

**LIMIT EXPRESSIONS FOR INTERMEDIATE SPEEDS OF SOUND IN NONEQUILIBRIUM FLOWS WITH AN ARBITRARY NUMBER OF CHEMICAL REACTIONS**

PMM Vol.41, № 1, 1977, pp.102-112

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(Received June 4, 1976)

It is shown that the Gibbs relation remains invariant under linear transformations which are used for reducing the kinetic matrix of reactions to a unitary one, and the matrix of a system chemical stability to a diagonal one. This makes it possible to consider new variables as thermodynamic parameters that specify the state of a relaxing mixture. Formulas for intermediate propagation velocities of small amplitude waves are obtained also for the limit case when the characteristic numbers of the relaxation matrix are of different orders of magnitude. It was found that the limit expressions may be represented by formulas for partly frozen and partly equilibrium speeds of sound in new thermodynamic variables.

**1. The Gibbs relationship.** Let us consider a mixture of gases in which  $N$  independent relaxation processes take place. The change of chemical composition of the mixture is defined by vector  $\mathbf{q} = (q_1, \dots, q_N)$  of the completeness of reactions. We denote time by  $t$  and the vectors which specify the rate and affinity of chemical reaction by  $\mathbf{q}^* = (q_1^*, \dots, q_N^*)$  and  $\boldsymbol{\omega} = (\omega_1, \dots, \omega_N)$ , respectively. The total derivative  $d/dt$  with respect to time of the reaction completeness vector is obviously

$$d\mathbf{q}/dt = \mathbf{q}^* \quad (1.1)$$

This equation introduces in the mathematical description of the relaxing mixture  $N$  supplementary functions  $q_1, \dots, q_N$ . The components  $\omega_1, \dots, \omega_N$  of chemical affinity vector play the part of adjoint thermodynamic variables. The closing of Euler's equations is achieved by Gibbs relationship which defines the increment of internal energy  $e$  by [1, 2]

$$de = \boldsymbol{\omega} d\mathbf{q} - p dV + T ds \quad (1.2)$$

where  $p$  is the pressure,  $V$  is the specific volume,  $T$  is the temperature, and  $s$  is the specific entropy. The first partial derivatives

$$\omega_i = \left( \frac{\partial e}{\partial q_i} \right)_{q_1, \dots, q_{i-1}, q_{i+1}, \dots, q_N, V, s} = \left( \frac{\partial e}{\partial q_i} \right)_{q_j, V, s} \quad (1.3)$$

expressed in terms of  $\mathbf{q}$ ,  $V$  and  $s$  represent the  $N$  lacking equations of state of the matter.

Let us consider the propagation of small amplitude waves in a quiescent mixture in a state of complete thermodynamic equilibrium. The equilibrium state of a system is defined by the equality  $\boldsymbol{\omega} = 0$  [1, 2]. In that state vector  $\mathbf{q}^*$  of the chemical reaction rate also vanishes. We select  $\boldsymbol{\omega}$ ,  $V$  and  $s$  as the independent thermodynamic variables, and denote parameters of the quiescent mixture by zero subscripts. If an analytic dependence of vector  $\mathbf{q}^*$  on  $\boldsymbol{\omega}$  is assumed, then in the system close to the equilibrium state

$$\mathbf{q}' = -\mathbf{H}(V_0, s_0)\boldsymbol{\omega} + \dots \quad (1.4)$$

The kinetic matrix  $\mathbf{H} = \|\| h_{i10} \|\|$  of reactions is positive definite and, in conformity with the Onzager reciprocity principle, it is also symmetric. We expand vector  $\boldsymbol{\omega}$  in a series. For this we introduce in conformity with formulas (1.3) the constant vectors

$$\begin{aligned} \mathbf{e}_{V_0} &= (e_{1V_0}, \dots, e_{NV_0}), & e_{iV_0} &= \left( \frac{\partial^2 e}{\partial q_{i0} \partial V_0} \right)_{q_j, s} \\ \mathbf{e}_{s_0} &= (e_{1s_0}, \dots, e_{Ns_0}), & e_{is_0} &= \left( \frac{\partial^2 e}{\partial q_{i0} \partial s_0} \right)_{q_j, V} \end{aligned}$$

and matrix  $\boldsymbol{\Omega} = \|\| (\partial \omega_l / \partial q_{i0})_{q_j, V, s} \|\|$ . Restricting the expansion to its principal terms, we have

$$\boldsymbol{\omega} = \boldsymbol{\Omega}(\mathbf{q} - \mathbf{q}_0) + \mathbf{e}_{V_0}(V - V_0) + \mathbf{e}_{s_0}(s - s_0) + \dots \quad (1.5)$$

The condition of thermodynamic stability of the system implies the positive definiteness of matrix  $\boldsymbol{\Omega}$  [1, 2]. Since

$$\left( \frac{\partial \omega_l}{\partial q_{i0}} \right)_{q_j, V, s} = \left( \frac{\partial^2 e}{\partial q_{i0} \partial q_{l0}} \right)_{q_j, V, s}$$

that matrix is also symmetric.

Below we assume that in the unperturbed state the frozen  $a_{f0}$  and the equilibrium  $a_{i0}$  speeds of sound are close to each other. We assume the difference between these to be proportional to  $\varepsilon_\alpha^2$ , where  $\varepsilon_\alpha$  is a small positive parameter. It was shown in [3] the closeness of these two speeds of sound is ensured by subjecting the equations of state of the mixture to the following conditions:

$$e_{iV_0} = - \left( \frac{\partial p}{\partial q_{i0}} \right)_{q_j, V, s} = \varepsilon_\alpha \frac{p_0}{q_{i0}} e'_{iV_0}, \quad i = 1, \dots, N \quad (1.6)$$

where  $e_{iV_0}$  is a dimensionless quantity of order unity.

We restrict the analysis of the propagation of small perturbations in the relaxing mixture to short waves which have either a plane, axis, or center of symmetry. We assume that the wave propagation velocity  $a_0$  does not greatly differ from the frozen  $a_{f0}$  and equilibrium  $a_{e0}$  speeds of sound. We introduce a moving system of coordinates to an element of the propagating wave, and denote by  $L$  a characteristic length in that system. We specify the width of the perturbed region by the small parameter  $\Delta$ , and represent time  $t$  and distance  $r$  from the origin of the Cartesian, cylindrical, or spherical system of coordinates in the form

$$t = \frac{L}{\Delta a_0} t', \quad r = a_0 t' + Lr' \quad (1.7)$$

To define deviations of unknown functions from their equilibrium values we introduce one more small parameter  $\varepsilon$ . In conformity with [3] we consider that the velocity  $v$  of particles of the mixture and its thermodynamic parameters can be expressed as follows:

$$\begin{aligned} v &= \varepsilon a_0 v', & V &= V_0 (1 + \varepsilon V') \\ p &= p_0 (1 + \varepsilon p'), & T &= T_0 (1 + \varepsilon T') \\ q_i &= q_{i0} (1 + \varepsilon \varepsilon_\alpha q_i'), & \omega_l &= \varepsilon \varepsilon_\alpha \frac{V_0 p_0}{q_{l0}} \omega_l', \quad i, l = 1, \dots, N \end{aligned} \quad (1.8)$$

The estimate of entropy increment yields the equality

$$s = s_0 (1 + \varepsilon^2 \varepsilon_\alpha^2 s') \quad (1.9)$$

When passing to dimensionless variables it is necessary to transform also the kinetic matrix  $\mathbf{H}$ . Let its elements be

$$h_{i10} = \frac{q_{i0}q_{10}}{\tau_{i1}V_0P_0} h'_{i10} \quad (1.10)$$

where  $\tau_{i1}$  has the meaning of the relaxation time of the  $i$ -th element, which depends on the chemical affinity of the  $l$ -th element, and  $h'_{i10}$  is a quantity of order unity. Since matrix  $\|h_{i10}\|$  is symmetric, it is convenient to choose  $\tau_{i1} = \tau_{1i}$ .

Now, substituting formulas (1.7) and (1.8) into Eq. (1.1) which determines the rate of chemical reactions, taking into consideration equalities (1.4) and (1.10), retaining in the obtained relation only the principal terms, and omitting the prime at all dimensionless variables, we obtain [3]

$$\partial \mathbf{q} / \partial r = \mathbf{F} \boldsymbol{\omega}, \quad \mathbf{F} = \|f_{il}\| = \|N_{il} h_{i10}\| \quad (1.11)$$

where the numerical parameters  $N_{il}$  are the ratios of the macroscopic time  $\tau = L/a_0$  to the relaxation time  $\tau_{il}$ .

Equality (1.5) can be similarly transformed for the expansion in series of the chemical affinity vector. First, we note that the entropy increment in formula (1.9) can be neglected, since its order of smallness is the next following that of the considered here. Passing from the input matrix  $\boldsymbol{\Omega}$  of chemical stability of the system to the matrix

$$\mathbf{G} = \|g_{il}\| = \left\| \frac{1}{V_0 P_0} q_{i0} q_{l0} \left( \frac{\partial \omega_l}{\partial q_{i0}} \right)_{q_j, v, s} \right\|$$

and allowing for the ordinal formulas (1.6), we obtain

$$\boldsymbol{\omega} = \mathbf{G} \mathbf{q} + eV = \mathbf{G} \mathbf{q} - e v, \quad \mathbf{e} = \mathbf{e}_{V_0} \quad (1.12)$$

where the prime at dimensionless variables is, as above, omitted; it will be, henceforth, omitted everywhere.

Since both matrices  $\mathbf{F}$  and  $\mathbf{G}$  are symmetric and positive definite, a matrix  $\mathbf{C}$  and a unitary matrix  $\mathbf{U}$  can be found so that the linear transformation

$$\mathbf{q}_2 = \mathbf{U}^{-1} \mathbf{C}^* \mathbf{q}, \quad \boldsymbol{\omega}_2 = \mathbf{U}^{-1} \mathbf{C}^{-1} \boldsymbol{\omega} \quad (1.13)$$

in which  $\mathbf{C}^{-1}$  and  $\mathbf{U}^{-1}$  are reciprocal matrices, and  $\mathbf{C}^*$  is the transpose matrix of  $\mathbf{C}$ , makes possible the reduction of the system of Eqs. (1.11) and (1.12) to the form [3]

$$\partial \mathbf{q}_2 / \partial r = \mathbf{E} \boldsymbol{\omega}_2, \quad \boldsymbol{\omega}_2 = \mathbf{D} \mathbf{q}_2 - \mathbf{e}_2 v \quad (\mathbf{e}_2 = \mathbf{U}^{-1} \mathbf{C}^{-1} \mathbf{e}) \quad (1.14)$$

where  $\mathbf{E}$  denotes a unitary matrix and  $\mathbf{D}$  is a diagonal matrix with elements  $d_{ii}$  equal to the characteristic numbers  $\lambda_i$  of the relaxation matrix  $\mathbf{R}$ .

The relaxation matrix  $\mathbf{R}$  is nothing else than the product  $\mathbf{F}\mathbf{G}$  of the kinetic matrix  $\mathbf{F}$  by matrix  $\mathbf{G}$  of the system chemical stability. The reduction of the first of these two matrices to a unitary and of the second to a diagonal matrix considerably simplifies the mathematical analysis of wave motions. There arises, however, the question whether the components of vectors  $\mathbf{q}_2$  and  $\boldsymbol{\omega}_2$  can be used as the new thermodynamic parameters which specify the multicomponent relaxing mixture and play the same part as the components of vectors of reaction completeness and chemical affinity. Otherwise the linear transformations (1.13) must be treated as purely formal substitutions of variables, and the "true" vector of reaction completeness must satisfy the input relaxation equation (1.1) or Eq. (1.11) which follows from it.

The question posed above can be readily solved with the use of Gibbs relationships. We introduce in conformity with formulas (1.13) the auxiliary vectors

$$\mathbf{q} = (\mathbf{C}^{-1})^* \mathbf{q}_1, \quad \boldsymbol{\omega} = \mathbf{C}\boldsymbol{\omega}_1$$

Let matrices  $\mathbf{C} = \|c_{il}\|$ ,  $\mathbf{C}^{-1} = \|c_{il}^{-1}\|$  and  $(\mathbf{C}^{-1})^* = \|(c^{-1})_{li}^*\|$ . Since elements  $(c^{-1})_{li}^* = c_{li}^{-1}$ , hence

$$\boldsymbol{\omega} d\mathbf{q} = \sum_{i,l=1}^N \omega_i (c^{-1})_{li}^* dq_{1l} = \sum_{i,l=1}^N c_{il}^{-1} \omega_l dq_{1i} = \boldsymbol{\omega}_1 d\mathbf{q}_1$$

As shown by the linear transformations (1.13), the auxiliary vectors

$$\mathbf{q}_1 = \mathbf{U}\mathbf{q}_2, \quad \boldsymbol{\omega}_1 = \mathbf{U}\boldsymbol{\omega}_2$$

Since  $\mathbf{U} = \|u_{il}\|$  is a unitary matrix, the elements of the inverse matrix  $\mathbf{U}^{-1} = \|u_{il}^{-1}\|$  are  $u_{il}^{-1} = u_{li}$ . This implies that

$$\boldsymbol{\omega}_1 d\mathbf{q}_1 = \sum_{i,l=1}^N \omega_{1i} u_{il} dq_{2l} = \sum_{i,l=1}^N u_{il}^{-1} \omega_{1l} dq_{2i} = \boldsymbol{\omega}_2 d\mathbf{q}_2$$

Thus the form of the scalar product  $\boldsymbol{\omega} d\mathbf{q} = \boldsymbol{\omega}_2 d\mathbf{q}_2$  in the right-hand side of formula (1.2) is not affected by the transition to new variables. This implies that the components of vectors  $\mathbf{q}_2$  and  $\boldsymbol{\omega}_2$  may be taken as the new thermodynamic parameters that determine the state of the multicomponent relaxing mixture by attributing to them the part of components of vectors of reaction completeness and chemical affinity. The invariance of Gibbs formula with respect to linear transformations (1.13) virtually means that any of vectors  $\mathbf{q}$  or  $\mathbf{q}_2$  play the part of the true vector of reaction completeness and any of vectors  $\boldsymbol{\omega}$  or  $\boldsymbol{\omega}_2$  may be considered as the true vector of chemical affinity.

The relaxation matrix in transformed variables is  $\mathbf{R}_2 = \mathbf{E}\mathbf{D} = \mathbf{D}$ , i.e. the characteristic numbers of the relaxation matrix are invariant with respect to linear transformations.

**2. Intermediate speeds of sound.** The missing equation that links the dimensionless velocity of particles and the vector of the perturbed completeness of chemical reactions was obtained in [3]. In variables defined in (1.13) it is of the form

$$2(\varepsilon m_0 v - \varepsilon_a^2 \beta_f) \frac{\partial v}{\partial r} + \Delta \left[ 2 \frac{\partial v}{\partial t} + (v - 1) \frac{v}{t} \right] = \varepsilon_a^2 \frac{V_0 p_0}{a_0^2} \mathbf{e}_2 \frac{\partial \mathbf{q}_2}{\partial r} \quad (2.1)$$

where the coefficients  $v = 1, 2, 3$  relate, respectively, to waves with a plane, axis, or center of symmetry, and the constants  $m_0$  and  $\beta_f$  are defined by formulas

$$m_0 = \frac{V_0^3}{2a_0^2} \left( \frac{\partial^2 p}{\partial V_0^2} \right)_{q_j, s}, \quad \beta_f = \frac{a_0 - a_{f_0}}{\varepsilon_a^2 a_0} \quad (2.2)$$

Equations (1.14) and (2.1) form a closed system. The input dimensional quantities are used for calculating  $(\partial^2 p / \partial V_0^2)_{q_j, s}$ , and all thermodynamic derivatives.

It is convenient to pass from Eqs. (1.14) and (2.1) to a single equation of order  $(N + 1)$  for the particle velocity  $v$ . For this we, first, introduce the following constants [4-6]:

$$\alpha_{\mu 0} = a_{f_0} + \frac{1}{2} \varepsilon_a^2 \frac{V_0 p_0}{a_0} \sum_{m=\mu+1}^N (-1)^{m-\mu} \frac{\sigma_{N-m}}{\sigma_{N-\mu}} \mathbf{e}_2 \mathbf{D}^{m-\mu-1} \mathbf{e}_2 \quad (2.3)$$

whose dimension is that of speed, and  $\sigma_l$  denotes the sum of all possible products of the characteristic numbers  $\lambda_1, \dots, \lambda_N$  by  $l$  in each product. When  $\mu = N$  the sum in the right-hand side of formula (2.3) vanishes, hence  $\alpha_{N0} = a_{f0}$ . The estimate of that sum for any arbitrary  $\mu$  is most rapidly obtained by passing to the auxiliary diagonal matrix

$$\mathbf{D}^{(\mu)} = \sum_{m=\mu+1}^N (-1)^{m-\mu} \frac{\sigma_{N-m}}{\sigma_{N-\mu}} \mathbf{D}^{m-\mu-1} \quad (2.4)$$

whose elements are

$$d_{ii}^{(\mu)} = \sum_{m=\mu+1}^N (-1)^{m-\mu} \frac{\sigma_{N-m}}{\sigma_{N-\mu}} \lambda_i^{m-\mu-1} = -\frac{\sigma_{N-\mu-1}^{(i)}}{\sigma_{N-\mu}} \quad (2.5)$$

where the superscript  $(i)$  at the sum  $\sigma_l^{(i)}$  indicates that  $\lambda_i$  is excluded from the complete set of characteristic numbers  $\lambda_1, \dots, \lambda_N$ . This immediately shows that formula

$$d_{ii}^{(0)} = -\frac{\sigma_{N-1}^{(i)}}{\sigma_N} = -\frac{1}{\lambda_i} \quad (2.6)$$

is valid for elements  $d_{ii}^{(0)}$  of matrix  $\mathbf{D}^{(0)}$ .

Substituting equalities (2.4) and (2.6) in formula (2.3) that defines constants  $\alpha_{\mu 0}$ , for the first  $\alpha_{00}$  we obtain

$$\alpha_{00} = a_{f0} + \frac{1}{2} \varepsilon_a^2 \frac{V_0 p_0}{a_0} \sum_{i=1}^N \left( -\frac{1}{\lambda_i} \right) e_{2i}^2 = a_{f0} - \frac{1}{2} \varepsilon_a^2 \frac{V_0 p_0}{a_0} \mathbf{e}_2 \mathbf{D}^{-1} \mathbf{e}_2$$

For any three matrices  $\mathbf{Q}_1$ ,  $\mathbf{Q}_2$  and  $\mathbf{Q}_3$ , whose product is  $\mathbf{W} = \mathbf{Q}_1 \mathbf{Q}_2 \mathbf{Q}_3$ , the equality  $\mathbf{W}^{-1} = \mathbf{Q}_3^{-1} \mathbf{Q}_2^{-1} \mathbf{Q}_1^{-1}$  is valid. Hence the inverse matrix is

$$\mathbf{D}^{-1} = \mathbf{U}^{-1} \mathbf{C}^* \mathbf{G}^{-1} \mathbf{C} \mathbf{U}$$

Using the last relation and recalling formula  $\mathbf{e}_2 = \mathbf{U}^{-1} \mathbf{C}^{-1} \mathbf{e}$ , we can easily verify that the product  $\mathbf{e}_2 \mathbf{D}^{-1} \mathbf{e}_2 = \mathbf{e} \mathbf{G}^{-1} \mathbf{e}$ . Since by the definition of matrix  $\mathbf{G}$  the elements  $g_{il}^{-1}$  of the inverse matrix  $\mathbf{G}^{-1}$  are

$$g_{il}^{-1} = \frac{V_0 p_0}{q_{i0} q_{l0}} \left( \frac{\partial q_l}{\partial \omega_{i0}} \right)_{\omega_k, V, s}$$

$$\left( \frac{\partial q_l}{\partial \omega_i} \right)_{\omega_k, V, s} = \left( \frac{\partial q_l}{\partial \omega_i} \right)_{\omega_1, \dots, \omega_{i-1}, \omega_{i+1}, \dots, \omega_N, V, s}$$

and the components of vector  $\mathbf{e}$  obey conditions (1.6), the expressions for  $\alpha_{00}$  in terms of the input dimensional variables assume the form

$$\alpha_{00} = a_{f0} - \frac{V_0^2}{2a_0} \sum_{i,l=1}^N \left( \frac{\partial q_l}{\partial \omega_{i0}} \right)_{\omega_k, V, s} \left( \frac{\partial p}{\partial q_{i0}} \right)_{q_j, V, s} \left( \frac{\partial p}{\partial q_{l0}} \right)_{q_j, V, s}$$

This is nothing else than the equilibrium speed of sound  $a_{e0}$  in the quiescent mixture [1, 2]. The remaining constants  $\alpha_{\mu 0}$  satisfy the inequalities

$$a_{e0} = \alpha_{00} < \alpha_{10} < \dots < \alpha_{N-1,0} < \alpha_{N0} = a_{f0} \quad (2.7)$$

as was strictly proved in [6].

We introduce now coefficients  $\gamma^{(\mu)}$  defined by formulas

$$a_0 - \alpha_{\mu 0} = \varepsilon_a^2 \gamma^{(\mu)} a_0 \quad (2.8)$$

In the limit cases of  $\mu = 0$  and  $\mu = N$  we have  $\gamma^{(0)} = \gamma_e$  and  $\gamma^{(N)} = \gamma_f$ , respectively. Using equalities (2.3) and (2.8) it is possible to reduce the system of Eqs. (1.14) and (2.1), after some very cumbersome calculations [6], to the following  $(N + 1)$ st order equation:

$$\sum_{\mu=0}^N (-1)^{\mu+1} \sigma_{N-\mu} \frac{\partial^\mu}{\partial r^\mu} \left\{ 2(\epsilon m_0 v - \epsilon_a^2 \gamma^{(\mu)}) \frac{\partial v}{\partial r} + \right. \quad (2.9)$$

$$\left. \Delta \left[ 2 \frac{\partial v}{\partial t} + (v - 1) \frac{v}{t} \right] \right\} = 0$$

which defines the particle dimensionless velocity  $v$ . Here the thermodynamic coefficient  $m_0$  is specified by the first of formulas (2.2).

The symmetric form of Eq. (2.9) makes it possible to interpret quantities  $\alpha_{\mu 0}$  as the velocity of acoustic wave propagation. In fact, the coefficient at the derivative  $\partial v / \partial r$  in the differential operator, appearing in braces in the left-hand side of the equation, contains two terms. The first of these depends on  $v$ ; its origin is due to that the velocity of signal transmission varies with the wave amplitude [7]. The second term is proportional to  $\gamma^{(\mu)}$ , i.e. to the difference between the wave propagation velocity and the quantity  $\alpha_{\mu 0}$ . The limit values  $\alpha_{00}$  and  $\alpha_{N0}$  of that quantity, that correspond to indices  $\mu = 0$  and  $\mu = N$  are equal, respectively, to the equilibrium  $a_{e0}$  and frozen  $a_{f0}$  speeds of sound in the quiescent mixture. Both are thermodynamic derivatives which are determined by the equations of state of the medium and are in no way related to the relaxation matrix  $\mathbf{R}$ . When  $0 < \mu < N$  expressions for  $\alpha_{\mu 0}$  contain also the characteristic numbers  $\lambda_1, \dots, \lambda_N$  of that matrix, which depend, in particular, on the relaxation times  $\tau_{ij}$ .

When  $\gamma^{(\mu)} = 0$ , the propagation velocity of small oscillations  $a_0 = \alpha_{\mu 0}$ . This means that quantities  $\alpha_{\mu 0}$  play the part of intermediate velocities at which waves may propagate in the perturbed flow zone with small variations of mixture parameters. As shown by inequalities (2.7), when  $0 < \mu < N$  these intermediate velocities  $\alpha_{\mu 0}$  are strictly confined to the interval between the frozen and equilibrium speeds of sound.

The presented reasoning does not in any way imply that the propagation velocity of signals in a relaxing mixture must necessarily be equal to one of the quantities  $\alpha_{\mu 0}$ . It was shown in [1, 2, 7] that the translation velocity  $a_0$  of small perturbations in the presence of chemical reactions depends on the wave length and varies continuously from the equilibrium  $a_{e0}$  to the frozen  $a_{f0}$  speed of sound. These results make it, however, possible to assert that perturbations will cluster around those which propagate at velocities  $\alpha_{\mu 0}$ .

The effect of intermediate speeds of sound becomes particularly clear after considering the following particular case. Let us assume that the wave propagation velocity  $a_0$  is exactly equal  $\alpha_{M0}$ , then  $\gamma^{(M)} = 0$ . We impose on the characteristic numbers of the relaxation matrix the conditions

$$\lambda_1, \dots, \lambda_M \ll 1, \quad 1 \ll \lambda_{M+1}, \dots, \lambda_N \quad (2.10)$$

The inequalities (2.10) show that "elements"  $q_{21}, \dots, q_{2M}$  vary very slightly, while elements  $q_{2,M+1}, \dots, q_{2N}$  relax at the same time in a nearly equiponderant manner. The greatest of all sums in Eq. (2.9) is  $\sigma_{N-M}$  followed by  $\gamma_{N-M-1}$  and  $\sigma_{N-M+1}$ . Their first approximations can be presented as

$$\sigma_{N-M} = \prod_{N \geq i \geq M+1} \lambda_i, \quad \sigma_{N-M-1} = \prod_{N \geq i \geq M+1} \lambda_i \sum_{n=M+1}^N \frac{1}{\lambda_n}$$

$$\sigma_{N-M+1} = \prod_{N \geq i \geq M+1} \lambda_i \sum_{m=1}^M \lambda_m$$

We assume that sums  $\sigma_{N-M-1}$  and  $\sigma_{N-M+1}$  are of the same order. We retain in Eq. (2.9) only the principal terms and, as the result, obtain

$$\frac{\partial^M}{\partial r^M} \left\{ 2\epsilon m_0 v \frac{\partial v}{\partial r} + \Delta \left[ 2 \frac{\partial v}{\partial t} + (v-1) \frac{v-1}{t} \right] \right\} + \quad (2.11)$$

$$2\epsilon a^{2\gamma(M-1)} \sum_{m=1}^M \lambda_m \frac{\partial^M v}{\partial r^M} + 2\epsilon a^{2\gamma(M+1)} \sum_{n=M+1}^N \frac{1}{\lambda_n} \frac{\partial^{M+2} v}{\partial r^{M+2}} = 0$$

We specify the relations

$$m_0 \epsilon = \frac{\alpha_{M0} - \alpha_{M-1,0}}{\alpha_{M0}} \sum_{m=1}^M \lambda_m = \Delta$$

between the small parameters and define the effective Reynolds number by

$$Re^* = \left[ \frac{\alpha_{M+1,0} - \alpha_{M0}}{\alpha_{M0} - \alpha_{M-1,0}} \sum_{n=M+1}^N \frac{1}{\lambda_n} \left( \sum_{m=1}^M \lambda_m \right)^{-1} \right]^{-1}$$

The  $M$ -fold integration of Eq. (2.11) yields

$$v \frac{\partial v}{\partial r} + \frac{\partial v}{\partial t} + \left( 1 + \frac{v-1}{2} \frac{1}{t} \right) v = \frac{1}{Re^*} \frac{\partial^2 v}{\partial r^2} \quad (2.12)$$

This clearly implies that in chemically active mixtures the effect of quasi-equilibrium "reactions" taking place at rates proportional to the characteristic numbers  $1 \ll \lambda_{M+1}, \dots, \lambda_N$  is the same as that of viscosity and thermal conductivity of inert gases. If inequalities (2.10) hold, the fastest relaxing elements that reach the equilibrium state are  $q_{2M+1}, \dots, q_{2N}$  which are linear combinations of all components  $q_1, \dots, q_N$  of the input vector of chemical reaction completeness. In other words, the equilibrium state is successively reached not by components of that vector but by their combinations defined by the first of formulas (1.13).

Let us now determine the first approximation of the intermediate velocity  $\alpha_{M0}$  of propagation of small perturbations in the quiescent mixture. We recall formula (2.5) which defines elements  $d_{ii}^{(M)}$  of the auxiliary diagonal matrix  $D^{(M)}$ . The principal terms of these elements are

$$d_{ii}^{(M)} = - \sum_{n=M+1}^N \frac{1}{\lambda_n} \quad \text{for } 1 \leq i < M, \quad (2.13)$$

$$d_{ii}^{(M)} = - \frac{1}{\lambda_i} \quad \text{for } M+1 \leq i \leq N$$

We substitute formulas (2.4) and (2.13) into (2.3) and obtain

$$\alpha_{M0} = a_{f0} - \frac{1}{2} \epsilon a^2 \frac{V_0 p_0}{a_0} \left[ \sum_{n=M+1}^N \frac{1}{\lambda_n} \sum_{l=1}^M e_{2l}^2 + \sum_{l=M+1}^N \frac{e_{2l}^2}{\lambda_l} \right] =$$

$$a_{f0} - \frac{1}{2} \varepsilon_a^2 \frac{V_0 p_0}{a_0} \left[ \sum_{l=1}^M \frac{e_{2l}^2}{\lambda_l} \sum_{n=M+1}^N \frac{\lambda_l}{\lambda_n} + \sum_{l=M+1}^N \frac{e_{2l}^2}{\lambda_l} \right]$$

We assume that the order of magnitude of the ratio  $e_{2l}^2 / \lambda_l$  is unity. Then by virtue of inequalities (2.10) the sum

$$\sum_{n=M+1}^N \frac{\lambda_l}{\lambda_n} \ll 1, \quad l = 1, \dots, M$$

The final form of the expression for the intermediate velocity of small oscillation propagation is

$$\alpha_{M0} = a_{f0} - \frac{1}{2} \varepsilon_a^2 \frac{V_0 p_0}{a_0} \sum_{l=M+1}^N \frac{e_{2l}^2}{\lambda_l} \quad (2.14)$$

Pressure  $p$  may be considered as a function of specific volume  $V$ , entropy  $s$  and such  $N$  quantities from the sequence  $q_{21}, \dots, q_{2N}$  and  $\omega_{21}, \dots, \omega_{2N}$  which do not contain conjugate ones. Such selection of independent variables can be achieved by  $2N$  different means.

We introduce the  $M$ -fold frozen and  $(N - M)$ -fold equilibrium speeds of sound

$$a_{2fe}^{(M)} = \left[ \left( \frac{\partial p}{\partial \rho} \right)_{q_{2j}, \omega_{2k}, s}^{(M)} \right]^{1/2}$$

where  $\rho = 1/V$  is the density and the superscript at the thermodynamic derivatives indicates that the first  $M$  components of vector  $\mathbf{q}_2$  of reaction completeness and the last  $N - M$  components of vector  $\omega_2$  which specifies chemical affinity are taken as independent variables. In conformity with the above  $j = 1, \dots, M$  and  $k = M + 1, \dots, N$ . Obviously

$$a_{2f0} = a_{f0} = \left[ \left( \frac{\partial p}{\partial \rho_0} \right)_{q_{2j}, \omega_{2k}, s}^{(N)} \right]^{1/2} = \left[ \left( \frac{\partial p}{\partial \rho_0} \right)_{q_{2j}, s} \right]^{1/2}$$

$$a_{2e0} = a_{e0} = \left[ \left( \frac{\partial p}{\partial \rho_0} \right)_{q_{2j}, \omega_{2k}, s}^{(0)} \right]^{1/2} = \left[ \left( \frac{\partial p}{\partial \rho_0} \right)_{\omega_{2k}, s} \right]^{1/2}$$

Differentiating the identity

$$p(q_{21}, \dots, q_{2M}, \omega_{2,M+1}, \dots, \omega_{2N}; \rho, s) = p(q_{21}, \dots, q_{2M}, q_{2,M+1}(q_{21}, \dots, q_{2M}, \omega_{2,M+1}, \dots, \omega_{2N}, \rho, s), \dots, q_{2N}(q_{21}, \dots, \dots, q_{2M}, \omega_{2,M+1}, \dots, \omega_{2N}, \rho, s); \rho, s)$$

with respect to  $\rho$ , for the quiescent mixture we have

$$(a_{2fe}^{(M)})^2 = a_{f0}^2 + \sum_{n=M+1}^N \left( \frac{\partial p}{\partial q_{2n0}} \right)_{q_{2j}, V, s} \left( \frac{\partial q_{2n}}{\partial \rho_0} \right)_{q_{2j}, \omega_{2k}, s}^{(M)} \quad (2.15)$$

Using the second of Eqs. (1.14) we immediately obtain

$$\left( \frac{\partial q_{2n}}{\partial \rho_0} \right)_{q_{2j}, \omega_{2k}, s}^{(M)} = \varepsilon_a V_0 q_{2n0} \frac{e_{2n}}{\lambda_n}$$

since in the considered approximation the density increment is  $\rho = v$  [3]. The simplest way of determining the derivatives  $(\partial p / \partial q_{2n0})_{q_{2j}, V, s}$  is to recall the definition of the auxiliary vector  $\mathbf{q}_1$

$$\left( \frac{\partial p}{\partial q_{2n0}} \right)_{q_{2j}, V, s} = \frac{1}{q_{2n0}} \sum_{l=1}^N q_{1l0} \left( \frac{\partial p}{\partial q_{1l0}} \right)_{q_{1j}, V, s} u_{ln} =$$



$$\frac{1}{q_{2n0}} \sum_{l=1}^N q_{1l0} u_{nl}^{-1} \left( \frac{\partial p}{\partial q_{1l0}} \right)_{q_j, V, s}$$

and similarly

$$\begin{aligned} \left( \frac{\partial p}{\partial q_{1l0}} \right)_{q_j, V, s} &= \frac{1}{q_{1l0}} \sum_{m=1}^N q_{1m0} \left( \frac{\partial p}{\partial q_{m0}} \right)_{q_j, V, s} (c^{-1})_{ml}^* = \\ &= \frac{1}{q_{1l0}} \sum_{m=1}^N q_{1m0} c_{lm}^{-1} \left( \frac{\partial p}{\partial q_{m0}} \right)_{q_j, V, s} \end{aligned}$$

We collect together the obtained results, and using equalities (1.6), present these in the form

$$\left( \frac{\partial p}{\partial q_{2n0}} \right)_{q_{2j}, V, s} = -\varepsilon_a \frac{p_0}{q_{2n0}} \sum_{l, m=1}^N u_{nl}^{-1} c_{lm}^{-1} e_m = -\varepsilon_a \frac{p_0}{q_{2n0}} e_{2n}$$

With allowance for the last equality, formula (2.15) can be written in the form

$$(a_{2f0}^{(M)})^2 = a_{f0}^2 - \varepsilon_a^2 V_0 p_0 \sum_{n=M+1}^N \frac{e_{2n}^2}{\lambda_n} \quad (2.16)$$

The second of formulas (2.2) shows that the rest  $a_0 - a_{f0} \sim \varepsilon_a^2$ , hence the comparison of formulas (2.14) and (2.16) yields

$$\alpha_{M0} = a_{2f0}^{(M)}$$

Thus, when the characteristic numbers of the relaxation matrix  $\mathbf{R}$  satisfy conditions (2.10), the  $M$ -th intermediate velocity of small perturbation propagation in a chemically active gas mixture is simply the  $M$ -frozen and the  $(N - M)$ -fold equilibrium speed of sound calculated in terms of variables  $q_{21}, \dots, q_{2M}, \omega_{2, M+1}, \dots, \omega_{2N}, V$  and  $s$ .

When the characteristic numbers are of the same order of magnitude, the intermediate velocity of acoustic wave propagation is not defined by such simple expression. According to the general formula (2.3) it depends not only on thermodynamic derivatives, but also on the rate of all chemical reactions that take place. In that case the input equation (2.1) may not be replaced by the simpler equation (2.12) and, consequently, the clustering of perturbations in wave packets at velocities  $\alpha_{u0}$  does not have a clearly defined character. The considered wave packet moving at velocity  $\alpha_{M0}$  is also blurred. When all chemical reactions affect the perturbation field, which occurs when the characteristic numbers of the relaxation matrix do not greatly differ, the wave propagation pattern is of a dispersing character with a continuous dependence of velocity on frequency.

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Translated by J. J. D.

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