

ON THE RELAXATION OF NONEQUILIBRIUM GAS SYSTEMS

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Usp. Fiz. Nauk 72, 741-764 (December, 1960)

AT the present time, both in very different fields of physics and in many applied fields of technology, more and more attention is being devoted to systems which are in a state different from the state of thermodynamic equilibrium. Plasma physics, astrophysics and atmospheric physics, supersonic gas dynamics, etc. all deal with such systems. One of the most important and of the most frequently occurring cases of departure from thermodynamic equilibrium is the delay in the establishment of equilibrium with respect to the inert degrees of freedom of the molecules of a gas subjected to rapid oscillations or having high gradients of some of its parameters. Such departures from equilibrium may be grouped together under the common name of relaxation phenomena. A characteristic example of such phenomena is the existence of a more or less extensive nonequilibrium zone behind the front of a shock wave propagated in a gas. From a practical point of view considerable importance attaches to the question of the numerical values of the constants characterizing the rate of relaxation processes. The majority of papers dealing with relaxation processes in gases are devoted specifically to the theoretical or experimental determination of these constants. During the last 10 – 15 years a large number of such papers has appeared, but until now there has been no attempt to make a systematic study of the investigations that have been carried out and to pick out the most reliable values of the constants from among the frequently contradictory and greatly varying values. In this connection the time seems to be ripe for a systematic study of the available papers, so as to compare the results of the different investigators and to recommend the most reliable values of the constants. The present paper is an attempt to fill this gap. The authors restrict themselves to a discussion of the problems of the establishment of equilibrium with respect to the translational, rotational, and vibrational degrees of freedom, and also with respect to dissociation and ionization, and make no reference to other chemical reactions. Moreover, wishing to avoid undue lengthening of the tables, the authors have restricted themselves to the most important molecules from a practical point of view (primarily to the constituents of air).

POTENTIAL ENERGY OF COLLIDING PARTICLES

Thermodynamic equilibrium is established in a nonequilibrium gas primarily by means of elastic and inelastic collisions. Radiation transitions do not play

an important role in the relaxation process in cases of interest to us (i.e., for the constituents of air at relatively low temperatures). Even in the case of dipolar molecules the deactivation of vibrational and rotational levels as a result of radiation plays an important role⁶⁵ only at pressures of the order of 10^{-3} – 10^{-4} mm Hg. Therefore, in discussing the process of the establishment of equilibrium in a gas we shall take into account only elastic and inelastic collisions.

For the calculation of the cross sections for elastic and inelastic collisions it is necessary to know the interaction potential between the colliding molecules. Usually the Lennard-Jones empirical expression is utilized for this potential:

$$V(r) = 4\epsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right], \quad (1)$$

which holds in the absence of chemical interaction between the molecules. Here ϵ is the depth of the potential well, r_0 is the classical distance of closest approach of molecules whose relative velocity at infinite separation is equal to zero. The term corresponding to attractive forces has also been obtained theoretically. The values of ϵ and r_0 are at present known for many molecules; they have been chosen to satisfy the experimental values of the coefficients of viscosity and diffusion. However, we note that values of these coefficients which agree with the experimental values can also be obtained with the aid of potentials of other shapes. Moreover, for the coefficients of viscosity and diffusion the behavior of the potential at relatively large r is important and, therefore, the interaction potential has been studied best of all at these large distances; in the case of inelastic collisions the behavior of the potential at considerably smaller r is important, in the range where it is described by the Lennard-Jones formula only approximately. Since in the case of inelastic collisions only the short range interaction forces are important (Landau and Teller²⁷), it is customary to take for the interaction potential the exponential repulsive function:

$$V_{\text{exp}}(r) = Ae^{-\alpha r}. \quad (2)$$

The quantity α^{-1} characterizes the range of the interaction forces. In references 35 and 36, the Lennard-Jones potential was approximated by an exponential repulsive potential whose parameters were so chosen that the values of V and dV/dr for these potentials would coincide at the classical distance of closest approach. The additional condition $V_{\text{exp}} \rightarrow -\epsilon$ was imposed at $r \rightarrow \infty$, which takes into

account the acceleration of the colliding molecules in the field of their mutual attraction. It has turned out that in a number of cases the following approximate relation holds

$$\alpha \cong \frac{17.5}{r_0}. \quad (3)$$

In the presence of chemical and semi-chemical forces the interaction between the molecules is no longer described by the Lennard-Jones potential; an interaction of this type occurs,¹⁵² for example, in the collision of NO molecules (cf. also reference 46).

ENERGY TRANSFER IN COLLISIONS

In the study of the phenomena of the approach to equilibrium in gases it is important to know the energy transfer in elementary processes. In an elastic collision of two atoms or two molecules a fraction of the translational energy $\overline{\Delta K}/K$ transferred on the average in a collision is of the order of

$$\frac{\overline{\Delta K}}{K} \cong \frac{2m_1m_2}{(m_1+m_2)^2}. \quad (4)$$

Thus, a collision of molecules with masses of the same order of magnitude is effective from the point of view of transferring the kinetic energy from one molecule to the other, while in the collision of a light particle with a heavy one the fraction of the energy transferred in the collision is small.

For a qualitative investigation of the nature of an inelastic collision we consider the following classical model. We assume that a diatomic molecule can be represented by a harmonic oscillator and that when it approaches another molecule or atom the oscillator is acted upon by a time dependent force $F(t)$. The equation of motion for such an oscillator has the form

$$\ddot{x} + \omega_0^2 x = \frac{1}{m} F(t), \quad (5)$$

where ω_0 is the characteristic frequency of the oscillator, and m is its mass. On introducing the new variable $\xi = \dot{x} + i\omega_0 x$ and on assuming that for $t \rightarrow -\infty$ the oscillator was at rest, we obtain the following expression for $\xi(t)$ for $t \rightarrow \infty$ (i.e., after collision)

$$\xi(t) = \frac{1}{m} e^{i\omega_0 t} \int_{-\infty}^{\infty} F(t) e^{-i\omega_0 t} dt. \quad (6)$$

After the collision the energy of the oscillator is equal to

$$E = \frac{m}{2} (\dot{x}^2 + \omega_0^2 x^2) = \frac{m}{2} |\xi|^2 = \frac{1}{2m} \left| \int_{-\infty}^{\infty} F(t) e^{-i\omega_0 t} dt \right|^2. \quad (7)$$

Since $F(t)$ differs from zero only during the collision time Δt , it may be easily seen that (7) has a maximum value for $\omega_0 \Delta t \sim 1$, while $E \cong 0$ for $\omega_0 \Delta t \gg 1$. Since $\Delta t = a/v$, where a is the range of the

intermolecular potential and v is the relative velocity of the colliding particles, the condition for the probability of energy transfer in a collision to be small assumes the form

$$\frac{a\omega_0}{v} \gg 1. \quad (8)$$

The simple physical meaning of this inequality is that when the condition (8) is satisfied the collision process will be so slow (adiabatic) that the internal configuration of the colliding particles has time to change and to adjust to the slowly varying interaction energy. In a quantum mechanical problem this criterion retains its form, only we have to replace ω_0 by $2\pi\Delta E/h$:

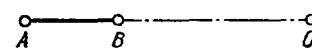
$$\frac{2\pi a \Delta E}{hv} \gg 1. \quad (9)$$

The inequality (9) (Massey's criterion) is the condition that the effective cross section σ_i for an inelastic collision accompanied by a change of internal energy by an amount ΔE should be much smaller than the cross section σ_e for an elastic collision. Usually one introduces into the discussion the value of the probability of an inelastic transition in an "elastic" collision $P = \sigma_i/\sigma_e = 1/z$, where z is the number of elastic collisions which a molecule experiences on the average before undergoing an inelastic collision. The arbitrary nature of such a quantity is obvious, but it is convenient to use due to its simple nature.

QUANTUM MECHANICAL DESCRIPTION OF A COLLISION

Classical considerations can give only a rough qualitative description of an inelastic collision. Therefore, it is necessary to use quantum mechanical methods for the evaluation of the quantities σ_i (or P). As an example we shall discuss the excitation of oscillations of a diatomic molecule AB, which is in a vibrational state i , as a result of a one-dimensional (frontal) collision with the atom C (cf. diagram).

Frontal collision of molecule AB with atom C.



In the case of inelastic collisions the principal role is played by the short range repulsive potential between molecules which we can assume to be of the form

$$V = Ae^{-\alpha r_{BC}} \quad (10)$$

(we can neglect the interaction between the distant atoms A and C). If r is the distance between the centers of mass of the molecule AB and atom C, and s is the normal coordinate for the vibration of the molecule AB, then r_{BC} may be written in the form

$$r_{BC} = r + A_0 + A_1 s, \quad (11)$$

$$V(r) = V_0 e^{-\alpha r} e^{-\alpha A_1 s} = V_0 V_r(r) V_s(s). \quad (12)$$

In order to obtain the probability of the transition of the molecule as a result of the collision from the state i into the state f — $P_{if}(v_i)$ — we use the method of distorted waves. $P_{if}(v_i)$ is determined by the square of the matrix element of the perturbing energy evaluated between the wave functions of the initial and the final states. The latter are obtained on the assumption that the motion of particles before the collision occurs in the field $V_i(r)$ with relative energy $mv_i^2/2$, while after the collision it occurs in the field $V_f(r)$ with relative energy $mv_f^2/2$ (m is the reduced mass of the colliding particles). We obtain for $P_{if}(v_i)$

$$P_{if}(v_i) = \frac{16\pi^2 V_0^2}{v_i v_f} |V_{i,f} R|^2, \quad (13)$$

where

$$R = \int_{-\infty}^{\infty} F_i F_f V_r dr, \quad (14)$$

$$V_{i,f} = \int_{-\infty}^{\infty} u_i(s) u_f(s) V_s ds. \quad (15)$$

Here u_i and u_f are harmonic oscillator wave functions; F_i and F_f are solutions of the wave equation for relative motion:

$$\frac{d^2 F_{i,f}}{dr^2} + \frac{8\pi^2 m}{h^2} \left[\frac{mv_{i,f}^2}{2} - V_0 V_r \right] F_{i,f} = 0. \quad (16)$$

The quantity R for the potential (2) has been calculated by Jackson and Mott.²⁵ On averaging the quantity $P_{if}(v_i)$ over the velocities we obtain

$$P_{i,f}(T) \sim \exp(-CT^{-\frac{1}{3}}); \quad C > 0. \quad (17)$$

This relation was first obtained by Landau and Teller.²⁷

In a more rigorous treatment of the problem one should take into account the fact that the collision has a three-dimensional nature, and that a significant contribution to the cross section is made not only by frontal collisions (i.e., such collisions for which the relative angular momentum $l = 0$), but also by collisions with l different from zero. Such a calculation was carried out in reference 36, where the potential for the interaction between the particles was taken to be spherically symmetric (the "breathing" sphere model for the oscillating molecule). This enabled the partial wave analysis to be applied to the investigation of the collision cross section. It is essential to take into account values of l different from zero;^{11,34} for example, it turned out that in the collision of an H_2 molecule with another H_2 molecule the principal contribution to the total cross section for the excitation of the first vibrational level is made by the partial cross sections with $l \sim 10 - 20$, and that to obtain the total cross section one must take into account partial cross sections up to $l \sim 80$. If we assume that the interaction potential is not spherically symmetric, then rotational-vibrational transitions must be taken into account in a collision.

In a number of cases one can treat the relative motion of the colliding particles classically. If the de Broglie wavelength $\lambda_0 \ll \alpha^{-1}$ we can approximately assume that the particles move along definite trajectories smeared out by an amount $\sim \lambda_0$ which is small compared with the spatial extension of the field in which the collision takes place. Moreover, the momentum Δp transferred in the collision will be of the order of

$$\Delta p \sim \int \nabla V dt \sim \frac{V \Delta t}{\alpha^{-1}} \sim \frac{V m}{h k}. \quad (18)$$

If

$$\frac{h}{\Delta p} = \frac{h^2 k}{V m \alpha^{-1}} \ll 1,$$

the motion can be treated classically; but if this ratio is ~ 1 , then even if the de Broglie wavelength is small the motion must be treated quantum mechanically.

We assume that both these conditions are satisfied and that, therefore, we can treat the relative motion of the colliding particles classically. Then as the particles move with respect to each other their interaction energy depends only on t , namely $V(t) = V[r(t)]$, where $r(t)$ is a classical integral of the motion. In this case we can apply time dependent perturbation theory for the evaluation of the transition probabilities. Since the energy of relative motion is not conserved in an inelastic collision usually the mean values of the translational energy and of the interaction energy before and after the collision are used for the evaluation of $r(t)$. Such a semiclassical theory is a good approximation if the relative translational energy is much greater than the energy transferred in the collision.

Nikitin⁶ has taken into account in a semiclassical treatment the role of long-range attractive forces; it turned out that taking such forces into account simply by increasing the kinetic energy of the colliding particles by an amount ϵ (the acceleration in the attractive field occurs at infinity) is insufficient.

RELAXATION OF TRANSLATIONAL, ROTATIONAL AND VIBRATIONAL ENERGY

We now consider the nature of the relaxation process for a gas in a nonequilibrium state. It follows from formula (4) that if at a certain instant the gas molecules have a nonequilibrium velocity distribution, then a Maxwellian equilibrium distribution will be established rapidly, during a few collision times, since the fraction of energy transferred in each collision is large. In the papers by Mott-Smith and others^{69,70} a discussion is given of the establishment of a new Maxwellian velocity distribution in a shock-wave front corresponding to the gas temperature beyond the shock wave. In these papers it is shown that the molecular velocity distribution function in the transition region can be approximately represented

in the form of a superposition of two Maxwellian distributions with temperatures corresponding to the temperature of the gas before and after the shock wave has passed through it:

$$f(v, x) = \nu_1(x) f_1(v) + \nu_2(x) f_2(v). \quad (19)$$

The functions $\nu_1(x)$ and $\nu_2(x)$ are such that at distances of the order of two or three mean free paths the Maxwellian distribution function $f_1(v)$ corresponding to the gas temperature before the shock wave has passed through it goes over into the distribution function $f_2(v)$ corresponding to the temperature of the gas after the shock wave has passed through it. Thus, the new Maxwellian distribution is established as a result of 2 or 3 collisions between molecules. Approximately the functions $\nu_1(x)$ and $\nu_2(x)$ may be written in the following form

$$\nu_1(x) = \frac{1}{2} \left(1 - \tanh \frac{2x}{L} \right); \quad \nu_2(x) = \frac{1}{2} \left(1 + \tanh \frac{2x}{L} \right). \quad (20)$$

Here L is the width of the shock wave front.

A simple investigation of the criterion (9) shows that in a number of cases the effective cross sections for inelastic collisions will be small compared to the cross sections for elastic collisions. For example, qualitative estimates lead to the conclusion that the effective cross section for rotational excitation is smaller than the cross section for an elastic collision and at the same time, as a rule, is considerably larger than the effective cross section for vibrational excitation.

The conversion of translational energy of molecules into rotational energy in inelastic collisions has been studied in a number of references.^{12,13,18,37-42} Brout¹³ found that for molecules of molecular weight greater than 20 the probability of the conversion of kinetic energy into rotational in a collision is of the order of $\frac{1}{2} (r_e/r_0)^2$, where r_e is the internuclear separation in the molecule, r_0 is its gas-dynamic collision diameter. From this it follows that the establishment of equilibrium over the rotational degrees of freedom for such molecules as N_2 and O_2 requires approximately 20 collisions between molecules. In the case of the H_2 molecule, owing to the large size of the rotational quantum, the probability of rotational excitation in a collision is relatively small and in order for an equilibrium distribution over the rotational levels to be established approximately 300 collisions are needed.

Effective cross sections for the conversion of vibrational energy into translational energy as a result of collisions turn out to be very small for the majority of molecules, and for equilibrium with respect to the vibrational degrees of freedom to be established it is necessary, as a rule, to have not less than $10^3 - 10^4$ collisions. An exception is provided by molecules the interaction between which is due to forces of

chemical nature. For such molecules the probability of excitation of vibrations in a collision is relatively great; this corresponds to the concept of the vibrational excitation of such molecules as the beginning of a chemical reaction.^{19,152}

The fact that exchanges between the kinetic energy of the gas molecules and their internal energy are difficult makes deviations from thermodynamic equilibrium possible in the case of a sufficiently rapid variation in the parameters that describe the gas. The time τ during which equilibrium is established is called the relaxation time. The relaxation time has a fully defined meaning if the quantity y which at an initial time had the value y_1 , approaches its equilibrium value y_2 in a manner described by the relaxation equation

$$\frac{dy}{dt} = -\frac{1}{\tau} (y - y_2). \quad (21)$$

For $\tau = \text{const}$ this equation has the solution

$$\frac{y - y_2}{y_1 - y_2} = e^{-\frac{t}{\tau}} \quad (22)$$

and then the relaxation time τ is the time at the expiration of which the quantity $y - y_2$ differs from its initial value by the factor e^{-1} .

The relaxation equation (21) holds, for example, for the case^{51,52} when the molecules can exist in two quantum states of energies E_1 and E_2 . Landau and Teller have investigated the case of the relaxation of harmonic oscillators in a thermal bath under the condition that the interaction between the internal degrees of freedom and the translational motion is small. As a result of this the interaction potential between the molecules may be expanded in series with respect to the normal coordinate of the vibration Q and consideration may be restricted to the linear term. Therefore, the probabilities of transition between harmonic oscillator levels will differ from zero only for adjacent levels and are equal to $P_{V, V+1} = P_0 (V + 1)$. The relaxation of the average energy of such harmonic oscillators also obeys Eq. (21). For the relaxation time in this case we obtain the expression

$$\frac{1}{\tau} = P_{10} (1 - e^{-\frac{h\nu}{kT}}), \quad (23)$$

where $h\nu$ is the size of the vibrational quantum, T is the temperature of the thermal bath, P_{10} is the probability of deactivation (per unit time) of the first excited vibrational level of the molecule in a collision.

The relaxation of harmonic oscillators in a thermal bath has been investigated in greater detail in a series of papers by Schuler and co-workers.⁵³⁻⁶⁴ In references 54-57 it was shown that the nature of the relaxation of the average energy of harmonic oscillators, distributed over the different levels at the initial instant in any arbitrary manner, is independent of the initial distribution. The relaxation time in this case

does not depend on the value of the average energy of the oscillators. If the oscillators are initially distributed over the levels in accordance with a pseudo-Boltzmann distribution with a "temperature" $T > T_{\text{gas}}$, then the relaxation proceeds through a sequence of pseudo-Boltzmann distributions with a time dependent temperature $T(t)$, with $T > T(t) > T_{\text{gas}}$. Thus, in this case the distribution of molecules over the vibration levels is determined by a single parameter, the vibrational "temperature." Taking dipole radiation transitions into account changes only the relaxation time without affecting the process of the establishment of equilibrium. It must be noted that such a relaxation process is intimately connected with the assumption $Q \ll \alpha^{-1}$. In reference 54 it was shown that if we assume the transition probability to have the form $P_{v,v+1} = P_0 \exp[\alpha(v+1)]$, then the intermediate states can no longer be characterized by a "temperature". Moreover, in this case since $P_{v,v+1}$ increases rapidly with increasing v , a distribution corresponding to the final temperature is rapidly established at the upper levels, while at the lower levels the distribution still corresponds to the initial vibrational "temperature." This shows that one must adopt a cautious attitude to the experimentally determined effective "temperatures." Taking anharmonicity into account introduces insignificant changes into the preceding results. In investigating simultaneously vibrational and rotational relaxation it turned out that they occur independently due to the great difference in the probabilities of excitation of vibration and of rotation. In references 73 — 76 it was shown that taking dissociation into account significantly changes the distribution of molecules in the upper vibrational levels.

DISSOCIATION AND IONIZATION

At high temperatures relaxation phenomena associated with the fact that the values of the constants describing the rates of dissociation and recombination reactions are finite become important. According to current concepts, the dissociation process has the following character. In collisions primarily those molecules dissociate of which one is in a vibrational level close to the dissociation limit, while the total energy (vibrational, rotational, and translational energy) is sufficient to produce dissociation. But if the colliding molecules are in lower vibrational levels, then even if the total energy is sufficient for dissociation the probability of dissociation is negligibly small. In reference 76 it was shown that the probability of transition from a vibrational level v into the continuum for the model of a diatomic molecule in the form of a Morse oscillator falls off very rapidly with increasing $(v - v_{\text{max}})$ and is negligibly small for the lower levels. In this connection the hypothesis proposed in a number of papers⁸⁰⁻⁸¹ with respect to the possibility of dissociation in collisions from any arbitrary

vibrational level appears to be very improbable.

The dissociation of diatomic molecules situated in a heat bath may be visualized in the following manner. As a result of the high probability of transition into the continuum in a collision the upper vibrational levels are practically empty (the distribution for these levels differs sharply from a Boltzmann distribution) and the rate of dissociation is determined by the probabilities of transition between discrete levels, since as a result of these transitions molecules are "supplied" to upper vibrational levels where the molecules dissociate. Moreover, at the upper levels an important role is played by transitions between nonadjacent levels.

Quantitatively the dissociation process can be described in the following manner. If we denote by N the molar concentration of molecules X_2 , and by n the molar concentration of atoms X , then the concentration of molecules N varies with time in accordance with the equation

$$\frac{dN}{dt} = -k_{d1}N^2 - k_{d2}nN + k_{r1}n^2N + k_{r2}n^3. \quad (24)$$

Here k_{d1} , k_{d2} are the reaction rate constants for the dissociation of molecules X_2 in collisions respectively with molecules X_2 and with atoms X , while k_{r1} , k_{r2} are the reaction rate constants for recombination in corresponding three-body collisions. These constants are related by the expression

$$\frac{k_{d1}}{k_{r1}} = \frac{k_{d2}}{k_{r2}} = k,$$

where k is the equilibrium constant.

From simple collision theory one can obtain the following expression for the constant of the rate of dissociation

$$k_d = A(l) PT^l e^{-\frac{D}{kT}},$$

where D is the dissociation energy for the molecule X_2 , while the constants l and $A(l)$ depend on the degree of participation of vibrational and rotational energy in the dissociation process. The quantity P has the meaning of the probability of dissociation of the molecule in a binary collision of molecules with an energy sufficient for dissociation. This quantity is usually obtained by making the theoretical curve for the dependence of k_d on T fit the experimental one; since agreement can be achieved for different values of l and P , it is clear that the quantity P has to a large extent an arbitrary nature. As we have seen, the value of the constant for the dissociation rate depends very strongly on the temperature.

The process of the establishment of equilibrium ionization in gases is at the present time almost completely uninvestigated. A study of the ionization of argon behind a strong shock wave¹⁴⁷ has shown that even in this simple case the process has a quite complicated character. It has turned out that ionization occurs primarily as a result of collisions of electrons

with atoms, while the ionization rate is determined primarily by the rate of exchange of energy between electrons and ions in elastic collisions, and is almost independent of the value of the cross section for inelastic collisions accompanied by ionization and excitation. No one has succeeded in giving a satisfactory explanation for the initial degree of ionization; apparently, in the initial stages of ionization an important role is played by the processes of photoionization and of ionization as a result of collisions with impurity atoms.

METHODS OF DETERMINING THE RELAXATION CONSTANTS

As already indicated, for the description of nonequilibrium gas systems it is necessary to know the effective cross sections both for elastic and for various types of inelastic collisions. A large number of papers has been devoted to the experimental⁸⁹⁻¹⁷⁰ and theoretical¹⁻⁵⁰ determination of these cross sections. The theoretical calculation of the probabilities of inelastic transitions presents great difficulties which are due mostly to our incomplete knowledge of the interaction potential between the molecules. The commonly used empirical expressions for this potential describe more or less well the interaction between molecules that are separated by large distances. In the evaluation of the constant for the rate of dissociation the difficulty also consists of the fact that we do not have an exact expression not only for the intermolecular but also for the intramolecule potential (the dissociation occurs primarily from the upper vibrational levels; moreover the motion of the atoms forming the molecule occurs in a field which is known only approximately). Nor do we have, at present a clear idea of the relative role played in the dissociation process by the translational, rotational, and vibrational energy of the molecules. In calculating the effective cross sections for inelastic collisions approximate quantum mechanical methods are utilized. All this causes the cross sections for the different inelastic collisions to be evaluated at present only with order-of-magnitude accuracy. The experimental values of the constants characterizing the processes of approach to equilibrium are usually of like accuracy. On taking this circumstance into account we can, for qualitative purposes, treat the relaxation process itself approximately. As we have seen already, the approach to equilibrium with respect to the vibrational degrees of freedom, at not very high temperatures, can be described by means of a relaxation equation by introducing the concept of a relaxation time. Although processes of approach to equilibrium with respect to rotational levels and with respect to the degree of dissociation are not described by a relaxation equation, it is possible for the sake of a simple treatment to describe these processes by means of relaxation times.

For the experimental determination of the constants characterizing nonequilibrium processes it is necessary in some way to make the gas depart from a state of thermodynamic equilibrium. This can be achieved, for example, by the following means:

1. Both the initial substances and the resultant products are in a nonequilibrium state as a result of a rapidly occurring chemical reaction (cf., for example, references 106, 139).
2. Gas flows with rapidly varying parameters (supersonic flows in nozzles, shock wave, density discontinuity in supersonic flow around a body).
3. Ultrasonic methods (the gas is situated in the sound field and is subjected to a rapid variation of parameters during a time of the order of the period of oscillations).
4. The spectrophone method (the gas has a nonequilibrium distribution with respect to the vibrational levels as a result of being irradiated by infrared radiation).
5. If energy is supplied in pulses to the plasma in an arc discharge, deviations from thermodynamic equilibrium are observed in the plasma.

Usually the following methods are used for the measurement of the relaxation time:

1. Measurement of relaxation time from the dispersion and absorption of an ultrasonic wave in the gas under investigation (cf., for example, reference 32).
2. Ultrasonic interferometer.¹⁶²
3. An ingenious method proposed by Hornig and based on the measurement of the coefficient of reflection of light from the front of a shock wave propagated in the gas.¹¹⁷
4. The method of Kantrowitz which utilizes the efflux of a gas from a shock tube through a nozzle.^{133,128}
5. A. N. Terenin and G. G. Neušmin⁹³ have proposed a method based on the fact that in an electric discharge in molecular gases the molecules have a nonequilibrium distribution with respect to the vibrational and rotational levels. By varying the gas pressure it is possible to vary the ratio between the probabilities of optical deactivation of vibrational levels and of the deactivation due to inelastic collisions. By measuring the intensity of the infrared radiation as a function of the pressure it is possible to obtain data on the probabilities of the deactivation of vibrational levels in inelastic collisions.
6. The method of the spectrophone, which is applicable in the case of vibrations active in the infrared spectrum. If the gas is irradiated by light of a definite wavelength and of an intensity modulated in time, a definite oscillation of the molecules is excited; by measuring the difference in phase between the change in pressure arising as a result of the heating of the gas and the intensity of the incident light, it is possible to determine the relaxation time.⁹⁴

7. As a result of certain chemical reactions, the molecules are produced predominantly in a single vibrational level characteristic of the given conditions. By measuring the dependence of the intensity of the different lines of ultraviolet absorption bands as a function of the time it is possible to obtain values of the relaxation time for a given vibrational level.¹³⁹

8. If the plasma in an arc discharge is "heated" by means of a current pulse, the molecules turn out to have a nonequilibrium distribution with respect to energy levels. The study of the subsequent process of approach to equilibrium enables us to determine the relaxation time.⁹²

9. The determination of the time τ for the establishment of equilibrium for the exchange of translational energy in collisions between radiating atoms having a nonequilibrium velocity distribution and molecules of the original gas, by means of a simultaneous measurement of the kinetic temperature of the radiating atoms and of the gas temperature.¹⁷¹

By now a large number of experimental investigations have been carried out which are devoted to the determination of constants characterizing the processes of the approach to equilibrium in gases. Usually the quantitative results of these investigations are given either in the form of a relaxation time τ , or in the form of the number Z_{eff} of collisions needed for the establishment of equilibrium with respect to a given degree of freedom, or in the form of the probability P of the corresponding elastic transition in a collision. Let us establish the relation between these quantities. For this purpose we consider the case of the approach to equilibrium with respect to the vibrational degrees of freedom (the concept of a relaxation time is, strictly speaking, applicable only in this case). We introduce the following notation: $p_{10} = 1/Z_{10}$ is the probability of deactivation of the first vibrational level in a collision, Z_{10} is the number of elastic collisions which the molecule experiences on the average before deactivation of the first vibrational level occurs. We shall define the quantity Z_{eff} as the number of elastic collisions which the molecule experiences on the average during the time τ , i.e., $Z_{\text{eff}} = \bar{v}\tau/\lambda$ (λ is the mean free path of the molecule, \bar{v} is its mean thermal velocity). The following relations hold between these quantities

$$\frac{1}{\tau} = P_{10} (1 - e^{-\frac{h\nu}{kT}}); \quad P_{10} = \frac{\bar{v}}{\lambda Z_{10}} = \frac{\bar{v}}{\lambda} P_{10}; \quad Z_{10} = Z_{\text{eff}} (1 - e^{-\frac{h\nu}{kT}}).$$

We shall also use the same quantities for an approximate description of the process of rotational relaxation.

DISCUSSION OF THE RELAXATION CONSTANTS

Tables I, II, III, and IV give a collection of the data obtained in investigations on the determination of constants characterizing relaxation processes. We have deemed it useful to give values of the quantities Z_{10}

and Z_{eff} , since they are easy to visualize. The quantity Z_{eff} is of a somewhat indefinite character, if in the course of the establishment of equilibrium with respect to a given degree of freedom the temperature of the gas and, consequently, the probability of inelastic collision which depends on it, undergo significant changes. In this case the Z_{eff} calculated by us differs from the actual number of collisions needed for the establishment of equilibrium with respect to a given degree of freedom.

An analysis of the material presented in the tables enables us to draw the following conclusions:

1. The effective cross sections for different elementary processes are essentially different, and one can divide the degrees of freedom of a gas into "active" ones for which the process of the establishment of equilibrium occurs during a few collisions (translational motion and rotation), and "inert" ones for the establishment of an equilibrium distribution with respect to which a considerable number of collisions are needed (vibrations).

2. The relaxation times for the vibrational degrees of freedom, and the constants for the rates of dissociation reactions, show a strong dependence on the gas temperature T . Moreover, for the vibrational degrees of freedom this relationship agrees with the theoretical expression of Landau and Teller $\ln \tau \sim eT^{-1/3}$ (i.e., the relaxation time decreases sharply as the temperature is increased²⁷). A paper that is instructive in this respect is the work of Lukasik and Young¹⁴⁰ in which the vibrational relaxation times of nitrogen were measured as a function of T in the temperature range 778 – 1186° K by ultrasonic methods. These relaxation times were compared with the data of Blackman⁹⁷ (temperature range 3500 – 5600° K); it turned out that the data of both papers are in good agreement with a common linear dependence of $\ln \tau$ on $T^{-1/3}$. Thus, although theoretical calculations yield values of τ which agree only roughly with experiment, the character of the dependence of τ on T is predicted by the theory with a considerably greater degree of accuracy. Widom,⁴⁷ in investigating the problem of vibrational excitation in an inelastic collision of diatomic molecules with a Maxwellian repulsive potential $V \sim R^{-4}$ (this potential gives a poor description of the repulsion), has obtained for the dependence of the relaxation time on the temperature the somewhat strange expression $\ln \tau \sim -BT^{1/3}$ instead of the Landau-Teller expression.

The constant for the rate of dissociation increases sharply with increasing temperature (and the corresponding "relaxation time" falls off sharply), with this dependence obeying the relation

$$k_d \sim T^l \cdot e^{-\frac{D}{kT}}.$$

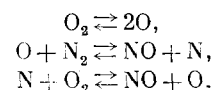
In this expression the principal role is played by the exponential term, so that to a high degree of accuracy $\ln k_d$ is directly proportional to $1/T$. Even an ele-

mentary collision theory for a dissociation reaction agrees well with this relationship.

The nature of the dependence of the rotational relaxation time on the temperature is not completely clear at the present time. On the one hand, as the temperature is increased the mean thermal velocity of the molecules increases and with it the collision frequency. On the other hand, as the temperature is raised, an ever more significant role in the relaxation process is played by transitions between the upper levels, the distance between which, and consequently also the transition probabilities, is smaller than in the case of the lower levels. For hydrogen experiment yields an increase in the rotational relaxation time with increasing temperature; for other molecules the

temperature dependence has not yet been established.

3. The relaxation times for the vibration of nitrogen, and for the dissociation of oxygen at a temperature of 3000° K turn out to be of the same order of magnitude. Also in the same temperature range a significant role is played by the reaction for the production of NO, which, apparently, proceeds in accordance with the scheme proposed by Ya. B. Zel'dovich:



In virtue of these circumstances the process of the establishment of equilibrium in air at such temperatures must be of a very complex nature.

Table I. Rotational Relaxation

T °K	τ , sec*	Z_{eff}	Reference	Method of determination
H₂ molecule				
193	$1.4 \cdot 10^{-8}$	250	131	Absorption and dispersion of sound
213	$1.4 \cdot 10^{-8}$	240		
233	$1.6 \cdot 10^{-8}$	260		
253	$1.7 \cdot 10^{-8}$	270		
273	$1.8 \cdot 10^{-8}$	270		
288	$2 \cdot 10^{-8}$	290		
275	$1.8 \cdot 10^{-8}$	270	129	Absorption of sound
291	$2.1 \cdot 10^{-8}$	310		
321	$2.1 \cdot 10^{-8}$	290		
340	$2.1 \cdot 10^{-8}$	280		
354	$2 \cdot 10^{-8}$	270		
273	$2.3 \cdot 10^{-8}$ $2.1 \cdot 10^{-8}$	350 320	163	Dispersion of sound. Absorption of sound
288	$2.1 \cdot 10^{-8}$	310	121	Pitot tube
		>150	118	Reflection from the front of a shock wave
	$2.3 \cdot 10^{-8}$	340	130	Dispersion of sound
298	$1.8 \cdot 10^{-8}$	260	162	Ultrasonic interferometer
285 207		160 200	123	Pitot tube
300		300	169	Absorption and dispersion of sound
300		300	127	Reflection from the front of a shock wave
290	$1.7 \cdot 10^{-8}$	250	161	Absorption and dispersion of sound
290	$\sim 10^{-4}$	~ 15	12	Theory
D₂ molecule				
70	$0.3 \cdot 10^{-8}$	60	131	Absorption and dispersion of sound
90	$0.3 \cdot 10^{-8}$	60		
193	$0.9 \cdot 10^{-8}$	110		
213	$0.9 \cdot 10^{-8}$	110		

Table I (continued)

T °K	τ , sec*	Z _{eff}	Reference	Method of determination
233 253 273 288	10^{-8} $1.1 \cdot 10^{-8}$ $1.3 \cdot 10^{-8}$ $1.5 \cdot 10^{-8}$	120 120 140 160	131	Absorption and dispersion of sound
274 288 328 351	10^{-8} $1.1 \cdot 10^{-8}$ $1.2 \cdot 10^{-8}$ $1.2 \cdot 10^{-8}$	110 110 120 110	129	Absorption of sound
273	$2 \cdot 10^{-8}$ $1.8 \cdot 10^{-8}$	210 190	163	Dispersion of sound, Absorption of sound
N ₂ molecule				
300		5.26	119	Absorption and dispersion of sound
300 273		5 3	165 144	Absorption of sound
300	$1.2 \cdot 10^{-9}$	9	170	Absorption and dispersion of sound
300 289	$< 10^{-9}$ $< 2 \cdot 10^{-9}$	7 15	138 121	Pitot tube
		5.5 5.3	96 156	
300 300		20 20	117 118	Reflection from the front of a shock wave
300		23	13	Theory
O ₂ molecule				
314	$2.176 \cdot 10^{-9}$	12	109	Dispersion of sound
300 273		5 3	165 144	Absorption of sound
300		30	166	Dispersion and absorption of sound
		5	96	
300		20	118	Reflection from the front of a shock wave
300		17	13	Theory
Dry air				
	$1.28 \cdot 10^{-8}$	90	100	
305	$3 \cdot 10^{-9}$ $2.29 \cdot 10^{-9}$	21 16	110	Absorption of sound, Dispersion of sound

*The values of τ have been reduced to 1 atm pressure.

Table II. Vibrational Relaxation

T °K	τ , sec	Z_{10} , Z_{eff}	Notes	Reference	Method of determination
3000	$4.2 \cdot 10^{-5}$	$\sim 2 \cdot 10^{5*}$	H ₂ molecule 2	106	Absorption of x-rays
300-600		N ₂ molecule 3.3 · 10 ⁵ 1.67 · 10 ⁵ 1.25 · 10 ⁶	3 a 3 b 3 c	98	Measurement of the intensity of infra-red radiation from a gas discharge
778 1020 1186	$17.6 \cdot 10^{-4}$ $14.4 \cdot 10^{-4}$ $7.96 \cdot 10^{-4}$	$6.55 \cdot 10^6$ $4.55 \cdot 10^6$ $2.29 \cdot 10^6$		140	Ultrasonic measurements
556 680 694 761		$3.1 \cdot 10^7$ $1.4 \cdot 10^7$ $1.6 \cdot 10^7$ $1.2 \cdot 10^7$	5 a		Pitot tube
413 575 733		$3.6 \cdot 10^4$ $3.4 \cdot 10^4$ $2.4 \cdot 10^4$	5 b	128	
3000 3500 4000 5000 5500 6000	$3.5 \cdot 10^{-5}$ $1.9 \cdot 10^{-5}$ $1.3 \cdot 10^{-5}$ $7 \cdot 10^{-6}$ $5 \cdot 10^{-6}$ $4 \cdot 10^{-6}$	$8 \cdot 10^{4*}$ $4 \cdot 10^{4*}$ $2.6 \cdot 10^{4*}$ $1.2 \cdot 10^{4*}$ $8.5 \cdot 10^3$ $6.5 \cdot 10^3$		98	Interferometer in a shock tube
2250 2450	$1.6 \cdot 10^{-4}$ $8 \cdot 10^{-5}$	$4.2 \cdot 10^{5*}$ $2 \cdot 10^{5*}$		107	Spectroscopic measurements in a shock tube
900	$> 1.5 \cdot 10^{-4}$	$> 6.25 \cdot 10^{5*}$		123	Interferometer in a shock tube
2200	10^{-4}	$2.7 \cdot 10^{5*}$	6	104	Reflected shock wave
288 600 900 1200 1800 2400 3000		$> 10^{12}$ $5 \cdot 10^9$ $3.1 \cdot 10^8$ $2 \cdot 10^7$ $9 \cdot 10^5$ $1.25 \cdot 10^5$ $6.2 \cdot 10^4$		35	Theory
1900 2100 2400	10^{-6} $4 \cdot 10^{-7}$ $2.5 \cdot 10^{-7}$	$2.5 \cdot 10^{3*}$ $9.4 \cdot 10^{2*}$ $5.5 \cdot 10^{2*}$		114	Schlieren measurements in a shock tube

T °K	τ , sec	Z_{10} , Z_{eff}	Notes	Reference	Method of determination
2700 2900	$2 \cdot 10^{-7}$ $8 \cdot 10^{-8}$	$4.2 \cdot 10^{2*}$ $1.6 \cdot 10^{2*}$		114	Schlieren measurements in a shock tube
800 1000 1400 2000 3000	$5.4 \cdot 10^{-5}$ $4 \cdot 10^{-5}$ $2 \cdot 10^{-5}$ $7 \cdot 10^{-6}$ $1.3 \cdot 10^{-6}$	$2 \cdot 10^{5*}$ $1.4 \cdot 10^{5*}$ $5.8 \cdot 10^{4*}$ $1.7 \cdot 10^{4*}$ $2.6 \cdot 10^{3*}$		98	Interferometer in a shock tube
4000 1400 1600 1800 2000 2200 3000	$< 2 \cdot 10^{-6}$ $4 \cdot 10^{-6}$ $2.5 \cdot 10^{-5}$ $1.5 \cdot 10^{-5}$ $6 \cdot 10^{-6}$ $3 \cdot 10^{-6}$ $2 \cdot 10^{-6}$		7 a 7 b 7 c 7 d	105	Absorption and radiation of ultraviolet in a shock tube
300		$> 5 \cdot 10^5$ $\sim 10^5$ $\sim 2 \cdot 10^4$ $\sim 2.5 \cdot 10^4$ $\sim 7.7 \cdot 10^3$	3 a 3 b 3 c 3 d	135	Ultrasonic measurements
1200 1500	$\sim 2 \cdot 10^{-5}$ $\sim 2 \cdot 10^{-5}$	$\sim 6.25 \cdot 10^{4*}$ $\sim 5.6 \cdot 10^{4*}$		126	From the width of the front of a shock wave
286 374	$1.6 \cdot 10^{-6}$ $2.6 \cdot 10^{-6}$	10^{4*} $1.5 \cdot 10^{4*}$		129	Dispersion and absorption of sound
~ 3200	$\sim 10^{-6}$	$1.9 \cdot 10^{3*}$	2	106	Absorption of x-rays
300	$\sim 3 \cdot 10^{-4}$	$1.9 \cdot 10^{6*}$	8	139	Absorption in the ultraviolet
288 600 900 1200 1800 2400 3000		$3.3 \cdot 10^8$ $3.3 \cdot 10^6$ $3.3 \cdot 10^5$ $7.7 \cdot 10^4$ $1.2 \cdot 10^4$ $1.8 \cdot 10^3$ $6.7 \cdot 10^2$		35	Theory
288 600 900 1200 1800 2400 3000		$5 \cdot 10^7$ $3.3 \cdot 10^5$ $3.3 \cdot 10^4$ $8.4 \cdot 10^3$ $1.4 \cdot 10^3$ $5 \cdot 10^2$ $2.5 \cdot 10^2$	3 a		Theory

Table II (continued)

T °K	τ , sec	Z_{10} , Z_{eff}	Notes	Reference	Method of determination
NO molecule					
500 1000		1.43·10 ³ 3.3·10 ²		152	Spectrophotometric measurements in a shock tube
500 1000		1.25·10 ³ 10 ³		153	Theory
CN molecule					
6300 7500 9550	4.2·10 ⁻⁵ 2.6·10 ⁻⁵ 1.4·10 ⁻⁵			153	Measurement of the ultraviolet absorption in a shock tube
~5600	~2-2.5·10 ⁻⁵			92	Measurement of the vibrational temperature in an arc
CO molecule					
300-600		1.67·10 ⁵ 1.33·10 ⁵ 8.3·10 ⁴	3 a 3 b 4 c	93	Measurement of the intensity of infrared radiation from a gas discharge
1000 1200 1400 1600 1800	10 ⁻⁵ 1.2·10 ⁻⁵ 1.15·10 ⁻⁵ 1.1·10 ⁻⁵ 10 ⁻⁵	2.9·10 ^{4*} 3.1·10 ^{4*} 2.8·10 ^{4*} 2.5·10 ^{4*} 2.1·10 ^{4*}	9	157	Dispersion of sound
2200 3500	10 ⁻⁵ 2.7·10 ⁻⁶	1.9·10 ^{11*} 4.1·10 ^{9*}		120	Interferometer in a shock tube
1470	1.9·10 ⁻⁵	4.5·10 ^{13*}		168	Infrared radiation in a shock tube
H₂O molecule					
486 585 796		4·10 ² 2.9·10 ² 1.9·10 ²		128	Pitot tube
CO₂ molecule					
300-600		1.25·10 ⁶ 2.27·10 ⁵ 1.67·10 ⁵ 4.17·10 ⁵ 5·10 ⁵	3 a 3 b 4 c 4 d 3 e	93	Measurement of the intensity of infrared radiation from a gas discharge
300		6.25·10 ⁴ 3.6·10 ⁴ 1.45·10 ⁴	10 a 10 b 10 c	94	Spectrophone
~300	5.7·10 ⁻⁶ 1.6·10 ⁻⁷ 2.7·10 ⁻⁶ 2.8·10 ⁻⁹	51000 1700 480 34		111	Absorption of sound

Notes: 1. The values of τ have been reduced to a pressure of 1 atm. The values of Z_{eff} have been marked by an asterisk.
2. Mixed with 25% Xe.

T °K	τ , sec	Z_{10} , Z_{eff}	Notes	Reference	Method of determination
273 373 473 573 673	7·10 ⁻⁶ 4.5·10 ⁻⁶ 3.2·10 ⁻⁶ 2.4·10 ⁻⁶ 2·10 ⁻⁶	57000 29000 17000 10000 8000		112	Absorption and dispersion of sound
273 373 473 573 673	9.6·10 ⁻⁹ 7.3·10 ⁻⁹ 1.5·10 ⁻⁸ 3·10 ⁻⁸ 5·10 ⁻⁸	105 65 102 150 250	3 f		
291 304 313 323	12.3·10 ⁻⁶ 10.9·10 ⁻⁶ 8.7·10 ⁻⁶ 6.8·10 ⁻⁶	1.1·10 ^{5*} 9.4·10 ^{4*} 7.4·10 ^{4*} 5.7·10 ^{4*}		130	Absorption of sound
300 450 750 1400	5·10 ⁻⁶ 2.5·10 ⁻⁶ 10 ⁻⁶ 5·10 ⁻⁷	4.3·10 ^{4*} 1.8·10 ^{4*} 5.5·10 ^{3*} 2·10 ^{3*}		123	Interferometer in a shock tube
291	6.95·10 ⁻⁶ 2.02·10 ⁻⁶	6.1·10 ^{4*} 1.8·10 ^{4*}	11	121	Pitot tube
600 2200	2·10 ⁻⁶ 3.5·10 ⁻⁶	1.2·10 ^{4*} 1.1·10 ^{4*}	12 13	120	Interferometer in a shock tube
300	10 ⁻⁶	8.6·10 ^{3*}		132	Spectrophone
900	10 ⁻⁷	5·10 ^{2*}		159	Interferometer in a shock tube
300		4.85·10 ⁴		124	Dispersion of sound
288		9·10 ⁴		35	Theory

3. In collisions with the following molecules: a) N₂; b) CO; c) CO₂; d) H₂; e) O₂; f) H₂O.
4. In collisions with the following atoms: a) He; b) Ar.
5. With the impurity: a) 0.05% H₂O; b) 2% H₂O.
6. At higher temperatures the data of this paper agree with the data of reference 98.
7. Mixture A: a) 0.25% O₂; b) 1% O₂; c) 5% O₂; d) 33% O₂.
8. For the 6-th excited vibrational level.
9. The absence of temperature dependence is surprising.
10. For vibrations corresponding to the wavelengths: a) 4.3 μ ; b) 2.7 μ ; c) 14.8 μ .
11. For industrial gas.
12. For a deformation type vibration.
13. For a fully symmetric vibration.

Table III. Dissociation relaxation

T °K	τ , sec	k_d , cm ³ /mole sec	k_p , $\frac{\text{cm}^3}{\text{mole}^2 \text{ sec}}$	Refer- ence	Method of determination
N ₂ molecule					
2850		1.5 · 10 ⁸	a	106	Absorption of x rays
3250		2.5 · 10 ⁸			
O ₂ molecule					
3100		1.4 · 10 ⁸	a	106	Absorption of x rays
3500		4.1 · 10 ⁸			
3500		4.6 · 10 ⁷	b	105	Absorption and emission of ultraviolet in a shock tube
4000		4.6 · 10 ⁸			
4500		2.6 · 10 ⁹			
5000		9 · 10 ⁹			
5500		2.2 · 10 ¹⁰			
3100	2 · 10 ⁻⁶			114	Schlieren-measurements in a shock tube
3400	5 · 10 ⁻⁷				
3800	6 · 10 ⁻⁸				
2540	~10 ⁻⁴			107	Spectroscopic measurements in a shock tube
3500	2 · 10 ⁻⁵			126	From the width of the front of a shock wave
3500			0.8 · 10 ¹⁵ 0.5 · 10 ¹⁵	141 104	Interferometer in a shock tube
			3 · 10 ¹⁴	116	Discharge in a capillary
300			9.8 · 10 ¹⁴	148	Afterglow
N ₂ molecule					
300			6.3 · 10 ¹⁴	148	Afterglow
			1.2 · 10 ¹⁶	167	Electrodeless discharge
297			5.4 · 10 ¹⁵	125	Afterglow

In accordance with measurements carried out in reference 141 the constant for the rate of dissociation of oxygen in collisions of type O₂ - O₂ in the temperature range 2500-4500°K can be given in the form

$$k_d = 7.43 \cdot 10^{11} P T^{1/2} \left(\frac{59380}{T} \right)^3 \exp \left(-\frac{59380}{T} \right) \text{ cm}^3/\text{mole sec}, \quad P = 0.074.$$

In reference 104 it was found that the variation with time of the concentration of oxygen atoms is described in the case of dissociation by the following equation:

$$\frac{d[O]}{Dt} = 2 \left(\frac{Q}{m} \right)^2 D^2 \bar{v} \exp \left(-\frac{T_{\text{diss}}}{T} \right) \left\{ k_1 \frac{c_1^2 (1-\alpha)^2}{2 (n_1!)^2} \left(\frac{T_{\text{diss}}}{T} \right)^{n_1} \cdot 1.052 \right. \\ \left. + k_2 \frac{c_1 (1-c_1) (1-\alpha)}{n_2!} \left(\frac{T_{\text{diss}}}{T} \right)^{n_2} + 2k_3 c_1^2 \alpha (1-\alpha) \frac{T_{\text{diss}}}{T} \cdot 1.034 \right\};$$

$$n_1 = 2, \quad n_2 = 1, \quad k_1 = 0.24, \quad k_2 = 0.1, \quad k_3 = 1.7.$$

The measurements were made in a mixture of oxygen with argon; c₁ is the ratio of the number of O₂ molecules to the total number of molecules.

Notes: a. mixed with 25% Xe. b. mixture of Ar and 1% O₂.

4. The relaxation times for the vibrations of oxygen in the case when the molecules are initially primarily in a single vibrational level (for example, $v = 6$), and in the case of an initial pseudo-Boltzmann distribution, turn out to be of the same order of magnitude. This also follows from theoretical considerations.⁵⁴⁻⁵⁷

5. The probabilities for inelastic transitions in a collision depend much less strongly on the nature of the colliding particles. For example, the probability of deactivation of the first vibrational level of the oxygen molecule is approximately ten times greater

in a collision of this molecule with another oxygen molecule, than in its collision with an argon atom. There is about the same difference in the efficiency of oxygen molecules and of argon atoms in the case of the dissociation of oxygen molecules in a collision.¹⁰⁵ According to Blackman's data the efficiency of the N₂ - O₂ collisions for the excitation of the vibrations of O₂ is approximately by a factor of 2.5 smaller than the efficiency of O₂ - O₂ collisions.⁹⁸ For the dissociation of oxygen, collisions of type N₂ - O₂ have a relatively low efficiency, while collisions of O atoms with O₂ molecules have an efficiency greater

Table IV. Relaxation of ionization in a shock tube

a) For air			b) For argon (from refs. 146, 147)	
M	τ μ sec	Reference	T °K	τ μ sec
8	3	88	10 ⁴	100
9	2		2·10 ⁴	1.5
10	1		3·10 ⁴	0.3
11	0.65		4·10 ⁴	0.15
12	0.45	142	5·10 ⁴	0.1
13	0.3			
14	0.22			
15	0.15			
16	0.11			
17	0.075			

M — Mach number for the shock wave propagated in the gas. The values of τ have been reduced to a pressure of 1 cm Hg.

According to reference 90, the time for the establishment of an equilibrium degree of ionization in the plasma of a spark discharge in air at atmospheric pressure (T ~ 40,000° K) is approximately equal to 10⁻⁷ sec.

by a factor of approximately seven compared to collisions of the O₂ — O₂ type.¹⁰⁴ In a number of cases the efficiency of impurity molecules so greatly exceeds the efficiency of the molecules of the original gas in the case of inelastic collisions, that even a low concentration of impurities has a significant effect on the process of establishment of equilibrium.^{128,112}

6. It can be seen from the tables that there exist wide discrepancies between the relaxation times obtained experimentally by different investigators. In a number of cases these discrepancies are explained by an insufficient purity of the gas under investigation. For example, a particularly important role for the vibrational relaxation of nitrogen is played by the H₂O impurity.¹²⁸ The discrepancies between the theoretical and the experimental data have, as a rule, the same order of magnitude as the discrepancies between experimental data of different investigators. There is a large discrepancy, for example, in the values of the relaxation times for the rotational degrees of freedom of oxygen and nitrogen. Some values for the effective number of collisions ($Z_{\text{eff}} \approx 3 - 5$) are most likely too small; on the other hand the value $Z_{\text{eff}} = 90$ for air is too large.

Thus, there exist large discrepancies between the values obtained by different authors for the constants characterizing processes of approach to equilibrium. A number of experimental papers is of a qualitative nature. In this connection there arises the necessity of picking out the most reliable ones of all the experimental data. For the rotational degrees of freedom of hydrogen apparently the most accurate measurements of the relaxation time are measurements reported in reference 169. The rotational relaxation times for oxygen and hydrogen, in contrast to hydrogen, are, as has been indicated already, somewhat indefinite; the most probable values of Z_{eff} for these molecules should be taken as $Z_{\text{eff}} \sim 10 - 25$.

Blackman's measurements⁹⁷⁻⁹⁸ should be recognized as the most accurate measurements of the vibrational relaxation time for oxygen. For the vibrational relaxation time for nitrogen one should also utilize the results of this paper supplementing them for lower temperatures by the data of references 140 and 164. It is necessary to note in general that the results of most investigations of vibrational relaxation times of oxygen and nitrogen agree, as a rule, with the results of Blackman's work, differing from them only by a considerably greater scatter of the measured quantities. The most accurate determination of the constant for the rate of dissociation of oxygen was carried out in references 104 and 141. However, the data of these papers differ approximately by a factor two, and their authors have not yet found an explanation for this discrepancy.

In making a general summary it should be noted that at the present time the work on relaxation times cannot be regarded as complete. The relaxation times are determined only with order-of-magnitude accuracy; there are large discrepancies between theoretical and experimental work. Experimental values are lacking for several important cases: dissociation of nitrogen, ionization of air, etc. The general theory of the relaxation of a nonequilibrium gas mixture is poorly developed. There is no doubt that in subsequent years a large amount of attention will be devoted to these problems.

¹ A. E. Glauberman, JETP 23, 182 (1952).

² A. E. Glauberman and V. I. Dorgon', JETP 23, 430 (1952).

³ V. N. Kondrat'ev, Кинетика химических газовых реакций (Kinetics of Chemical Gaseous Reactions), Moscow, Academy of Sciences, U.S.S.R., 1958.

⁴ M. A. El'yashevich, Physik. Z. Sowjetunion 1, 510 (1932).

- ⁵ M. A. El'yashevich, JETP 2, 59 (1932).
- ⁶ E. E. Nikitin, Оптика и спектроскопия (Optics and Spectroscopy) 6, 141 (1959).
- ⁷ A. I. Osipov, Bull. Moscow State Univ. No. 4, 97 (1958).
- ⁸ H. Aroeste, J. Chem. Phys. 21, 870 (1953).
- ⁹ Bates, Massey, and Stewart, Proc. Roy. Soc. A216, 437 (1953).
- ¹⁰ E. Bauer, Phys. Rev. 84, 315 (1951); 85, 277 (1952).
- ¹¹ E. Bauer, J. Chem. Phys. 23, 1087 (1955).
- ¹² J. C. Beckerle, *ibid.* 21, 2034 (1953).
- ¹³ R. Brout, *ibid.* 22, 934, 1189, 1500 (1954).
- ¹⁴ G. W. Castellan and H. M. Hulburt, *ibid.* 18, 312 (1950).
- ¹⁵ Curtiss, Hirschfelder, and Adler, *ibid.* 18, 1638 (1950).
- ¹⁶ C. F. Curtiss and F. T. Adler, *ibid.* 20, 249 (1952).
- ¹⁷ C. F. Curtiss, *ibid.* 21, 2045 (1953).
- ¹⁸ E. Fermi, Z. Phys. 40, 399 (1927).
- ¹⁹ J. Franck and A. Eucken, Z. Phys. Chem. B20, 460 (1933).
- ²⁰ T. Z. Hearon, Bull. Math. Biophys. 15, 121 (1953).
- ²¹ K. F. Herzfeld and V. Griffing, J. Phys. Chem. 61, 844 (1957).
- ²² K. F. Herzfeld and T. Q. Litovitz, Dispersion and absorption of ultrasonic waves, N. Y., 1959.
- ²³ K. F. Herzfeld, Z. Phys. 156, 265 (1959).
- ²⁴ T. Inoue and T. Takahashi, J. Phys. Soc. Japan 9, 199 (1954); 10, 208 (1955).
- ²⁵ J. M. Jackson and N. F. Mott, Proc. Roy. Soc. A137, 703 (1932).
- ²⁶ E. H. Kerner, Phys. Rev. 91, 1174 (1953); 92, 899 (1953).
- ²⁷ L. Landau and E. Teller, Phys. Z. Sow. 10, 34 (1936); 11, 18 (1937).
- ²⁸ O. Oldenberg, Phys. Rev. 37, 194 (1931).
- ²⁹ J. G. Parker, Phys. Fluids 2, 449 (1959).
- ³⁰ H. C. Penny and H. Aroeste, J. Chem. Phys. 23, 1281 (1955).
- ³¹ N. Rosen and C. Zener, Phys. Rev. 40, 502 (1932).
- ³² F. D. Rossini, ed., Thermodynamics and Physics of matter, 1955.
- ³³ A. S. Roy and M. E. Rose, Proc. Roy. Soc. A149, 511 (1935).
- ³⁴ M. Salkoff and E. Bauer, J. Chem. Phys. 29, 26 (1958).
- ³⁵ Schwartz, Slawsky, and Herzfeld, *ibid.* 20, 1591 (1952).
- ³⁶ R. N. Schwartz and K. F. Herzfeld, *ibid.* 22, 767 (1954).
- ³⁷ K. Takayanagi, Progr. Theor. Phys. 8, 111, 497 (1952); 11, 557 (1954).
- ³⁸ K. Takayanagi and T. Kishimoto, *ibid.* 9, 578 (1953).
- ³⁹ K. Takayanagi and S. Kanako, Sci. Rep. Saitama Univ. A1, 111 (1954).
- ⁴⁰ K. Takayanagi and K. Ohno, Progr. Theor. Phys. 13, 243 (1955).
- ⁴¹ K. Takayanagi, The threshold of space, ed. M. Zelikoff, 1957, p. 191.
- ⁴² K. Takayanagi, Proc. Phys. Soc. A70, 348 (1957).
- ⁴³ K. Takayanagi, J. Phys. Soc. Japan 14, 75 (1959).
- ⁴⁴ K. J. Tanczos, J. Chem. Phys. 25, 439 (1956).
- ⁴⁵ F. D. de Wette and Z. I. Slawsky, Physica 20, 1169 (1954).
- ⁴⁶ B. Widom and S. H. Bauer, J. Chem. Phys. 21, 1670 (1953).
- ⁴⁷ B. Widom, *ibid.* 27, 940 (1957); 28, 918 (1958).
- ⁴⁸ Ta-You Wu, Canad. J. Phys. 33, 151 (1958).
- ⁴⁹ C. Zener, Phys. Rev. 37, 556, 38, 277 (1931); 40, 335 (1932).
- ⁵⁰ C. Zener, Proc. Cambr. Phil. Soc. 29, 136 (1933).
- ⁵¹ H. O. Kneser, Ann. der Phys. 16, 337, 360 (1933).
- ⁵² A. J. Rutgers, *ibid.* 16, 350 (1933).
- ⁵³ K. E. Shuler, Fifth Symp. on Combustion, N. Y., 1955, p. 56.
- ⁵⁴ R. J. Rubin and K. E. Shuler, J. Chem. Phys. 25, 59, 68 (1956).
- ⁵⁵ K. E. Shuler, Sixth Symp. on Combustion, N. Y., 1957, p. 371.
- ⁵⁶ R. J. Rubin and K. E. Shuler, J. Chem. Phys. 26, 137 (1957).
- ⁵⁷ E. W. Montroll and K. E. Shuler, J. Chem. Phys. 26, 454 (1957).
- ⁵⁸ K. E. Shuler, J. Phys. Chem. 61, 849 (1957).
- ⁵⁹ N. W. Bazley et al., J. Chem. Phys. 28, 700 (1958).
- ⁶⁰ R. Herman and K. E. Shuler, J. Chem. Phys. 29, 366 (1958).
- ⁶¹ E. W. Montroll, Intern. Symp. transport processes in statistical mech. (Brussels, 1956), 1958.
- ⁶² E. W. Montroll and K. E. Shuler, Adv. Chem. Phys. 1, 1958.
- ⁶³ K. E. Shuler, Phys. Fluids 2, 442 (1959).
- ⁶⁴ R. Herman and R. J. Rubin, Phys. Fluids 2, 547 (1959).
- ⁶⁵ S. J. Lukasik, J. Acoust. Soc. Amer. 28, 455 (1956).
- ⁶⁶ S. H. Bauer, J. Chem. Phys. 21, 1888 (1953).
- ⁶⁷ R. O. Davies and J. Lamb, Proc. Phys. Soc. B69, 293 (1956).
- ⁶⁸ F. C. Roesler and W. A. Twyman, Proc. Phys. Soc. B68, 97 (1955).
- ⁶⁹ H. M. Mott-Smith, Phys. Rev. 82, 885 (1951).
- ⁷⁰ A. Sakurai, J. Fluid. Mech. 3, 255 (1957).
- ⁷¹ H. A. Bethe and E. Teller, Aberdeen Proving Ground, BRL, Report X-117, 1941.
- ⁷² J. G. Logan, Механика (Mechanics), No. 1, 1 (1959).
- ⁷³ E. E. Nikitin, Dokl. Akad. Nauk SSSR 116, 584 (1957) and 119, 526 (1958, Soviet Phys.-Doklady).
- ⁷⁴ E. E. Nikitin, Thesis, Moscow, 1958.
- ⁷⁵ E. E. Nikitin, J. Phys. Chem. (U.S.S.R.) 33, 572 (1959).
- ⁷⁶ E. V. Stupochenko and A. I. Osipov, J. Phys.

- Chem. (U.S.S.R.) **32**, 1673 (1958); **33**, 1526 (1959).
- ⁷⁷G. Jarre, *Z. angew. Math. Phys.* **9b**, 389 (1958).
- ⁷⁸E. Wigner, *J. Chem. Phys.* **5**, 720 (1937); **7**, 646 (1939).
- ⁷⁹O. K. Rice, *J. Chem. Phys.* **9**, 258 (1941); **21**, 750 (1953).
- ⁸⁰G. Careri, *Nuovo cimento* **6**, 94 (1949); **7**, 155 (1950).
- ⁸¹G. Careri, *J. Chem. Phys.* **21**, 749 (1953).
- ⁸²R. E. Duff, *Phys. Fluids* **1**, 242 (1958).
- ⁸³R. E. Duff, *J. Chem. Phys.* **28**, 1193 (1958).
- ⁸⁴R. E. Duff and N. Davidson, *J. Chem. Phys.* **31**, 1018 (1959).
- ⁸⁵D. W. Jepsen and J. O. Hirschfelder, *J. Chem. Phys.* **30**, 1032 (1959).
- ⁸⁶B. Widom, *J. Chem. Phys.* **31**, 1027 (1959).
- ⁸⁷J. W. Bond, *Phys. Rev.* **105**, 1683 (1957).
- ⁸⁸Y. Manheimer-Timnat and W. Low, *J. Fluid. Mech.* **6**, 449 (1959).
- ⁸⁹Losev, Generalov, and Terebina, *Оптика и спектроскопия (Optics and Spectroscopy)* **8**, 569 (1960).
- ⁹⁰S. L. Mandel'shtam and N. K. Sukhodrev, *ЖЕТП* **24**, 701 (1953).
- ⁹¹G. G. Neuĭmin and A. N. Terenin, *Izv. Akad. Nauk SSSR, Ser. Fiz. No. 4*, 529 (1936).
- ⁹²Prokof'ev, Gurevich, Belousova, and Snegirev, *Оптика и спектроскопия (Optics and Spectroscopy)* **7**, 14 (1959).
- ⁹³A. N. Terenin and G. G. Neuĭmin, *Acta physico-chim. URSS* **16**, 257 (1942).
- ⁹⁴P. V. Slobodskaya, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **12**, 656 (1948).
- ⁹⁵W. H. Andersen and D. F. Hornig, *J. Chem. Phys.* **24**, 767 (1956).
- ⁹⁶W. H. Andersen and D. F. Hornig, *Metcalf Res. Lab., Brown Univ. Techn. Rep.*, N 8, May 22, 1958.
- ⁹⁷V. H. Blackman, *Techn. Rep. II-20*, Dept. of phys., Princeton Univ., May 1955.
- ⁹⁸V. H. Blackman, *J. Fluid. Mech.* **1**, 61 (1956).
- ⁹⁹W. Bleakney, *The Threshold of Space*, 1957, p. 275.
- ¹⁰⁰J. W. Braithwaite and F. D. Werner, *Univ. of Minnesota, Dep. aeron Engng., Res. Rep.* **58**, 1950.
- ¹⁰¹D. Britton et al., *J. Chem. Phys.* **25**, 804 (1956).
- ¹⁰²D. Britton and N. Davidson, *J. Chem. Phys.* **25**, 810 (1956).
- ¹⁰³D. L. Bunker and N. Davidson, *J. Amer. Chem. Soc.* **80**, 5090 (1958).
- ¹⁰⁴S. R. Byron, *J. Chem. Phys.* **30**, 1380 (1959).
- ¹⁰⁵M. Camac et al., *Avcores. lab., preprint*, N 802, 1958.
- ¹⁰⁶J. P. Chesick and G. B. Kistiakowsky, *J. Chem. Phys.* **28**, 956 (1958).
- ¹⁰⁷Clouston, Gaydon, and Glass, *Proc. Roy. Soc. A248*, 429 (1958).
- ¹⁰⁸J. V. Connor, *J. Acoust. Soc. Amer.* **30**, 297 (1958).
- ¹⁰⁹G. R. Cowan and D. F. Hornig, *J. Chem. Phys.* **18**, 1008 (1950).
- ¹¹⁰Ener, Gabrysh, and Hubbard, *J. Acoust. Soc. Amer.* **24**, 474 (1952).
- ¹¹¹A. Eucken and R. Becker, *Z. Phys. Chem.* **B27**, 235 (1934).
- ¹¹²A. Eucken and E. Neumann, *ibid.* **B36**, 163 (1937).
- ¹¹³E. F. Fricke, *J. Acoust. Soc. Amer.* **12**, 245 (1940).
- ¹¹⁴H. S. Glick and W. H. Wurster, *J. Chem. Phys.* **27**, 1224 (1957).
- ¹¹⁵H. S. Glick and W. H. Wurster, *Bull. Amer. Phys. Soc., ser. II* **2**, 47 (1957).
- ¹¹⁶J. A. Golden and A. L. Myerson, *J. Chem. Phys.* **28**, 978 (1958).
- ¹¹⁷Greene, Cowan, and Hornig, *J. Chem. Phys.* **19**, 427 (1951).
- ¹¹⁸E. F. Greene and D. F. Hornig, *J. Chem. Phys.* **21**, 617 (1953).
- ¹¹⁹M. Greenspan, *J. Acoust. Soc. Amer.* **30**, 672 (1958).
- ¹²⁰W. D. Greenspan and V. H. Blackman, *Bull. Amer. Phys. Soc., ser. II* **2**, 217 (1957).
- ¹²¹W. Griffith, *J. Appl. Phys.* **21**, 1319 (1950).
- ¹²²W. Griffith, *Phys. Rev.* **87**, 234 (1952).
- ¹²³Griffith, Brickl, and Blackman, *Phys. Rev.* **102**, 1209 (1956).
- ¹²⁴M. C. Henderson and L. Peselnick, *J. Acoust. Soc. Amer.* **29**, 1074 (1957).
- ¹²⁵J. T. Herron et al., *J. Chem. Phys.* **29**, 230 (1958).
- ¹²⁶A. Hertzberg and J. G. Logan, *The Threshold of Space*, 1956, p. 276.
- ¹²⁷D. F. Hornig, *J. Phys. Chem.* **61**, 856 (1957).
- ¹²⁸P. W. Huber and A. Kantrowitz, *J. Chem. Phys.* **15**, 275 (1947).
- ¹²⁹A. van Itterbeek and P. Mariens, *Physica* **4**, 207, 609 (1937); **7**, 938 (1940).
- ¹³⁰van Itterbeek, de Bruyn, and Mariens, *Physica* **6**, 511 (1939).
- ¹³¹A. van Itterbeek and R. Vermaelen, *Physica* **9**, 345 (1943).
- ¹³²M. E. Jacox and S. H. Bauer, *J. Phys. Chem.* **61**, 833 (1957).
- ¹³³A. Kantrowitz, *J. Chem. Phys.* **10**, 145 (1942); **14**, 150 (1946).
- ¹³⁴G. B. Kistiakowsky and G. G. Volpi, *J. Chem. Phys.* **27**, 1141 (1957).
- ¹³⁵H. O. Kneser and V. O. Knudsen, *Ann. Phys.* **21**, 682 (1935).
- ¹³⁶H. Knotzel and L. Knotzel, *Ann. Phys.* **21**, 682 (1935).
- ¹³⁷V. O. Knudsen, *J. Acoust. Soc. Amer.* **5**, 112 (1933).
- ¹³⁸L. Lamb and S. C. Lin, *J. Appl. Phys.* **28**, 754 (1957).
- ¹³⁹Lipskomb, Norrish, and Thrush, *Proc. Roy. Soc. A233*, 455 (1956).

- ¹⁴⁰S. J. Lukasik and J. E. Young, *J. Chem. Phys.* **27**, 1149 (1957).
- ¹⁴¹O. Matthews, *Phys. Fluids* **2**, 170 (1959).
- ¹⁴²V. Niblett and V. H. Blackman, *J. Fluid. Mech.* **4**, 191 (1958).
- ¹⁴³H. B. Palmer and D. F. Hornig, *J. Chem. Phys.* **26**, 98 (1957).
- ¹⁴⁴Parker, Adams, and Stavseth, *J. Acoust. Soc. Amer.* **25**, 263 (1953).
- ¹⁴⁵H. E. Petschek et al., *J. Appl. Phys.* **26**, 83 (1955).
- ¹⁴⁶H. E. Petschek and S. Byron, *The Threshold of Space*, ed. M. Zelikoff, 1957, p. 270.
- ¹⁴⁷H. E. Petschek and S. Byron, *Ann. phys.* **1**, 270 (1957).
- ¹⁴⁸Reeves, Manella, and Narteck, *J. Chem. Phys.* **29**, 608 (1958); **32**, 632 (1960).
- ¹⁴⁹E. L. Resler and B. B. Cary, *The Threshold of Space*, 1957, p. 320.
- ¹⁵⁰J. E. Rhodes, *Phys. Rev.* **70**, 932 (1946).
- ¹⁵¹W. T. Richards and J. A. Reid, *J. Chem. Phys.* **2**, 193 (1934); **4**, 561 (1936).
- ¹⁵²F. Roblen, *J. Chem. Phys.* **31**, 420 (1959).
- ¹⁵³W. Roth, *J. Chem. Phys.* **31**, 720 (1959).
- ¹⁵⁴R. N. Schwartz and J. Eckerman, *Phys. Rev.* **94**, 1441 (1954).
- ¹⁵⁵R. N. Schwartz and J. Eckerman, *J. Appl. Phys.* **27**, 169 (1956).
- ¹⁵⁶F. S. Sherman, NACA Technical Note, 3298 (1955).
- ¹⁵⁷G. G. Sherratt and E. Griffiths, *Proc. Roy. Soc.* **A147**, 292 (1934).
- ¹⁵⁸L. S. Sinnes and W. E. Roseveare, *J. Chem. Phys.* **4**, 427 (1936).
- ¹⁵⁹Smiley, Winkler, and Slawsky, *J. Chem. Phys.* **20**, 293 (1952).
- ¹⁶⁰E. F. Smiley and E. H. Winkler, *J. Chem. Phys.* **22**, 2018 (1954).
- ¹⁶¹E. S. Stewart, *Phys. Rev.* **69**, 632 (1946).
- ¹⁶²J. L. Stewart, *Rev. Sci. Instr.* **17**, 59 (1946).
- ¹⁶³E. S. Stewart and J. L. Stewart, *J. Acoust. Soc. Amer.* **24**, 194 (1952).
- ¹⁶⁴R. Strehlow and A. Cohen, *J. Chem. Phys.* **30**, 297 (1959).
- ¹⁶⁵W. Tempest and H. P. Parbrook, *Acustica* **7**, 354 (1954).
- ¹⁶⁶W. J. Thaler, *J. Acoust. Soc. Amer.* **24**, 15 (1952).
- ¹⁶⁷Wentink, Sullivan, and Wray, *J. Chem. Phys.* **29**, 231 (1958).
- ¹⁶⁸Windsor, Davidson, and Taylor, *J. Chem. Phys.* **27**, 315 (1957).
- ¹⁶⁹I. Zartmann, *J. Acoust. Soc. Amer.* **21**, 171 (1949).
- ¹⁷⁰A. J. Zmuda, *J. Acoust. Soc. Am.* **23**, 472 (1951).
- ¹⁷¹Vasin, Leskov, and Savin, Paper presented at the XIII All-Union Conference on Spectroscopy (in press).
- ¹⁷²Kudryavtsev, Sobolev, Tunitskiĭ, and Faizullof, Paper presented at the XIII All-Union Conference on Spectroscopy (in press).
- ¹⁷³S. A. Losev and N. A. Generalov, Paper presented at the XIII All-Union Conference on Spectroscopy (in press).
- ¹⁷⁴A. I. Osipov, Paper presented at the XIII All-Union Conference on Spectroscopy (in press).

Translated by G. Volkoff