THE SPEED OF SOUND IN A REACTING GAS MIXTURE

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The one-dimensional problem of the propagation of sound in a two-component mixture is solved. An expression is obtained for the speed of sound under conditions of chemical equilibrium. The results for the dissociation of hydrogen are compared with similar results in [1].

In problems of gas dynamics the velocity of sound is usually calculated from the formula $c = \sqrt{\gamma p/\rho}$, where $\gamma = c_p/c_v$ is the ratio of the specific heat capacities at a given temperature. However, if sound travels in a mixture of gases, this formula will be valid only for a nonreacting mixture. When the composition of the mixture changes as a consequence of chemical reaction, and the specific heat capacities do not remain constant, the coefficient γ will have some other significance.

An expression for the speed of sound is derived below directly from the solution of the equations describing the propagation of small perturbations in a reacting medium. The mixture is assumed to be a two-component one. Its state is characterized by the temperature T, the mass density of the mixture $\rho = \rho_1 + \rho_2$, and the mass concentrations $C_1 = \rho_1/\rho$, $C_2 = \rho_2/\rho$; since $C_1 + C_2 = 1$, then one of the concentrations, C_1, for example, will be independent in the chemical reaction process; we shall denote it by C. Assuming that the flow is one-dimensional and employing, as usual in the theory of sound, the adiabatic approximation, i.e., neglecting viscosity, diffusion and thermal conduction, we write the equations characterizing the behavior of the mixture.

The continuity equation for a particular component in the presence of a chemical reaction will be

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} = -m. \tag{1}$$

Here v is the mean flow velocity of the mixture, and m is the mass rate of the chemical reaction, which depends on concentration and temperature. In the case in question, in the presence of a reversible stoichiometric equilibrium reaction [2], we can write:

$$m = M(\nu_1' - \nu_1)\left[k_b\left(\frac{C}{\mu_1}\right)^{\nu_1'}\left(\frac{1-C}{\mu_2}\right)^{\nu_2'}\rho^{\nu_1'+\nu_2'-1} - k_f\left(\frac{C}{\mu_1}\right)^{\nu_1}\left(\frac{1-C}{\mu_2}\right)^{\nu_2}\rho^{\nu_1+\nu_2-1}\right] \tag{2}$$

where M is the mass of a molecule of the first component, ν_i and ν_i' are stoichiometric numbers, μ_1 and μ_2 are the molecular weights of the components, and k_f and k_b are the rate constants of the forward and reverse reactions, depending exponentially on activation energy (Arrhenius' hypothesis):

$$k_f = k\exp\frac{-E}{RT}, \qquad k_b = k\exp\frac{-(E+r)}{RT}. \tag{3}$$

It is assumed that the excitation times of the forward and reverse reactions are the same, and therefore the steric factor k is the same for k_f and k_b. We note at once that $m = 0$ will be the condition of chemical equilibrium.

The continuity equation and the momentum equation for the mixture have the form

$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial x}\rho v = 0, \qquad \rho\frac{\partial v}{\partial t} + \rho v\frac{\partial v}{\partial x} = -\frac{\partial p}{\partial x}. \tag{4}$$

The condition of conservation of energy in the presence of a chemical reaction has the form

$$\rho c_p\left(\frac{\partial T}{\partial t} + v\frac{\partial T}{\partial x}\right) = \frac{\partial p}{\partial t} + v\frac{\partial p}{\partial x} - \rho m Q \qquad (c_p = Cc_{p_1} + (1-C)c_{p_2}), \tag{5}$$

where c_p is the specific heat capacity of the mixture, and p is the pressure, equal to the sum of the partial pressures. For the quantity of heat Q in Eq. (5) we have

$$Q = r + \int_0^T (c_{p_2} - c_{p_1})\,dT.$$

Here r is the specific heat of reaction and the second term is conditioned by the temperature dependence of the heat capacities.

Finally, in order to close the system, it is necessary to add the equation of state of the mixture, obtained by summation of the equations of state for the individual components (R is the gas constant of the mixture):

$$p = \rho RT \qquad (R = CR_1 + (1 - C) R_2). \tag{6}$$

We linearize the system of equations (1), (4)-(6) in the following manner. We represent all the parameters of the mixture in the form of a sum of the undisturbed part – denoted by the subscript 0 – and the perturbation – denoted by a prime. The undisturbed parameters relate to the state of chemical equilibrium, so that the condition m = 0 is fulfilled, while the following limitations are imposed on the perturbations: their squares and products may be neglected, perturbations of dependent quantities are obtained as the linear part of the expenaion of these quantities at the point of chemical equilibrium:

$$\begin{matrix} C = C_0 + C', \\ \rho = \rho_0 + \rho', \end{matrix} \qquad m = \frac{\partial m}{\partial C_0} C' + \frac{\partial m}{\partial \rho_0} \rho' + \frac{\partial m}{\partial T_0} T' = m' \quad \text{etc.} \tag{7}$$

If only the speed of sound is to be determined, and not the entire mechanism of sound wave propagation, then the undisturbed mixture may be assumed to be at rest, $v_0 = 0$ and $v' = v$.

Substituting (7) in the system of equations (1), (4)-(5), and discarding terms containing only undisturbed quantities, since they satisfy these equations, we obtain for the perturbations the system of linear differential equations

$$\begin{gathered} \frac{\partial \rho'}{\partial t} + \rho_0 \frac{\partial v'}{\partial x} = 0, \qquad \rho_0 \frac{\partial v'}{\partial t} + \frac{\partial p'}{\partial x} = 0, \qquad \frac{\partial C'}{\partial t} = - m' \\ \rho_0 c_{p0} \frac{\partial T'}{\partial t} = \frac{\partial p'}{\partial t} - \rho_0 Q_0 m', \qquad p' = \frac{\partial p}{\partial \rho_0} \rho' + \frac{\partial p}{\partial T_0} T' + \frac{\partial p}{\partial C_0} C' \end{gathered} \tag{8}$$

the solution of which is sought in the form:

$$\rho' = \rho_0 \zeta_\rho e^{i(ax - 2\pi\nu t)}, \qquad C' = C_0 \zeta_c e^{i(ax - 2\pi\nu t)} \qquad (a = 2\pi / \lambda + i\varkappa) \quad \text{etc.}, \tag{9}$$

where λ is the wavelength, $\varkappa$ is the absorption coefficient , ν is the frequency, ζ_ρ, ζ_c, etc., denote dimensionless wave amplitudes; and ρ_0, C_0, etc., are associated with the condition m = 0.

For the rate of propagation of the perturbations we have, from the known formula,

$$c = \lambda\nu = \frac{2\pi\nu}{\operatorname{Re} a} = \frac{\omega}{\operatorname{Re} a} \qquad (\omega = 2\pi\nu). \tag{10}$$

Substituting (9) in (8), we obtain a homogeneous system of linear algebraic equations for the amplitudes ζ_ρ, ζ_c, etc. Its solution will be nontrivial if the determinant of its coefficients is zero. From this condition, after expansion of the determinant, we find the relation between a and the frequency ω:

$$\frac{a^2}{\omega^2} = \frac{c_{v_0}\omega + i \left[\frac{\partial m}{\partial C} c_v + \frac{\partial m}{\partial T} \left(Q + \frac{1}{\rho} \frac{\partial p}{\partial C} \right) \right]_0}{\frac{\partial p}{\partial \rho_0} \left\{ c_{p_0}\omega + i \left[\frac{\partial m}{\partial C} c_p + Q \frac{\partial m}{\partial T} - \frac{\partial m}{\partial \rho} \left(\frac{Q\rho}{T} + \frac{c_p}{RT} \frac{\partial p}{\partial C} \right) \right]_0 \right\}} \tag{11}$$

$$(c_{v_0} = c_{p_0} - R).$$

By separating the real part of Eq. (11), we can find from (10) the speed of sound c as a function of ω. The formulas for c will be simplest in two limiting cases: 1) The system follows the oscillations of the wave without inertia, so that chemical equilibrium is established all the time, and, 2) the system can not keep up with changes in the wave. In the first case the relaxation time τ is small compared with ω^{-1}. It was shown in [2] that for a mixture of gases reacting stoichiometrically the relation between the relaxation time and the derivative of the reaction rate with respect to concentration is $\tau = (\partial m/\partial C)^{-1}$.

Then the condition $\tau < \omega^{-1}$ implies that $\omega < \partial m/\partial C$. It can be shown that in this case ω will also be small compared with $\partial m/\partial \rho$ and $\partial m/\partial T$. Expanding with respect to the small parameter $\omega\,(\partial m/\partial C)^{-1}$ the expression for a from (11), we obtain, by confining ourselves to first-order terms, for the speed of sound at small values of ω:

$$c_0^2 = \frac{\partial p}{\partial \rho} \left. \frac{\frac{\partial m}{\partial C} c_p + Q \frac{\partial m}{\partial T} - \rho \frac{Q}{T} \frac{\partial m}{\partial \rho} - \frac{c_p}{RT} \frac{\partial p}{\partial C} \frac{\partial m}{\partial \rho}}{\frac{\partial m}{\partial C} c_v + Q \frac{\partial m}{\partial T} + \frac{1}{\rho} \frac{\partial m}{\partial T} \frac{\partial p}{\partial C}} \right|_0 . \tag{12}$$

In the second limiting case the system can be considered "frozen" at $c = c_0$, $\rho = \rho_0$ and $T = T_0$. In this case, $\tau > \omega^{-1}$ and $\omega > \partial m/\partial C$, and expansion with respect to the small parameter ω^{-1} and $\omega > \partial m/\partial C$ for the speed of sound, denoted in this case by c_∞ gives

$$c_\infty^2 = \frac{c_{p_0}}{c_{v_0}} \frac{\partial p}{\partial \rho_0}. \tag{13}$$

The real value of the speed of sound, calculated from (11) for a completely defined ω, lies between the values c_0 and c_∞. It can be seen from the results just given that the formula $c = \sqrt{\gamma p/\rho}$, in which c_p and c_v are taken for ρ_0

and T_0 is suitable for calculating the speed of sound in the mixture only if it is in the "frozen" state, when its composition remains unchanged. Hence, the rate of transmission of very high frequency waves is almost unaffected by the presence of a reaction in the gas mixture. Formula (12) is also suitable for calculating the velocity of long waves; for this calculation it is necessary to know from the chemical kinetics the actual relation between the reaction rate m and C, ρ, and T.

We shall apply the result obtained to a dissociation reaction of the type $X_2 \rightleftarrows 2X - r$, where r (taken with the minus sign) denotes the heat absorbed in the process of dissociation of unit mass of gas, i. e., this is nothing other than the heat of formation of X from the elements of X_2 on the assumption that the heat of formation of X_2 is equal to zero. Using expressions (2) and (3), written for dissociation, we obtain for the derivatives at the equilibrium point:

$$\frac{\partial m}{\partial C_0} = \frac{Mk_b}{\mu_2{}^2}\rho_0\frac{1-C_0{}^2}{C_0}, \qquad \frac{\partial m}{\partial \rho_0} = -\frac{Mk_b}{\mu_2{}^2}(1-C_0)^2$$
$$\frac{\partial m}{\partial T} = \frac{Mk_b}{\mu_2{}^2}\rho_0\frac{r}{RT^2}(1-C_0)^2 . \tag{14}$$

Substitution in Eq. (12) gives

$$c_0{}^2 = \frac{p}{\rho}\left(c_p\frac{2}{(1-C)\,C\,(2-C)} + \frac{rQ}{RT^2} + \frac{Q}{T}\right)\left(c_v\frac{1+C}{(1-C)\,C} + \frac{rQ}{RT^2} - \frac{r}{T\mu_1}\right)^{-1}\Bigg|_0 . \tag{15}$$

Introducing the true isentropic exponent for dissociation $\gamma_D = c_0^2\rho_0/p_0$, where c_0^2 is calculated from formula (15), we see that it does not coincide with the ratio c_p/c_v.

Using formula (15) to calculate the dissociation of hydrogen (chemical kinetics data taken from the handbook [3]), we obtain, for example, for

$T = 3000°$ K, $p = 0.010$ abs atm, $\gamma_D = 1.123$, $c_p/c_v = 1.264$;
$T = 3000°$ K, $p = 0.500$ abs atm, $\gamma_D = 1.120$, $c_p/c_v = 1.206$;
$T = 2200°$ K, $p = 0.010$ abs atm, $\gamma_D = 1.123$, $c_p/c_v = 1.164$.

For these same values of temperature and pressure, the corresponding values of γ_D and c_p/c_v obtained in [1] (by means of a purely thermodynamic calculation) are, respectively:

$$\gamma_D = 1.117,\quad 1.122,\quad 1.117,\quad c_p/c_v = 1.260,\quad 1.180,\quad 1.162 .$$

The agreement may be considered satisfactory.

REFERENCES

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