DIFFUSION DESCRIPTION OF VIBRATIONAL RELAXATION IN A BINARY MIXTURE OF DIATOMIC MOLECULES AS QUANTUM ANHARMONIC OSCILLATORS – RESULTS OF A CALCULATION

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In the general case, vibrational relaxation in a binary mixture of anharmonic oscillators as a function of concentration is characterized as a complex interaction of energy exchange processes: vibration–translation VT, vibration–vibration VV, and vibration–vibration between different types of molecules VV'. Here it is impossible to separate the dominant process at a given time interval over the whole range of vibrational energy. As in the case of a single-component gas (see [1-3] for details), triple distributions are formed in each of the components at the lower vibrational levels as a result of a single-quantum VV exchange. The relation between the distributions within the different components occurs through VV' processes. For relatively close fundamental vibration frequencies of the mixture components, the single-quantum process plays the main role in the VV' processes. This case has often been studied, in particular in relation to its application to laser systems [2, 4-6]. In the more general case of two-quantum VV'-exchange processes, the relaxation of the average vibration energy, in the form of a distribution function in the quasistationary relaxation regime, has been examined in the weak anharmonic* approximation [3] (see also [2]) on the basis of previous results [7, 8]. This approach [2, 3, 7, 8] has been applied [9] to studying the effect of multiple (two) quantum VV' exchanges on the quantitative characteristics of the kinetic cooling effect in the process of vibrational relaxation in a binary mixture of molecular gases.

Here we present the results of a numerical investigation of a transient kinetic vibrational relaxation in a binary mixture of diatomic molecules for arbitrary concentrations, initial vibration excitation levels, and ratios of the fundamental vibrational frequencies $W=\omega_0^{(2)}/\omega_0^{(1)}$ (which implies discarding the approximation of weak anharmonicity and considers the processes of single-quantum energy exchange caused by the multimode character of the anharmonic vibrations). Here the initial kinetic equations are the kinetic diffusion equations in discrete quantum-number space [10]. They are a generalization of the diffusion theory of vibrational relaxation for a binary mixture of diatomic molecules or quantum oscillators. The results illustrate the effect of multiquantum vibrational exchange for components with significantly different vibrational frequencies for different concentrations and initial conditions. We also include a comparison, based on the example of a binary mixture of diatomic molecules, of microscopic (on the level of vibrational state population densities) and macroscopic (on the level of average energies) descriptions of vibrational relaxation, in order to determine the limits of applying the macroscopic description, which is widely used in complex multicomponent mixtures in combination with the gas dynamic description (acoustic and shock waves, gas lasers of various types, etc.).

1. Initial Equations and Initial Conditions. A system of finite-difference diffusion equations provides the initial kinetic equations for calculating the population density x_{v_i} of the vibrational levels v_i of the i-th component of a gas mixture:

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*In the calculations, the dependence of the rate constant on the degree of vibrational excitation of the oscillators is considered single-mode (quasiharmonic), but multiquantum transitions are caused by nonlinear terms in the expansion of the intermolecular potential.

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$$\frac{dx_{v_i}}{dt} = \sum_{j=1}^{2} \Delta J_{v_i}^{(j)}, \; i = 1, 2, \; v_i = 0, 1, 2, \ldots; \tag{1.1}$$

$$J_{v_i}^{(j)} = \left[\sum_{v_j} B_{11}^{ij}(v_i, v_j)\, x_{v_j}^0 \varphi_{v_j}\right] x_{v_i+1} \Delta\varphi_{v_i+1} - x_{v_i+1}^0 \varphi_{v_i} \sum_{v_j} \varphi_{v_j} \Delta' \left[x_{v_j}^0 B_{12}^{ij}(v_i, v_j)\right]. \tag{1.2}$$

Here $\phi_V = x_V/x_V^0$; $x_V^0 = x_V(\infty)$; and $J_{vi}^{(j)}$ is the flux of molecules of type i from the vibrational state v_i as a result of collisions with molecules of type j, and Δ and Δ' are first-order finite difference operators

$$(\Delta A_{v,v'} = A_{v,v'} - A_{v-1,v'}, \quad \Delta' A_{v,v'} = A_{v,v'} - A_{v,v'-1}).$$

The dynamic aspect of the problem is localized in the coefficients $B_{hs}^{(ij)}(v_i, v_j)$, which are expressed in terms of the rate constants of the process

$$\{v_i, v_j\} \rightarrow \{v_i \pm n_i, v_j \mp n_j\}, \; n_i = 1, 2, \ldots \tag{1.3}$$

by the formulas [10]

$$B_{11}^{(i,j)} \cong \sum_{n_i, n_j \geqslant 1} n_i^2 Q_{v_i, v_i - n_i}^{v_j, v_j + n_j}, \; B_{12}^{(i,j)} \cong -\sum_{n_i, n_j} n_i n_j Q_{v_i, v_i - n_i}^{v_j, v_j + n_j}. \tag{1.4}$$

With respect to the Boltzmann population-density balance equations, from which they were obtained [10] for the weak-interaction condition $n_i < v_i$, Eqs. (1.1)-(1.4) are approximate in the general case with respect to n_i and exact in the single-quantum case ($n_i = 1$ and $i = 1, 2$). The last property of these equations and the absence of the limitation $\hbar\omega_0^{(i)}/kT \leqslant 1$ [11, 12] makes the application of Eqs. (1.1) preferable in comparison to the corresponding equations of classical (continuum) diffusion [13], which are the limiting case of Eqs. (1.1) for $\hbar\omega_0^{(i)}/kT \ll 1$.

In the system of harmonic oscillators corresponding to Eqs. (1.1), (1.2), and (1.4), the equations for the average energies E_i (macroscopic description) have the form [10]

$$\frac{dE_i}{dt} = \sum_{j=1}^{2} \gamma_j \sum_{n_i, n_j} n_i Q_{n_i 0}^{0 n_j}(i, j) \frac{E_i^0 E_i^{n_i - 1}(1 + E_i)(1 + E_j)^{n_j}}{1 + E_j^0} \left[\frac{n_i (E_i^0 - E_i)}{E_i^0 (1 + E_i)} - \frac{n_j (E_j^0 - E_j)}{E_j^0 (1 + E_j)}\right], \; i = 1, 2. \tag{1.5}$$

For n_i, $n_j > 1$, they are approximate in the sense of that the diffusion Eqs. (1.1) are approximate. The single-quantum exchange processes (1.1) are described exactly.

Below we present the results of a numerical solution of Eqs. (1.1) and (1.5) (transient isothermal problem) for a binary mixture of anharmonic oscillators with greatly differing fundamental frequencies. As an example to illustrate the results, we chose systems with fundamental frequency ratios W = 0.73, 1.47, and 1.9, which correspond to the mixtures $CO + O_2$, $HCl + H_2$, and CO (or N_2) + HF. As initial conditions we used the Boltzmann distribution with a temperature T_0;

$$x_v(0) \equiv x_v^0(T_0) = c \exp\left(-\frac{D}{kT_0} y_v\right) \tag{1.6}$$

and a strongly inverse distribution of the form

$$x_v(0) = c\exp\left[-(y_v - y_m)^2/2\rho^2\right], \tag{1.7}$$

where m is the number of the level which corresponds to the maximum of the distribution; the c are the normalizing constants; $y_v \equiv \varepsilon_v/D = (2v/N)(1 - v/2N)$ is the degree of excitation of the oscillator with the vibrational state v; ε_V is the energy of the oscillator with the vibrational state v; D is the dissociation energy; and N is the total number of the oscillator levels.

2. Characteristic Times and the Role of Various Processes. Numerical Solution Method. In calculating the vibrational relaxation process in a binary mixture of quantum anharmonic oscillators of types i and j, we will represent the probabilistic processes of exchanging vibrational energies (rate constant processes) $Q_{kl}^{ps}(i, j)$ by functions which correspond to first-order "forced oscillator" excitation functions with a linear expansion of the interaction potential in the vibrational coordinates r and r' [12]:

$$P_{kl}(i,j) = P_{10}(i,j)(r_{kl}/r_{10})^2\,\Phi\left(\xi_0^{ij}\omega_{kl}/\omega_0\right)/\Phi\left(\xi_0^{ij}\right), \tag{2.1}$$

$$Q_{kl}^{ps}(i,j) = Q_{10}^{01}(i,j)(r_{kl}/r_{10})^2\left(r'_{sp}/r_{10}\right)^2\Phi\left(\xi_0^{ij}\left|\frac{\omega_{kl}}{\omega_0} - W\frac{\omega'_{sp}}{\omega'_0}\right|\right)\Big/\Phi\left(\xi_0^{ij}\left|1-W\right|\right),$$

where $r_{k\ell}$ and r'_{sp} are matrix elements of the trajectories of unperturbed vibrational motion of the i-th and j-th oscillators, respectively; $W = \omega'_0/\omega_0$; $\xi_0^{(ij)} = \tau_*^{(i,j)}\omega_0$ is the adiabatic parameter ($\tau_*^{(ij)}$ is the characteristic interaction time for colliding oscillators); and the function $\Phi(x)$ is defined by the known relationship

$$\Phi(x) = x^2\int\limits_0^\infty e^{-z}\operatorname{csch}^2\left(x/\sqrt{z}\right)dz \simeq$$

$$\simeq \begin{cases} 8\sqrt{\pi/3}\,x^{7/3}\exp\left(-3x^{2/3}\right), & x \gg 1, \\ \frac{1}{2}\left[3 - \exp\left(-\frac{2}{3}x\right)\right]\exp\left(-\frac{2}{3}x\right), & 0 \leqslant x \leqslant 20. \end{cases}$$

Although the function (2.1) is obtained as the result of solving a linear (collinear) dynamic problem by using an exponential repulsive potential, it can be considered universal for the purpose of a series of colliding pairs, because the selection of the parameters $P_{10}(i,j)$, $Q_{10}^{01}(i,j)$ and $\xi_0^{(ij)}$ can be approximated satisfactorily by the effect of rotation and long-range attraction in the vibrational energy exchange process [14, 15].

Besides the transition probabilities between the lower states $P_{10}(i, j)$ and $Q_{10}^{01}(i,j)$ the basic parameters of the problem are the ratio W of the fundamental frequencies and the adiabatic collision parameter $\xi_0^{(ij)}$. In the general case, the characteristic times γ_i for the VT, VV, and VV' exchange processes (including the multiquantum processes) can be both close to each other and far apart, in terms of these parameters. Here, as a rule, the most rapid processes are the single-quantum VV processes, which form a triple distribution in each of the components at lower levels:

$$x_{v_i} = x_{0i}C_i^{v_i}\exp\left(-\varepsilon_{v_i}/kT\right). \tag{2.2}$$

Therefore, in a numerical solution, the characteristic time $\tau_{VV}^{AA}(1, 1)$ for single-quantum VV exchange at the lower levels in one of the components (A, for example) is chosen as the time scale for the numerical solution of the problem. In this scale, accordng to (1.1)-(1.4) and (2.1), the rate of change of the relative population density x_{v_i} due to the q-th relaxation channel is chosen proportional to the quantity

$$\gamma_j\frac{\tau_{VV}^{AA}(1,1)}{\tau_q^{ij}(n_i,n_j)}\Phi\left(\xi_0^{ij}\left|\frac{\omega_{v_i+n_i,v_i}}{\omega_{0i}} - W\frac{\omega_{v_j+n_j,v_j}}{\omega_{0j}}\right|\right). \tag{2.3}$$

It also depends on the population densities x_{v_i} and x_{v_j} and their gradients. Here $\tau_q^{ij}(n_i, n_j) \sim \left[Q_{n_i,0}^{0,n_j}(i,j)\right]^{-1}$ is the characteristic time of the q-th vibrational relaxation channel (of the process of transferring n_i quanta of oscillation type i to n_j quanta of oscillation type j).

Distributions of the type (2.2), with a constant C_i, which do not depend on the level number, and which are due to a single-quantum VV exchange within each of the components, are established on a time scale $\tau_{VV}^{ii}(1, 1)$ and are completed after a time $\tau = t/\tau_{VV}^{AA}(1,1) \leqslant 10^2$. This follows from special calculations which consider only single-quantum VV exchange (the rate constants of other possible processes are set to zero). In these calculations, the quantities $\delta_{v_i}(\tau)$ for the lower levels ($y_V < 0.25$) are determined from (2.2) by the relationship $\delta_{v_i} = \left[\ln\left(x_{v_i}/x_{0i}\right) + \varepsilon_{v_i}/kT\right]/v_i$. For $\tau > 10^2$, they do not depend on the level number v_i.

Under actual conditions, a fast single-quantum VV exchange process ($n_i = n_j = 1$) occurs in a background VV (n_i, $n_j > 1$), VV' (n_i, $n_j \gtrsim 1$), and (as a rule, single-quantum) VT exchange processes of a slower or similar rate. In particular, the slower VV' (n_i, $n_j \gtrsim 1$) exchanges (e.g. for a CO + O_2 mixture with W = 0.73), of which in this case (A = CO and B = O_2) the main process is a single-quantum one ($n_A = n_B = 1$), there is a "mixing" of the vibrational quanta. As a result, in times $\tau \gtrsim 10^4$, the distribution (2.2) with $C_A = C_B$ is established at the lower levels. This can be seen from Fig. 1, which shows the function $\delta_{v_i}(\tau)$ (solid curves) for complete calculation (including all processes) of the actual case of relaxation in a mixture A = CO and B = O_2 ($\gamma_A = 0.1$ and $\gamma_B = 0.9$), which corresponds approximately to fast cooling (T ≈ 500 K) of a mixture of heated molecular oxygen ($T_0^B \approx 2500$

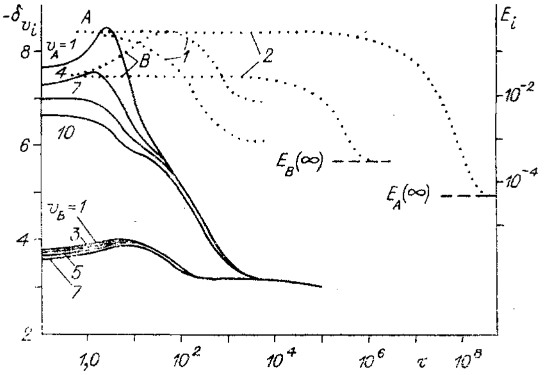

Fig. 1

K) and carbon monoxide with an inverse initial distribution (1.7) (m = 12 and ρ = 0.07), which is formed for example, as a result of a chemical reaction or of optical excitation.

As noted previously, the characteristic times for various processes can differ strongly. Namely such a situation is characteristic for the example in Fig. 1 ($CO + O_2$, $T \approx 500$ K). The quantities $\tau_q^{ij}(n_i, n_j)$ on a scale of $\tau_{VV}^{AA}(1,1)$ are as follows: $\tau_{VV}^{BB}(1,1) - 0.7$, $\tau_{VV'}(1,1) - 4\cdot10^2$, $\tau_{VT}^{AA} - 10^7$, $\tau_{VT}^{AB} - 2\cdot10^7$, $\tau_{VT}^{BA} - 7\cdot10^4$, $\tau_{VT}^{BB} - 10^5$). The dotted curves show the average vibrational energy (as a fraction of the dissociation energy) $E_i = \sum\limits_{v_i} y_{v_i} x_{v_i}$ for two variants of the calculation: 1) considers VV (n_A, $n_B \geq 1$) and VV' (n_A, $n_B \geq 1$) exchange (without considering VT exchange processes), and 2) considers only VT exchange processes. From Fig. 1 it can be seen that the VV (n_A, $n_B \geq 1$) and VV' (n_A, $n_B \geq 1$) processes occur after a time $\tau \sim 10^3$, and the VT process occurs after a time $\tau \sim 10^5$-10^6 for component A and $\tau \sim 10^8$ for component B.

If it is necessary to account correctly for processes with different time scales, there is a basic difficulty in the calculation; that is, the calculations must be done such that (on one hand) they are sufficiently accurate to follow the fast processes and (on the other that) they can proceed to large times on a scale for establishing total equilibrium. This difficulty is overcome within the framework of the double-sweep (modified Gaussian elimination) method by an approach whose essence is an alternation of a large time step (for the slow process) and a series of fine steps (for the fast process). Due to the extreme stability of the solution, a large error, which arises in the large time step, is decreased to an allowable value in the subsequent fine time steps of integration. The selection and sequence of steps in τ is given at the beginning of the calculation, starting from the value $\tau_q^{ij}(n_i, n_j)$.

3. Effect of Concentrations. In the general case, the mole fractions γ_i are important parameters on which depends the effective relaxation rate of the components. Thus, in the $CO + O_2$ system [16] for $T \simeq 1600$ K ($\tau_{VT}^{AA} \simeq \tau_{VT}^{AB} \simeq 2\cdot10^3$, $\tau_{VT}^{BB} \simeq \tau_{VT}^{BA} \simeq 65$) and $T_0^A = T_0^B \simeq 3600$ (a Boltzmann distribution (1.6) in both components), a change in the concentration of component $B = O_2$ from 0.01 to 0.5 decreases the effective relaxation time for the average energies by an order of magnitude.

Figure 2 shows the average energies E_A and E_B as a function of τ for A = CO, $B = O_2$, and $T \approx 500$ K [A has the initial distribution (1.7), m = 12, ρ = 0.07; B has the initial distribution (1.6), $T_0^B \approx 500$ K] for various concentrations: 1) $\gamma_A = 0.1$ and $\gamma_B = 0.9$; 2) $\gamma_A = 0.01$ and $\gamma_B = 0.99$; and 3) $\gamma_A = 10^{-4}$ and $\gamma_B = 0.9999$. The character of the relaxation depends especially strongly on the concentration when even a small number of high-energy molecules are added. Thus, for relaxation of a relatively small addition ($\gamma_A \gtrsim 10^{-3}$, see curves 1 and 2) of high-energy CO molecules (for example, those formed in the reaction $CS + O_2 \rightarrow CO^* + SO$) in relatively cold molecular oxygen, initially (for times $\tau \lesssim 10^2$), the VV' exchange process leads to the excitation of O_2, which in turn leads to a slowing of the CO relaxation in the subsequent ($\tau > 10^3$) near-equilibrium stage. Thus, in the example illustrated in Fig. 2 for times $\tau \sim 10^4$, the system goes into a very slowly relaxing quasistationary state (after time $\tau > 10^8$). In this case, for concentrations $\gamma_A \lesssim 10^{-4}$, the effect of excited additions of A on the vibrational state of gas B can be neglected; that is, the model of a small addition of nonequilibrium molecules into a Boltzmann thermostat [12, 17] is correct.

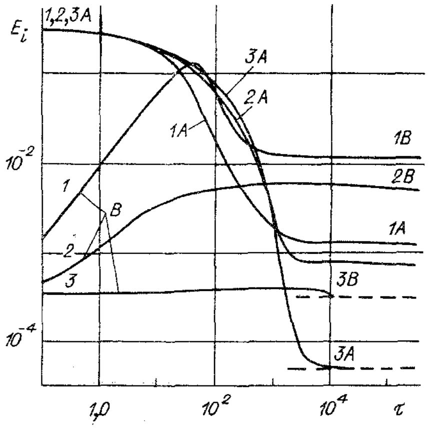

Fig. 2

4. Effect of Multiquantum Exchange Processes. According to (2.3), the maximum of one or another VV (VV') exchange process can mainly be expected in the excitation energy ranges which satisfy the relationship

$$\omega_{v_i+n_i}/\omega_{0i} - W\omega_{v_j-n_j,v_j}/\omega_{0j} = 0, \tag{4.1}$$

under conditions of large values of the corresponding quantities x_{v_i}. Equation (4.1) determines the level numbers v_i and v_j for resonance processes of the type (1.3). According to (4.1), the largest effect of the multiquantum (mainly two-quantum) VV' exchange processes should be expected for $W \approx 2^{\pm 1}$, and for $W \approx (1.5)^{\pm 1}$ in those cases, where there is significant excitation of the component with the smaller vibrational quantum. Thus, in a mixture A = CO and B = O_2 (W = 0.73), the process of two-quantum exchange (n_A = 1 and n_B = 2) occurs almost at resonance for v_A = 0-1 and v_b = 18-22, and in a mixture A = HCl and B = H_2 (W = 1.47), this is related to a VV' exchange process (n_A = 2 and n_B = 1) for v_B = 0-1 and v_A = 1-3. Thus, the effect of multiquantum exchange processes has different effects at different temperatures, concentrations, and initial conditions. Thus, in the previous case A = CO, B = O_2, T ≈ 1600 K, and $T_0^A = T_0^B \approx$ 3600 K [16], and also for cases 2 ($\gamma_A = 10^{-2}$) and 3 ($\gamma_A = 10^{-4}$) in Fig. 2, the multiquantum effect does not appear, which agrees completely both with what was discussed previously and with conclusions [17] obtained in the classical (continuum) approximation for a small admixture of excited molecules in a Boltzmann thermostat. Actually, in these cases there is no excitation of component B with a smaller quantum [in the first case T ≈ 1600 K due to intensive VT deactivation of component B) or it is relatively small (Fig. 2, curves 2 and 3) due to small γ_A. In the mixture A = CO and B = O_2, the effect of multiquantum exchanges appears with increasing γ_A, due to a large excitation of component B in the relaxation process (for $\tau > 10$); however, it has a purely quantitative character, and does not make a qualitative change in the relaxation process as a whole (see [16] for details).

A similar (quantitative) effect of the multiquantum VV' (and VV) exchange processes is illustrated in Fig. 3, which shows the function $E_i(\tau)$ (curve 1 is E_A and curve 2 is E_B) for the mixture A = HCl and B = H_2 (N_A = 28, N_B = 18, and W = 1.47) under conditions of vibrational and translational (equilibrium) temperatures ($T_0^A = T_0^B \approx$ 2500 K, T ≈ 500 K, $\xi_0^{AA} \approx 7.5$, $\xi_0^{AB} \approx 20$, $\xi_0^{BB} \approx 12$, $\gamma_A = 0.05$, and $\gamma_B = 0.95$), which correspond to conditions in a gas dynamic laser (see [18] for example). From Fig. 3 it can be seen that the effect of multiquantum VV' exchanges, which lead to an increase in E_{HCl} (compare curve 1), are small (insignificant initial excitations of components A and B, and intensive VT deactivation), and this effect is observed for relatively small times ($\tau \approx 10^3$).*

In the situation illustrated in Fig. 4 (A = CO, B = HF, and W = 1.9), multiquantum VV' exchanges completely determine the character of the relaxation of the mixture (compare curves 1 and 4.** In this case one of the components (A = CO) relaxes almost completely due

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*As applied to gas dynamic laser conditions, these are nozzles of small diameters with characteristic flow times $\tau_g \lesssim 10^3 \cdot \tau_{VV}^{AA}$ (1, 1).

**Curves 4 of Fig. 4 correspond to a calculation that only considers the single-quantum exchange process ($n_A = n_B = 1$).

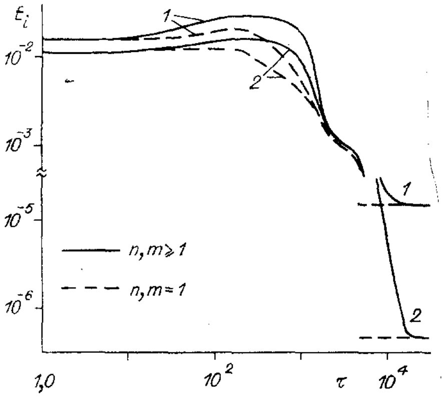

Fig. 3

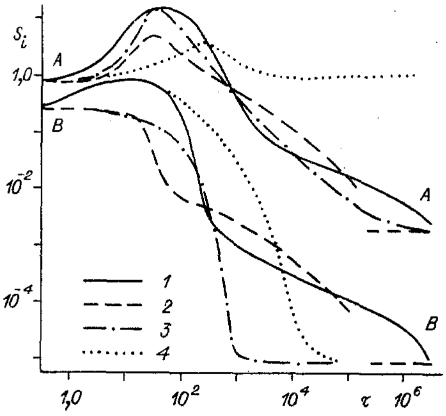

Fig. 4

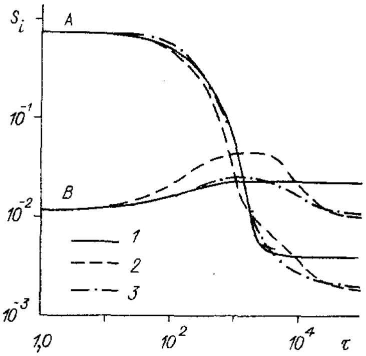

Fig. 5

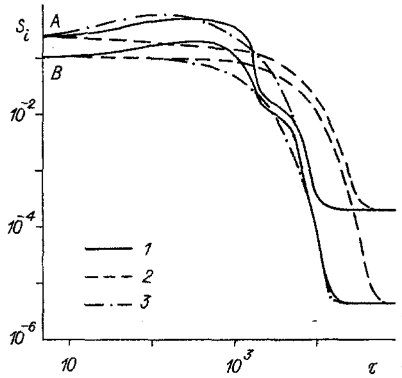

Fig. 6

to a multiquantum exchange with the other component (B = HF), which in turn has an inverse effect on the relaxation process of component B, accelerating it in the initial stage ($\tau \lesssim 10^3$) and decelerating it in the near-equilibrium stage ($\tau \lesssim 10^6$).

5. Macroscopic Description of Vibrational Relaxation in a Binary Mixture of Diatomic Molecules. As noted previously, macroscopic descriptions of vibrational kinetics are widely used in kinetic calculations of multicomponent systems. These descriptions use equations for the average energies (or the average number of vibrational quanta of the components (vibrational modes), which are modeled by harmonic oscillators. Within the framework of the diffusional approximation, this is Eq. (1.5). Below we present several results of comparing the microscopic [Eqs. (1.1), (1.2), and (1.4)] and macroscopic [Eq. (1.5)] descriptions of the vibrational kinetics in a binary mixture of diatomic molecules. For a comparison characteristic, we use the magnitude of S_i, the average number of vibrational quanta in the i-th component of the mixture. For anharmonic oscillators $S_i = \sum_{v_i} v_i x_{v_i}$, as a result of solving Eqs. (1.1), but for harmonic oscillators $S_i \equiv E_i$ as a result of solving Eqs. (1.5). The corresponding functions $S_i(\tau)$ are shown in Figs. 4-6, where curves 1 correspond to the solution of Eqs. (1.1) and 2 to the solution of Eqs. (1.5). Overall, the correspondence of curves 1 and 2 can be described only as qualitative (Fig. 4: 90% CO + 10% HF, $T_0^A = 3500$ K, $T_0^B \simeq 3500$ K, and $T \simeq 500$ K; Fig. 5: 1% CO + 99% O_2, $T_0^A = 3500$ K, $T_0^B \simeq 500$ K, and $T \simeq 500$ K; Fig. 6: 5% HCl + 95% H_2, $T_0^A = T_0^B \simeq 2500$ K, and $T \simeq 500$ K). This correspondence can be improved and brought to an approximate quantitative agreement at specific stages or for the whole process by introducing into the calculation constant corrections $\alpha_q^{(i)}$ (i is the component, and q is the relaxation channel) to the rate constants (characteristic times) for processes which approximately consider the effect of anharmonicity (averaged over time). These calculations are shown in Figs. 4-6 by curves 3 (Fig. 4: $\alpha_{VT}^{(B)} = 90$, $\alpha_{VV}^{(B)} = 10^5$, $\alpha_{VV'}^{(A)} = 1.2$, $\alpha_{VV'}^{(B)} = 10^{-3}$; Fig. 5: $\alpha_{VV'}^{(A)} = 0.8$, $\alpha_{VV'}^{(B)} = 0.33$; Fig. 6: $\alpha_{VT}^{(B)} = 9$, $\alpha_{VV}^{(A)} = 3$, $\alpha_{VV}^{(B)} = 1.4 \cdot 10^4$, $\alpha_{VV'}^{(A)} = 3$, $\alpha_{VV'}^{(B)} = 0.05$).

However, a macroscopic parametric method of calculating anharmonicity as a whole is limited to either the simplest system compositions (for example a small admixture to a Boltzmann thermostat) or to systems with a relatively low vibrational excitation [$S_i(0) \lesssim 1.0$].

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LITERATURE CITED

1. E. E. Nikitin and A. I. Osipov, "Vibrational relaxation in gases," in: Advances in Science and Technology, Kinetics and Catalysts Series [in Russian], Vol. 4, VINITI [All-Union Institute of Scientific and Technical Information of the State Committee of the Council of Ministers, USSR, for Science and Technology and of the Academy of Sciences USSR] (1977).
2. Sh. S. Mamedov, "Methods of vibrational kinetics and their application to molecular lasers and laser chemistry," in: Molecular Kinetics, Molecular Lasers, and Laser Chemistry, Trans. P. N. Lebedev Physics Institute of the Academy of Sciences, USSR [in Russian], Vol. 107 (1979), p. 3.
3. B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, Kinetic Processes in Gas and Molecular Lasers [in Russian], Nauka, Moscow (1980).
4. E. R. Fisher and R. H. Kummler, "Relaxation by vibration—vibration exchange. Part II, Binary Mixtures," J. Chem. Phys., 49, No. 4 (1968).
5. A. A. Likal'ter, "Vibrational relaxation in strongly excited molecular mixtures," Teplofiz. Vys. Temp., 17, No. 5 (1979).
6. S. A. Zhdanok, R. I. Soloukhin, and S. M. Khizhnyak, "Analytic theory of the CO gas dynamic laser and its application to analyzing gas dynamic methods of obtaining inversion in carbon monoxide," Preprint No. 7 [in Russian], A. V. Lykov Institute of Heat and Mass Transfer of the Academy of Sciences, Belorussian SSR, Minsk (1985).
7. B. F. Gordiets, Sh. S. Mamedov, and L. A. Shelepin, "Vibrational kinetics of anharmonic oscillators under highly nonequilibrium conditions," Zh. Tekh. Fiz., 67, No. 4 (1974).
8. B. F. Gordiets and Sh. S. Mamedov, "Separating isotopes in chemical reactions of vibrationally excited molecules," Kvantavaya Élektron., 2, No. 9 (1975).
9. U. S. Dzhurabekov, A. I. Osipov, and V. Ya. Panchenko, "Kinetics of multiquantum vibrational exchange in molecular gases and its appearance in the process of kinetic cooling," in: Chemical Physics of Combustion and Explosion, Kinetics of Chemical Reactions, Proc. 8th All-Union Symposium on Combustion and Explosion, Tashkent (1986) and Chernogolovka (1986).
10. O. V. Skrebkov, "Diffusion description of vibrational relaxation in binary mixtures of diatomic molecules—quantum oscillators," Prikl. Mekh. Tekh. Fiz., No. 6 (1987).
11. M. N. Safaryan and O. V. Skrebkov, "Comparison of the results of classical-diffusion and quantum calculations of vibrational—translational relaxation of diatomic molecules," Prikl. Mekh. Tekh. Fiz., No. 4 (1978).
12. V. M. Volokhov and O. V. Skrebkov, "Classical-diffusion and quantum calculations of vibrational—translational relaxation in binary mixtures of diatomic molecules—anharmonic oscillators," Khim. Fiz., 3, No. 2 (1984).
13. V. M. Volokhov, M. N. Safaryan, and O. V. Skrebkov, "Diffusion description of vibrational relaxation of anharmonic oscillators in a two-component system," Teor. Éksp. Khim., 14, No. 4 (1978).
14. O. V. Skrebkov and A. L. Smirnov, "Effect of rotation on the energy exchange process of diatomic molecules — of an anharmonic oscillator with an atom," Preprint [in Russian] of the Department of the Institute of Chemical Physics of the Academy of Sciences USSR (1988).
15. V. M. Volokhov and O. V. Skrebkov, "Consideration of noncollinearity of collisions and long-range attraction in the diffusion of vibrational relaxation," Khim. Fiz., No. 11 (1983).
16. O. V. Skrebkov, Z. G. Vakina, and V. M. Vasil'ev, "Vibrational relaxation in a binary mixture of diatomic molecules; quantum (discrete) diffusion model," in: Chemical Physics of Combustion and Explosion, Kinetics of Chemical Reactions, Proc. 8th All-Union Symposium on Combustion and Explosion, Tashkent (1986) and Chernogolovka (1986).
17. V. M. Volokhov and O. V. Skrebkov, "Vibrational relaxation of diatomic molecules — anharmonic oscillators in a Boltzmann thermostat, two-component system," Prikl. Mekh. Tekh. Fiz., No. 5 (1982).
18. V. A. Vostryakov, I. P. Kirmusov, and A. M. Starik, "Numerical modeling of the effect of the supersonic nozzle on the generation spectrum and energetic characteristics of a HCl gas dynamic laser," Academic seminar "Fundamental Problems of Shock Wave Physics"

[in Russian], Azau (1987); Abstracts of an All-Union Seminar, Vol. 1, Part II. Chernogolovka (1987).

A GAS EJECTOR SYSTEM AND A DIFFERENTIAL EJECTOR

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1. Introduction. A theoretical investigation is conducted on the efficiency of using a system of gas ejectors with cylindrical mixing chambers and the limiting case of this system – the differential ejector. Mixing is examined for gases with equal stagnation temperatures and identical physical characteristics. The process of mixing gases in a differential ejector was first investigated in [1], where an error in the solution of the system of equations led to the loss of one condition of optimizing each stage of the differential ejector.

Here this error is corrected and the solution to the problem of a differential ejector is presented.

The transition from a single-stage ejector with a cylindrical mixing chamber to a system of sequential ejectors with cylindrical mixing chambers (Fig. 1) can improve the characteristics of a single stage ejector. The improvement is possible for two reasons. First, the differential mixing process can prolong the formation of the critical regime [1-3], which leads to a more efficient operation of the ejector. Second, differentiation increases the number of variable parameters in the ejector design, which can improve the efficiency of the mixing process. Here we investigate the effect only of the last factor; that is, it is assumed that the critical regime does not prevent optimization of the mixing process in each of the ejectors of the system. This approach is correct, because the effect of forming the critical regime is practically uncoupled with the ejector design specifics [1].

2. Optimization Criteria for a Single-Stage Ejector. We will examine mixing in an ejector with a cylindrical mixing chamber for two gases with identical physical characteristics c_p, κ, and stagnation temperature T_0. The total pressures are p_{01} and p_{02}; the mass flow rates are G_1 and G_2, where $p_{01} < p_{02}$. The gases are totally mixed in the chamber and there are no losses. In this case, the laws of conservation of mass flows, momenta and energies for a cylindrical mixing chamber are [4]

$$p_{0m}=\frac{1}{q(\lambda_m)\left(\frac{\gamma_1}{p_{01}q(\lambda_1)}+\frac{\gamma_2}{p_{02}q(\lambda_2)}\right)}; \tag{2.1}$$

$$z(\lambda_m)=\gamma_1 z(\lambda_1)+\gamma_2 z(\lambda_2), \tag{2.2}$$

where $z(\lambda)=\lambda+1/\lambda$, $q(\lambda)=\lambda\left(1-\frac{\varkappa-1}{\varkappa+1}\lambda^2\right)^{1/(\varkappa-1)}$, $\gamma_1=G_1/(G_1+G_2)$; $\gamma_2=G_2/(G_1+G_2)$, and p_{0m} is the total pressure of the gas mixture. From Eq. (2.2) it follows that for given values of the reduced velocities λ_1 and λ_2 there are two values of the reduced velocity of the gas mixture λ_m. One of these corresponds to the subsonic velocity of the gas mixture ($\lambda_m = \lambda_{m\ell} < 1$) and

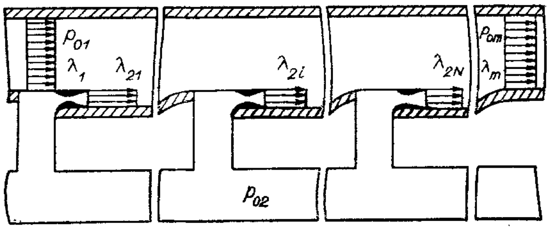

Fig. 1

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