxation permits us to some extent to fill this gap. The data thus obtained on the intermolecular-interaction potential (Fig. 3) fit well with the results of studies in the ranges of small and large energies. [26,27]
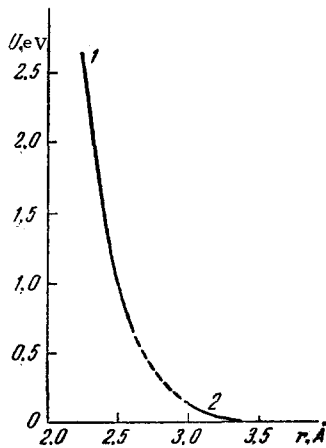

FIG. 3. Potential energy of the O_2-O_2 interaction as calculated: (1) from vibrational-relaxation data, and (2) from viscosity data.

Thus, the study of vibrational relaxation gives us information not only on the mechanism of energy exchange in molecular collisions, but also permits us to answer a number of related questions, in particular, such as that of the intermolecular interaction.

2.5. Vibrational relaxation in an isothermal system. Distribution of the molecules over the vibrational levels. By studying vibrational relaxation by optical methods, in particular ultraviolet absorption, [18] one can measure the number of molecules in the different vibrational levels. Here the question arises of deriving a complete solution of the system of equations in (2.15) describing the distribution of the molecules over the individual vibrational levels.

Before we take up the methods of deriving the general solution, let us discuss a particular solution of great practical interest. Just as in the preceding Sec. 2.5, we shall consider only a harmonic-oscillator model. That is, we shall study the system of (2.17). The system of (2.17) has a solution of the form

$$x_n(t) = (1 - e^{-\vartheta(t)}) e^{-n\vartheta(t)}, \qquad (2.21)$$

where $\vartheta(t)$ is a known function of the time independent of n. This latter fact is important.

We can convince ourselves of the correctness of the solution (2.21) by substituting it into (2.17). Then the system of equations (2.17) is reduced to one equation determining the function $\vartheta(t)$:

$$\frac{d\vartheta}{dt} = ZP_{10}(1 - e^{-\vartheta})(e^{-\vartheta} - e^{-\theta}) e^{\vartheta}.$$

The solution of the equation obtained has the form

$$\vartheta(t) = \ln\left[\frac{e^{-\frac{t}{\tau}}(1 - e^{\theta - \vartheta_0}) - e^{\theta}(1 - e^{-\vartheta_0})}{e^{-\frac{t}{\tau}}(1 - e^{\theta - \vartheta_0}) - (1 - e^{-\vartheta_0})}\right], \qquad (2.22)$$

where τ is the time of vibrational relaxation determined by Eq. (2.19), and $\vartheta_0 = \vartheta(0)$.

The physical meaning of the equation obtained is obvious. We assume that at the initial instant of time the distribution function of the molecules over the vibrational levels has the form of a Boltzmann function with a temperature different from that of the surrounding monatomic gas. That is to say, $x_0(0) = (1 - e^{-\vartheta_0}) e^{-n\vartheta_0}$. Then the vibrational-relaxation process will take place in such a way that the distribution function will keep its original form, but vary only in the vibrational temperature. In other words, the process of vibrational relaxation obeys the law of conservation of the form of the distribution function when the initial distribution is a Boltzmann distribution. An analogous situation is also observed in the relaxation of the translational degrees of freedom in a gas consisting of molecules obeying the Maxwellian statistics. [28]

The particular solution (2.21) of the system (2.17) was first discovered in [29], and has been widely used in practical calculations. [30,31] However, we must emphasize that the law of conservation of the form of a Boltzmann distribution is valid only in a system of harmonic oscillators.

The general solution of the system (2.17) can be sought by ordinary methods. System (2.17) is a system of linear differential equations with constant coefficients. Hence, its solution can be written in the form

$$x_n(t) = \sum a_{nm} e^{-\mu_m t}$$

It is shown in [29] that, as applied to the system of (2.17),

$$a_{nm} = \alpha_m l_n(m), \quad \mu_m = m[ZP_{10}(1 - e^{\theta})],$$

where the $l_n(m)$ are the Gottlieb polynomials.

Thus, the general solution of the system (2.17) has the form

$$x_n(t) = \sum \alpha_m l_n(m) e^{-\frac{mt}{\tau}}, \qquad (2.23)$$

where τ is the relaxation time [see Eq. (2.19)], and the α_m are determined by the initial conditions.

An essential peculiarity of the solution (2.23) is the fact that the longest relaxation times, which essentially determine the trend in time of the $x_n(t)$, coincide with the relaxation time of the vibrational energy.

Solution (2.23) is not always convenient for practical calculations. Hence, often several other forms of the solution derived by the generating-function method are used.[29]

Let

$$G(z, t) = \sum z^n x_n(t).$$

Then, by multiplying (2.17) by z^n, and summing over all values of n, we obtain an equation for $G(z,t)$:

$$\frac{1}{k}\frac{\partial G}{\partial t} = (z-1)e^{-\theta}\left\{\frac{\partial G}{\partial z}[(z-1)+(1-e^{\theta})]+G\right\},\quad(2.24)$$

where $k = zP_{10}$.

The solution of Eq. (2.24) has the form

$$G(z, t) = \frac{1-e^{\theta}}{(z-e^{\theta})-(z-1)e^{-t/\tau}}G_0\left(\frac{(z-1)e^{-\frac{t}{\tau}}e^{\theta}-(z-e^{\theta})}{(z-1)e^{-t/\tau}-(z-e^{\theta})}\right),$$

$$(2.25)$$

where $G_0(y)$ is an arbitrary function defined by the initial conditions $G_0(z) \equiv G(z, 0) = \Sigma z^n X_n(0)$.

In certain cases of practical interest, we can limit ourselves to studying the simpler special solutions, rather than using the general expressions (2.23) or (2.25). From this viewpoint, we shall study the process of vibrational relaxation in oxygen in the experiments of Norrish et al.[32]

In these experiments, vibrationally-excited oxygen molecules with a distribution favoring the eighth level were obtained by flash photolysis of chlorine dioxide in the presence of large amounts of nitrogen. By measuring the intensity of the oxygen absorption band corresponding to the sixth vibrational level at various instants of time after cessation of the illumination, they determined the lifetime of oxygen molecules in the sixth vibrational level. The lifetime was found to be inversely proportional to the initial ClO_2 pressure, which was varied from 0.25 to 0.75 mm Hg, and was practically independent of the nitrogen pressure (145—730 mm). The latter result shows that the fundamental process leading to deactivation of the oxygen is the transfer of energy in the collisions of oxygen molecules with one of the molecules produced by the decomposition of chlorine dioxide. According to Norrish's estimates, this molecule could be chlorine monoxide (ClO). If we know the lifetime of the oxygen molecules and the mechanism leading to deactivation, we can try to determine the probability of transformation of the vibrational energy of the oxygen in a collision with a molecule of chlorine monoxide.

The system of equations describing the process of vibrational relaxation of an oxygen molecule in the sixth vibrational level has the form

$$\frac{dx_n}{dt} = -ZP_{n,n-1}x_n,$$

$$\frac{dx_{n-1}}{dt} = Z(P_{n,n-1}x_n - P_{n-1,n-2}x_{n-1}),$$

$$\frac{dx_{n-2}}{dt} = Z(P_{n-1,n-2}x_{n-1} - P_{n-2,n-3}x_{n-2}),\quad x_m(0) = \delta_{n8}\quad(2.26)$$

and can be derived from (2.15) by dropping all terms

describing processes of excitation of oxygen molecules.

Under the given conditions (T = 288°K, n = 6—8), it is valid to drop these terms, since the probability of excitation $P_{n,n+1} = P_{n+1,n}e^{-\Delta E_{n,n+1}/kT}$ is about a thousand times smaller than the probability of deactivation. The latter condition makes it possible to reduce the infinite system of equations of (2.15) to a system of three equations. System (2.26) describes transitions between levels which can be considered equidistant in the first approximation, and we can use (2.16) to find P_{nm}. However, we must remember that in this case the quantity P_{10} characterizes the transition probability for an oscillator having a vibrational quantum equal to the mean vibrational quantum of the oxygen molecule for the given levels. Z in Eq. (2.26) is equal to the number of collisions of oxygen molecules with chlorine monoxide molecules per second. Since the concentration of ClO molecules varies during the process of vibrational relaxation, Z is a function of time. This function is easily found: $Z = Z_0[ClO]$. The concentration of ClO varies, owing to the reaction $ClO + ClO \rightarrow Cl_2 + O_2$, the rate constant of which is known: $d[ClO]/dt = -k[ClO]^2$. Hence, $[ClO] = c_0/(1 + c_0kT)$, where c_0 is the initial concentration of ClO. If we know Z as a function of time, we can easily integrate the system of equations and find $x_6(t)$:

$$x_6(t) = x_8(0)\,28e^{-6\sigma}(1-e^{-\sigma})^2,$$

where

$$\sigma = \frac{Z_0c_0P_{10}}{c_0k}\ln(1+c_0kt).\quad(2.27)$$

We can find P_{10} and P_{65} from Eq. (2.27), using the known values of the concentration c_0 and the corresponding lifetimes. P_{65} is approximately 2.5×10^{-3}. According to Norrish's estimates, $P_{65} \sim 5 \times 10^{-4}$. In calculating P_{65}, Norrish started with the following concepts. He considered that the process of deactivation of an oxygen molecule in the sixth level can be described by the equation

$$-\frac{d[O_2^*]}{dt} = k'[ClO][O_2^*].$$

If we know the time-dependence of the concentration [ClO] as well as the lifetime of the oxygen molecule, we can find k' and estimate P_{65}. This estimate will be very rough, since it is based on an equation for the reaction rate not in accord with the system (2.26).

The result which we have obtained is also qualitative in nature. This involves the fact that in Norrish's experiments[32] the exact form of the initial distribution of the molecules over the vibrational levels was not known. This latter fact, which was noted in [34], hinders any exact theoretical calculation.

2.6. Vibrational relaxation in an isolated system. Gas-kinetic equations. Thus far, in the systems discussed the diatomic molecules were present in low

concentration in a monatomic gas. The study of vibrational relaxation in pure diatomic gases is also of practical interest. In such a system, besides the transformation of translational into vibrational energy, the processes of energy transfer among the vibrational and rotational degrees of freedom, as well as exchange of vibrational energy, are also essential.

The process of transformation of rotational into vibrational energy is in itself improbable, in view of the large difference between the energies of the vibrational and rotational quanta. A simultaneous transformation of rotational and translational into vibrational energy, or vice versa, could be significant. In this case,[35] the probability of loss or gain of a vibrational quantum becomes several times greater than the analogous probability that one would calculate without taking the transformation of the rotational energy into account. Such a calculation was made in [35], and showed that the transformation of the rotational energy leads to a three- to fivefold increase in the probability of vibrational excitation in O_2 in O_2-O_2 collisions, as compared with O_2-Ar collisions. The experimental data, which were obtained over the wide temperature range $1200-7000°K$,[19] show that the vibrational relaxation time of O_2 in the O_2-O_2 case is about five times shorter than that in O_2-Ar mixtures. Thus, although the processes of transformation of rotational into translational energy do not change the general picture of the relaxation phenomena discussed in Secs. 2.3−2.5, they can lead only to an increase in the transition probabilities, or a decrease in the relaxation time.

The processes of vibrational exchange lead to a fundamental change in the picture of establishment of equilibrium. This and the next section are concerned with elucidating the role of these processes in the establishment of equilibrium. For harmonic oscillators, the transformation of translational into vibrational energy takes place, as was shown above, by one-quantum transitions, in which the transition probabilities $P_{n,n+1}$ are determined by the Landau-Teller formula. In the collision of oscillators, in addition to the processes discussed above, vibrational energy is also transferred from one oscillator to another. As will be shown below, these processes are also one-quantum in type. The probability of transfer of a vibrational quantum from an oscillator in the $(m+1)$-st state to an oscillator in the n-th state will be denoted by $Q_{n,n+1}^{m+1,m}$.

The set of equations describing vibrational relaxation in an isolated system of oscillators is a set of balance equations for the numbers of molecules in each vibrational level, just as in the case of the isothermal system (Sec. 2.2).

In the notation adopted in Sec. 2.2, this system of equations has the following form:

$$\frac{dx_n}{dt} = Z\{P_{n-1,n}x_{n-1} - P_{n,n-1}x_n + P_{n+1,n}x_{n+1} - P_{n,n+1}x_n$$

$$+ \left(\sum_l Q_{n-1,n}^{l+1,l}x_{l+1}\right)x_{n-1} - \left(\sum_m Q_{n,n-1}^{m,m+1}x_m\right)x_n$$

$$+ \left(\sum_l Q_{n+1,n}^{l,l+1}x_l\right)x_{n+1}$$

$$- \left(\sum_m Q_{n,n+1}^{m+1,m}x_{m+1}\right)x_n\}, n = 0, \quad 1, \quad 2 \ldots, \tag{2.28}$$

where

$$Q_{n,n-1}^{m,m+1}(T) = 2\left(\frac{\mu}{2kT}\right)^2 \int_0^\infty v^3 q_{n,n-1}^{m,m+1}(v) \exp\left(-\frac{\mu v^2}{2kT}\right) dv. \tag{2.29}$$

The notation is the same as in Sec. 2.3: $q_{n,n-1}^{m,m+1}(v)$ is the probability of transition of oscillators from the state (n, m) to the state $(n-1, m+1)$ on collision with a relative velocity v. The value of $q_{n,n-1}^{m,m+1}(v)$ is calculated by quantum-mechanical methods. The calculations of q are given in [6,12].

We shall merely sketch the conclusions here. Just as in Sec. 2.3, we shall consider the simplest one-dimensional case. In order to determine the transition probabilities, we can conveniently use the Schrödinger equation written in a representation in terms of the eigenfunctions of the unperturbed Hamiltonian of the molecule. In this representation, the Schrödinger equation practically coincides with the system (2.3). The only difference is the fact that the index k characterizes the state of two independent molecules, rather than that of one molecule. The index k is actually a double index $k(n, m)$. In addition, the quantity $\hbar\omega km$, which corresponds to the difference in vibrational energies before and after collision, is zero in the transfer of vibrational energy between two identical oscillators. In this case, Eq. (2.3) is simplified, and the expression for the transition probability (2.4) takes the form

$$\left.\begin{array}{l} q_m(v) = \left|\frac{1}{\hbar}\int_{-\infty}^\infty V_{nm}(r(t))\,dt\right|^2, \\ V_{nm}(r) \equiv (n_1, n_2|V(r, x_1, x_2)|m_1, m_2). \end{array}\right\} \tag{2.30}$$

Just as in Sec. 2.3, $V(r,x_1,x_2)$ can be expanded in a power series in $(x_1 - x_1,\text{equil})$ and $(x_2 - x_2,\text{equil})$. The term responsible for exchange of vibrational quanta is $x_1x_2(\partial^2 V/\partial x_1\partial x_2)$. In this case,

$$V_{nm}(r) = x_{n_1m_1}x_{n_2m_2}\frac{\partial^2 V}{\partial x_1\partial x_2}. \tag{2.31}$$

Since

$$V(r_1, x_1, x_2) = V(r - \lambda_1 x_1 - \lambda_2 x_2),$$

where λx is the distance of a colliding atom from the center of gravity of its molecule, then

$$\frac{\partial^2 V}{\partial x_1\partial x_2} = \lambda_1\lambda_2\frac{d^2 V}{dR^2}. \tag{2.32}$$

By substituting Eqs. (2.32) and (2.31) into (2.30), we obtain an equation for the transition probability

$$q_{n_1m_1}^{n_2m_2}(v) = \left|\frac{1}{\hbar}x_{n_1m_1}x_{n_2m_2}\lambda_1\lambda_2\int_{-\infty}^\omega\frac{d^2 V}{dR^2}dt\right|^2, \tag{2.33}$$

where $d^2V/dR^2 \sim v_0/a^2$, a is the radius of intermolecular interaction, and $V_0 \sim \mu v^2/2$. The integration in (2.33) is limited to a time of the order of the duration of the collision, i.e., a/v. If we take into account the fact that x_{nm} differs from zero only if $m = n \pm 1$, we obtain

$$q_{n_1, n_1+1}^{n_2, n_2-1} = (n_1 + 1) n_2 q_{10}, \qquad (2.34)$$

where $q_{10} \sim 1/(\omega\tau)^2$ $(\omega\tau \gg 1)$, ω being the frequency of the oscillator.

We see by comparing (2.34) with (2.7) that the probability of exchange of vibrational quanta is considerably greater than that of transformation of a vibrational quantum into translational energy. This statement is valid for $\omega\tau \gg 1$, which is the condition for applicability of perturbation theory in the form discussed here. As $\omega\tau \to 1$, the value of p_{10} becomes of the order of q_{10}. The averaging of q_{10} over the Maxwell velocity distribution is not difficult, and has been performed in [6].

In calculating the probabilities q, we do not have to use the perturbation theory (2.30). The system of equations determining the probabilities of exchange of vibrational quanta can be solved exactly by using the method which was used in solving Eq. (2.3) under the condition $\omega\tau \ll 1$. The probabilities of exchange of vibrational quanta thus obtained are analogous to (2.11), and go over into (2.34) when $\omega\tau \ll 1$. Hereinafter, however, all we shall need is Eq. (2.34). When we take into account Eqs. (2.34) and (2.16), the system of equations (2.28) is simplified, and can be written in the form

$$\frac{dx_n}{dt} = ZP_{10}\{(n+1)x_{n+1} - [(n+1)e^{-\theta} + n]x_n + ne^{-\theta}x_{n-1}\}$$

$$+ ZQ_{10}\{(n+1)(1+\alpha)x_{n+1} - [(n+1)\alpha$$

$$+ n(1+\alpha)]x_n + n\alpha x_{n-1}\},$$

$$n = 0, 1, 2, \ldots \qquad (2.35)$$

where $\alpha(t) = \Sigma nx_n(t)$ is the total number of vibrational quanta at the instant t of time.

2.7. Vibrational relaxation in an isolated system. Distribution of the molecules over the vibrational levels. In the general case, the solution of the non-linear system of equations of (2.35) involves considerable difficulties. However, in this problem we are aided by the fact that $Q_{10} \gg P_{10}$. [36-38] We see from studying system (2.35) that the establishment of equilibrium in the vibrational degrees of freedom involves two relaxation times, $\tau_1 \sim 1/ZQ_{10}$ and $\tau_2 \sim 1/ZP_{10}$. Here, in accordance with what has been said, $\tau_2 \gg \tau_1$. The latter inequality permits us to distinguish two stages in the process of establishment of equilibrium. During the first rapid stage, which occurs with the relaxation time τ_1, the vibrational degrees of freedom behave as an isolated system, practically unconnected with the translational motion. This stage results in establishment of a quasi-steady-state distribution,

owing to the elementary events of exchange of vibrational quanta. During the second slow stage, which occurs with the relaxation time τ_2, the translational and vibrational degrees of freedom interact, with the result of establishment of a single equilibrium distribution.

The establishment of equilibrium in the first rapid stage (i.e., at times $t \ll \tau_2$) is described by the following system of equations derived from (2.35) by neglecting the terms of the order of τ_1/τ_2 in the latter:

$$\frac{dx_n}{dt} = ZQ_{10}\{(n+1)(1+\alpha)x_{n+1}$$

$$- [(n+1)\alpha + n(1+\alpha)]x_n + \alpha nx_{n-1}\},$$

$$n = 0, 1, 2, \ldots \qquad (2.36)$$

The value of α in (2.36) is constant to an accuracy of terms of the order of τ_1/τ_2. In fact, if we multiply (2.35) by n and sum over all values of n, we obtain after simple transformations

$$\frac{d\alpha}{dt} = -ZP_{10}(1 - e^{-\theta})[\alpha(t) - \alpha(\infty)]. \qquad (2.37)$$

If we neglect the terms of the order of τ_1/τ_2 in (2.37), we obtain, in the same approximation as in (2.36), the equation

$$\frac{d\alpha}{dt} = 0, \quad \text{or} \quad \alpha = \text{const.}$$

The latter result is obvious, since during the first rapid stage, the vibrational degrees of freedom (in this approximation) behave like an isolated system.

Thus, system (2.36) is a system of linear equations coinciding in form with the system studied in Sec. 2.4. The general solution (2.36) has the form of (2.23), or can be derived from (2.25). However, the solution of practical interest is the steady-state solution of the system, which is appropriate to times $\tau_1 \ll t \ll \tau_2$.

The steady-state solution, as we can easily see, has the form

$$x_n = (1 - e^{-\theta_0})e^{-n\theta_0}, \qquad (2.38)$$

where

$$\theta_0 = \ln(1 + \alpha^{-1}). \qquad (2.39)$$

Thus the first rapid stage in the isolated system of oscillators results in establishment of a quasi-steady-state Boltzmann distribution with a temperature determined by the initial supply of vibrational quanta, but independent of the form of the initial distribution function of the oscillators over the vibrational levels.

The second slow stage of the process of establishment of equilibrium is described by the system of complete equations. Here, according to what has been said, the solution is sought in the form of (2.39), where θ_0 is now an unknown function of time. We can easily see that, with such a choice of solution, the last parenthesis on the right-hand side of (2.35) becomes iden-

tically zero, and the following system of equations for determining $x_n(t)$ is left:

$$\frac{dx_n}{dt} = ZP_{10}\{(n+1)x_{n+1} - [(n+1)e^{-\theta} + n]x_n + ne^{-\theta}x_{n+1}\},$$
$$n = 0, 1, 2, \ldots \qquad (2.40)$$

The system (2.40) differs from the analogous system (2.17) in that the value of θ, and hence also of P_{10}, are functions of time. The form of these functions can be found by solving (2.37).

Thus, the establishment of equilibrium in the vibrational degrees of freedom in an isolated system of oscillators takes place as follows. First, in a period of time of the order of τ_1, a quasi-steady-state Boltzmann distribution is established, with a temperature determined by the initial number of vibrational quanta, but independent of the other initial conditions. In this process, the fundamental elementary event which occurs in the collision of oscillators is the exchange of vibrational quanta; here the total number of vibrational quanta remains practically constant. After the quasi-steady-state Boltzmann distribution has been established, the elementary processes of energy transformation of translational into vibrational motion initiate the relatively slow evolution of the quasi-steady-state Boltzmann distribution into an equilibrium state. In this stage, the distribution function remains always a Boltzmann function, but its parameter varies from the initial value θ_0 to a final value corresponding to the temperature in a state of complete equilibrium.

At temperatures considerably lower than the characteristic temperature, the difference between Q_{10} and P_{10} amounts to several orders of magnitude. Thus, the cited stages in the process of establishment of equilibrium can be observed experimentally. A practical example in which one can follow the first stage of the establishment of equilibrium is given by the experiments of Cashion and Polanyi,[39,40] who studied the infrared emission of vibrationally-excited HCl molecules formed in a system consisting of atomic hydrogen and chlorine. In these experiments, which were conducted at room temperature, it was found that the HCl molecules have a Boltzmann distribution with a vibrational temperature of 2700°K. This phenomenon can be explained within the framework of the ideas which have been presented here.

In the experiments under discussion, the vibrationally-excited HCl molecules formed in the exchange reaction $H + Cl_2 \rightarrow HCl + Cl$ lost their vibrational energy through spontaneous emission and collisions with the molecules of the surrounding gas. We shall consider only the processes of energy transfer in collisions of HCl molecules with one another.

In this case, two types of processes are possible: transformation of vibrational into translational energy, and exchange of vibrational quanta. The probability of the former process has been calculated in [41], and at room temperature is 5.2×10^{-9}. A calculation of the probability of the latter process using the formulas

from [6] gives a value of 10^{-1}–10^{-2}. Thus, the establishment of complete statistical equilibrium requires about $(1/P_{10}) = 1/(5.2 \times 10^{-9}) \sim 2 \times 10^8$ collisions. However, the establishment of equilibrium among the vibrational degrees of freedom requires about $(1/Q_{10} \sim 100$ collisions. In these experiments, the HCl molecules undergo about 10^4 collisions while they are within the cone of observation. As we can easily see, this number is just bracketed between the characteristic numbers of collisions for the first and second stages

$$\frac{1}{Q_{10}} \ll 10^4 \ll \frac{1}{P_{10}}.$$

Thus, in this time interval, which corresponds to 10^4 collisions, the first stage of the process of establishment of equilibrium has already been completed, but the second stage has not yet started. This explains the existence of different temperatures for the vibrational and translational degrees of freedom in the experiments of [39]. The estimates given are qualitative in nature, since they neglect the processes of energy transfer in collisions with other molecules, as well as spontaneous emission. However, we must emphasize that it would not change the overall picture of the relaxation phenomenon to take into account these processes, whose characteristic time constants are longer than the shorter time constant in the given problem. Taking these processes into account would only affect the total supply of vibrational energy, which would then differ from the total vibrational energy of the newly-formed HCl molecules.

3. DISTRIBUTION OF VIBRATIONAL ENERGY IN SYSTEMS CONTAINING PARTICLE SOURCES

3.1. Introduction. The preceding section discussed the process of establishment of equilibrium in a system under arbitrary initial conditions. If chemical reactions occur in the system, or it is subjected to some external influence producing vibrationally-excited molecules, we cannot justly speak of establishment of equilibrium during the period while these factors are acting. As has been stated, these systems may formally be described a systems containing particle sources.

Thus, the problem arises of studying the distribution of vibrational energy in systems containing sources of vibrationally-excited particles. We very often encounter sources of this sort in practice. Thus, for example, vibrationally-excited molecules are formed in electric discharges in gases,[42] in flash photolysis of gas mixtures,[32,22] and in exchange reactions of the type $A + BC \rightarrow AB + C$ or $A + BCD \rightarrow AB + CD$.[34] Finally, the process of thermal dissociation of molecules is also formally a source or sink (negative source) of vibrationally-excited particles,[43–45] etc. The practical interest of these systems is obvious. Constant sources distort the equilibrium distribution

of the energy among the vibrational degrees of free-
dom of the molecules, and this distortion can have a
considerable effect on the behavior of the system.

The study of these systems is also of interest in
that the ordinary perturbation theory cannot be applied
here. In fact, the result of the presence of constantly-
acting perturbations (sources) is that the ordinary
power-series expansion in the perturbation theory con-
tains secular terms which increase with time. This
situation is typical, not only of problems of statistical
kinetics, but is encountered in astronomy in the study
of planetary motion, and also in mechanics in the study
of nonlinear vibrational processes.

In mechanics and statistical physics, methods have
been developed for eliminating these difficulties in-
volving the appearance of secular terms. In the kinetic
problems with which this review is concerned, an addi-
tional difficulty arises. As has been stated, here finite
perturbations introduced by particle "sources" are of
interest. Hence, the method of solution must be adapted
to the description of the finite perturbations. However,
this fact is not always properly taken into account.

3.2. Thermal dissociation as a negative source of
vibrationally-excited molecules. We encounter negative
sources of vibrationally-excited particles in reactions
in which the activated molecules are vibrationally-
excited particles. A typical example of such a reaction
is the thermal dissociation of diatomic molecules. As
is known, this reaction results from the transition of
molecules from high vibrational levels to an energy
continuum.[43,45] This section will be concerned with
a discussion of this case.

We shall begin with the simplest problem, that of
thermal dissociation in a system in which the diatomic
molecules are a minor constituent in a monatomic gas.
Here we can neglect the mutual collisions of the disso-
ciating molecules, and consider only the collisions of
the latter with the monatomic gas. In order to esti-
mate the probabilities of transitions of the molecules
from the excited vibrational levels to the continuum,
we can use the Landau-Teller formula (2.9). We see
from Eq. (2.9) that the only practically-allowed transi-
tions are those from the upper vibrational levels to the
continuum. Owing to the small size of the vibrational
quanta for the upper levels, the transitions to the con-
tinuum will be many-quantum transitions. This means
that, in the range of vibrational energies for which the
probabilities of transition to the continuum differ from
zero, the probabilities of many-quantum transitions
between the discrete vibrational levels will also differ
from zero. Thus, the dissociation process can be
schematically represented as a stochastic process of
random walk of the molecules among the vibrational
levels, with a negative source acting on the upper lev-
els. The length of the walk will differ for the different
levels. In the lower vibrational levels, the molecules
can undergo only one-quantum transitions, i.e., jump
to adjacent levels. In the region of high enough vibra-

tional energies, many-quantum transitions are also
allowed; in this energy region, the probabilities of
transition to the continuum also differ from zero.

For convenience of discussion, we shall schematize
the problem even further. We shall consider that a
molecule will undergo one-quantum transitions up to
the k-th vibrational level, from which it can jump over
to the continuum.

This scheme of dissociation is described by a sys-
tem of gas-kinetic equations analogous to those for vi-
brational relaxation (2.15), with the sole difference
that a negative source will act on the upper level k,
describing the process of decomposition of the mole-
cules into atoms.

If we denote as $\frac{1}{2}x_d$ the concentration of molecules
which have dissociated, the system of equations will
have the form

$$
\begin{cases}
\frac{dx_n}{dt} = Z(P_{n+1,\,n} - P_{n,\,n+1}\,x_n + P_{n-1,\,n}\,x_{n-1} - P_{n,\,n-1}\,x_n), \\
\qquad\qquad n = 0,\ 1,\ 2,\ \ldots,\ k-1, \\
\frac{dx_k}{dt} = Z(P_{dk}\,x_d^2 - P_{kd}\,x_k + P_{k-1,\,k}\,x_{k-1} - P_{k,\,k-1}\,x_k), \\
\frac{1}{2}\frac{dx_d}{dt} = Z(P_{kd}\,x_k - P_{dk}\,x_d^2);
\end{cases}
$$
(3.1)

where $ZP_{dk}x_d^2$ is the number of molecules formed per
second by recombination.

In the general case, the solution of the system (3.1)
involves considerable difficulties, since this system
describes two processes, vibrational relaxation and
establishment of dissociation equilibrium. The relax-
ation times of these processes, as has been shown in
[18,46], are quite different, such as to permit a consid-
erable simplification of the solution of the problem.
Since we are interested in the slow process, the estab-
lishment of dissociation equilibrium, the system (3.1)
can be considered on a macroscopic time scale whose
unit of measurement is considerably longer than the
relaxation time of the rapid process.

In such a case, the rapid process is not considered
at all. The essential point thenceforth is only the re-
sult of this process, which leads to a synchronization
of the initial distribution function with the macroscopic
parameters of the problem.

Thus, on a macroscopic time scale, the solution of
system (3.1) can be sought in the form

$$x_n(t) = x_n^{(0)}(v) + \varepsilon x_n^{(1)}(v) + \ldots, \tag{3.2}$$

where $v = \frac{1}{2}(dx_d/dt)$ is the reaction rate, and ε is a
small parameter of the order of magnitude of τ_1/τ_2,
where τ_1 is the vibrational relaxation time, and τ_2 is
the time of establishment of dissociation equilibrium.

This form of solution assumes that at each given
moment of time, there is a certain quasi-steady-state
distribution of molecules, which is determined by the
value of the reaction rate at that moment of time. Thus,
this distribution depends on the time implicitly through
the parameter v, the rate of dissociation.

In order to simplify the problem, we shall consider the case in which the total number of vibrationally-excited molecules is small in comparison with the number of molecules in the ground state. Thus we obtain the condition

$$\frac{dx_n}{dv}\frac{dv}{dt} \ll v, \qquad n \neq 0, d. \tag{3.3}$$

On substituting Eq. (3.2) into (3.1), and taking (3.3) into account, we obtain the following system of equations for determining $x_n^0(v)$ (we shall omit the superscript zero below):

$$
\left.
\begin{aligned}
v &= Z(P_{n-1, n} x_{n-1} - P_{n, n-1} x_n) \\
&\qquad (n = 1, 2, \ldots, k), \\
v &= Z(P_{kd} x_k - P_{dk} x_d^2),
\end{aligned}
\right\} \tag{3.4}
$$

where

$$v = -\frac{dx_0}{dt} = \frac{1}{2}\frac{dx_d}{dt}. \tag{3.5}$$

The results obtained under these limitations are also valid under more general conditions, since the essential points involved are the behavior of the distribution function on the upper levels and the rate of dissociation. The only distinction between the more general case and that discussed here is in the behavior of the distribution function on the lower levels. However, the latter fact is not important, since in both cases this distribution is a Boltzmann distribution to a high degree of accuracy.

If we assume the upper limit of the reaction rate to be of the order of $ZP_{kd}x_0 e^{-D/kT}$ ($E_k \approx D$), we obtain from the condition $\tau_2 \gg \tau_1$ the following condition for validity of Eq. (3.4):

$$P_{10} \gg P_{kd} e^{-\frac{D}{kT}}. \tag{3.6}$$

We should emphasize still another fact. If, instead of the expansion in (3.2) we use the ordinary series from perturbation theory:

$$x_n(t) = x_n^{(0)}(t) + \varepsilon x_n^{(1)}(t) + \ldots, \tag{3.7}$$

we can then analyze only the first rapid stage of the process of establishment of equilibrium. In fact, in the zero-order approximation, the quantity $N = \sum_0^k x_n(t)$ is independent of time. The time-dependence of N, which characterizes the dissociation process, can be obtained only by taking into account a correction term proportional to ε. Thus we see that the series expansion of (3.7) can be used only in a time interval during which N varies little from its initial value. This means that the series expansion of (3.7) is practically inapplicable for description of the dissociation process.

We shall seek a solution of system (3.4) in the form

$$x_n = x_0 e^{-\varepsilon_n}(1 + \varphi_n), \qquad \varepsilon_n = \frac{E_n - E_0}{kT}, \tag{3.8}$$

where φ_n characterizes the deviation of the quasi-steady-state distribution from the equilibrium Boltzmann distribution. Here, $\varphi_0 = 0$, while φ_n is not necessarily much smaller than unity. By substituting (3.8) into (3.4), and taking into account the fact that, according to the principle of microscopic equilibrium

$$\frac{P_{n, n-1}}{P_{n-1, n}} = e^{-(\varepsilon_{n-1} - \varepsilon_n)},$$

we obtain

$$\varphi_l = -\frac{v}{Zx_0}\sum_{n=1}^{l}\frac{e^{\varepsilon_{n-1}}}{P_{n-1, n}}. \tag{3.9}$$

In order of magnitude, $v \sim ZP_{kd}x_0 e^{-D/kT}$. Hence, on the lower levels, $\varphi_l \ll 1$, but on the upper levels $\varphi_l \sim 1$ (excluding the case of very low temperatures). Thus, the dissociation process leads to a finite distortion of the equilibrium distribution of the molecules over the vibrational levels. This distortion is practically confined to the region of vibrational energies from which the molecule can go over to the energy continuum. This distortion has a considerable effect on the rate of dissociation. If we substitute (3.8) and (3.9) into the last equation of (3.4), we obtain

$$\frac{1}{2}\frac{dx_d}{dt} = \left(P_{kd} ZN \frac{e^{-\varepsilon_k}}{\sum_{i=0}^{k} e^{-\varepsilon_i}} - \frac{1}{2}\frac{dx_d}{dt}P_{kd}e^{-\varepsilon_k}\sum_{i=1}^{k}\frac{e^{\varepsilon_{i-1}}}{P_{i-1, i}}\right) - P_{dk}Zx_d^2,$$

or, neglecting recombination,

$$v = \frac{1}{2}\frac{dx_d}{dt} = NZ \frac{P_{kd}e^{-\varepsilon_k}}{\sum_{i=0}^{k} e^{-\varepsilon_i}\left\{1 + P_{kd}e^{-\varepsilon_k}\sum_{i=1}^{k}\frac{e^{\varepsilon_{i-1}}}{P_{i-1, i}}\right\}},$$

$$N = \sum_{i=0}^{k} x_i. \tag{3.10}$$

Equation (3.10) is also correct for a more general case than is assumed in condition (3.3). Here we need only assume that we can specify a region of large vibrational energies having a relatively low population density, but having a negligibly small value of φ at its lower limit.

In most cases of practical interest, $P_{kd}\exp(-\varepsilon_k)$ $\Sigma[(\exp \varepsilon_{i-1})/P_{i-1, i}] \gg 1$. Hence, we can neglect the term unity in the curly brackets of (3.10). For comparison, we might point out that in elementary collision theory, in which the distortion of the Boltzmann distribution is neglected, the expression for the dissociation rate v will have the form of (3.10), but with the term $P_{kd}\exp(-\varepsilon_k)\Sigma[(\exp \varepsilon_{i-1})/P_{i-1, i}]$ taken as negligible in comparison with unity. The mode of reasoning giving this result is not the only one, although perhaps it is the simplest. Analogous results (by several other methods) have been obtained in [47,48].

Thus, the distortion of the equilibrium energy distribution over the vibrational levels caused by the dissociation process has a considerable influence on the rate of dissociation.

We shall cite two examples as possible applications of the results obtained.

1. The fact that the rate of thermal dissociation is determined by a non-equilibrium distribution of the molecules over the vibrational levels complels us to criticize the application of the well-known relation of statistical thermodynamics

$$\frac{k_{\text{dissoc}}}{k_{\text{recomb}}} = K_{\text{equil}} \qquad (3.11)$$

under non-equilibrium conditions. Here, K_{equil} is the chemical equilibrium constant, while k_{dissoc} and k_{recomb} are the rate constants for dissociation and recombination, respectively. In particular, in the present case of the thermal dissociation of diatomic molecules occurring as a minor constituent in a monatomic gas, the rate "constant" of the forward reaction differs from its equilibrium value. This involves the distortion of the Boltzmann distribution in the upper levels. The rate constant of the reverse reaction retains its equilibrium value, since under the stated conditions this reaction takes place through triple collisions of the atoms of the dissociating gas with the thermal-reservoir atoms, and the Maxwell distribution in the velocities of these particles is practically unaltered. Hence, Eq. (3.11) does not hold for the reaction being discussed; (3.10) has the form $v = -k_1 N$, where the proportionality coefficient k_1 depends only on T (and on the density of the thermal-reservoir gas). Hence we can write

$$\frac{k_1}{k_2} = K^*, \qquad (3.12)$$

where k_2 is the rate constant of the reverse reaction, that is, k_{recomb}, while K^* is a quantity independent of the concentrations of the reacting components.

Equation (3.12) has the same form as (3.11), and permits us to determine k_1 from the constant k_2. However, (3.12) differs in meaning from (3.11): K^* is not equal to the equilibrium constant, and besides, we must bear in mind the fact that k_1 is the rate constant for dissociation at the initial instant of time, when we can neglect the recombination processes.

The publication of studies predicting from theory an appreciable effect of the distortion of the equilibrium distribution functions on the course of chemical reactions [43,44,45] has stimulated anew the discussion of the old question of the applicability of Eq. (3.11) in systems not in chemical equilibrium. [49-52]

2. The expression found for the rate constant for dissociation can be compared with experimental data. Equation (3.10) can be simplified by using some concrete model of the molecule. In particular, for an oscillator having a Morse potential function in a temperature range above the characteristic temperature, Eq. (3.10) has the form

$$k_{\text{dissoc}} = Z\overline{P_{k,\,k-1}} \left(\frac{\hbar\omega}{D} \right)^2 \left(\frac{D}{kT} \right)^{1.5} \exp\left(-\frac{D}{kT} \right). \qquad (3.13)$$

In comparing Eq. (3.13) with the experimental data, we must take into account the effect of the rotational and vibrational degrees of freedom of the dissociating molecule. The estimates made in [47] lead to the appearance in (3.13) of additional factors with values larger than unity. For the reaction $Br_2 + Ar \rightarrow 2Br + Ar$, which has been studied over a temperature range up to 2000°K in a shock tube, [53] the dissociation rate constant has the form

$$k_{\text{dissoc}} = 5 \cdot 10^{-2} Z \left(\frac{D}{kT} \right)^{1.5} \exp\left(-\frac{D}{kT} \right).$$

The experimental value of the rate constant for this reaction is [53]

$$k_{\text{dissoc}} = 6 \cdot 10^{-2} Z \left(\frac{D}{kT} \right)^{1.97} \exp\left(-\frac{D}{kT} \right).$$

These expressions give values agreeing in order of magnitude.

3.3. Distribution of vibrational energy in an isolated system of dissociated molecules. The previous section discussed the distribution function for the vibrational energy in the thermal dissociation of diatomic molecules occurring as a minor constituent in a monatomic gas. The distribution of vibrational energy in an isolated system of dissociating molecules is also of interest.

We shall consider the simplest model of a molecule, a truncated harmonic oscillator. [54] This model has been used repeatedly in calculations of the rate of dissociation of molecules occurring as a minor constituent in a monatomic gas. [55-57]

In calculating the distribution function for the vibrational energy in an isolated system of oscillators, we must take into account the exchange of vibrational quanta in the molecular collisions, as well as the transformation of translational into vibrational energy.

The process of dissociation in such a system is described by the following equations:

$$\frac{dx_n}{dt} = ZP_{10} \{(n+1) x_{n+1} - [(n+1) e^{-\theta} + n] x_n + ne^{-\theta} x_{n-1}\}$$

$$+ ZQ_{10} \{(n+1)(1+\alpha) x_{n+1} - [(n+1)\alpha$$

$$+ n(1+\alpha)] x_n + n\alpha x_{n-1}\},$$

$$n = 0, 1, 2, \ldots, k-1$$

$$\frac{dx_k}{dt} = ZP_{10} \{ke^{-\theta} x_{k-1} - kx_k\} + ZQ_{10} \{k\alpha x_{k-1} - k(1+\alpha) x_k\}$$

$$- ZP_{kd} x_k; \qquad (3.14)$$

where $\alpha = \dfrac{1}{N} \displaystyle\sum_{n=0}^{k} nx_n(t)$, and N(t) is the total number of oscillators. The system (3.14) is analogous to the equations of (2.35) describing vibrational relaxation in an isolated system of harmonic oscillators, but differs from (2.35) in the last equation, which describes the transition of the molecules to the dissociated state. As before, we shall assume that the dissociation of the

molecules arises from the transition of the molecules from some level k to the continuum. We shall consider only the initial stage of dissociation, and hence will neglect recombination.

The solution of the nonlinear system (3.14) involves considerable difficulties. In the general case, the system (3.14) describes complex relaxation processes. First, energy is exchanged between the translational and vibrational degrees of freedom, and vibrational quanta are exchanged as well. It is only in the region of high vibrational energies that these processes very rapidly establish, to a first approximation, a Boltzmann distribution (quite perturbed). The second slow stage of the process involves the establishment of dissociation equilibrium. In kinetic problems of the type under discussion, it is the second, slow stage which is of especial interest.

It is an easier problem to derive the quasi-steady-state distribution function, which is established as a result of the rapid process, and which subsequently changes slowly with the time.

The quasi-steady-state distribution, as was shown in Sec. 3.2, differs appreciably from a Boltzmann distribution only in the upper vibrational levels. This is true even when we take into account only the transformation of translational into vibrational energy. Hence, it is all the more valid when we also take into account exchange of vibrational quanta. On the basis of this conclusion, we can simplify system (3.14). The quantity α in (3.14) is mainly determined by molecules occurring in the first few vibrational levels. In the quasi-steady-state process being discussed, these levels obey a Boltzmann distribution to a high degree of accuracy. Hence

$$\alpha = \frac{1}{N} \sum_{n=0}^{h} n x_n (t) = (1 - e^{-\theta}) \sum n e^{-n\theta} = \frac{1}{e^{\theta} - 1} . \quad (3.15)$$

Taking (3.15) into account, we can write the system (3.14) in the following form:

$$\frac{dx_n}{dt} = Z P_{10}^* \{ (n+1) x_{n+1} - [(n+1) e^{-\theta} + n] x_n + n e^{\theta} x_{n-1} \},$$

$$n = 0, 1, 2, \ldots, k-1,$$

$$\frac{dx_k}{dt} = Z P_{10}^* \{ k e^{-\theta} x_{k-1} - k x_k \} - Z P_{kd} x_k,$$

$$(3.16)$$

where

$$P_{10}^* = P_{10} \left[1 + (1 - e^{-\theta})^{-1} \frac{Q_{10}}{P_{10}} \right] \equiv \beta P_{10}. \quad (3.17)$$

Thus the nonlinear system (3.14) is reduced to the linear system (3.16). Formally, we can derive the equations of (3.16) from system (3.14) by substituting into the latter x_n in the form given by (3.2), and keeping only the zero-order terms.

The system of equations (3.16) coincides in form with the analogous system derived in Sec. 3.2. The only difference is that instead of P_{10}, we have here

$P_{10}^* = \beta P_{10}$. The system of equations of (3.16) has been solved in Sec. 3.2. The solution is of the form

$$x_n = x_0 e^{-\varepsilon_n} (1 + \varphi_n).$$

For the molecular model under discussion, in a temperature range lower than or of the order of the characteristic temperature, φ_n differs appreciably from zero only when $n \approx k$.

In particular,

$$x_k = x_0 e^{-\varepsilon_k} \frac{1}{P_{kd} e^{-\varepsilon_k} \sum_{n=1}^{k} \frac{e^{\varepsilon_{n-1}}}{n P_{10}}} .$$

The substitution of P_{10}^* for P_{10} results in the multiplication of x_k by the factor β. At temperatures below the characteristic temperature, $Q_{10} \gg P_{10}$, and hence, $\beta \gg 1$. At temperatures of the order of the characteristic temperature, $Q_{10} \sim P_{10}$, and $\beta \sim 1$.

Thus, the exchange of vibrational quanta upon collision of molecules in the dissociation process increases the quasi-steady-state population of molecules in the upper vibrational levels, and brings it closer to the equilibrium value. This increase is considerable at temperatures below the characteristic temperature, but plays no appreciable role at temperatures above or of the order of the characteristic temperature.

The physical reason for the increase in the number of molecules in the upper vibrational levels is obvious. At low temperatures, energy transfer from the highly-excited molecules through exchange of vibrational quanta proceeds more rapidly than energy transfer involving translation-vibration transition. The rate of supply of molecules to the upper vibrational levels is increased, while the probability of transition to the continuum ($P_{kd} \sim 1$) remains unchanged. Thus the quasi-steady-state population is increased.

In comparing the obtained results with the experimental data, we must bear in mind the fact that the model being discussed does not take into account anharmonicity. Hence, the present results are qualitative in nature as applied to diatomic molecules. However, in the case of polyatomic molecules whose thermal dissociation involves change of multiplicity, the interaction potential along the broken bond can be approximated quite well by a model of formation of a harmonic oscillator. In particular, this is true of N_2O dissociating to N_2 and O. In the latter case we can state that the dissociation rate in pure N_2O will exceed the dissociation rate of N_2O mixed with a monatomic gas. There are as yet no comparative experiments of this sort.

3.4. Distribution of vibrational energy in a system containing positive sources (case of low concentration). We shall consider the simplest case. We shall assume that in a system consisting of a monatomic or polyatomic gas A, whose internal degrees of freedom do not participate in the deactivation process, vibration-

ally-excited molecules of B are generated with a certain supply of vibrational energy E_{n_0}. We are to find the distribution function of the B molecules over the vibrational levels. We shall consider only conditions under which the concentration of B molecules is considerably smaller than the concentration of A molecules.[58] In this case, the mutual collision of A molecules need not be considered.

The vibrational relaxation of the B molecules in the presence of a source is described by the following system of equations:

$$\frac{dx_n}{dt} = Z\left(P_{n+1,\,n}x_{n+1} - P_{n,\,n+1}x_n + P_{n-1,\,n}x_{n-1} \right.$$
$$\left. - P_{n,\,n-1}x_n\right) + N\delta_{nn_0}, \quad n = 0, 1, 2, \ldots \quad (3.18)$$

where N is the strength of the source, i.e., the number of vibrationally-excited molecules with energy E_{n_0} produced per unit time per unit volume; and δ_{nn_0} is the Kronecker delta.

The system (3.18) can describe the vibrational deactivation of molecules also when the vibrational degrees of freedom of the surrounding gas participate in this process. Under these conditions, we must take certain effective values $(P_{ik})_{eff}$ for the P_{ik}. In the special case of resonance transfer discussed in the previous section, $(P_{ik})_{eff} = P_{ik}^*$. The system of equations (3.18) differs from the analogous system (2.15) in the presence of the source, whose strength N is generally a function of time.

In solving system (3.18), we encounter the same difficulties as in the problem involving dissociation. In fact, the equations of (3.18) involve two time scales. One time scale involves the vibrational relaxation time, while the other involves the characteristic time constant of the source. Under practical conditions, these time constants commonly differ greatly from each other. These facts permit us to simplify the problem considerably. Just as in the case of dissociation, we can avoid discussing the process leading to synchronization of the distribution function with the acting source, and discuss only the quasi-steady-state distribution, which is determined by the strength of the source at the particular instant of time. For simplicity, we shall assume a constant source. The problem formulated in this way is analogous to the problems of the distribution of kinetic energy in systems containing particle sources,[59,60] where solutions have been discussed satisfying the condition

$$\frac{dx_n}{dt} = Nx_n^{(0)}; \quad (3.19)$$

where $x_n^{(0)}$ is the normalized Boltzmann function. This method can be applied to the given problem as well. Condition (3.19) implies that systems are being studied in which the source has been acting for a sufficiently long time. If we were to classify at each given moment all of the existing particles produced by the source in terms of their age, we would find in the course of time that their distribution would be enriched only in "old"

molecules having a Boltzmann distribution. This fact is reflected by Eq. (3.19).

Equation (3.19) can be integrated. Then,

$$x_n(t) = tNx_n^{(0)} + f_n; \quad (3.20)$$

where f_n is an unknown function which we shall call the perturbation function.[59] The perturbation function f_n is assumed to be independent of time.

Upon substitution of Eq. (3.20) into (3.18), we obtain the following inhomogeneous system of algebraic equations for determining the perturbation function:

$$(P_{n+1,\,n}f_{n+1} - P_{n,\,n+1}f_n) - (P_{n,\,n-1}f_n - P_{n-1,\,n}f_{n-1})$$
$$= \frac{N}{Z}(x_n^{(0)} - \delta_{nn_0}). \quad (3.21)$$

A solution of this system exists when the solution of the corresponding homogeneous conjugate system of equations is orthogonal on the right-hand side. The latter condition can be written in the form

$$\frac{N}{Z}\sum (x_n^0 - \delta_{nn_0}) = 0, \quad (3.22)$$

which, as we can easily see, is fulfilled identically.

If we carry out the double summation, and take into account the fact that

$$P_{n+1,\,n} = P_{n,\,n+1}e^{-\varepsilon_n + \varepsilon_{n+1}},$$

we obtain the solution in the form

$$f_{n+1} = \left[\frac{N}{Z}\sum_{m=0}^{n}\frac{e^{\varepsilon_{m+1}}}{P_{m+1,\,m}}\sum_{l=0}^{m}(x_l^{(0)} - \delta_{ln_0}) + f_0\right]e^{-\varepsilon_{n-1}}. \quad (3.23)$$

Solution (3.23) is correct only for a source described by a δ-function. The perturbation function for an arbitrary source may be represented as a superposition of solutions of the type of (3.23), owing to the linearity of the equations of (3.18).

For performing concrete calculations, it is convenient to select a Morse oscillator as the model. We shall consider only the lower levels, i.e., the condition $E_{n_0} \ll D$ (where D is the dissociation energy), at low temperatures ($e^{-\theta} \ll 1$), and can then write (3.23) in the form

$$f_n = B(n)e^{-n\theta}, \quad n \leqslant n_0,$$
$$f_n = B(n_0)e^{-n\theta}, \quad n > n_0, \quad (3.24)$$

where

$$B(n) = \frac{Ne^{n\theta}}{ZP_{n,\,n-1}},$$
$$P_{n,\,n-1} = nP_{10}\gamma^{n-1}, \quad \gamma \gg 1^{17}.$$

The expressions derived here permit us to guess at the nature of the perturbation in the vibrational energy distribution caused by the particle source. In the present approximation, the perturbation function f_n is of Boltzmann type in the region $n > n_0$, with a false total number of particles $B(n_0)$. In the region $n \leq n_0$, the perturbation function f_n differs appreciably from the Boltzmann distribution, and behaves approximately

like $1/n$. Within a period of time of the order of mag-
nitude of the vibrational relaxation time, the distribu-
tion of the particles which have been created is deter-
mined primarily by the perturbation function f_n. In
fact, the vibrational relaxation time $\tau = 1/ZP_{10}$, and
hence, for moments of time $t > \tau$, the term $tNx_n^{(0)}$ in
Eq. (3.20) is of the order of $Ne^{-n\theta}/ZP_{10}$, which is
considerably smaller than the value of the perturba-
tion function f_n ($f_n \sim N/ZP_{10}n$, where $n \lesssim n_0$). Thus,
in this approximation, the particle source produces a
finite perturbation which is practically confined to the
region of vibrational energies less than the initial vi-
brational energy of the created molecules.

We should emphasize that the perturbation in the
distribution function for the vibrational energy in this
case resemble in nature the perturbation brought about
in the kinetic-energy distribution by a source of fast
particles acting under analogous conditions.[59,60]

The results obtained can be applied, for example,
to analyze the experiments of Norrish,[32] who studied
the process of deactivation of vibrationally-excited O_2
molecules. In these experiments, the vibrationally-
excited molecules were obtained by flash photolysis
of ClO_2 and NO_2 in the presence of large amounts of
N_2 and other gases. The method of calculating the
transition probabilities from the data of these experi-
ments is given in Sec. 2.5. One of the basic difficul-
ties in the analysis of this study is in determining the
form of the distribution function of the molecules over
the vibrational levels at the moment the flash stops. In
the flash photolysis of ClO_2 mixed with N_2, the dura-
tion of the flash ($\tau \sim 10 \ \mu sec$) was considerably
shorter than the lifetime ($\sim 500 \ \mu sec$). Hence, we
can assume to a high degree of accuracy that at the
moment the flash stops, the molecules are still in the
same levels in which they were formed (see Sec. 2.5.)
In these experiments, the molecules were formed pref-
erentially in the eighth level,[34] and hence we can take
a δ-function as the initial distribution. In the flash
photolysis of ClO_2 mixed with CO_2 and N_2, the flash
duration ($\sim 10 \ \mu sec$) was comparable to the lifetime
($\sim 65 \ \mu sec$), and hence, within the period of the flash
the molecules could jump to other vibrational levels.
The distribution of the molecules over the vibrational
levels at the moment the flash ceases can be approxi-
mated in this case by Eq. (3.24). By solving the sys-
tem (2.26) under the initial condition (3.24), taking into
account only the O_2-Cl_2 collisions, we can determine
x_6 as a function of time. We can find $P_{10}(O_2-CO_2)$
from the experimental value of the lifetime.* It turns
out that $P_{10}(O_2-CO_2) = 6 \times 10^{-5}$. According to the es-
timates of Norrish,[32] $P_{10}(O_2-CO_2) = 2 \times 10^{-5}$. From
ultrasonic data, $P_{10}(O_2-CO_2) = 4 \times 10^{-5}$. All of the
results are for room temperature. Analogously, from

Norrish's experiments one can determine the proba-
bility of transformation of the vibrational energy of
O_2 in a collision with an NO_2 molecule.[62]

However, we must bear in mind the fact that P_{10} as
determined by the ultrasonic method can differ from
the P_{10} found by the flash photolysis method.

It was stated in Sec. 2.5 that the value of P_{10} deter-
mined in Norrish's experiment refers to a certain av-
erage vibrational quantum, which corresponds approx-
imately to the sixth vibrational level. However, in the
ultrasonic experiments, P_{10} refers to the vibrational
quantum of the first excited state. In view of the an-
harmonicity of the actual potential curve, these values
of the vibrational quanta will differ among themselves.

3.5. Distribution of vibrational energy in a one-
component system containing positive sources. In the
study of systems containing positive sources of vibra-
tionally-excited molecules, not only is the above-dis-
cussed case of low concentrations of practical interest,
but also single-component systems in which the cre-
ated molecules are identical with the molecules of the
medium.

Thus, for example, in the experiments of Dwyer,[42]
vibrationally-excited I_2 molecules were generated by
passing an electric discharge through I_2 vapor. We
also may encounter an analogous situation when the
concentration of the created molecules is large enough
that we cannot neglect their collisions with one another.

In this case, the problem is considerably more
complicated, since in addition to the energy exchange
between the translational and vibrational degrees of
freedom, we must also take into account the exchange
of energy between the vibrational degrees of freedom
of the molecules under study.

In general, this process has already been discussed
in a previous section (Sec. 3.4), in which it was as-
sumed that the molecules of the medium have internal
degrees of freedom. However, there is an essential
difference between the present problem and the previ-
ous one, in which the vibrational energy distribution
was studied in a system whose molecules are products
of a reaction, but where we were not interested in the
perturbation of the equilibrium in the surrounding
medium.

In the problems discussed in this section, we can-
not distinguish the surrounding medium from the re-
action products. Hence, we are interested in the over-
all distribution of the vibrational energy of the mole-
cules of both the reaction products and their collision
partners.

We shall discuss the simplest case, a system of
harmonic oscillators containing a constant source gen-
erating vibrationally-excited oscillators having energy
E_{n0}.

The equations describing the relaxation in this sys-
tem are analogous to those for vibrational relaxation
in an isolated system of harmonic oscillators (2.35),
and differ from the latter in including the constant

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*The found value of P_{10} generally amounts to a lower bound for
the transition probability. However, as was shown in [62], the dif-
ference between the upper and lower bounds for P_{10} is insignificant.

source. In our notation, this system of equations has the form

$$\frac{dx_n}{dt} = ZQ_{10}\{(n+1)(1+\alpha)x_{n+1} - [(n+1)\alpha + n(1+\alpha)]x_n +$$
$$+ \alpha n x_{n-1}\} + ZP_0\{(n+1)x_{n+1} - [(n+1)e^{-\theta} + n]x_n +$$
$$+ ne^{-\theta}x_{n-1}\} + N\delta_{nn_0} \quad (n = 0, 1, 2, \ldots),$$
$$(3.25)$$

where $Z = Z_0\rho$, $\rho = \Sigma x_n(t)$, Z_0 is the number of collisions per unit time per unit volume which a certain molecule makes with the others when the latter have a concentration $\rho = 1$, and

$$\alpha = \frac{1}{\varrho}\sum n x_n(t).$$

The solution of the system (3.25) in the general case is difficult, since it is non-linear and inhomogeneous. However, just as in the previous cases, we are aided by the fact that the relaxation process described by the system (2.35) is characterized by relaxation times which differ considerably. First, there are two characteristic time constants $\tau_1 \sim 1/ZQ_{10}$, and $\tau_2 \sim 1/ZP_{10}$, whose meanings have been explained in Sec. 2.7. Besides, the system (3.25) possesses another characteristic time constant τ_3 involving the source. Since ordinarily $\tau_3 \gg \tau_2, \tau_1$, we can consider the source to be constant. Since in such problems we are interested only in the quasi-steady-state distribution brought about by the source, we can avoid studying the rapid process of "synchronization" of the distribution function with the characteristics of the source, assuming this process to have been completed.

Then, we can seek the distribution function $x_n(t)$ in the form

$$x(t) = x_n^{(0)}(\varrho, \alpha) + x_n^{(1)}(\varrho, \alpha) + \ldots \quad (3.26)$$

The series expansion is carried out in terms of a parameter of smallness ϵ, which is the dimensionless strength of the source $N/Z\rho Q_{10}$.

We shall take as the normalization conditions: $\rho = \Sigma x_n^{(0)}$, and $\alpha = (1/\rho)\Sigma n x_n^{(0)}$. To begin, we shall consider the case

$$\frac{1}{ZQ_{10}} \ll t \ll \frac{1}{ZP_{10}},$$

neglecting here the second curly bracket in Eq. (3.25).

In the zero-order approximation, we obtain the equation

$$L(\alpha, \varrho, x_n) \equiv ZQ_{10}\{(n+1)(1+\alpha)x_{n+1}$$
$$- [(n+1)\alpha + n(1+\alpha)]x_n$$
$$+ \alpha n x_{n-1}\} = 0 \quad (n = 0, 1, 2, \ldots), \quad (3.27)$$

where $d\alpha/dt$ and $d\rho/dt$ are of the order of ϵ. In fact, we can easily derive from Eq. (3.25) the following:

$$\frac{d\alpha}{dt} = \frac{N}{\varrho}(n_0 - \alpha),$$
$$\frac{d\varrho}{dt} = N. \qquad (3.28)$$

The solution of the system (3.27), taking into account the normalization conditions, has the form

$$x_n^{(0)} = \varrho(1 - e^{-\vartheta})e^{-n\vartheta},$$

where

$$e^{-\vartheta} = \frac{\alpha}{1+\alpha}.$$

Thus, in the zero-order approximation, a Boltzmann distribution is established in the system with a temperature determined by the supply of vibrational quanta existing at the given moment of time. The quantity α, which determines the temperature of the system, is a function of time, and can be found by solving system (3.28).

The equations of the first-order approximation have the form

$$\frac{\partial x_n^{(0)}}{\partial \alpha}\frac{d\alpha}{dt} + \frac{\partial x_n^{(0)}}{\partial \varrho}\frac{d\varrho}{dt} = L(\alpha, \varrho, x_n^{(0)}) + N\delta_{nn_0}, \quad n = 0, 1, 2, \ldots$$
$$(3.29)$$

The condition for solvability of system (3.29), which has the form

$$\sum_{n=0}^{\infty}\left\{(1 - e^{-\vartheta})e^{-n\vartheta} - \delta_{nn_0}\right.$$
$$\left. + (n_0 - \alpha)(1 - e^{-\vartheta})^2 e^{-n\vartheta}\left(\frac{n}{\alpha} - 1\right)\right\} = 0, \quad (3.30)$$

is satisfied identically, as can be easily seen.

The solution of (3.29) is obtained by direct summation, and can be written in the form

$$x_n^{(1)} = \frac{N}{\varrho Z}B(n)e^{-n\vartheta},$$

$$B(n) = \frac{1 - e^{-\vartheta}}{Q_{10}}\left(\sum_{m=1}^{n}\frac{e^{m\vartheta} - 1}{m} - \frac{(n_0 - \alpha)(1 - e^{-\vartheta})^2}{e^{-\vartheta}}n\right) + x_0,$$

$$B(n) = \frac{1 - e^{-\vartheta}}{Q_{10}}\left(\sum_{m=1}^{n_0}\frac{e^{m\vartheta} - 1}{m} - \sum_{n_0+1}^{n}\frac{1}{m} - \frac{(n_0 - \alpha)(1 - e^{-\vartheta})^2}{e^{-\vartheta}}n\right) + x_0,$$
$$n > n_0.$$

The normalization constant x_0 can be assumed to be zero or determined from the condition that $B(n)$ should always be positive. We note that the result of (3.30) is analogous to that in the corresponding problem of the perturbation of the kinetic-energy distribution in systems containing particle sources.[63,64]

We can easily see that an analogous expression can also be derived when

$$t \gg \frac{1}{ZP_{10}}.$$

In this case, Q_{10} must be replaced by some effective value Q_{eff}, such that

$$Q_{eff} = Q_{10} + \frac{P_{10}}{1+\alpha} \equiv Q_{10} + (1 - e^{-\vartheta})P_{10}.$$

We can appreciate the meaning of this substitution by referral to Sec. 3.3. When the source is weak enough and $\alpha \ll 1$, Eq. (3.31) becomes considerably simpler

in form:

$$B(n) \simeq \frac{1}{Q_{10}} \left(\frac{e^{n\vartheta}}{n} - n n_0 e^{\vartheta} \right) + x_0, \quad n \leqslant n_0.$$

When $n \approx n_0$,

$$B(n) \approx \frac{1}{Q_{10}} \frac{e^{n\vartheta}}{n} , \qquad (3.31)$$

in agreement with the analogous expression derived in the previous section (Sec. 3.4).

We note that the perturbation introduced by the particle source can be finite in the region of higher energies ($n \sim n_0$). This does not contradict the series expansion (3.26), since in any case the number of particles created per unit time will be smaller than the number of molecular collisions in the same time interval (the condition $N \ll \rho Z Q_{10}$ or $\epsilon \ll 1$).

The example discussed here is to a certain extent analogous to the conditions of Norrish's experiment,[32] and can be realized in practice.

We also encounter problems of this type in determining the distribution function for the vibrational energy in a homogeneous system at the moment of cessation of an electrical pulse. Such problems arise in the experimental determination of the lifetime of vibrationally-excited molecules.[42] The theoretical calculation is simplified in this case, since $d\rho/dt = 0$.

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