EXPERIMENTAL DETERMINATION OF THE PROBABILITY FOR EXCITATION OF BROMINE VIBRATIONAL LEVELS IN COLLISIONS WITH He, Ne, Ar, AND Xe ATOMS IN SHOCK WAVES

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Submitted June 27, 1969

The behavior of the transition probability $\Delta E/h\nu$ between bromine vibrational levels in mixtures containing He, Ne, Ar or Xe is investigated for adiabatic-factor values $0.5 \leq \omega\tau_{col} \leq 1.8$. It is shown that in mixtures containing Ne or Ar the quantity $\Delta E/h\nu$ goes through a maximum at $\omega\tau_{col} \sim 1$; in mixtures with He or Xe its variation is different and depends on $\omega\tau_{col}$. It is noted that for $\omega\tau_{col} > 1$ the experimental results can be satisfactorily described by the Landau–Teller theory. Theories developed for $\omega\tau_{col} < 1$ do not agree with data obtained in this range of $\omega\tau_{col}$ values.

1. INTRODUCTION

$\mathbf{A}$ sudden loss of statistical equilibrium in a molecular gas is accompanied by different relaxation processes, each with its own characteristic time. Measurement of these quantities makes it possible to determine experimentally the transition probabilities between the rotational, vibrational, and electronic levels. There is a large variety of experimental methods for investigating relaxation processes in gases. Initially, ultraacoustic methods were the most widely used.[1] However, the temperature interval of these methods was quite narrow and was limited to room temperatures or to temperatures close to them. Subsequently, methods covering a broader temperature interval were developed. These include, for example, the shock-wave method. In spite of the fact that this method is now used quite extensively, the results obtained with it pertain only to a rather narrow field of vibrational relaxation, namely the region of adiabatic collisions, where the period of the molecule vibrations is smaller than the duration of the collisions τ_{col}, i.e., $\omega\tau_{col} > 1$ (ω—vibrational frequency of the molecules).

In the present investigation, the shock-wave method was used to determine the vibrational relaxation times τ in mixtures of bromine with inert gases He, Ni, Ar, and Xe under conditions of both adiabatic and nonadiabatic collisions, and the adiabaticity factor $\omega\tau_{col}$ lies in the interval $0.5 \leq \omega\tau_{col} \leq 1.8$. As is well known[2,3], under the conditions of adiabatic collisions ($\omega\tau_{col} < 1$) almost all the experimental results pertaining to diatomic molecules agree quite well with the conclusions of the Landau–Teller theory[4] ($\ln \tau \sim \text{const}/T^{1/3}$). The only exceptions are certain molecules of the HI type.[5] In the region of nonadiabatic collisions ($\omega\tau_{col} < 1$) the existing theoretical analyses of vibrational relaxations[6,7] have not yet been confirmed experimentally, since there are practically[8,9] no experimental measurements of the value of τ under these conditions.

The choice of bromine as the object of investigation is governed by several factors. First, bromine has an intense well-investigated absorption spectrum in the visible region, making it possible to employ the method of molecular absorption spectroscopy to register the populations of the different vibrational levels of the Br_2 molecule. The semi-empirical Sulzer–Wieland formula[10] for the absorption coefficient $\epsilon_T(\nu)$ describes sufficiently accurately the experimental results in a wide range of temperatures and wavelengths

$$\epsilon_T(\nu) = \epsilon_0^m \left[\text{th}\left(\frac{\Theta_0}{2T}\right) \right]^{1/2} \exp\left[-\text{th}\left(\frac{\Theta_0}{2T}\right)\left(\frac{\nu - \nu_0}{\Delta\nu_0^*}\right)^2 \right], \quad (1)$$

where ϵ_0^m, ν_0, and $\Delta\nu_0^*$ are quantities determined from experiment, $\Theta_0 = h\nu/k = 465°\text{K}$ is the characteristic vibrational temperature of bromine, and T is the thermodynamic temperature of the gas. Second, the presence of a low characteristic vibrational temperature for bromine greatly simplifies the performance of the experiment in the region of nonadiabatic collisions of Br_2 molecules with inert gases; this investigation can be carried out under conditions in which there is still no overlap of the process of vibrational relaxation with dissociation. For almost all the remaining diatomic molecules, the region of nonadiabatic collisions lies at temperatures so high that an appreciable overlap is observed between the processes of dissociation and vibrational relaxation (for example O_2, N_2, CO, and others). However, in view of the high chemical activity of bromine, the experimental technique is greatly complicated, since the experimental setup must be made of a material that is not subject to corrosion.

2. EXPERIMENTAL SETUP

The experimental investigations aimed at determining the probabilities of the transition between vibrational levels of the Br_2 molecules were carried out with a shock tube made of stainless steel (Fig. 1). The shock tube consisted of sections with inside diameter 134 mm; the length of the low-pressure chamber (LPC) and the high pressure chamber (HPC) were respectively 7 and 12 meters. These chambers were separated by an aluminum membrane with a corrugation whose depth determined the strength of the shock wave. The vacuum seals
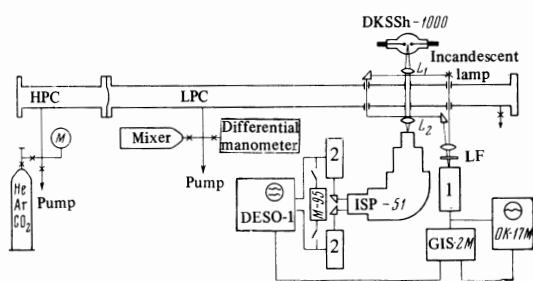
FIG. 1. Diagram of Experimental setup. 1–FÉU-36 photomultiplier, 2–FÉU-38 photomultiplier.

were made of teflon or silicone rubber. The shock-tube walls could be heated to 200°C with the aid of a special nichrome coil uniformly wound over the entire setup.

The low-pressure chamber was evacuated with a forevacuum pump to a pressure 2×10^{-2} mm Hg. The leakage due to the insufficient sealing did not exceed 10^{-4} mm Hg within the time necessary to perform the experiment.

The mixture of bromine with the inert gases was prepared in a special gas mixer, 20 liters in volume, which was connected to the shock tube through bellows and valves. The gases were mixed not less than one day. The pressure of the mixture on the shock tube was determined with the aid of a differential manometer specially designed and constructed to operate with corrosive media. This instrument was designed to operate at a temperature up to 200°C. The error in the measurement of a mixture pressure of several millimeters mercury did not exceed 2%.

The partial pressure P_1 of the bromine vapor was determined from the absorption of light in the visible region of the spectrum, $\lambda = 4140$ Å. To this end, an optical system was assembled where the light source was a DKSSh-1000 lamp. A lens L_1 was used to form an approximately parallel beam of light, which crossed the shock tube perpendicular to its axis, and was focused by a lens L_2 on the input slit of the ISP-51 spectrograph. The light receiver was an FÉU-38 photomultiplier, the output signal of which was fed to a moving-mirror microammeter M-95. Since the investigations were carried out in the region of continuous absorption of the light, the connection between the Br_2 molecule concentration (or the pressure P_1) and the absorptivity A was established on the basis of Beer's law

$$P_1 = -\frac{NkT\ln(1-A)}{10^3 \epsilon_{T_1}(\nu)d}, \qquad (2)$$

where $\epsilon_{T_1}(\nu)$ is the absorption coefficient (liters/mole-cm), N is Avogadro's number, T_1 the initial temperature of the gas in the shock tube, k is Boltzmann's constant, and d is the diameter of the shock tube (cm).

The same scheme with certain modifications was used to investigate the distribution of the absorptivity of the gaseous bromine behind the shockwave front. The difference lies in the fact that the registration of the absorptivity of the Br_2 molecules in the shock wave was carried out simultaneously at two wavelengths, $\lambda_1 = 4140$ and $\lambda_2 = 4900$ Å; two optical slits were placed at the output of the ISP-51 spectrograph and, accordingly, two FÉU-38 photomultipliers, the signals from which were fed not to the moving-mirror galvanometer, but to two

channels of a DÉSO-1 oscilloscope. To facilitate the calculation of the vibrational-relaxation time, the relative positions of the sweeps were calibrated before the experiment.

The widths of the slits on the sighting windows of the shock tube did not exceed 0.3 mm. This width determined the resolving power of the registration system, since the time constant of the electric circuit did not exceed 10^{-7} sec.

To determine the shock-wave velocity we measured the transit time of the shock wave through a tube 290 mm long; the instants of passage of the wave past two specified points of the apparatus were registered by the absorption-spectroscopy method. To this end, the light source was a tungsten incandescent lamp, and the necessary section of the spectrum was separated with the aid of an interference light filter (LF). The beams of light after passing through the shock tube were aimed on the same FÉU-36 photomultiplier, the output signal of which was fed to an OK-17M oscilloscope.

3. DETERMINATION OF THE VIBRATIONAL RELAXATION TIME

The study of the vibrational relaxation (and consequently of the probabilities of the transition between the vibrational levels) of the Br_2 molecules behind the front of the shock wave was carried out in a mixture of bromine with the inert gases He, Ne, Ar, and Xe. The percentage content of the bromine in the mixtures with He, Ne, and Xe was respectively 5, 10, 20, 50%; 10%; and 5, 10, 20%; 20%. Typical oscillograms of the distribution of the absorptivity of bromine vapors behind the shock wave front are shown in Fig. 2. Both oscillograms were obtained in the same experiment, but for different sections of the spectrum, $\lambda_1 = 4140$ Å and $\lambda_2 = 4900$ Å. The absorption of the light in the region of $\lambda_1 = 4140$ Å is connected with transitions between the Br_2 molecules from the zeroth vibrational level of the ground electronic state $^1\Sigma_g^+$ to the excited state $^3\Pi_{1u}$. The other section of the spectrum, at $\lambda_2 = 4900$ Å, corresponds to transitions from the lower vibrational levels of the state $^1\Sigma_g^+$ to the excited states $^1\Pi_{0+u}$ and $^3\Pi_{1u}$. Since the transitions begin from the zeroth vibrational level in the spectral regions $\lambda_1 = 4140$ Å and $\lambda_2 = 4900$ Å, the gas is not perfectly transparent even at room temperatures. (It must be noted that under the experimental conditions inert gases are fully transparent to light
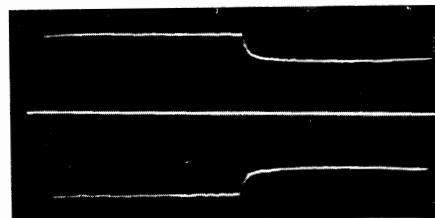

FIG. 2. Oscillograms of the absorptivity of bromine in a mixture 10% Br_3 + 90% He behind the front of the shock wave. The sweep duration is 50 μsec, $P_1 = 10$ mm Hg, v = 1.24 mm/μsec. The upper curve corresponds to absorption of light in the region $\lambda_1 = 4140$ Å, and the lower at $\lambda_2 = 4900$ Å.

with wavelength $\lambda_1 = 4140$ Å and $\lambda_2 = 4900$ Å.)

The gas is heated and compressed in the front of the shock wave. The compression leads to an increase of the total density of the gas, and consequently to an increase of the absorptivity, while heating of the gas causes a decrease in the population of the zeroth vibrational level and, naturally, a decrease of its absorptivity. The total contribution of these processes to the absorption is such that an increase of the absorptivity is observed in the front of the shock wave. With increasing distance from the front, the absorption continues to increase. This is connected with the growth of the gas density and with the drop of the translational temperature during the process of population of the upper vibrational levels of the Br_2 molecules. During the course of this process, the vibrational temperature increases from room temperature to the equilibrium value of the translational temperature. The change of the absorptivity of the gas behind the shock-wave front continues for several microseconds, after which a constant level is established (region of statistical equilibrium). The absorption coefficient of bromine in this equilibrium region of the shock wave coincides, within the limits of experimental error, with the values calculated in accordance with formula (1).

The time of vibrational relaxation of the Br_2 molecules was determined in the following manner. For the spectral regions $\lambda_1 = 4140$ Å and $\lambda_2 = 4900$ Å, the oscillograms were used to determine the distribution of the absorptivity of the bromine behind the shock wave front $A_1(t)$ and $A_2(t)$. Then, using the relation derived from Beer's law and formulas (1)

$$\frac{\ln(1-A_1)}{\ln(1-A_2)} = \frac{\varepsilon_T(\nu_1)}{\varepsilon_T(\nu_2)} = \exp\left\{-\left[\th\left(\frac{\Theta_0}{2T}\right)\right]\frac{(\nu_1-\nu_2)(\nu_1+\nu_2-2\nu_0)}{\Delta\nu^{*2}}\right\}.$$ (3)

we determined the distribution of the vibrational temperature $T_V(t)$, and accordingly, of the vibrational energy $E_V(t)$ behind the shock wave front. The profiles of the density $\rho_2(t)$ and of the translational temperature of the gas were determined from the data on the distribution of the absorptivity $A_1(t)$ and of the vibrational temperature $T_V(t)$, using Beer's law and the laws of mass and momentum conservation. These data suffice for the determination of the relaxation time of the vibrational energy in the laboratory system, if the following formula is used:

$$\tau_{lab} = \frac{E_v(T) - E_v(T_v)}{dE_v(T_v)/dt_{lab}}.$$ (4)

Since we know now the profiles of the quantities $E_V(t)$, $E_V(T_v)$ and $dE_V(T_v)/dt_{lab}$ behind the shock-wave front, obtained from the oscillograms, we calculate from formula (4) the dependence of the time of vibrational relaxation on the translational temperature T in the laboratory frame. Then, using the results of the calculation of τ_{lab}, we determine the relaxation time τ_{eff} in a coordinate system connected with a physically small volume of the gas. The values of τ_{eff} obtained in this manner correspond to a concrete mixture. To find the vibrational relaxation time τ_{Br_2-M} due only to the collisions between the Br_2 molecules and the atoms of the inert gases (M), we used the equation

$$\frac{1}{\tau_{eff}} = \frac{x}{\tau_{Br_2-Br_2}} + \frac{1-x}{\tau_{Br_2-M}},$$ (5)

where $\tau_{Br_2-Br_2}$ is the time of vibrational relaxation of pure bromine[9] and x is the concentration of the Br_2 molecules in the mixture.

Experiment has shown that the time τ_{Br_2-M} does not depend on the percentage composition of the mixture, thus demonstrating the validity of formula (5). The results of the measurements of τ_{Br_2-M} were reduced to normal density (n = 2.69×10^{19} cm^{-3}) and are shown in Figs. 3 and 4 as functions of the translational gas temperature. These data have much in common and their temperature dependences deviate greatly from the experimental results available for other molecules.[2,3] Notice should be taken of three characteristic segments on the curves of Figs. 3 and 4. The first pertains to the region of low temperatures, where the vibrational relaxation time decreases with increasing temperature T. Such a dependence of τ on T ($\omega\tau_{col} > 1$) is characteristic of adiabatic collisions and is sufficiently well described by the Landau-Teller theory. However, there is no agreement between theory and experiment when it comes to the absolute values. Thus, for example, the experimental and theoretical values of τ_{Br_2-Ne}, τ_{Br_2-Ar}, and τ_{Br_2-Xe} differ by 90, 60, and 4 times respectively. (Figs. 3 and 4; they show τ_{Br_2-M} already multiplied by the foregoing numbers.)

The range of adiabatic collisions depends on the type of incoming particle, particularly on its mass. Whereas for the Br_2-Xe mixture it extends up to 1000-1100°K, and for Br_2-Ar up to 800-900°K, for the lighter neon it decreases to 600-700°K. In the Br_2-He system, adiabatic collisions are possible only at T < 500°K. Therefore in Fig. 3 there is no section in which τ_{Br_2-He} decreases.
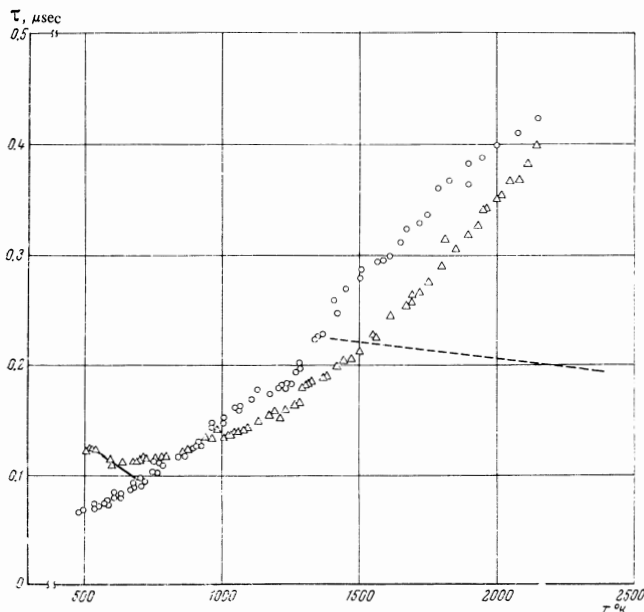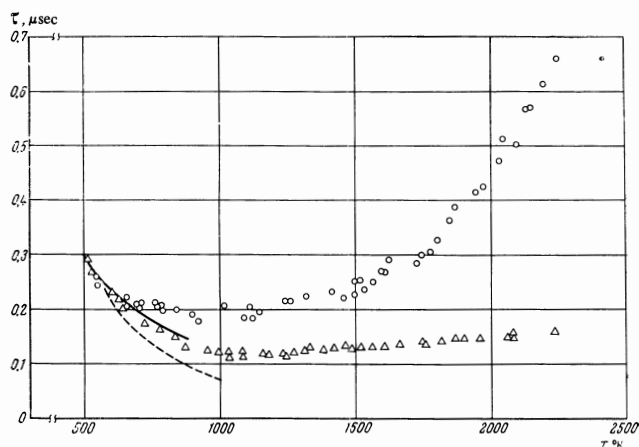

FIG. 3. Dependence of the vibrational-relaxation time of bromine on the gas temperature. O and Δ — results of the present investigation for the mixtures Br_2-He and Br_2-Ne, respectively; solid line — 90 τ_{Br_2-Ne} (where τ_{Br_2-Ne} was calculated in accordance with the Landau-Teller theory), dashed — 200τ_{Br_2-He} (where τ_{Br_2-He} was calculated in accordance with the theory of [7]).

FIG. 4. Dependence of the time of vibrational relaxation of bromine on the gas temperature. $\bigcirc$ and $\triangle$ — results of the present investigation for the mixtures Br_2-Ar and Br_2-Xe, respectively; solid line — $60\tau_{Br_2-Ar}$; dashed line — $4\tau_{Br_2-Xe}$ (where τ_{Br_2-Ar} and τ_{Br_2-Xe} are calculated by the Landau-Teller theory).

Adjacent to the region of adiabatic collisions is a segment in which the time of vibrational relaxation ceases to change with increasing temperature. Its dimensions, just as in the case of the first segment, are determined by the nature of the incoming particle. The vibrational relaxation under these conditions is characterized by a transition from adiabatic collisions to non-adiabatic ones ($\omega\tau_{col} \sim 1$). It should be noted that when $\omega\tau_{col} \sim 1$ the Landau–Teller theory can no longer be used for the description of the excitation of the molecular vibrations; no theory has yet been developed for these conditions.

Finally, the region of nonadiabatic collisions ($\omega\tau_{col} < 1$) differs from the two preceding ones in that the time of vibrational relaxation increases appreciably with increasing temperature. This is connected with the decrease of the vibration-excitation probability of the Br_2 molecules, or at least with its constancy. For the Br_2-Xe system, the range of nonadiabatic collisions begins at $T > 2200°K$, where an overlap of the relaxation and dissociation processes is observed. In the Br_2-He mixture, to the contrary, owing to the large relative velocities of the colliding particles, this range begins in the region of room temperatures ($T < 500°K$).

In theoretical investigations[6,7] of vibrational relaxation in the region $\omega\tau_{col} < 1$, it is assumed that the mass of the incoming particle is much smaller than the mass of the relaxing molecules. Therefore, only for the Br_2-He system can we compare the experimental and theoretical values. Figure 3 shows the results of a calculation of τ_{Br_2-M} by means of the formula of [7]. It turns out that the theory and experiment yield essentially different results.

4. PROBABILITY OF EXCITATION OF THE VIBRATIONAL LEVELS OF Br_2 MOLECULES BY COLLISION WITH ATOMS OF He, Ne, Ar, AND Xe

In the present study, the main experimental result is the time of vibrational relaxation τ_{Br_2-M}. It is connected with the probability of excitation of the vibrations of the molecules Br_2 (in our case the probability

is equal to $\Delta E/h\nu$) by the relation[11]

$$\tau = \left[z\frac{\Delta E}{h\nu}(e^{h\nu/kT}-1) \right]^{-1}, \qquad (6)$$

where ΔE is the energy acquired by the molecule in one collision, $h\nu$ is the quantum of the vibrational energy, and z is the frequency of collisions of the molecules with the incoming particle (in our case with the atom of the inert gases). We shall use formula (6) and calculate the probability $\Delta E/h\nu$ of excitation of the vibrations of the Br_2 molecules. We assume here that the gas-kinetic cross section of the collision between the molecule and the atom of the inert gas is $\sigma_{Br_2-M} = \frac{1}{2}(\sigma_{Br_2} + \sigma_M)$ and remains constant in the entire investigated range $T = 500$–$2250°K$; σ_{Br_2} and σ_M are respectively the cross sections for the collisions between the Br_2 molecules and the inert-gas atoms. The obtained values of $\Delta E/h\nu$ are shown in Figs. 5 and 6 as functions of the gas temperature.

As seen from Figs. 5 and 6, the probability $\Delta E/h\nu$ of excitation of vibrational levels of bromine molecules in collisions Br_2-Ne, Ar, Xe increases with increasing T, in the region of relatively low temperatures, and reaches a section with a constant value. For the Br_2-Xe system, the probability $\Delta E/h\nu$ assumes a constant value in the region $T \sim 1500°K$ and remains unchanged up to the upper limit of the investigation, whereas for the mixtures Br_2-Ar, Br_2-Ne it goes through a maximum at $T \sim 1300°K$ and $T \sim 1000°K$ respectively. In the Br_2-He mixture, the probability $\Delta E/h\nu$ of excitation of the vibrational levels decreases in the region

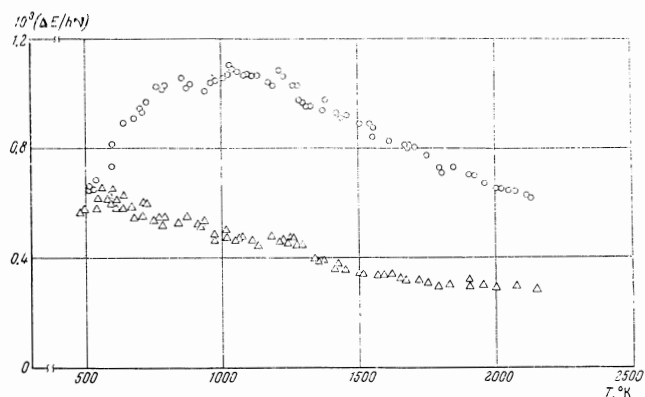FIG. 5. Probability of transition between vibrational levels of Br_2 molecules as a function of the gas temperature. $\bigcirc$ and $\triangle$ — the results for the mixtures Br_2-He and Br_2-Ne, respectively.
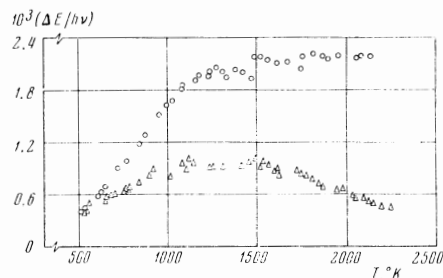

FIG. 6. Probability of transition between vibrational levels of the Br_2 molecules as a function of the gas temperature. $\bigcirc$ and $\triangle$ — results for the mixtures Br_2-Xe and Br_2-Ar, respectively.

T = 500–1500°K and remains practically unchanged at T = 1500–2150°K.

The behavior of the probability $\Delta E/h\nu$ of the transition between the vibrational levels and the behavior of the time of vibrational relaxation τ_{Br_2-M} as functions of the temperature have much in common for all the investigated mixtures. The only difference is that the common characteristic sections of $\Delta E/h\nu$ pertain to different values of the temperature. We therefore present the results not as functions of the temperature but as functions of a quantity characterizing the ratio of the period of the oscillations to the duration of the particle collision, i.e., as a function of $\omega\tau_{col}$. The duration of the collision is defined as $\tau_{col} = 1/\alpha v^*$, where α is one of the constants of the exponential potential of the interaction between the Br_2 molecules and the atoms of the inert gas, $V = V_0 \exp -\alpha r$, and v^* is the relative velocity of the colliding particles making the largest contribution to the excitation of the vibrations of the Br_2 molecule; it is determined from the Landau–Teller theory. The parameter α was obtained from the experimental results at low temperatures, where agreement between theory and experiment is observed. For the

systems Br_2–Ne, Br_2–Ar, and Br_2–Xe, α turned out to be equal respectively to 5.0×10^8, 5.5×10^8, and 5.0×10^8 cm^{-1}; the parameter α for the Br_2–He mixture was assumed equal to 4.0×10^8 cm^{-1}. All the experimental results are presented on a common plot (Fig. 7).

The quantity $\omega\tau_{col}$ turned out to be the smallest for the mixture Br_2–He ($\omega\tau_{col} \sim 0.5$), and largest for Br_2–Xe. The reason is that the temperature interval of the investigation was approximately the same for all systems, but the reduced masses differ greatly. It is seen from Fig. 7 that the probability of excitation of the vibrational levels of bromine in mixtures with argon and neon goes through a clearly pronounced maximum in the region $\omega\tau_{col} \sim 1$, i.e., the most effective collisions are those whose duration is close to the period of vibration of the molecules.

Analyzing the results, we can apparently suggest that when $\omega\tau_{col} \sim 1$ there is a maximum of the probability of excitation of the vibrations of the Br_2 molecules also for the mixtures Br_2–He and Br_2–Xe. It is possible that this dependence of $\Delta E/h\nu$ on the temperature or on the parameter $\omega\tau_{col}$ is typical also of many other diatomic molecules.

In conclusion, the authors are grateful to E. V. Stupochenko and A. I. Osipov for a discussion of the results.
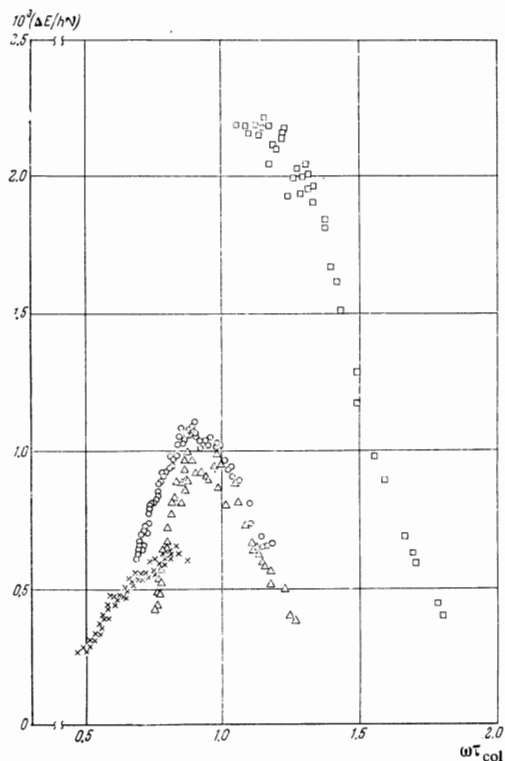

FIG. 7. Dependence of the probability of transition between vibrational levels of Br_2 molecules on the adiabatic factor $\omega\tau_{col}$ in the following mixtures: Br_2 – He (X); Br_2 – Ar (△); Br_2 – Ne (O); Br_2 – Xe (□).

[1] K. F. Herzfeld and T. Litovitz, Absorption and Dispersion of Ultrasonic Waves (Academic Press, New York, 1959).

[2] R. C. Millikan and D. R. White, J. Chem. Phys. 39, 3209 (1963).

[3] E. V. Stupochenko, S. A. Losev, and A. I. Osipov, Relaksatsionnye protsessy v udarnykh volnakh (Relaxation Processes in Shock Waves), Nauka, 1965.

[4] L. D. Landau and E. Teller, Phys. Z. Sowjetunion 10, 34 (1936).

[5] C. C. Chow and E. F. Greene, J. Chem. Phys. 43, 324 (1965).

[6] A. I. Osipov, Zh. fiz. khim. 37, 2757 (1963).

[7] M. N. Safaryan and E. V. Stupochenko, Prik. Mat. Teor. Fiz. 1, 93 (1965).

[8] N. A. Generalov and V. D. Kosynkin, Dokl. Akad. Nauk 175, 1033 (1967) [Sov. Phys.-Dokl. 12, 796 (1968)].

[9] N. A. Generalov and V. A. Maksimenko, ibid. 186, 5 (1969) [sic!].

[10] P. Sulzer and K. Wieland, Helv. Phys. Acta 25, 653 (1962).

[11] A. I. Osipov and N. A. Generalov, Fiz. goreniya i vzryva 2, 83 (1966).

Translated by J. G. Adashko
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