

ENTROPY CHANGE DURING RELAXATION OF A GAS BEHIND A SHOCK WAVE

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We have investigated entropy changes which take place in shock waves as translational, rotational and vibrational degrees of freedom are successively excited and as dissociation is induced. It is shown that the largest entropy change takes place when the translational degrees of freedom are excited; excitation of other degrees of freedom involves smaller entropy variations.

1. INTRODUCTION

In a previous paper,¹ the author set forth a method of consideration of nonequilibrium processes in a shock wave, making use of the introduction of zones of "quasi-equilibrium." The process of transition is as follows: a sudden throttling of the gas over several mean free path lengths produces an increase of temperature of the translational degrees of freedom, the remaining degrees of freedom remaining "frozen" because of their large relaxation times. Further, an additional retardation of the gas takes place and there is a transfer of energy from the translational degrees of freedom to the rotational; the vibration are "frozen" in this case. Then the vibrations are excited, and later there is dissociation of the gas.

Let us denote by the index 1 parameters of the inflowing current; by the indices 2, 3, and 4 the parameters in zones where the translational, rotational and vibrational degrees of freedom are completely excited; and by the index 5 the parameters in the zone of equilibrium dissociation. In what follows, we limit ourselves to diatomic gases. The introduction of zone 2 is strictly valid only for hydrogen and deuterium; in the heavier gases, the relaxation times of the translational and rotational degrees of freedom differ less.

In zones 2, 3:

$$\frac{p_k}{p_1} = \frac{2\gamma_1 M_1^2 \gamma_1}{\gamma_k + 1} - \frac{\gamma_k - 1}{\gamma_k + 1}, \tag{1}$$

$$\frac{\rho_k}{\rho_1} = \left(\frac{\gamma_k + 1}{\gamma_k - 1} \frac{p_k}{p_1} + 1 \right) / \left(\frac{\gamma_k + 1}{\gamma_k - 1} + \frac{p_k}{p_1} \right), \tag{2}$$

$$T_k/T_1 = p_k \rho_1 / \rho_1 p_k. \tag{3}$$

In zones 4, 5 (cf. reference 1):

$$\frac{p_k}{p_1} = \frac{\gamma_1 M_1^2 + 1}{\gamma'_k + 1} + \left[\left(\frac{\gamma_1 M_1^2 + 1}{\gamma'_k + 1} \right)^2 - \left(\frac{2\gamma_1 M_1^2}{\gamma'_1 - 1} - 1 \right) \frac{\gamma'_k - 1}{\gamma'_k + 1} \right]^{1/2}. \tag{4}$$

$$\frac{\rho_k}{\rho_1} = \left(\frac{\gamma'_k + 1}{\gamma'_k - 1} \frac{p_k}{p_1} + 1 \right) / \left(\frac{\gamma'_k + 1}{\gamma'_k - 1} + \frac{p_k}{p_1} \right), \tag{5}$$

$$T_k/T_1 = (p_k \rho_1 / \rho_1 p_k) / (1 + \kappa), \tag{6}$$

$$\gamma'_k / (\gamma'_k - 1) = H_k / (1 + \kappa) RT_k; \tag{7}$$

$H_k = H_k(p_k, T_k)$ is the enthalpy, referred to one mole μ of the inflowing gas, and κ is the degree of dissociation.

Making use of the method outlined above, we obtain the entropy change of the gas in transition from zone to zone.

2. GENERAL RELATIONS

In the absence of dissociation, the entropy change per mole of gas is equal to

$$dS = c_p dT/T - R dp/p; \tag{8}$$

whence

$$\frac{S_2 - S_1}{R} = \frac{5}{2} \ln \frac{T_2}{T_1} - \ln \frac{p_2}{p_1}, \tag{9}$$

$$\frac{S_3 - S_2}{R} = \frac{5}{2} \ln \frac{T_3}{T_2} + \ln \frac{T_3}{T_1} - \ln \frac{p_3}{p_2}. \tag{10}$$

$$\begin{aligned} \frac{S_4 - S_3}{R} = & \frac{7}{2} \ln \frac{T_4}{T_3} + \frac{e^{T_c/T_4} (T_c/T_4)}{e^{T_c/T_4} - 1} \\ & - \frac{e^{T_c/T_1} (T_c/T_1)}{e^{T_c/T_1} - 1} - \ln \frac{e^{T_c/T_4} - 1}{e^{T_c/T_1} - 1} - \ln \frac{p_4}{p_3}, \end{aligned} \tag{11}$$

T_c is the characteristic vibration temperature.

When $T_1 \gg T_c$, i.e., the vibrations are already excited in the flow, we have

$$\frac{S_4 - S_3}{R} = \frac{7}{2} \ln \frac{T_4}{T_3} + \ln \frac{T_4}{T_1} - \ln \frac{p_4}{p_3}. \tag{12}$$

If $T_1 \ll T_c \ll T_4$, which is the case in strong shocks,

$$\frac{S_4 - S_3}{R} = \frac{7}{2} \ln \frac{T_4}{T_1} + 1 + \frac{T_c}{T_4} + \ln \frac{T_4}{T_c} - \ln \frac{p_4}{p_3}. \quad (13)$$

In the presence of dissociation,

$$dS = (1 - \kappa) c_{p2} \frac{dT}{T} + 2\kappa c_{p1} \frac{dT}{T} + D(T) \frac{dx}{T} - (1 + \kappa) R \frac{dp}{p}. \quad (14)$$

We can set the energy of dissociation $D(T)$ equal to the energy of dissociation at absolute zero D_0 .

To compute $S_5 - S_4$, we need to know the dependence of κ on T on p in the nonequilibrium region between zones 4 and 5. We make use of the conservation equations and the equation of state

$$\rho u = \alpha, \quad p + \rho u^2 = \beta, \quad H + \mu u^2/2 = \epsilon; \quad (15)$$

$$p/\rho = RT(1 + \kappa)/\mu \quad (16)$$

α , β , ϵ are expressed in terms of the boundary conditions;

$$H = (1 - \kappa) \int_0^T c_{p2} dT + 2\kappa \int_0^T c_{p1} dT + \kappa D_0. \quad (17)$$

The four equations in (15) and (16) contain five unknowns, ρ , u , p , T and κ . We can therefore express κ as a function of p or T alone. The exact evaluation of such functions is difficult; therefore, we make use of approximate relationships.

We set

$$c_{p2} = a + Tb, \quad c_{p1} = c + Td; \quad (18)$$

a , b , c , and d are certain constants. From Eqs. (15) and (16) we have

$$u \approx (1 + \kappa) \alpha RT/\beta\mu; \quad u^2 \approx (1 + 2\kappa) (\alpha RT/\beta\mu)^2. \quad (19)$$

Substitution of (18) and (19) in (15) yields

$$\kappa = \frac{\epsilon - aT - (e+b)T^2/2}{D_0 + mT + (2e+n)T^2/2} \equiv \frac{1}{X(T)} \left[\epsilon - aT - \frac{1}{2}(e+b)T^2 \right], \quad (20)$$

where $e = \mu(\alpha R/\beta\mu)^2$, $m = 2c - a$, $n = 2d - b$.

In a similar fashion, we find

$$\begin{aligned} \kappa &= (2D_0)^{-1} \left\{ \epsilon - D_0 - \left(\frac{\beta}{p} - 1 \right) \frac{mR}{e} \right. \\ &\quad \left. + \left[\left[\epsilon - D_0 - \left(\frac{\beta}{p} - 1 \right) \frac{mR}{e} \right]^2 \right. \right. \\ &\quad \left. \left. + 4D_0 \left[\epsilon - \left(\frac{\beta}{p} - 1 \right) \frac{aR}{e} \right]^{1/2} \right\} = (2D_0)^{-1} [F - m\beta R/ep \right. \\ &\quad \left. + \sqrt{(m\beta R/ep)^2 + Gm\beta R/ep + H}] \\ &= (2D_0)^{-1} [F - m\beta R/ep + \sqrt{Q(p)}]. \end{aligned} \quad (21)$$

In the integration of Eq. (14) over p , we introduce the variable $x = m\beta R/ep$. Then

$$\begin{aligned} \frac{S_5 - S_4}{R} &= L_1(T_4 - T_5) + L_2 \ln \frac{X(T_4)}{X(T_5)} - \frac{L_3(T_5)}{X(T_5)} + \frac{L_3(T_4)}{X(T_4)} \\ &\quad + L_4 [J(T_4) - J(T_5)] \\ &\quad + \left(1 + \frac{\sqrt{H} + F}{2D_0} \right) \ln \frac{p_4}{p_5} - \frac{1}{2D_0} \left\{ \frac{m\beta R}{e} \left(\frac{1}{p_5} - \frac{1}{p_4} \right) \right. \\ &\quad \left. - \sqrt{Q(p_5)} + \sqrt{Q(p_4)} + \sqrt{H} \ln \frac{H + m\beta GR/2ep_5 + \sqrt{HQ(p_5)}}{H + m\beta GR/2ep_4 + \sqrt{HQ(p_4)}} \right. \\ &\quad \left. - G \ln \frac{\sqrt{Q(p_5)} + m\beta R/ep_5 + G/2}{\sqrt{Q(p_4)} + m\beta R/ep_4 + G/2} \right\}, \end{aligned} \quad (22)$$

where the following notation has been introduced:

$$\begin{aligned} L_1 R &= \frac{e(n-2b)}{2e+n}; \quad L_2 R = \frac{2an + m(e+b)}{2(2e+n)} - \frac{mn(e+b)}{(2e+n)^2} - \frac{a}{2}; \\ L_3 R &= aD_0 + \epsilon m + \frac{1}{2} [D_0(e+b) + \epsilon(2e+n)] T \\ &= q_1 + q_2 T; \\ L_4 R &= q_2 + mL_2 + \left[\epsilon + \frac{D_0(e+b)}{2e+n} \right], \end{aligned} \quad (23)$$

$$J = \frac{2}{\sqrt{2D_0(2e+n) - m^2}} \tan^{-1} \frac{m + (2e+n)T}{\sqrt{2D_0(2e+n) - m^2}}.$$

In order to obtain the explicit dependence of the entropy change in every region of M_1 and γ_1 , we consider the limiting cases of weak and strong shocks.

3. SHOCK WAVES OF WEAK INTENSITY

In this case the specific heat of the gas can be considered constant; we need consider only $S_2 - S_1$, $S_3 - S_2$, $S_4 - S_3$:

$$\frac{p_k}{p_1} = 1 + \Delta, \quad \Delta = \frac{2\gamma_k}{\gamma_k + 1} \left(M_1^2 \frac{\gamma_1}{\gamma_k} - 1 \right) \ll 1. \quad (24)$$

We employ a power series expansion in Δ , whence

$$\frac{S_k - S_1}{R} = \frac{2\gamma_k}{3(\gamma_k + 1)^2} \left(M_1^2 \frac{\gamma_1}{\gamma_k} - 1 \right)^3, \quad (25)$$

$$\gamma_2 = 5/3, \quad \gamma_3 = 7/5, \quad 7/5 > \gamma_4 > 9/7.$$

Obviously, for given γ_k and M_1 , the entropy change is the greater the larger the value of γ_1 ; it has a maximum value for monatomic gases.

For given γ_1 and M_1 , the entropy increases with decrease in γ_k , i.e., successive excitation of the degrees of freedom of the molecules is accompanied by an increase in the entropy.

From Eq. (25) we have

$$\frac{S_2 - S_1}{R} = \frac{5}{32} \left(\frac{3}{5} \gamma_1 M_1^2 - 1 \right)^3, \quad (26)$$

$$\frac{S_3 - S_2}{R} = \frac{35}{216} \left(\frac{5}{7} \gamma_1 M_1^2 - 1 \right)^3 - \frac{5}{32} \left(\frac{3}{5} \gamma_1 M_1^2 - 1 \right)^3 < \frac{S_2 - S_1}{R}, \quad (27)$$

$$\frac{S_4 - S_3}{R} = \frac{2\gamma_4}{3(\gamma_4 + 1)^2} \left(\frac{\gamma_1}{\gamma_4} M_1^2 - 1 \right)^3$$

$$- \frac{35}{216} \left(\frac{5}{7} \gamma_1 M_1^2 - 1 \right)^3 < \frac{S_3 - S_2}{R}. \quad (28)$$

For $\gamma'_5 > M_1^2 > 1$, the excitation of the translational and rotational degrees of freedom takes place without entropy change, and only the subsequent excitation of vibrations leads to its increase. This phenomenon is known as the Kantrowitz effect² for supersonic velocities. No sharp front of the shock wave will be observed, but rather a gradual change of the parameters over distances of several tens of mean free path lengths.

4. STRONG SHOCK WAVES

In this case, considering $M_1 > 10$, Eqs. (1) to (6) are written in the form

$$\frac{p_h}{p_1} = \frac{2\gamma_1 M_1^2}{\gamma_h + 1}, \quad \frac{\rho_h}{\rho_1} = \frac{\gamma'_h + 1}{\gamma'_h - 1}, \quad \frac{T_h}{T_1} = \frac{2\gamma_1 M_1^2}{(\gamma'_h + 1)^2} \frac{\gamma'_h - 1}{1 + \alpha}, \quad (29)$$

where $\gamma'_2 = 5/3$, $\gamma'_3 = 7/5$, $\gamma'_4 \geq 9/7$; in accord with Refs. 3, 4, and 5, $\gamma'_5 = 1.2$. Making use of Eqs. (9), (10), (12), (13), and (29) we obtain

$$(S_2 - S_1)/R = 3 \ln M_1 + \frac{3}{2} \ln \gamma_1 - 3.897, \quad (30)$$

$$(S_3 - S_2)/R = 2 \ln M_1 + \ln \gamma_1 - 2.829 < (S_2 - S_1)/R, \quad (31)$$

$$(S_4 - S_3)/R|_{T_1 > T_c} = 2 \ln M_1 + \ln \gamma_1 - 3.098 < (S_3 - S_2)/R. \quad (32)$$

For most practical problems, $T_c/T_1 \leq 10$; therefore,

$$(S_4 - S_3)/R|_{T_1 < T_c < T_4} = 2 \ln M_1 + \ln \gamma_1 + 91.43/\gamma_1 M_1^2$$

$$- 4.401 < (S_4 - S_3)/R|_{T_1 > T_c}. \quad (33)$$

It follows from Eqs. (32) and (33) that in a gas in which the vibrations are already appreciably excited in the flow, the entropy change, for the same values of M_1 , is larger than in a gas with the vibrations unexcited.

The expression for $S_5 - S_4$ is rather complicated. We shall simplify it, in order to estimate the dependence of the entropy change in dissociation upon M_1 , γ_1 , and D_0 . Tabulated data give $a \approx 4R$, $c \approx 2R$, $m \approx R$, $b \approx d \approx 3 \text{ to } 6 \times 10^{-2} R/T_1$,

$n \approx b$; moreover, $D_0 \approx 2 \times 10^2 RT_1 \approx \gamma_1 M_1^2 RT_1$. Making use of these values, we obtain

$$(S_5 - S_4)/R \approx (A + B\gamma_1 M_1^2 RT_1/D_0) \cdot 10^{-2}$$

$$< (S_4 - S_3)/R|_{T_1 < T_c < T_4}; \quad (34)$$

A and B are constants on the order of unity. It is clear that the entropy change depends more strongly on M_1 in the dissociation of a gas than ΔS does in the excitation of arbitrary degrees of freedom of the molecules. For a given M_1 this change increases with diminishing energy of dissociation.

On the basis of Eqs. (26) to (28) and (30) to (34), it can be verified that the maximum entropy change takes place in the excitation of the successive degrees of freedom. For subsequent excitation of rotation, vibration and dissociation of the gas, the increase in entropy is lessened. This is explained by the fact that in an isolated system tending toward equilibrium, an increase in the total entropy can be accompanied by a decrease in the entropy of its separate parts; for a gas these will be the different degrees of freedom of the molecules. As is easily seen, in the successive excitation of the degrees of freedom of the gas, less of it is throttled, and a smaller fraction of the directed motion is transformed into heat energy. Such an excitation takes place therefore more and more at the expense of the redistribution of the already excited degrees of freedom.

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DISPERSION RELATIONS AND THE DERIVATION OF THE EQUATIONS FOR K-MESON SCATTERING

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A study is made of the scattering of K mesons by nucleons, with inclusion of effects of the possible formation of Ξ particles. In addition to the other propositions of the standard theory, special use is made of the conditions of causality and of the unitary nature of the S matrix. These conditions, together with the additional hypothesis that the interaction is invariant with respect to rotations in four-dimensional isotopic spin space, enable us to obtain equations which are valid at not too high energies and are of the type of Low's equations^{1,2} in the theory of π -meson scattering. The form of the interaction is involved in the equations through the inhomogeneous term. These equations are at the same time a generalization of the dispersion relations for scattering at arbitrary angles. Analogous equations for π -meson scattering have been obtained in reference 2, where, however, use was made of a special spectral representation of the scattering matrix.³⁻⁵ This spectral representation is not used in the present paper.

THE fact that it is not a trivial problem to go from the scattering of π mesons to a treatment of K-meson scattering is mainly due to the special nature of the behavior of the K mesons with respect to transformations in ordinary space and isotopic spin space, and also to the fact that in the case of the K mesons it turns out to be necessary from the very beginning to take into account the interactions with particles that do not play any direct part in the scattering, in particular Σ and Λ particles, and also π mesons. In addition, one must give more careful attention to relativistic effects. The interactions are here taken to be the renormalized ones; effects of weak interactions are neglected. This last condition is formulated as the requirement that all interactions be invariant with respect to rotations in the four-dimensional isotopic space.⁶ In this space nucleons, Ξ particles, and K mesons form the four-dimensional isotopic spinors:

$$\Psi_N = \begin{pmatrix} \psi_p \\ \psi_n \\ \psi_{\Xi^0} \\ \psi_{\Xi^-} \end{pmatrix} \text{ and } K = \begin{pmatrix} K^+ \\ K^0 \\ \tilde{K}^0 \\ K^- \end{pmatrix} = \|K^i\|, \quad (i = 1, 2, 3, 4); \tag{1}$$

The following representation is chosen for the isotopic matrices:*

*Hereafter, where no special stipulation is made, the notations of reference 7 are used.

$$\gamma_i^i = \begin{pmatrix} 0 & \tau_i \\ -\tau_i & 0 \end{pmatrix} \quad (i = 1, 2, 3); \quad \gamma_0^i = \begin{pmatrix} 0 & E_2 \\ E_2 & 0 \end{pmatrix};$$

$$\gamma_5^i = \begin{pmatrix} iE_2 & 0 \\ 0 & -iE_2 \end{pmatrix}. \tag{2}$$

This way of writing makes it possible to give a unified description of the dynamical behavior of all K mesons, and furthermore the "hypercharge" Y^6 of the heavy fermions is given apart from a factor i by the eigenvalue of the matrix γ_5^i . Unlike the convention of reference 6, we regard the isotopic space as pseudo-Euclidean, since only in this kind of a space can an isotopic spinor K that does not vanish identically be taken to be self-conjugate:

$$K = -i\gamma_5^i K^*. \tag{3}$$

It is necessary, however, to impose the invariant requirement that K be self-conjugate, owing to the existence of only four different K mesons. In connection with the experimental facts that are interpreted in terms of the presence of different parities of K mesons, one can assume* that an

*One can try to give this fact a general explanation through the idea of a fusion of the ordinary and isotopic spaces.⁸ We note also that the definition of the hypercharge is here an obvious four-dimensional way of writing the isotopic fermion number of d'Espagnat and Prendtki. The reflections in this four-dimensional isotopic space for the K mesons are analogous to the Pauli transformations⁹ for spinor particles.