SOVIET PHYSICS JETP VOLUME 35, NUMBER 2 AUGUST, 1972

Theory of Relaxation and Transfer Processes in Molecular Gases II

L. I. Podlubnyi

Moscow Power Institute

Submitted July 11, 1971

Zh. Eksp. Teor. Fiz. **62**, 593–605 (February, 1972)

The contribution of vibrational and rotational transitions to the kinetic coefficients is calculated for polyatomic gases and molecular mixtures. The general generating function for the kinetic coefficients can be expressed in the impulse approximation in terms of correlation functions which describe the translational and internal motion of the colliding molecules. The vibrational and rotational relaxation times and shear viscosity coefficient are obtained for diatomic and polyatomic molecules.

In an earlier paper[1] (referred to as I throughout) we proved the compactness of the arrival term of the inelastic-collision integral of diatomic molecules with structureless particles, and considered the question of perturbation of the spectrum of the Boltzmann integral operator when account is taken of the inelastic collisions. In the impulse approximation, the form of the spectrum and the eigenvalues of the Boltzmann operator are determined by the type of the pseudopotential V and the values of the parameters that specify the function V = V(r). The characteristic features of the behavior of the pseudopotential V(r) can be explained by calculating, with the aid of a corresponding collision integral (see I, formula (2.1)), the rate of inelastic energy loss, the viscosity, the thermal conductivity, and other kinetic coefficients in high-temperature molecular mixtures and by comparing the results with experiment.

1. GENERATING FUNCTION FOR THE KINETIC COEFFICIENTS. ALLOWANCE FOR ROTATIONAL TRANSITIONS

The problem of calculating the kinetic coefficients with allowance for the inelastic collisions was considered many times by many authors (see the reviews[2,3]). Usually, a joint analysis of the kinetic equations for the distribution functions and of the balance equations for the populations[1)] is used first to construct a general theory of the relaxation and transport processes, in which the kinetic coefficients are expressed in terms of the cross sections for elastic and inelastic collisions. Only then are the cross sections, rate constants, and kinetic coefficients calculated with the aid of quantum-mechanical or classical methods. For rarefied systems with weak nonequilibrium, the kinetic part of the problem was solved by the Chapman-Enskog method by Wang-Chang and Uhlenbeck (see, for example,[4]) and also by Zhdanov[5], who used the Grad method[5]. The kinetic coefficients for a diatomic nonisothermal gas were calculated by Kuznetsov[6]. The present author (see[7] considered, using the method of correlation functions with allowance for rotational transitions, the kinetics of electrons in a nonisothermal molecular plasma without first calculating the probabilities of the elementary processes. By an analogous method it is possible to express any kinetic coefficient in terms of the correlator of the collision operator, which contains only the collision potential and the internal potential (for structural particles). In the case of dense media, general expressions of this type were obtained, with allowance for elastic collisions only, for the diffusion, viscosity, etc. (see[8]). Irreversible processes with allowance for inelastic collisions were considered recently by Pokrovskiĭ[9] and Peletminskiĭ[10].

For rarefied systems, the linearized collision integral and the kinetic coefficients are determined by equilibrium two-particle correlation functions that describe the internal and translational degrees of freedom (see I and[7]). In this case, different kinetic coefficients L (obtained, for example, in[4]) can be expressed in terms of a general generating function Z:

$$L = \hat{L}Z(\mathbf{x}, \mathbf{y}, u_1, \ldots, u_N, s_1, \ldots, s_N),$$

$$Z = \int_{-\infty}^{\infty} dt \left\langle \exp\left(i\mathbf{x}\hat{\mathbf{p}} + i\sum_{j=1}^{N} u_j\hat{H}_j\right)\hat{\tau}(t)\exp\left(-i\mathbf{y}\hat{\mathbf{p}} - i\sum_{j=1}^{N} s_j\hat{H}_j\right)\hat{\tau}^*(0)\right\rangle$$

$$\hat{L} = L(\nabla_x,\ \nabla_y,\ \partial/\partial u_1, \ldots, \partial/\partial s_N). \tag{1.1}$$

In (1.1), $N = 3(N_1 + N_2) - 6$ is the total number of vibrational and rotational degrees of freedom of the colliding polyatomic molecules[2)]. To each kinetic coefficient there corresponds a separate operator $\hat{L}$. For example, the number of collisions is determined by the quantity $Z|_0$; for the rate of the inelastic energy loss we have

$$L_j = -i(\partial/\partial u_j + \partial/\partial s_j)_0 Z = \int_{-\infty}^{\infty} dt\langle[\hat{H}_j\hat{\tau}(t)]\hat{\tau}^*(0)\rangle; \tag{1.2}$$

and for the rate of the elastic loss $\hat{L}_\epsilon = (\nabla_x^2 - \nabla_y^2)/2\mu$; for the shear-viscosity coefficient (see[4,11])

$$\frac{1}{\eta} \sim \sum_{\alpha\alpha'}\int d^3p\, d^3p' N_\alpha f(p) W_\alpha{}^{\alpha'}(\mathbf{p}, \mathbf{p}')\,[p^4\sin^2\theta$$

$$+ {}^2/{}_3 p^2(1 - {}^3/{}_2\sin^2\theta)(\varepsilon_{\alpha'} - \varepsilon_\alpha)] \tag{1.3}$$

we can easily obtain

$$\hat{L}_\eta \sim {}^2/{}_3\Delta_x^2 + {}^1/{}_3\Delta_x\Delta_y - (\nabla_x\nabla_y)^2. \tag{1.3'}$$

It is possible to consider analogously the bulk viscosity ($\sim \overline{\Delta\epsilon^2}$) the thermal conductivity, the thermal diffusion,

---

[1)] With respect to the internal degrees of freedom, the system is more frequently considered to be in local equilibrium.

[2)] The system of units and the notation in (1.1) and throughout this paper (unless specially stipulated) coincide with those of I and [7].

etc. For various concrete kinetic coefficients it is possible to use for the generating function Z a less general expression than (1.1), but one that is more convenient for practical calculations (see Sec. 3).

In the pseudopotential approximation

$$\hat{\tau} = \sum_{\nu=1}^{N_1}\sum_{n=1}^{N_2} V_{\nu n}$$

and for a nonisothermal system (the translational temperatures of the colliding molecules are T and T′, the rotational ones T_r and T'_r, and the vibrational ones T_v and T'_v) the function Z is determined by a correlator product of the type

$$\langle \exp(iu_j\hat{H}_j)\exp(i\mathbf{q}\mathbf{r}_j(t))\exp(-is_j\hat{H}_j)\exp(-i\mathbf{q}\mathbf{r}_j)\rangle_{Tj} = \Phi_{\beta_j}(q, t+s_j),$$

$$\beta_j = i(s_j - u_j) + 1/T_j; \tag{1.4}$$

The correlation functions $\Phi_\beta(q, t)$ were calculated in I (see also[7]). For the correlation function describing the relative motion with a "reduced" translational temperature $\overline{T} = \mu(T/M_1 + T'/M_2)$, we can easily obtain

$$\Phi_{\overline{T}}(q,t) = \langle \exp(i\mathbf{x}\hat{\mathbf{p}})\exp(i\mathbf{q}\mathbf{R}(t))\exp(-i\mathbf{y}\hat{\mathbf{p}}) \cdot\exp(-i\mathbf{q}\mathbf{R})\rangle_{\overline{T}} = \exp[-{}^1\!/_2 q^2(it+t^2\overline{T})/\mu - {}^1\!/_2\mu\overline{T}(\mathbf{x}-\mathbf{y})^2 - i\mathbf{q}\mathbf{y} - t\overline{T}\mathbf{q}(\mathbf{x}-\mathbf{y})], \tag{1.5}$$

where $\mu = M_1M_2/(M_1 + M_2)$. We finally obtain for the generating function

$$Z(\mathbf{x}, \mathbf{y}, \ldots) = \sum_{\nu=1}^{N_1}\sum_{n=1}^{N_2}\int d^3q\, dt\, |V_{\nu n}(q)|^2 \Phi_{\overline{T}} \times\left\langle \Phi_{\beta_r}\Phi_{\beta_{r'}} \sum_{v=1}^{v_m}\Phi_{\beta_v}\prod_{v'=1}^{v_m'}\Phi_{\beta_{v'}}\right\rangle_{\Omega_1\Omega_2}. \tag{1.6}$$

For linear molecules ($v_m = 3N_1 - 5$) and for spherical-top molecules ($v_m = 3N_1 - 6$) we obtain in the reciprocal-mass-tensor approximation

$$\Phi_{T_r}(q,t) = \exp[-{}^1\!/_2 a_\nu^2 I_1^{-1} q^2(1-z_1^2)(it + t^2T_r)]; \tag{1.7}$$

here $z_1 = \cos\theta_1$, a_ν is the distance between the ν-th atom and the center of inertia of the molecule, and I_1 is the moment of inertia of the molecule.

We shall consider throughout homonuclear molecules and also centrally-symmetrical molecules of the type XY_4 (tetrahalides with X = C, Si, Ge, Sn and Y = Cl, Br, F, and I) and XY_6 (hexafluorides, for example sulfur hexafluoride SF_6, uranium hexafluoride UF_6), which consist of identical atoms of mass $M_Y = m$ (the central atom M_X does not take part in the collisions). We note that to calculate the probabilities of the elementary processes and of the corresponding transport coefficients one uses, as a rule, not realistic models, but rough classical approximations such as loaded and rough spheres, sphero-cylinders, etc. (see[3,11]). Even for the simplest models where the molecules are regarded as rigid bodies, calculation of the collision integral and of the kinetic coefficients is quite complicated (considerable difficulties arise, in particular, when it comes to choosing the integration region, see, for example,[12]) and it is hardly possible to obtain the generating functions, whereas the proposed approach takes into account the spatial geometry of real molecules and requires less labor.

To calculate the time of rotational relaxation in a mixture of rigid-rotator molecules it is necessary to use the generating function

$$Z(u_1,u_2) = \int_{-\infty}^{\infty} dt\langle\exp[i(u_1\hat{H}_1 + u_2\hat{H}_2)]\hat{\tau}(t)\exp[-i(u_1\hat{H}_1+u_2\hat{H}_2)]\hat{\tau}^*(0). \tag{1.8}$$

From expansions of the type (see also[7])

$$Z(0,0) = \sum_{\alpha\alpha'} N_\alpha k_\alpha^{\alpha'} = \int d^3p\, d^3p'\, f(p)\, W(\mathbf{p},\mathbf{p}') \tag{1.8′}$$

we can obtain the probabilities of the inelastic transitions $\alpha\mathbf{p} \to \alpha'\mathbf{p}'$, the moments of different orders of the inelastic energy losses, etc. Thus, for the nonisothermal rate constant ($T \neq T'$) we easily obtain[3)]

$$k_\alpha^{\alpha'} = \sum_{\nu,n}\int d^3q\, dt\, |V_{\nu n}(q)|^2 \times|(\exp[i\mathbf{q}(\mathbf{R}_\nu - \mathbf{R}_n)])_{\alpha\alpha'}|^2\exp\left[-\frac{q^2}{2\mu}(it+t^2\overline{T}) + it(\varepsilon_\alpha - \varepsilon_{\alpha'})\right]. \tag{1.9}$$

It is impossible to carry out the summation in (1.8) and (1.8′) with exact rate constants and corresponding rotational correlators. We shall therefore use the mass-tensor approximation (1.7). In the case of rotational relaxation in a nonisothermal mixture ($T \neq T' \neq T_r$) of structureless hard-sphere molecules and rigid-rotator molecules we have for the generating function

$$Z(u) = Z_0\left\langle\frac{(1+\mu\alpha T_r/\overline{T})^{1/2}}{(1+\mu\alpha)^2 + 4iu\mu\alpha(\overline{T}-T_r)/\overline{T} + 4u^2\mu\alpha T_r/\overline{T}}\right\rangle_\Omega. \tag{1.10}$$

Here

$$\alpha q^2 = q\rho q = (\rho_1\sin^2\theta\cos^2\varphi + \rho_2\sin^2\theta\sin^2\varphi + \rho_3\cos^2\theta)q^2, \tag{1.11}$$

$Z_0 = Z(0)$ and ρ_i are the components of the reciprocal mass tensor ρ (see I) in the diagonal representation.

For the rate of energy loss we obtain from (1.10)

$$-\overline{\frac{d\hat{H}_r}{dt}} = 4\mu Z_0\Delta T\left\langle\frac{\alpha(1+\mu\alpha T_r/\overline{T})^{1/2}}{(1+\mu\alpha)^4}\right\rangle_\Omega. \tag{1.12}$$

In the case of linear molecules and spherical-top molecules ($\rho_1 = \rho_2 = a^2/I$, $\rho_3 = 0$) we obtain from (1.12)

$$\frac{1}{\tau_r} = 4\frac{\gamma Z_0}{C_r}\int_0^1 dz\frac{(1-z^2)[1+\gamma(1-z^2)T_r/\overline{T}]^{1/2}}{[1+\gamma(1-z^2)]^4}, \tag{1.13}$$

$\gamma = \mu a^2/I$ and C_r is the rotational specific heat. In particular, for $\gamma \ll 1$ (relaxation of heavy molecules in a light thermostat) we have

$$1/\tau_r = (8\gamma Z_0/3C_r)\left[1 + \frac{16}{5}\gamma(T_r/8\overline{T} - 1)\right] + 0(\gamma). \tag{1.14}$$

In the case of molecules of the XY_4 or XY_6 type, we have respectively $\gamma = 3\mu/8m$ and $\mu/4m$, and for the number of rotational collisions we have $Z_{rot} = Z_0\tau_r \sim m/\mu \gg 1$.

For a nonisothermal mixture, the integration in (1.13) leads to a cumbersome algebraic expression, which becomes much simpler if $T_r = \overline{T}$. Namely,

---

[3)] For nonrigid rotators it is necessary to introduce in (1.9) the product of oscillator correlation functions from (1.6); in the isothermal case a formula of the type (1.9) was used in[13] to calculate the Born rate constants of transitions between strongly excited states of hydrogen atoms in collisions with electrons.

$$1/\tau_r = 8Z_0\gamma(\gamma+5)/15C_r(\gamma+1)^3. \tag{1.15}$$

For example, for He + O_2 we have $Z_r = Z_0\tau_r \approx 4$; experiment yields (see the review[14]) $Z_r \sim 2$.

In a rigid-rotator molecule mixture it is also necessary to take into account the transfer of excitation (and the simultaneous excitation (quenching) of the two colliding molecules). It is necessary to use the generating function (1.8) for this purpose. In analogy with (1.10) we obtain (we consider for simplicity the case $T_r = \overline{T}$)

$$Z(u_1, u_2) = Z_0\left\langle \frac{(1+\mu\alpha_1+\mu\alpha_2)^{1/2}}{(1+\mu\alpha_1+\mu\alpha_2)^2+4\mu^2\alpha_1\alpha_2(u_1-u_2)^2+4\mu(\alpha_1u_1^2+\alpha u_2^2)}\right\rangle_{\Omega_1\Omega_2} \tag{1.16}$$

The rotational-relaxation time is

$$\frac{1}{\tau_r} = 4\frac{\mu Z_0}{C_r}\left\langle \frac{\alpha_1+\mu\alpha_1\alpha_2}{(1+\mu\alpha_1+\mu\alpha_2)^{7/2}}\right\rangle_{\Omega_1\Omega_2}. \tag{1.17}$$

After averaging over the angle variables we obtain a final expression for the time of rotational relaxation in the case of linear and spherical molecules:

$$\frac{1}{\tau_r} = 4\frac{\gamma_1 Z_0}{C_r}\iint_0^1 dz\, dz_1 \frac{(1-z^2)[1+\gamma_2(1-z_1^2)]}{[1+\gamma_1(1-z^2)+\gamma_2(1-z_1^2)]^{7/2}}, \tag{1.18}$$

$\gamma_{1,2} = \mu a_{1,2}^2/I_{1,2}$. For a pure rotator-molecule gas we have[4]

$$\frac{1}{\tau_r} = \frac{4Z_0}{15C_r(1+2\gamma)^2}\left[\frac{3\gamma^2-\gamma-2}{(1+\gamma)^2} + \frac{11\gamma^2+11\gamma+2}{\gamma(1+2\gamma)^{1/2}}\operatorname{arctg}\frac{\gamma}{(1+2\gamma)^{1/2}}\right]. \tag{1.19}$$

In the case of XY_4 molecules, the parameter $\gamma = 3/4 + 3M_X/16m$ and, for example, $Z_r \approx 22$ for CH_4 and $Z_r \approx 6$ for CF_6. The experimental values of Z_r are (see[14,15]) 9–17 for CH_4 and ~3 for CF_4. In a pure gas of homonuclear molecules $\gamma = 1/2$ and $Z_r = 5$ (experiment[14] yields approximately 2–10) for N_2 and O_2. For SF_6 the parameter is $\gamma = 3/4 + M_X/8m$ and $Z_r \approx 6$ (experiment yields ~2.5). Taking into account the considerable scatter of the experimental data, the agreement should be regarded as satisfactory.

2. VIBRATIONAL RELAXATION

We consider in this section collisions of simple particles (n_1, M_1, T) with molecules (n_2, M_2, T', T_V, T_r). According to I, the number of collisions is equal to

$$Z_{12} = n_2\int_{-\infty}^{\infty} dt\langle\hat{\tau}_{12}(t)\hat{\tau}_{12}^*(0)\rangle = \frac{Z_0}{8\pi^{3/2}}\int d^3q\, dt \exp[-q^2(it+t^2)]\int_0^1 dzF;$$

$$F = \exp[-\gamma q^2(1-z^2)(it+t^2T_r/\overline{T}) - {}^1/_2\gamma q^2z^2\Gamma(t)],$$

$$\Gamma(t) = \varphi^{-1}\operatorname{cth}(\varphi\overline{T}/T_v)(1-\cos 2\varphi t) + i\varphi^{-1}\sin 2\varphi t, \tag{2.1}$$

$\varphi = \omega/2\overline{T}$ and $\gamma = \mu/M_2$. The normalization in (2.1) satisfies the condition $Z_{12} = Z_0$ and F = 1 (collisions of structureless particles).

In I we used instead of the colliding-particle interaction potential an equivalent pseudopotential chosen such that exact scattering by the true potential coincided with the Born approximation for the pseudopotential. In particular (2.1) corresponds to a pseudopotential V(r) ~ δ(r), which leads to isotropic scattering with an amplitude independent of the momentum transfer, ~V(q) = const (hard-sphere collisions). The pseudopotential $V(q) \sim \exp(-x_0q^2/2)$ used in I, which is the simplest generalization of a δ potential to the case of nonisotropic scattering, can be regarded as a consequence of the "smearing" of the δ potential:

$$\delta(r) = \lim_{R_0\to 0}(\pi R_0^2)^{-3/2}\exp(-r^2/R_0^2).$$

In the general case (see I)

$$|V(q)|^2 \sim \int dx\, v(x)e^{-xq^2}$$

and

$$Z_{12} = \frac{Z_0}{8\pi^{3/2}}\int dx\, v(x)\int d^3q\, dt\exp[-q^2(it+t^2+x)]\int_0^1 dz\, F\Big/\int\frac{dx\, v(x)}{1+4x}. \tag{2.2}$$

The pseudopotential in (2.2) is so normalized that we have $Z_{12} = Z_0$ at F = 1, and when v(x) = δ(x) (hard-sphere collisions) Eq. (2.2) goes over into (2.1). We confine ourselves below to the simplest Gaussian pseudopotential with $v(x) = \delta(x - x_0)$, for which

$$Z_{12} = \frac{1+4x_0}{8\pi^{3/2}}Z_0\int d^3q\, dt\exp[-q^2(it+t^2+x_0)]\int_0^1 dz\, F, \tag{2.2'}$$

$x_0 = \mu\overline{T}R_0^2$. In the limit as $R_0 \to 0$ and $x_0 \to 0$ we have (2.1) as before; when $R_0 \neq 0$ the factor $x_0 \neq 0$ is, generally speaking, an empirical parameter (see below).

The procedure for calculating integrals of the type (2.2) was discussed in detail in I[5]. As a result of the integration we obtain

$$Z_{12} = Z_0\frac{1+4x_0}{2\gamma}\varphi\operatorname{sh}\left(\varphi\frac{\overline{T}}{T_v}\right)\overline{T}^{1/2}\int_0^1\frac{dz}{z^2[\overline{T}+\gamma(1-z^2)T_r]^{1/2}}$$

$$\times\left\{[a_1(a_1+2)]^{-1/2} + \sum_{\Delta=1}^{\infty}F_\Delta\operatorname{ch}(A\varphi\Delta)\right\},$$

$$F_\Delta = -4\frac{d}{da_1}[K_\Delta(X_+\Delta)I_\Delta(X_-\Delta)], \qquad X_\pm = (a_1a_2+2a_2)^{1/2}\pm(a_1a_2)^{1/2},$$

$$A = \frac{\overline{T}-T_v+(T_r-T_v)\gamma(1-z^2)}{\overline{T}+T_r\gamma(1-z^2)},$$

$$a_1 = \frac{[1+\gamma(1-z^2)]^2T_v\varphi\operatorname{sh}(\varphi\overline{T}/T_v)}{2\gamma z^2[\overline{T}+\gamma(1-z^2)T_r]} + 2\frac{x_0\varphi}{\gamma z^2}\operatorname{sh}\left(\varphi\frac{\overline{T}}{T_v}\right)$$

$$+\operatorname{ch}\left(\varphi\frac{\overline{T}}{T_v}\right) - 1,\quad a_2 = \frac{\gamma\varphi T_v}{2[\overline{T}+\gamma(1-z^2)T_r]\operatorname{sh}(\varphi\overline{T}/T_v)}, \tag{2.3}$$

where K and I are Bessel functions of imaginary argument.

The first term in the curly brackets of (2.3) describes elastic collisions (Δ = 0) between structureless particles and oscillator-molecules in the ground and ex-

---

[4] We note that in the case of centrally-symmetrical molecules at different ratios of the masses of the central and surface atoms, the parameters $1/2\gamma = I/Ma^2$ varies within the same limits as the analogous parameter $K = 4I/Md^2$ in the rough-sphere model (for different radial distributions of the sphere density $0 \le K \le 2/3$; d is the diameter of the molecule). The dependence of τ_r (of η—see Sec. 3—and of other kinetic coefficients) on γ differs, of course, from the classical model of rough-sphere molecules (see[3,11]).

[5] In the expressions given in I for F and Φ, the factor 1/2 for Γ was left out (see formulas (2.4) and (2.5) of I), so that the substitution $\gamma z^2 \to \gamma z^2/2$ must be made in the corresponding formulas of Secs. 2 and 3 of I.

cited vibrational states. The number of such collisions Z_0' in the important practical case of an isothermal ($T_r = \overline{T} = T_v$) molecular mixture at $\varphi^2 \ll 1$, $\gamma \ll 1$, but $\varphi^2/\gamma \sim 1$, is

$$Z_0' \approx Z_0 \cdot 2^{-1/2} f \int_0^1 \frac{dz}{(z^2 + f^2/2)^{1/2}} = Z_0 \cdot 2^{-1/2} f \ln\left[\frac{2^{1/2}}{f} + \left(1 + \frac{2}{f^2}\right)^{1/2}\right],$$

$$f = \varphi\left(\frac{1 + 4x_0}{2\gamma}\right)^{1/2}. \tag{2.4}$$

For the rate of loss of the vibrational energy we obtain in analogy with (2.1)—(2.3) (see (1.2) with u = s)

$$-\overline{\frac{d\hat{H}}{dt}} = 2Z_0 \overline{T} f^2 \operatorname{sh}\left(\varphi \frac{\overline{T}}{T_v}\right) \int_0^1 \frac{dz}{z^2[1 + \gamma(1 - z^2) T_r/\overline{T}]^{1/2}}$$

$$\times \sum_{\Delta=1}^{\infty} F_\Delta \Delta \operatorname{sh}(A\gamma\Delta). \tag{2.5}$$

In particular, in the isothermal limit A → 0 and the vibrational-relaxation time

$$\frac{1}{\tau} = \frac{1}{C_v \Delta T} \overline{\left(-\frac{d\hat{H}}{dt}\right)} = \frac{\overline{\Delta\varepsilon^2}}{2C_v T^2} \tag{2.6}$$

is given by ($C_V = \varphi^2/\sinh^2\varphi$ is the specific heat)

$$\frac{1}{\tau} = \sum_{\Delta=1}^{\infty} \frac{1}{\tau_\Delta}, \quad \frac{1}{\tau_\Delta} = 2Z_0 \Delta^2 \frac{f^2}{\varphi} \operatorname{sh}^3 \varphi \int_0^1 \frac{dz\, F_\Delta}{z^2[1 + \gamma(1 - z^2)]^{1/2}}. \tag{2.7}$$

The terms $1/\tau_\Delta$ in the sum of (2.7) take into account the contribution of the collisions in which the vibrational quantum number changes by Δ. For a molecular mixture with $\varphi^2 \ll 1$, $\gamma \ll 1$, and $\varphi^2/\gamma \sim 1$ we have

$$\frac{1}{\tau_\Delta} \approx 2\sqrt{2} Z_0 f \varphi^2 \Delta^3 \int_0^{\operatorname{arsh}(\sqrt{2}/f)} dx\, [X_+ K_{\Delta+1}(X_+\Delta) I_\Delta(X_-\Delta)$$

$$+ X_- K_\Delta(X_+\Delta) I_{\Delta+1}(X_-\Delta)],$$

$$X_+ = f(2\gamma)^{1/2} \operatorname{ch}^2(x/2), \quad X_- = f(2\gamma)^{1/2} \operatorname{sh}^2(x/2). \tag{2.8}$$

In the interval $0.1 \lesssim f \lesssim 10$ of interest to us, the second term in (2.8) is smaller than the first by 2—4 orders of magnitude, and for $\Delta \lesssim 10$ we have

$$\frac{1}{\tau_\Delta} \approx Z_0 \frac{\gamma}{\sqrt{2}} f^3 \varphi^2 \frac{\Delta^{\Delta+3}}{\Delta!} \int_0^{\operatorname{arsh}(\sqrt{2}/f)} dx \operatorname{sh}^2 x \left(\frac{1}{2} X_-\right)^{\Delta-1} K_{\Delta+1}(X_+\Delta). \tag{2.8}$$

For arbitrary Δ we can use the asymptotic formulas (with respect to the index) for the product of Bessel functions (accuracy ~ 5% for f = 8—0.2 and Δ ≥ 1 (see I)):

$$2\Delta K_\Delta(X_+\Delta) I_\Delta(X_-\Delta) \approx (B_+ B_-)^{-1/2} \left[\frac{X_- e^{B_-}}{X_+ e^{B_+}} \frac{1 + B_+}{1 + B_-}\right]^\Delta;$$

$$B_\pm = (1 + X_\pm^2)^{1/2}. \tag{2.9}$$

From (2.7) and (2.9) we have

$$\frac{1}{\tau_\Delta} = Z_0 \sqrt{2} f \varphi^2 \Delta^2 \int_0^{\operatorname{arsh}(\sqrt{2}/f)} dx \frac{1 + B_+}{B_+^{1/2}} \exp\left(-2\frac{\Delta}{\Delta_m}\right),$$

$$\frac{2}{\Delta_m} = \ln\left[\frac{4(B_+ - 1)}{\gamma f^2 \operatorname{sh}^2 x} \exp(B_+ - 1)\right]. \tag{2.10}$$

Summing in (2.10), we obtain finally for the vibrational-relaxation time

$$\frac{1}{\tau} = \frac{Z_0 f \varphi^2}{2\sqrt{2}} \int_0^{\operatorname{arsh}(\sqrt{2}/f)} dx \frac{B_+ + 1}{B_+^{1/2}} \operatorname{ch}\frac{1}{\Delta_m} \operatorname{sh}^{-3}\frac{1}{\Delta_m}. \tag{2.11}$$

If we average over the angles in the initial formula (2.4) after Krieger and Nelkin ($\overline{\exp[\Omega(z)]} \to \exp[\overline{\Omega(z)}]$), the main expression (2.8) goes over into

$$1/\tau_\Delta = Z_0 \Delta^3 (1 + 2/3f^2)^{-1/2} (\omega/T)^2 (X_+ K_{\Delta+1} I_\Delta + X_- K_\Delta I_{\Delta+1}) \tag{2.12}$$

and, further,

$$\frac{1}{\tau} = \frac{Z_0}{2(1 + 2/3f^2)^{1/2}} \left(\frac{\omega}{T}\right)^2 \frac{B_+ + 1}{B_+} \sum_{\Delta=1} \Delta^2 \exp\left(-2\frac{\Delta}{\Delta}\right). \tag{2.13}$$

Since $1/\tau_\Delta \sim \Delta^2 \exp(-2\Delta/\Delta m)$, Δ_m corresponds to the maximum of $1/\tau_\Delta$ as a function of Δ. At small Δ_m, the main contribution to the sums (2.7)—(2.13) is made by the term with Δ = 1, which describes single-quantum transitions

$$\frac{\tau_0}{\tau_1} = \frac{\gamma}{6(1 + 2/3f^2)^{1/2}} \left(\frac{\omega}{T}\right)^2 K_2(X_+)$$

$$\approx \left(\frac{\omega}{T}\right)^2 \frac{B_+ + 1}{2[B_+(1 + 2/3f^2)]^{1/2}} \exp\left(-\frac{2}{\Delta_m}\right). \tag{2.14}$$

The values of τ_0/τ_1 and τ_0/τ are given in the table for the Br_2 + He pair ($\gamma = 1/41$).

The vibrational relaxation in the molecular mixtures Br_2 + He, Ne, Ar under nonadiabatic conditions was investigated experimentally by Generalov and Maksimenko[16]. If we assume $\alpha_0 R_0 = 1$, where $1/\alpha_0$ is the radius of action of the collision potential (α_0 is determined by the Landau-Teller formula from the experimental data in the adiabatic region; α_0 is equal to 4×10^8, 5×10^8, and 5.5×10^8 cm^{-1} for Br_2 + He, Ne, Ar, respectively (see[16])), then, say at T = 500°K (f = 6—7), it follows from (2.13) and (2.14) that τ is equal to 0.12, 0.25, and 0.25 μsec for the relaxation of Br_2 + He, Ne, and Ar. The corresponding experimental values[16] of τ are 0.07, 0.12, and 0.25 μsec. At T = 2000°K (f = 2—3) the agreement between the theoretical values of τ (0.12, 0.25, and 0.3 μsec) and the experimental values (0.4, 0.35, and 0.15 μsec) can also be regarded as satisfactory[6]. The corrections connected with allowance for the temperature dependence of the effective radius of the hard-sphere molecule with allowance for the contribution made to τ_0 by the vibrationally-excited states (see (2.4)) are relatively small and cancel out in part, so that the discrepancy is apparently due to the anharmonic corrections and the inaccuracy of the pseudopotential.

It is seen from the table that the single-quantum transitions (2.14) make the main contribution to 1/τ, starting with $f \gtrsim 2$, with (2.14) following directly from (2.1)—(2.5) in the limit as γ → 0, when[7]

$$-\frac{d^2}{du^2}\Big|_0 \exp\left[-\frac{1}{2}\gamma q^2 z^2 \Gamma(t + u)\right] = \frac{1}{2}\gamma q^2 z^2 \Gamma''(t) + 0(\gamma), \tag{2.15}$$

$$\frac{\tau_0}{\tau_1} = \frac{\gamma}{6}\left(\frac{\omega}{T}\right)^2 K_2\left[\left(\varphi^2 + \frac{8}{\pi}\varkappa^2\right)^{1/2}\right], \quad \varkappa = \frac{\omega}{\alpha_0 \bar{v}}, \quad \bar{v} = \left(\frac{8T}{\pi\mu}\right)^{1/2}. \tag{2.16}$$

---

[6] We note that a comparison of the experimental data with other theories (see[16]) results in a difference by 1.5–2 orders of magnitude.

[7] In the expansion of (2.15) in powers of γ, the term with γΔ does not describe all the Δ-quantum transitions; substituting (2.15) in (2.1) and integrating there with respect to t, we can easily verify that single-quantum transitions are contained also in the term O(γ)—the contribution of these transitions can be neglected for the relaxation of heavy molecules in a light thermostat.

	f								
	0,2	0,4	0,6	0,8	1	2	4	6	8
Δ_m	4,25	2,22	1,53	1,09	0,98	0,61	0,42	0,35	0,31
$(T/\omega)^2\tau_0/\tau$	4,6	1,22	0,54	0,21	0,18	$5{,}1\cdot 10^{-2}$	$9{,}1\cdot 10^{-3}$	$3{,}3\cdot 10^{-3}$	$1{,}55\cdot 10^{-3}$
$(T/\omega)^2\tau_0/\tau_1$	0,15	0,18	0,165	0,12	0,1	$3{,}4\cdot 10^{-2}$	$8{,}8\cdot 10^{-3}$	$3{,}3\cdot 10^{-3}$	$1{,}55\cdot 10^{-3}$

In the other limiting case f → 0 we have

$$X_+ \approx X_- \approx (\gamma/3)^{1/2}, \quad 2/\Delta_m \approx \gamma/6 \ll 1. \tag{2.17}$$

In this high-temperature essentially multiquantum region, it is likewise easier to go to the limit in the initial expression (2.1)–(2.5). We have

$$\frac{1}{\tau} \to \frac{4}{15}\gamma Z_0 \frac{(1+4x_0)(5+2\gamma)}{(1+4x_0+\gamma)^2(1+\gamma)^{3/2}}, \quad \varphi \to 0. \tag{2.18}$$

Let us proceed to consider vibrational relaxation of central-symmetry molecules colliding with structureless particles. The rate of energy loss in the different vibrational modes is determined by the generating function (see (1.6); $\mathbf{A}_v$ are normal vectors)

$$Z(u_1, u_2, \ldots, u_{3N_2-6}) = \frac{Z_0(1+4x_0)}{8\pi^{3/2}} \int d^3q\, dt$$
$$\times \exp[-q^2(it+t^2+x_0)] \Big\langle \exp\Big[-\mu q\rho q(it+t^2)\frac{T_r}{\bar{T}}$$
$$-\frac{\mu}{2}\sum_{v=1}^{3N_2-6} |\mathbf{q}\mathbf{A}_v|^2 \Gamma_v(t+u_v)\Big]\Big\rangle_\Omega. \tag{2.19}$$

The pseudopotential parameter x_0, which is the same for all the surface atoms Y of the molecules XY_4 or XY_6, can be assumed approximately the same as for collisions of diatomic molecules Y_2 with the corresponding partner. In the case of heavy outer atoms, the inequality $kT \gg \hbar\omega_{\min}$ ($\omega_{\min}$ corresponds to surface oscillations with change of the valence angle YXY) is satisfied already at room temperatures. For example, the temperature $\Theta_{\min} = 175°$ for CBr_4, 92° for $SnBr_4$, and 69° for SnI_4. Using the expansion of the integrand in (2.9) in Bessel functions, we can separate (in analogy with the transition (2.2)–(2.3)) the contribution made to the total energy loss by the vibrational transitions with change Δ_v of the vibrational quantum number, but the resulting very cumbersome multiple sums do not make it possible to obtain simple formulas similar to (2.10)–(2.13). We therefore confine ourselves to a calculation of the contribution of the single-quantum transitions, assuming that $\mu/N_2m \ll 1$ (see, however, footnote 7). In analogy with (2.15) and (2.16), we obtain (for an isothermal mixture)

$$\frac{1}{\tau_v} = \frac{Z_0\mu(1+4x_0)}{32\pi^{3/2}C_v} \int d^3q\, dt\, \Gamma_v''(t) \exp[-q^2(it+t^2+x_0)]$$
$$\times \langle \exp[-\mu q\rho q(it+t^2)]\, |\mathbf{q}\mathbf{A}_v|^2\rangle_\Omega. \tag{2.20}$$

The connection between the normal vectors $\mathbf{A}_v$ and the force constants a, b, d, e of molecules of the XY_4 type were discussed by various authors[17,18]. For molecules of this type, the averaging over the angles reduces to a calculation of the integral

$$\langle \ldots \rangle_\Omega = \frac{q^2}{4m} \int_0^1 dz(\alpha_v + \beta_v z^2) \exp[-\gamma q^2(1-z^2)(it+t^2)], \tag{2.21}$$

so that ultimately ($\gamma < \mu/4m \ll 1$)

$$\frac{1}{\tau_v} = Z_0 \frac{\mu}{8m}\left(\frac{\omega_v}{T}\right)^2 \left(\alpha_v + \frac{1}{3}\beta_v\right) K_2\left[\left(\varphi_v^2 + \frac{8}{\pi}\varkappa_v^2\right)^{1/2}\right] \tag{2.22}$$

$\varphi_v = \omega_v/2T$ and $\kappa_v = \omega_v/\alpha_0\bar{v}$. In (2.21) and (2.22) we have for the four different frequencies (the vibrations with frequency ω_2 are doubly degenerate; the degeneracy multiplicity for ω_3 and ω_4 is equal to 3) with v = 1, 2, 3, 4 (see[18])

$$\alpha_1 = 0, \quad \alpha_2 = \beta_1 = -\beta_2 = 1, \quad \alpha_3 = 1/2 + 1/4\cos^2\beta - 1/4\sqrt{6}\sin 2\beta,$$
$$\alpha_4 = 1/2 + 1/4\sin^2\beta + 1/4\sqrt{6}\sin 2\beta, \quad \beta_3 = 3/2\sin^2\beta + 3/4\sqrt{6}\sin 2\beta,$$
$$\beta_4 = 3/2\cos^2\beta - 3/4\sqrt{6}\sin 2\beta, \quad \beta = \operatorname{arc\,tg}\,[4e\sqrt{3}/(6b-6d-a)]. \tag{2.23}$$

For example, for CBr_4 + He at T = 500°K the rate of vibrational relaxation of the mode with v = 2 ($\omega_2 = \Theta_{\min}$) amounts to $Z_0\tau_2 = 420$ (according to (2.16), $Z_0\tau = 600$ for Br_2 + He).

In analogy with (2.13)–(2.15), we can describe the vibrational relaxation of other polyatomic molecules. The general expansions for the energy loss and for the generating function Z take the form of complicated multiple sums and are not presented here. For diatomic molecules, the impulse approximation $v(x) = \delta(x)$ was also discussed by Ivanov and Sayasov[19], but the correlation functions were not used, and only the inelastic cross sections and the rate constants of the transitions from the ground vibrational level were calculated.

3. CALCULATION OF THE COEFFICIENT OF SHEAR VISCOSITY

To calculate the shear viscosity with allowance for the contribution of the rotational transitions of rigid-rotator molecules, we use a generating function simpler than (1.1):

$$Z(a,b,c) = \int d^3p\, d^3p'\, f(p) \sum_{\alpha\alpha'} N_\alpha W_\alpha^{\alpha'}(\mathbf{p},\mathbf{p}')$$
$$\times \exp\left[\frac{1}{2\mu T}(ap^2 + 2b\mathbf{p}\mathbf{p}' + cp'^2)\right]. \tag{3.1}$$

Here f(p) and N_α are the equilibrium Maxwell and Boltzmann distribution with identical temperature (the generalization to the nonisothermal case is obvious); $W_\alpha^{\alpha'}(\mathbf{p}, \mathbf{p}')$ is the inelastic-scattering probability. Changing over to dimensionless variables and using the integral representation of the probability from I, we obtain for the shear viscosity (see (1.3)),

$$1/\eta = \hat{L}_\eta Z(a, b, c),$$
$$\hat{L}_\eta = \frac{4\sigma}{5(2\pi\mu T)^{1/2}}\left(\frac{2}{3}\frac{\partial^2}{\partial a^2} + \frac{1}{3}\frac{\partial^2}{\partial a\,\partial c} - \frac{1}{4}\frac{\partial^2}{\partial b^2}\right)_0,$$
$$Z(a,b,c) = \frac{1}{8\pi^3}\int d^3p\, d^3p'\, dt\, \langle \Phi_{T_r} \Phi_{T'_r}\rangle_{\Omega_1\Omega_2}$$
$$\times \exp[ap^2 + 2b\mathbf{p}\mathbf{p}' + cp'^2 - p^2 + it(p^2 - p'^2)]. \tag{3.2}$$

The normalization in (3.2) is chosen such that for collisions between structureless particles and hard spheres

(σ is the scattering cross section), when $\langle\ldots\rangle = 1$, we obtain from (3.2) the usual result[11]

$$1/\eta_0 = 16\sigma/5(2\pi\mu T)^{1/2}.$$

The integration in (3.2), using the approximation (1.7), yields

$$Z=\left\langle\frac{[1-\mu A_2(\alpha_1+\alpha_2)]^{1/2}}{4A_1[1-\mu A_2(\alpha_1+\alpha_2)]+[c-a+1-\mu A_2(\alpha_1+\alpha_2)]^2}\right\rangle_{\Omega_1\Omega_2},$$
$$A_1=(a-1)c-b^2,\quad A_2=a+c+2b-1. \tag{3.3}$$

For the shear viscosity we obtain from (3.2) and (3.3) an expression of the type (1.18):

$$\frac{1}{\eta}=\frac{1}{\eta_0}\int_0^1\!\!\int\frac{dz\,dz_1[1+{}^5/_3\gamma_1(1-z^2)+{}^5/_3\gamma_2(1-z_1^2)]}{[1+\gamma_1(1-z^2)+\gamma_2(1-z_1^2)]^{7/2}}. \tag{3.4}$$

For example, for a mixture of structureless particles and rotators with $\gamma \ll 1$ we have $\eta^{-1} = \eta_0^{-1}(1 - {}^{11}/_9\gamma)$; in the case of a pure gas of homonuclear molecules $\gamma_1 = \gamma_2$ and $1/\eta \approx 0.4\eta_0^{-1}$, so that the contribution of the rotational transitions to the shear viscosity is quite appreciable.

For a mixture of structureless particles and homonuclear molecules, with allowance for the vibrational and rotational transitions, we can obtain a general multiquantum expansion

$$\frac{1}{\eta}=\sum_{\Delta=0}^{\infty}\frac{1}{\eta_\Delta},$$

analogous to the expansion (2.7)—(2.13) for the reciprocal relaxation time. Owing to the cumbersome character of the multiquantum expansion, we confine ourselves to a consideration of single-quantum transitions in the approximation $\gamma \ll 1$ for a Gaussian pseudopotential. For the generating function we have in place of (3.3)

$$Z=\frac{(1+4x_0)^3}{1-4x_0}\int_0 dz\,\frac{(A_2')^{1/2}}{A_1'}\left[1+2\gamma z^2\frac{A_2A_2'\operatorname{cth}\varphi}{\varphi A_1'}\right.$$
$$\left.-\frac{\gamma z^2A_2\varphi}{A_2'\operatorname{sh}\varphi}\operatorname{ch}\left(\frac{a-c}{A_2'}\varphi\right)K_2\left(\varphi\frac{(A_1')^{1/2}}{A_2'}\right)\right];$$
$$A_1'=4A_2'(A_1-x_0A_2)^2+(c-a+A_2')^2,\qquad A_2'=1-\gamma(1-z^2)A_2. \tag{3.5}$$

The terms in the square brackets in (3.5) describe, respectively, elastic (with respect to the vibrations) scattering by a rotator molecule, the contribution of the thermal vibrations to the elastic scattering (the Debye-Waller correction), and single-quantum vibrational transitions.

According to (3.2)—(3.5), the contribution of the single-quantum vibrational transitions is equal to

$$\frac{1}{\eta_1}\approx-\frac{4\sigma\gamma\varphi}{15(2\pi\mu T)^{1/2}\operatorname{sh}\varphi}\frac{(1+4x_0)^3}{1-4x_0}$$
$$\times\left(\frac{2}{3}\frac{\partial^2}{\partial a^2}+\frac{1}{3}\frac{\partial^2}{\partial a\,\partial c}-\frac{1}{4}\frac{\partial^2}{\partial b^2}\right)_0\frac{\operatorname{ch}[(a-c)\varphi]}{a+c-2b-4x_0-1}$$
$$\times K_2\left[2\varphi\left(x_0(1-a-c-2b)+b^2-\frac{1}{4}(c+a-1)^2\right)^{1/2}\right]. \tag{3.6}$$

Comparison with (2.16) yields

$$\eta_1^{-1}:\eta_0^{-1}\sim\gamma\varphi^2K_2[f(2\gamma)^{1/2}]\sim\tau_0/\tau_1\ll 1. \tag{3.7}$$

For example, for collisions of H, Ne, and Ar with Br$_2$ we have $\tau_0/\tau_1 \sim 10^{-3}$ at $T \sim 10^{3}$°K. Thus, the contribution of the vibrational transitions (~ 0.1%) can be neglected. In analogy with the shear viscosity, we can calculate the contribution of the inelastic collisions to the thermal conductivity, diffusion, and other kinetic coefficients in molecular mixtures.

The author is grateful to the participants of the seminar of the theoretical division of the High Temperature Institute of the USSR Academy of Sciences.

---

[1] L. I. Podlubnyĭ, Zh. Eksp. Teor. Fiz. **60**, 356 (1971) [Sov. Phys. JETP **33**, 194 (1971)].

[2] V. M. Zhigulev and V. M. Kuznetsov, Trudy TsAGI (Trans. Central Aerohydrodynamics Institute), No. 1136, Moscow, 1969.

[3] L. Vald'man, in Termodinamika gazov (Thermodynamics of Gases) Mashinostroenie, 1970.

[4] C. S. Wang-Chang, G. E. Uhlenbeck, and J. de Boer, Studies in Stat. Mech., Vol II, p. 243, Amsterdam 1964.

[5] V. M. Zhdanov, Zh. Eksp. Teor. Fiz. **53**, 2099 (1967) [Sov. Phys. JETP **26**, 1187 (1968)].

[6] V. M. Kuznetsov, Izv. Akad. Nauk SSSR Fiz. Zemli ,(3), 178 (1965).

[7] L. I. Podlubnyĭ, Zh. Eksp. Teor. Fiz. **57**, 1778 (1969) [Sov. Phys. JETP **30**, 962 (1970)].

[8] D. N. Zubarev, Neravnovesnaya statisticheskaya termodinamika (Nonequilibrium Statistical Thermodynamics), Nauka, 1971.

[9] L. A. Pokrovskiĭ, Teor. i Matem. Fiz. **2**, 103 (1970).

[10] S. V. Peletminskiĭ, Teor. i Matem. Fiz. **6**, 123 (1971).

[11] J. O. Hirschfelder, G. F. Curtiss, and R. B. Byrd, Molecular Theory of Gases and Liquids, Wiley, 1964.

[12] Yu. Kagan and A. M. Afanas'ev, Zh. Eksp. Teor. Fiz. **41**, 1536 (1961) [Sov. Phys. JETP **14**, 1096 (1962)].

[13] L. I. Podlubnyĭ and V. M. Sergeev, Opt. Spektrosk. **27**, 404 (1969).

[14] A. I. Osipov, Fiz. Goreniya Vzryva **4**, 139 (1968).

[15] H. O. Kneser, translation in: Fizicheskaya akustika (Physical Acoustics), **2A**, Mir, 1968.

[16] N. A. Generalov and V. A. Maksimenko, Zh. Eksp. Teor. Fiz. **58**, 420 (1970) [Sov. Phys. JETP **31**, 223 (1970)].

[17] M. Johnston and D. M. Dennison Phys. Rev. **48**, 868 (1935).

[18] A. M. L. Messiah, Phys. Rev. **84**, 204 (1951).

[19] G. K. Ivanov and Yu. S. Sayasov, Dokl. Akad. Nauk SSSR **154**, 1314 (1964) [Sov. Phys. Dokl. **9**, 171 (1964)].

Translated by J. G. Adashko
74