

EFFECT OF HEATS OF CHEMICAL REACTIONS ON TURBULENCE IN HOMOGENEOUS GAS MIXTURES

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UDC 532.517.4:541.124.7

The effect of the heats of chemical reactions on the turbulence in a turbulent gas flow is considered. An example of the application of the obtained results to a dissociating polyatomic gas is given.

It is known [1] that distributed energy sources can affect the degree of turbulence in a compressible turbulent gas flow. This is due to the fact that in a flow of compressible gas a component due to density (and pressure) fluctuations is added to the usual solenoidal vortical turbulence field of an incompressible medium. This compressible component is capable under certain conditions of receiving the energy of distributed sources and transmitting it in turn to the vortical turbulence field.

A typical example of distributed energy sources is the heat release due to chemical reactions in homogeneous gas mixtures.

In [1] an attempt was made to investigate theoretically the intensification of turbulence due to heats of chemical reactions in a reacting system composed of a monatomic and a diatomic gas. This paper, however, excludes a large number of practically important cases of reacting mixtures of polyatomic gases.

Below we consider the effect of heat release due to chemical reactions on the intensity of turbulence of a reacting mixture of polyatomic gases. The results obtained are used to determine the change in turbulence in the case of thermal dissociation of a dinitrogen tetroxide - nitrogen dioxide system. We assume that when the flow velocity of the reacting gas is low the compressibility properties depend on the molecular changes due to chemical reactions.

We will represent the fluctuations of a compressible medium as a harmonic oscillator:

$$\rho = \bar{\rho} + \rho' \sin \omega\tau, \quad (1)$$

$$p = \bar{p} + p' \sin(\omega\tau - \varphi). \quad (2)$$

According to [1], the energy transmitted from the compressible component to the vortical component is equal to the work performed. The work performed by unit mass in one oscillation cycle is given by the integral

$$B_\omega = \int_{v_\tau=0}^{v_\tau = \frac{2\pi}{\omega}} p dV. \quad (3)$$

Calculating (3) to second-order terms in fluctuation amplitude we have

$$B_\omega = \frac{p' \rho' \omega}{2\rho^2} \sin \varphi \frac{2\pi}{\omega}.$$

Relating the performed work to unit time we obtain

$$P_\omega = \frac{p' \rho' \omega}{2\rho^2} \sin \varphi. \quad (4)$$

If the phase difference between the density and pressure fluctuations is $\varphi = \pi/2$, then

Power Institute, Moscow. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 17, No. 4, pp. 648-654, October, 1969. Original article submitted November 23, 1968.

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$$P_\omega = \frac{\rho' p' \omega}{2\rho^2}. \quad (5)$$

Thus, energy P_ω is transmitted in unit time in unit mass from the compressible component to the vortical component, thus intensifying or reducing the turbulence (depending on the sign of P_ω).

We determine the relationship between p' and ρ' , which is required for the calculation of (4) or (5), for a system composed of a dissociating (or recombining) gas reacting according to the scheme $A_2 \rightleftharpoons 2A$, where A and A_2 are polyatomic molecules.

We define the degree of dissociation α as the mass fraction of dissociating gas, and the reaction rate ψ as $d\alpha/d\tau$.

In the general case

$$\frac{d\alpha}{d\tau} = \psi(\alpha, T, \rho). \quad (6)$$

The fluctuations of α and T may be shifted in phase relative to ρ .

We expand (6) in a series of fluctuation components α , T , and ρ , retaining only the first-order terms. Bearing in mind that differentiation alters the phase by $\pi/2$, we obtain

$$-\alpha'_1 \omega = \bar{\psi}_\alpha \alpha'_0 + \bar{\psi}_T T'_0 + \bar{\psi}_\rho \rho'_0, \quad (7)$$

$$\alpha'_0 \omega = \bar{\psi}_\alpha \alpha'_1 + \bar{\psi}_T T'_1. \quad (8)$$

We now have five unknowns (α'_0 , α'_1 , T'_0 , T'_1 , ρ'_1), for the determination of which in terms of ρ' we need five equations. Two of the five equations are provided by (7) and (8). The rest can be obtained by using two different expressions for the fluctuating part of the internal energy and the equation of state.

On one hand, the fluctuating part of the internal energy per unit mass e' can be calculated as the work performed by the fluctuations in one half cycle, which corresponds to the eddy kinetic energy

$$e' = \int_{v_\tau=0}^{v_\tau=\frac{\pi}{\omega}} p dV = \frac{\bar{p}}{\rho^2} \rho'. \quad (9)$$

In the calculation of (9) we retain only terms of the first order in fluctuation amplitude.

It follows from (9) that in a first approximation the fluctuations of e' are in phase with ρ' , i.e.,

$$e'_1 = 0, \quad (10)$$

$$e'_0 = \frac{\bar{p}}{\rho^2} \rho'. \quad (11)$$

On the other hand, the fluctuating part of the internal energy can be calculated from a thermodynamic standpoint in the following way.

The total internal energy U of the $A_2 \rightleftharpoons 2A$ system of volume V is given by the formula [2]

$$U = kT^2 \left\{ n_A \frac{\partial}{\partial T} \log f_A + n_{A_2} \frac{\partial}{\partial T} \log f_{A_2} \right\} + \frac{1}{2} n_A D. \quad (12)$$

The term $n_A D/2$ is required because of the difference in chemical binding energy in the molecules A and A_2 .

$$f_{A,A_2} = f_{A,A_2}^T f_{A,A_2}^R f_{A,A_2}^V f_{A,A_2}^E, \quad (13)$$

$$f_{A,A_2}^T = \frac{(2\pi m_{A,A_2} kT)^{3/2} V}{h^3}, \quad (14)$$

$$f_{A,A_2}^R = V \bar{\pi} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} (I_A^{A,A_2} I_B^{A,A_2} I_C^{A,A_2}), \quad (15)$$

$$f_{A,A_2}^V = [1 - \lambda(v_1^{A,A_2}, T)]^{-1} [1 - \lambda(v_2^{A,A_2}, T)]^{-1} \dots \quad (16)$$

The electronic distribution function is usually close to unity and it can be neglected.

Substituting (14)-(16) in (13) and (13) in (12), we obtain the following expression for the internal energy:

$$U = n_A \left(3kT + \sum_{i=1}^{i_A} h\nu_i \frac{\lambda(\nu_i, T)}{1 - \lambda(\nu_i, T)} \right) + n_{A_2} \left(3kT + \sum_{j=1}^{i_{A_2}} h\nu_j \frac{\lambda(\nu_j, T)}{1 - \lambda(\nu_j, T)} \right) + \frac{1}{2} n_A D. \quad (17)$$

We replace n_A and n_{A_2} in (17) by expressions in ρ and α . By definition

$$\alpha = \frac{n_A}{n_A + 2n_{A_2}}; \quad n_A + 2n_{A_2} = \frac{\rho V}{m}. \quad (18)$$

Hence, the internal energy per unit mass e ($e = U/\rho V$) is given by

$$e = \frac{3kT}{m} \frac{1 + \alpha}{2} + \frac{\alpha}{m} \sum_{i=1}^{i_A} h\nu_i \frac{\lambda(\nu_i, T)}{1 - \lambda(\nu_i, T)} + \frac{1 - \alpha}{2m} \sum_{j=1}^{i_{A_2}} h\nu_j \frac{\lambda(\nu_j, T)}{1 - \lambda(\nu_j, T)} + \frac{1}{2} D \frac{\alpha}{m}. \quad (19)$$

The quantities T and α in (19) fluctuate around their mean values

$$T = \bar{T} + T' \sin(\omega\tau - \varphi_1), \quad (20)$$

$$\alpha = \bar{\alpha} + \alpha' \sin(\omega\tau - \varphi_2). \quad (21)$$

Because of this the internal energy also fluctuates around a mean value e_0 , which is given by expression (19) with $T = \bar{T}$ and $\alpha = \bar{\alpha}$.

Substituting (20) and (21) in (19) we can determine the fluctuating part of the internal energy e' .

To first-order terms in fluctuation amplitude we have after some manipulation

$$e' = \alpha\alpha' + bT', \quad (22)$$

where

$$a = \frac{1}{m} \sum_{i=1}^{i_A} h\nu_i \frac{\lambda(\nu_i, \bar{T})}{1 - \lambda(\nu_i, \bar{T})} + \frac{3k\bar{T}}{2m} - \frac{1}{2m} \sum_{j=1}^{i_{A_2}} h\nu_j \frac{\lambda(\nu_j, \bar{T})}{1 - \lambda(\nu_j, \bar{T})} + \frac{1}{2} \frac{D}{m}; \quad (23)$$

$$b = \frac{3k}{m} \frac{1 + \bar{\alpha}}{2} + \frac{\bar{\alpha}}{m} \sum_{i=1}^{i_A} \frac{h\nu_i}{k\bar{T}^2} \left(\frac{\lambda(\nu_i, \bar{T})}{1 - \lambda(\nu_i, \bar{T})} + \frac{\lambda(2\nu_i, \bar{T})}{[1 - \lambda(\nu_i, \bar{T})]^2} \right) + \frac{1 - \bar{\alpha}}{2m} \sum_{j=1}^{i_{A_2}} \frac{(h\nu_j)^2}{k\bar{T}^2} \left(\frac{\lambda(\nu_j, \bar{T})}{1 - \lambda(\nu_j, \bar{T})} + \frac{\lambda(2\nu_j, \bar{T})}{[1 - \lambda(\nu_j, \bar{T})]^2} \right). \quad (24)$$

Comparing (22) and (10), (11), we obtain

$$e'_0 = \alpha\alpha'_0 + bT'_0 = \frac{\bar{p}}{\rho^2} \rho', \quad (25)$$

$$e'_1 = \alpha\alpha'_1 + bT'_1 = 0. \quad (26)$$

Using the equation of state for the mean values

$$\frac{\bar{p}}{\rho} = (1 + \bar{\alpha}) R\bar{T}, \quad (27)$$

we replace $\bar{p}/\bar{\rho}$ in (25) by $(1 + \bar{\alpha})R\bar{T}$. Then

$$\alpha\alpha'_0 + bT'_0 = (1 + \bar{\alpha}) R\bar{T} \frac{\rho'}{\rho}. \quad (28)$$

Using the equation of state for the fluctuating quantities, we obtain

$$\frac{p'}{p} - \frac{\rho'}{\rho} = \frac{T'}{T} + \frac{\alpha'}{1 + \bar{\alpha}}. \quad (29)$$

For components with a phase shift of $\pi/2$ relative to ρ' (29) becomes

$$\frac{\rho'_1}{\rho} = \frac{T'_1}{\bar{T}} + \frac{\alpha'_1}{1 + \bar{\alpha}} \quad (30)$$

Using the obtained equations (7), (8), (25), (26), and (30) we can express components α' , T' , and p' in terms of ρ' and derivatives of the reaction rate ψ and find a relationship between p'_1 and ρ' .

After the necessary operations we obtain

$$p'_1 = \frac{R(a + \bar{\alpha} - b\bar{T})[b\bar{\rho}\bar{\psi}_\rho/\bar{\psi} + R\bar{T}(1 + \bar{\alpha})\bar{\psi}_T/\bar{\psi}]\bar{\psi}}{b^2 + \frac{\bar{\psi}^2}{\omega}(a\bar{\psi}_T/\bar{\psi} - b\bar{\psi}_\alpha/\bar{\psi})^2} \frac{\bar{\psi}}{\omega} \rho' \quad (31)$$

If p is in advance of ρ by $\pi/2$, then $p'_1 = -p' \sin \varphi$ and the expression for the energy P_ω transmitted to the turbulence has the form

$$P_\omega = -\frac{1}{2} \frac{\omega p'_1 \rho'}{\bar{\rho}^2} \quad (32)$$

Substituting (31) in (32) we obtain the final expression for P

$$P_\omega = -\frac{R(a + \bar{\alpha} - b\bar{T})(b\bar{\rho}\bar{\psi}_\rho/\bar{\psi} + R\bar{T}(1 + \bar{\alpha})\bar{\psi}_T/\bar{\psi})\bar{\psi}}{b^2 + \left(\frac{\bar{\psi}}{\omega}\right)^2 (a\bar{\psi}_T/\bar{\psi} - b\bar{\psi}_\alpha/\bar{\psi})^2} \frac{\bar{\psi}}{2} \left(\frac{\rho'}{\bar{\rho}}\right)^2 \quad (33)$$

Thus, the effect of the heat of the chemical reaction on turbulence is a second-order effect in density fluctuation and is proportional to the reaction rate.

The expression (33) for P_ω is similar to that obtained by Eschenroeder in [1]. It differs in the coefficients a and b , which have a much simpler form for a reacting mixture of a monatomic and diatomic gas.

As an example of the use of the obtained expression for P_ω we use it to evaluate the effect of heat release on the turbulence of a reacting $N_2O_4 \rightleftharpoons 2NO_2$ system. The $N_2O_4 \rightleftharpoons 2NO_2$ reaction occurs at 300–400°K. We will determine the effect of the chemical reaction on the turbulence at $T = 320^\circ\text{K}$, $\alpha = 0.3$, for instance. When $\alpha = 0.3$ the predominant reaction is dissociation, which is accompanied by heat absorption. The reaction rate is positive and, hence, $P_\omega < 0$, i.e., the turbulence energy decreases.

Substituting in expressions (23) and (24) for a and b the oscillation frequencies of the N_2O_4 and NO_2 molecules, the reaction heat $D = 4.74 \cdot 10^{-19}$ J, and the mean mass per molecule $m = 7.64 \cdot 10^{-26}$ kg with $\alpha = 0.3$, we obtain $a = 2.23 \cdot 10^5$ J/kg and $b = 3.53 \cdot 10^2$ J/kg·deg.

The equation for the overall reaction rate has the form

$$\psi = \frac{d\alpha}{d\tau} = k_{\text{diss}}(1 - \alpha) - 4k_{\text{rec}}\rho\alpha^2$$

The reaction rate constants k_{diss} and k_{rec} are given by the expressions [4]

$$k_{\text{diss}} = 10^{16} \exp\left(-\frac{13000}{RT}\right) \text{ sec}^{-1},$$

$$k_{\text{rec}} = \frac{k_{\text{diss}}}{k_p/RT(1 + \alpha)},$$

where k_p is given by the expression [4]

$$\log k_p = -\frac{2930}{T} + 9, \quad k_p \text{ in atm.}$$

It can be shown [1] that

$$\frac{\rho'}{\bar{\rho}} = \frac{3/2u'^2}{c^2} \quad (34)$$

Assuming $u' = 25$ cm/sec [5], we have

$$\frac{\rho'}{\bar{\rho}} = 9.02 \cdot 10^{-7}.$$

Determining the numerical values of $\bar{\psi}$, $\bar{\psi}_T$, $\bar{\psi}_\alpha$, and $\bar{\psi}_\rho$, and substituting them in equation (33), we obtain, for any ω ,

$$|P_\omega| \leq 1.05 \text{ J/kg} \cdot \text{sec.}$$

For comparison we give the heat release per unit time per unit mass

$$\frac{D}{m} \bar{\psi} \approx 10^{13} \text{ J/kg} \cdot \text{sec.}$$

The energy P_ω is released in a very short period of time, equal to the chemical relaxation time τ_{chem} , which for the considered reaction is $\tau_{\text{chem}} = 10^{-7}$ sec.

The energy absorbed in this time is

$$P_\omega \tau_{\text{chem}} \leq 10^{-7} \text{ J/kg,}$$

which is negligibly small in comparison with the energy of turbulent pulsations per unit mass of gas

$$\frac{1}{2} u'^2 = 3 \cdot 10^{-2} \text{ J/kg.}$$

Thus, the reduction in turbulence due to heat absorption of the chemical reaction in a $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ system is not more than 0.001%, i.e., is of no practical importance.

NOTATION

p	is the pressure;
ρ	is the density;
φ	is the phase difference between density and pressure fluctuations;
V_τ	is the volume per unit mass at time τ ;
ω	is the fluctuation frequency;
α	is the degree of dissociation;
T	is the temperature;
ψ	is the reaction rate;
$\psi_\alpha, \psi_T, \psi_\rho$	are the derivatives of ψ with respect to α , T, and ρ ;
k	is the Boltzmann constant;
h	is the Planck constant;
n_A, n_{A_2}	are the number of molecules A and A_2 in volume V;
f_A, f_{A_2}	are the distribution functions for molecules A and A_2 ;
m	is the mass of molecule;
I	is the moment of inertia of molecule;
$\nu_i (i = 1, \dots, i_A)$,	
$\nu_j (j = 1, \dots, j_{A_2})$	are the oscillation frequencies of molecules A and A_2 ;
D	is the dissociation energy per A_2 molecule;
c	is the mean thermal velocity of molecules;
u'	is the pulsation velocity

Subscripts

dash	denotes the fluctuation amplitude;
bar	denotes the mean value;
0	denotes the component in phase with ρ' ;
1	denotes the component differing in phase from ρ' by $\pi/2$.

Superscripts

T, R, V, E denote the translational, rotational, vibrational, and electronic distribution functions;
 $\lambda(\nu, T) = \exp(-h\nu/kT)$.

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