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TRANSPORT PROCESSES IN VIBRATIONALLY EXCITED MOLECULAR GASES

S. V. Dobkin and É. E. Son

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There has recently been significantly increased interest in studies and applications of molecular gases in conditions far from equilibrium when the amount of vibrational energy of the molecules markedly exceeds the equilibrium value corresponding to the temperature of the gas. Such conditions occur in gaseous discharges, in outflow of a very hot gas from a nozzle, in relaxation zones behind shock waves, etc. The distribution of molecules in the vibrational states can be of a non-Boltzmann character in these conditions and therefore the transport processes in a vibrationally excited nonequilibrium gas differ from the equilibrium case. For a small difference between the vibrational and translational temperature when the Boltzmann distribution of vibrational degrees of freedom is realized via fast V-V processes, the transport coefficients are calculated in [1, 2]. Here we analyze the case of a large difference between the vibrational and translational temperature when the regime of quasisonance exchange is realized [3]. Moreover, for low vibrational levels ($i \leq i_*$) the distribution of molecules on the vibrational levels is of the Treanor type with a characteristic vibrational temperature T_V determined by the full margin of the vibrational energy; on higher levels ($i_* < i \leq i_{**}$) the distribution of molecules forms a plateau which for $i > i_{**}$ becomes the equilibrium Boltzmann distribution with the gas temperature T via a strong V-T exchange. We will limit ourselves to the case when the spatial inhomogeneities only slightly perturb the above distribution. For weak variations of the parameters in space and time one obtains a quasistationary and quasihomogeneous regime when the distribution preserves its form and is determined by its local parameters - gas and vibrational temperatures. This approximation holds when the flow of molecules in vibrational levels is much larger than the flow due to spatial diffusion [4].

The kinetic equation for the distribution function of molecules in velocities and non-equilibrium populations has the form of Wang Chang-Uhlenbeck equations [5]

$$\varepsilon(\partial f_{\alpha i} / \partial t + \mathbf{v}_\alpha \nabla f_{\alpha i}) = J_{\alpha i}^{TT} + \eta J_{\alpha i}^R, \quad J_{\alpha i}^R = J_{\alpha i}^{VV} + J_{\alpha i}^{VT} + J_{\alpha i}^l. \quad (1)$$

Here $f_{\alpha i}(\mathbf{v}_\alpha, \mathbf{r}, t)$ is the distribution function in velocities of particles of type α in vibrational state i with velocity \mathbf{v}_α ; on the right-hand side we have the collisional integrals taking into account the processes of elastic $J_{\alpha i}^{TT}$ and inelastic $J_{\alpha i}^R$ collisions including V-V ($J_{\alpha i}^{VV}$) and V-T ($J_{\alpha i}^{VT}$) exchanges and sources $J_{\alpha i}^l$ of population of the vibrational levels due to external interaction (excitation by electron impact, infrared radiation, laser-chemical reactions, etc.); $\varepsilon \ll 1$ is the Knudsen number; $\eta = \sigma_R / \sigma_{TT}$ is the ratio of the cross sections of the inelastic and elastic processes. In contrast to the equilibrium Boltzmann population of the vibrational levels when $\eta \ll 1$, in the considered conditions the effects of vibrational anharmonicity are substantial when the cross sections of the inelastic processes on upper vibrational levels equal the cross sections of the elastic processes and therefore $\eta \leq 1$. To obtain the solution of the kinetic equation in this case we will use the generalized Chapman-Enskog method [6] developed for arbitrary ratios of elastic and inelastic processes (i.e. the

parameter η can take the values $\varepsilon \leq \eta \leq 1$). The distribution function of particles will be expanded in powers of the small parameter ε :

$$f_{\alpha i} = f_{\alpha i}^{(0)} + \varepsilon f_{\alpha i}^{(1)} \quad (2)$$

In the zero-order (in ε) approximation for arbitrary values of η ($\varepsilon \leq \eta \leq 1$) the distribution function $f_{\alpha i}^{(0)}$ is Maxwellian [6]. For the population of the vibrational states n_i in the same approximation one obtains the usual equations of level kinetics [6] and for high pumping intensity one realizes a distribution function in vibrational levels that contains the plateau [3]. The integrals of inelastic collisions in (1) are of the order of ε [6] and must be taken into account in the next approximation (next power of the Knudsen number) to calculate the transport coefficients.

In the spatially inhomogeneous case, when the distributions in velocities and vibrational states are only slightly perturbed, the distribution parameters T , T_V , n_i depend only on the coordinates and time. The hydrodynamic equations of the zero-order approximation are obtained from (1) by substituting $f_{\alpha i}^{(0)}$ for $f_{\alpha i}$ and by integrating over velocities with weights corresponding to the collisional invariants. In order to find the equations determining the distribution function of the first-order approximation we substitute the expansion (2) into the kinetic equation (1). As a result we get a linearized Boltzmann equation where, according to [6], we need only the symmetrized part of the integral operator of the inelastic collisions, denoted by the superscript RS:

$$\frac{df_{\alpha i}^{(0)}}{dt} - J_{\alpha i}^R(f_{\alpha i}^{(0)}, f_{\alpha i}^{(0)}) = J_{\alpha i}^{TT}(f_{\alpha i}^{(0)}, f_{\alpha i}^{(1)}) + J_{\alpha i}^{RS}(f_{\alpha i}^{(0)}, f_{\alpha i}^{(1)}) \quad (3)$$

The most essential effect in an inhomogeneous vibrationally excited gas arises in calculation of the thermal fluxes of the translational q_T and vibrational q_V energy. A crude estimate of the energy transport by vibrationally excited molecules can be obtained by comparing the phenomenological expressions of the fluxes of vibrational and translational energy and finding the margin of vibrational quanta n_V using the distribution function discussed above [3]:

$$\frac{q_V}{q_T} \simeq \frac{\frac{1}{4} n_V E_1 v_T}{\frac{1}{4} n_0 k T v_T} \approx \frac{i_* E_1}{k T} \exp\left(-\frac{E_1 i_*}{k T_V}\right) \ln \frac{i_{**}}{i_*} \quad (4)$$

Here E_1 is the magnitude of a quanta; v_T is the thermal velocity. For instance, for the vibrationally excited CO for $T_V = 4500$ K, $T = 300$ K, $i_* = 6$, and $i_{**} \approx 49$ it follows from the estimate (4) that the vibrational levels transport twice as much energy as the translational degrees of freedom.

Since we are interested only in processes of thermal conduction we will write the part of the linearized equation (3) describing heat conduction in a one-component gas (omitting index α) of anharmonic oscillators:

$$f_i^{(0)} \left\{ \left[\left(w^2 - \frac{5}{2} \right) + \frac{\partial \ln n_i}{\partial \ln T} \right] \mathbf{v} \cdot \nabla \ln T + \frac{\partial \ln n_i}{\partial \ln T_V} \cdot \mathbf{v} \cdot \nabla \ln T_V \right\} = J_i^{TT}(f_i^{(0)}, f_i^{(1)}) + J_i^{RS}(f_i^{(0)}, f_i^{(1)}), \quad \mathbf{w} = (m/2kT)^{1/2} \cdot \mathbf{v} \quad (5)$$

The solutions of Eq. (5) have the form

$$f_i^{(1)} = -f_i^{(0)} [A_i^{(1)}(\mathbf{w}, n_i) \mathbf{w} \cdot \nabla \ln T + A_i^{(2)}(\mathbf{w}, n_i) \mathbf{w} \cdot \nabla \ln T_V]$$

with the normalization conditions

$$\sum_i \int f_i A_i^{(1),(2)} w^2 d^3 w = 0.$$

Equation (5) breaks down into two independent equations

$$f_i^{(0)} \left[w^2 - \frac{5}{2} + \frac{\partial \ln n_i}{\partial \ln T} \right] \mathbf{v} = J_i^{TT}(f_i^{(0)}, A_i^{(1)} \mathbf{w} f_i^{(0)}) + J_i^{RS}(f_i^{(0)}, A_i^{(1)} \mathbf{w} f_i^{(0)}); \quad (6)$$

$$f_i^{(0)} \left[\frac{\partial \ln n_i}{\partial \ln T_V} \right] \mathbf{v} = J_i^{TT}(f_i^{(0)}, A_i^{(2)} \mathbf{w} f_i^{(0)}) + J_i^{RS}(f_i^{(0)}, A_i^{(2)} \mathbf{w} f_i^{(0)}). \quad (7)$$

The expressions for fluxes are the following

$$\mathbf{q}_T = -\lambda_T^T \nabla T - \lambda_V^T \nabla T_{V_s}, \quad \mathbf{q}_V = -\lambda_T^V \nabla T - \lambda_V^V \nabla T_{V_s},$$

where the thermoconductivity coefficients can be determined from

$$\begin{aligned} \lambda_T^T &= \left(\frac{2kT}{m}\right)^{1/2} \frac{k}{3} \sum_i \int f_i^{(0)} A_i^{(1)} \left(w^2 - \frac{5}{2}\right) w^2 d^3 v_s, \\ \lambda_V^T &= \left(\frac{2kT}{m}\right)^{1/2} \frac{k}{3} \frac{T}{T_V} \sum_i \int f_i^{(0)} A_i^{(2)} \left(w^2 - \frac{5}{2}\right) w^2 d^3 v_s, \\ \lambda_T^V &= \left(\frac{2kT}{m}\right)^{1/2} \frac{k}{3} \frac{1}{T} \sum_i (E_i - \bar{E}) \int f_i^{(0)} A_i^{(1)} w^2 d^3 v_s, \\ \lambda_V^V &= \left(\frac{2kT}{m}\right)^{1/2} \frac{k}{3} \frac{1}{T_V} \sum_i (E_i - \bar{E}) \int f_i^{(0)} A_i^{(2)} w^2 d^3 v_s, \\ \bar{E} &= \sum_i E_i n_i, \quad \sum_i n_i = 1. \end{aligned}$$

The solution of Eqs. (6), (7) will be sought in the form of expansion in orthogonal polynomials Q^{TP} of Waldman-Trubenchacher for the expansion in the discrete internal energy levels [7] and of Sonine [8] for the reduced velocities with unknown coefficients a_{rp}^j :

$$A^{(j)} = \sum_{rp} a_{rp}^j Q^{rp}, \quad j = 1, 2. \quad (8)$$

Substituting the expansion (8) into Eqs. (6), (7), and integrating over velocities with corresponding weights and summation over the vibrational levels, we obtain a system of linear algebraic equations for the coefficients a_{rp}^j in the second approximation in Q^{TP}:

$$\begin{aligned} \sum_{s,q} G^{rpsq} a_{sq}^j &= R_{rp}^j, \quad j = 1, 2, \\ R_{10}^1 &= 7.5, \quad R_{01}^1 = 3 \frac{T}{T_V} \sum_i \frac{\partial n_i}{\partial T} (E_i - \bar{E}), \\ R_{10}^2 &= 0, \quad R_{01}^2 = 3 \sum_i \frac{\partial n_i}{\partial T_V} (E_i - \bar{E}). \end{aligned}$$

Using the standard transformations [8] the integral brackets G^{rpsq} reduce to expressions obtained by Wang Chang and Uhlenbeck [5], with appropriate replacement of the translational temperature T by the effective vibrational temperature T_V :

$$\begin{aligned} G^{rpsq} &= \sum_{ijkl} \int \int \exp(-g^2) g^3 n_i n_j F_0^{rpsq} \sigma_{ij}^{h1}(g, \chi) d^2 \Omega dg, \\ F_0^{1010} &= -4g^4 \sin^2 \chi - 4g^2 \frac{\Delta E_1}{kT} \sin^2 \chi - \frac{11}{2} \left(\frac{\Delta E_1}{kT}\right)^2, \\ F_0^{1001} &= -F_0^{0110} = -\frac{5}{2} \frac{(\Delta E_1)^2}{k^2 T_V T}, \\ F_0^{0101} &= \frac{3}{2} \left(\frac{\Delta E_1}{kT_V}\right)^2 + \left| g \left(\frac{E_i - E_j}{kT_V}\right) - g_1 \left(\frac{E_k - E_l}{kT_V}\right) \right|^2, \\ \Delta E_1 &= E_i + E_j - E_k - E_l, \quad g_1^2 = g^2 + \frac{\Delta E_1}{kT}. \end{aligned} \quad (9)$$

In order to evaluate the integral it is necessary to estimate the contribution of the elastic and inelastic collisions. At low gas temperatures ($T \sim 100-700$ K) the cross sections for the V-T exchange are far less than the cross sections for the V-V exchange [3], but in contrast with harmonic molecules in the anharmonic case this statement is not valid for the entire set of vibrational levels. The presence of the exponential factor in the expressions for the exchange probability in the anharmonic case leads to a situation where the probability of the V-T exchange grows faster and the probability of the V-V exchange slower than the corresponding probabilities for the harmonic oscillator [3]. Also, for large vibrational numbers i the probability of the V-V exchange begins to decrease with increasing i due to the growing resonance defect ΔE_1 . For high vibrational levels the corresponding probabilities become equal.

For example, for nitrogen $P_{i+1,i} = Q_{i+1,i}^{01}$ for $i_1 = 30$, $T = 700$ K and the number of this level increases slightly for lower temperatures (similar estimates hold for CO). However, the populations of these levels are extremely low, e.g., for $T_V \sim 2700$ K and $700 \text{ K} \leq T \leq 500 \text{ K}$ i_1 is in the region above the plateau where $n_{i_1}/n_0 \sim 10^{-6}-10^{-4}$; for $500 \text{ K} \leq T \leq 100 \text{ K}$ i_1 is in the region at the edge of the plateau where $n_{i_1}/n_0 \sim 10^{-4} - 5 \cdot 10^{-3}$. Therefore one can neglect the contribution of the V-T processes in comparison with the V-V processes to the integral of G^{rpsq} .

Now we estimate the contribution of the V-V processes to G^{rpsq} taking into account only the single-quantum transitions. In the regime of quiresonance exchange the resonance defect $\Delta E_1 = 2\Delta E|m - i|$ for a single-quantum V-V exchange $(i + 1, m) \rightarrow (i, m + 1)$ is far smaller than the gas temperature T [3]. Moreover, there is also a small parameter T/T_V . Therefore the terms in (9) that contain the parameters $\Delta E_1/kT$ and $\Delta E_1/kT_V$ can be neglected. It remains to estimate the term G^{0101} which can be brought to the form

$$G^{0101} = \sum_{ijkl} \int \int \exp(-g^2) 2g^5 n_i n_j \left[\left(\frac{E_i - E_j}{kT_V} \right)^2 - \frac{(E_i - E_j)(E_k - E_l)}{kT_V kT_V} \cos \chi \right] \sigma_{ij}^{kl} d^2 \Omega dg. \quad (10)$$

We will identify in (10) the contributions of the elastic and V-V processes. In the single-quantum V-V exchange approximation the cross section for the elastic process is equal $\sigma_{ij}^{ij} = \sigma_0(1 - Q_{ij}^{i+1,j-1} - Q_{ij}^{i-1,j+1})$, the cross section for the V-V exchange $\sigma_{ij}^{i+1,j-1} = \sigma_0 Q_{ij}^{i+1,j-1}$, $\sigma_{ij}^{i-1,j+1} = \sigma_0 Q_{ij}^{i+1,j-1}$ where σ_0 is the total elastic cross section, Q 's are the probabilities of the corresponding single-quantum transfers, depending on the relative velocities of the colliding molecules and the polar angle specifying the direction of the vector g_i relative to g .

To estimate the contribution of the V-V exchange in (10) we will put the resonance defect equal to zero in the probabilities Q . Further, the dependence of Q on the vibrational level is the same as in the harmonic oscillator [3], and the estimate of the contribution of the V-V processes is obviously a little too high.

By summing over the vibrational levels (10) can be written as

$$G^{0101} = 4c_V \frac{m}{kT_V^2} \int \int \exp(-g^2) g^5 [(1 - \cos \chi) + 2 \cos \chi Q_{10}^{01}(g, \chi)] \sigma_0 d^2 \Omega dg, \quad (11)$$

where c_V is the heat capacity of the vibrational degrees of freedom $Q_{10}^{01} = Q_{10}^S + Q_{10}^L$. The index S refers to the probabilities of the V-V exchange computed by taking into account only the short-range interactions of the colliding molecules, the index L denotes the calculation using the long-range forces. At low temperatures for dipole molecules $Q_{10}^L \gg Q_{10}^S$ [9]. Using the dependence of Q_{10}^S on velocity [10], the method of the modified quantum number, introduced by Takayanagi, for the dependence of the probability Q_{10}^{01} on the collision parameter [11], and the hard sphere model for σ_0 [8], we obtain $Q_{10}^S(g, \chi) = Q_{10}^S(T)g^2(1 - \cos \chi)/2$. Substituting this quantity into (11) and integrating we find out that the ratio of the V-V exchange contribution to the contribution of the elastic collisions in (11) is equal to $Q_{10}^S(T)$ - the magnitude of the V-V exchange probability averaged over the velocities of molecules. For nitrogen this quantity is calculated in [10]: $Q_{10}^S = 3.7 \cdot 10^{-6}T$. Consequently, in the temperature interval under consideration ($100 \text{ K} \leq T \leq 700 \text{ K}$) one can neglect the V-V exchange for nitrogen. Similar estimates can be easily carried out for CO using a more complicated dependence of Q_{10}^L on g and χ [9]. Having integrated (11) we find an estimate of the ratios of the contributions of the corresponding processes: $cQ_{10}^L(T)$ where $c \sim 1$. For $100 \text{ K} \leq T \leq 700 \text{ K}$ $1.5 \cdot 10^{-2} > Q_{10}^L(T) > 3 \cdot 10^{-3}$ [9]. Therefore in CO one can neglect the V-V exchange as well. In taking into account only the elastic collisions the integral reduces to standard Ω integrals [5] and the expressions for the heat conduction coefficients have the form

$$\begin{aligned} \lambda_T^T &= \frac{75kT}{32m\Omega^{(2.2)}}, \quad \lambda_V^T = 0, \\ \lambda_T^V &= \frac{3}{8} \frac{kT}{m\Omega^{(1.1)}} \sum_i \frac{\partial n_i}{\partial T} E_i = \rho D c_T, \\ \lambda_V^V &= \frac{3}{8} \frac{kT}{m\Omega^{(1.1)}} \sum_i \frac{\partial n_i}{\partial T_V} E_i = \rho D c_V. \end{aligned} \quad (12)$$

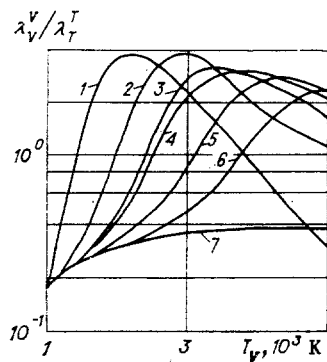


Fig. 1

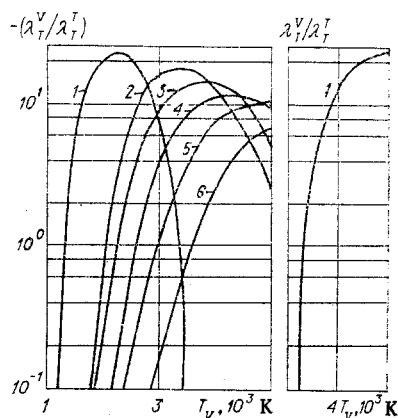


Fig. 2

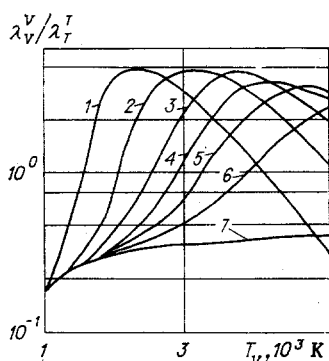


Fig. 3

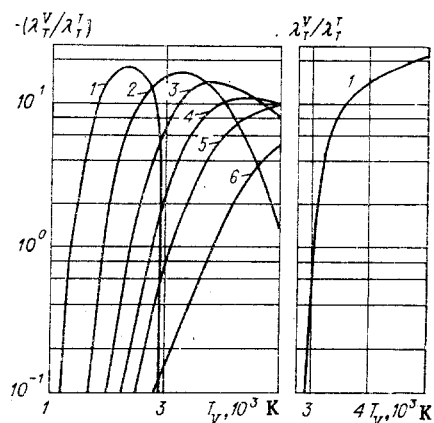


Fig. 4

Here D is the coefficient of mutual molecular diffusion; $c_{T,V}$ are the corresponding heat capacities. Accordingly, if the cross sections for inelastic processes are small, the processes of vibrational heat conduction can be reduced to the diffusion of vibrational energy [4]. For molecules with a large dipole moment (e.g., CO_2 and N_2O) the cross sections of the resonance V-V exchange can be significant and for the calculation of the coefficients of vibrational heat conduction it is necessary to use the general expressions of the integral (9). An approximate estimate in this case was given in [12]. For molecules with a small dipole moment (CO , HCl) there was no experimental evidence of the difference between the coefficients of vibrational diffusion and autodiffusion [13] which qualitatively supports the correctness of expressions (12).

In Figs. 1 and 2 we show the values of the heat conduction coefficients for vibrationally excited CO for $T = 100, 200, 300, 400, 500, 700$ K - curves 1-6; curve 7 represents the result for the Boltzmann distribution on vibrational levels. Figures 3 and 4 show analogous results for N_2 .

We will compare the heat conduction coefficients (12), computed for anharmonic molecules and a harmonic oscillator [2, 7]. Due to inelastic processes a distribution function n_i arises through which these processes influence λ_T^V , λ_V^V . For a harmonic oscillator [7] when only resonance transitions are taken into account $\lambda_T^V = 0$. For a gas of anharmonic oscillators there exist nonresonant processes whose result is an energy transfer between the translational and vibrational degrees of freedom and a strong dependence of n_i on T . For a large difference between the vibrational and gas temperature the value of λ_T^V can significantly exceed the value of the coefficient of the translational heat conduction λ_T^T (Fig. 2 and 4).

The sign of λ_T^V is related to the temperature dependence $n_i(T)$. For different ratios T_V/T the principal contribution to R_{01}^{-1} , which determined λ_T^V , comes from different groups of vibrational levels. For the lower levels $\partial n_i/\partial T < 0$, for the upper ones $\partial n_i/\partial T > 0$. Therefore the dependence of λ_T^V on the vibrational temperature will not be monotonous. For $T > 200$ K and < 5000 K the principal contribution to R_{01}^{-1} comes from the group of lower levels and $\lambda_T^V < 0$. Physically, it is related to the fact that the flux of the vibrationally excited

molecules from the hot region toward the cold region is smaller than the corresponding flux from the cold region to the hot one, so that the total flux of vibrational energy has the direction of the temperature gradient. One assumes that the vibrational temperature is constant in the considered region. Figures 1 and 3 show the comparison of the coefficient λ_V^V computed in the anharmonic case and for the Boltzmann distribution of molecules on vibrational levels [2, 7]. Exceeding the values of λ_V^V roughly by one order of magnitude is brought about by a strong temperature dependence on the vibrational temperature. The flux of vibrationally excited molecules due to the gradient of translational temperature vanishes in the Boltzmann case ($\lambda_T^V = 0$). In general in the Boltzmann case the Onsager reciprocity relations hold for the cross terms: $\lambda_T^V T^2 = \lambda_V^T T_V^2$ [14]

In the case under investigation the Onsager relations for λ_T^V and λ_V^T are not fulfilled for the following reason. For harmonic molecules the relaxation takes place in two phases. During the fast phase the vibrational degrees of freedom are actually an isolated subsystem where a quasistationary distribution of molecules in vibrational states with the temperature T_V , different from T , is established due to the V-V exchange. During the slow phase the V-T exchange takes place, leading to the full equilibrium. In the case being considered, it cannot be reckoned that the gas - being an aggregate of two subsystems - relaxes so that interaction initially takes place within the vibrational subsystem and then between this subsystem and the translational subsystem.

Preliminary results, published in [15, 16], were used later in papers on the dynamics of vibrational relaxation [17] and in studies of the processes of mixing of vibrationally excited molecules [18]. More complete results on the transport processes in the vibrationally excited gas obtained in the present article can be a basis for calculation of various phenomena in inhomogeneous vibrationally excited nonequilibrium gases.

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PARTICLE CHARGING IN "HOT" AEROSOLS

A. V. Fillipov

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Electrification of highly conductive alpha- and beta-active particles in dispersed media is studied. In order to do so, a single ideally conductive radioactive particle of spherical form, located within a nonmoving gas containing ions of both signs, is studied. It is assumed that the ion concentration and particle dimensions are so small that the intrinsic electric field of the ions may be neglected. In contrast to [3, 4], this study considers the case in which the contribution of external radiation sources (including the contribution of radiation of other particles in the aerosol) to gas ionization is the major one. The results of solution of the analogous problem for nonradioactive particles were presented in [5, 6]. We consider the problem of determining equilibrium concentrations of ions and radioactive particle charge with consideration of ion absorption by the particles. Relationships are obtained and studied, which describe the equilibrium state of a monodispersed radioactive medium, analogous to the Sach equations for ionized gases or the equations of the law of acting masses for chemically reacting gas masses [1].

1. In radioactive aerosols the charges of particles can change due to capture of gas ions and because of radiation of alpha- or beta-particles. Propagation of radiation through the gas leads to its ionization. In connection with this, the charge of particles and concentration of ions depend significantly on the concentration of particles and their individual activity, which for the most dangerous ("hot") particles can reach values of the order of hundreds of Bq (decays/sec) and more [7]. In order to study this phenomenon in the case of a low volume concentration of the dispersed phase we will first consider electrification of a single spherical particle in a gas which simultaneously contains ions of both signs. The equation describing particle electrification has the form

$$\frac{dQ}{dt} = Y + e(i_+ - i_-), \quad (1.1)$$

where Q is the particle charge; i_{\pm} is the flux of positive and negative ions toward the particle; e is the charge of a proton; Y is the rate of change of charge due to radioactive radiation. For definiteness, we will assume below that $Y \geq 0$, which does not affect the generality of the results obtained.

The quantity Y is related to the particle activity C by the equation $Y = e m C$ (where m is the mean number of elementary charges lost by the particle in a single decay). We assume that the particle diameter is so small that radiation braking within the particle can be neglected, so that the relationship $m \ll \eta$ is satisfied (where η is the mean number of ion pairs formed by radiation in the gas in a single decay).

In the case of electronic beta-decay $m = 1$, while for alpha-decay due to secondary electron emission the quantity m is positive and may reach values of the order of 10-20 [8].

We will consider the state of the electric field perturbed by a particle and the distribution of ion concentrations. We assume that the particle is ideally conductive and that all ions reaching the surface of the particle instantly transfer their charge to the particle.