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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE PROOF OF THE IMPOSSIBILITY OF STRONG DEFLAGRATIONS AND WEAK DETONATIONS

1. A proof of the impossibility of strong deflagrations has become widespread; its physical meaning is seen from Fig. 1, where the Hugoniot adiabat H is shown, constructed from the equation

$$\pi = \frac{q + \chi - \sigma}{\chi\sigma - 1}, \quad (1)$$

and the Michelson straight line 1—2—3, satisfying the relation

$$\pi = (1 + \operatorname{tg} \theta) - \operatorname{tg} \theta \cdot \sigma. \quad (2)$$

Fig. 1

The tangent of the angle of inclination

$$\operatorname{tg} \theta = \frac{1 - \pi_2}{\sigma_2 - 1} \quad (3)$$

determines the velocity of propagation of the deflagration, which depends on the physicochemical and aerodynamic characteristics of the gas mixture.

In equations (1)–(3), π and σ are the pressure and specific volume of the gas, normalized so that at the initial point $\pi_1 = 1$, $\sigma_1 = 1$, $\chi = (\gamma + 1)/\gamma - 1$, γ is the ratio of heat capacities, $q = 2\gamma Q/c_1^2$, where Q/c_1^2 is the ratio of the heat effect of combustion per unit mass to the square of the speed of sound in the initial state 1.

Fig. 2

Figure 2: Fig. 2

On the Hugoniot adiabat the Jouguet deflagration is denoted by the point K . Above the point K on the curve H lie the states of the combustion products of weak deflagrations, and below it, of strong ones. For a strong deflagration to be realized, the state of the gas must be carried along the straight line from the initial point 1 through 2 to 3. But all points on the segment of the Michelson straight line between 2 and 3 correspond to higher heat releases during combustion than on the curve H . The region between 2 and 3 is an energy barrier, for overcoming which the gas has no reserve of heat. This is the essence of the generally accepted proof of the impossibility of strong deflagrations.

In the Zeldovich–Neumann model, a detonation is represented in the form of a deflagration propagating behind a shock wave with the same velocity as it (in the laboratory coordinate system). The initial state for the deflagration is the shock-compressed gas. A strong detonation, therefore, is identified with a weak deflagration, and a weak detonation with a strong deflagration. The impossibility of weak detonations is proved in exactly the same way as the impossibility of strong deflagrations.

2. The proof given above, which has entered the most fundamental manuals ^(1,2), is valid in many practical cases, but in principle is incorrect. It is based on the nonobvious assumption—especially for detonation processes—that the rate of the chemical reaction along the Michelson straight line 1—2—3 is positive (in space, from the unburned gas to the burned gas).

Let us imagine dissociation of the combustion products, occurring with some delay. Then the assumption of the positivity of the reaction rate, and with it the entire proof, loses its force. Suppose, for example, that in the first stage of the reaction heat is released corresponding to the Hugoniot adiabat H' , shifted upward; then, after some time, part of the heat of reaction is spent on dissociation, and the stationary case—the curve H —will be determined by some part of the maximum thermal effect. Under these conditions, from the standpoint of the proof given above, it becomes possible to overcome the energy barrier 2—3 and to realize a strong deflagration and a weak detonation. But in reality, in this case too, strong deflagration, as well as weak detonation in the Zel' dovich–Neumann model, is unrealizable. This is due to a more general thermodynamic cause than the presence of an energy barrier between points 2 and 3.

Fig. 2

3. Figure 2 shows the entropy as a function of the specific volume along the Hugoniot adiabat (line H) and along the Michelson straight lines passing through points 2—3 (curve M_2) and K (curve M_K). Fig. 2 repeats Fig. 1 in the S — σ plane; corresponding points have the same notation. But in addition to deflagration (the segment $H2K2_13$), Fig. 2 also shows the

detonation part of the Hugoniot curve (to the left of $\sigma = 1$) with a sharp entropy minimum J . The initial point $\sigma_1 = 1$ and $S = 0$ did not fall on the graph; it is located far below.

As can be seen from Fig. 2, the entropy on the straight line 1—2—3 at point 3, belonging to strong deflagration, is lower than at point 2, which lies on the branch of weak deflagrations. Consequently, the transition from weak deflagrations to strong ones is accompanied by a decrease in entropy, in this case by the amount ΔS . But, since the thermal effect of the reaction at points 2 and 3 is the same and the process takes place in a tube of constant cross section, such a transition is impossible: it contradicts the second law of thermodynamics. The validity of this assertion for a deflagration propagating with any of the possible velocities can be proved by considering limiting cases. As point 3 approaches the point where the Hugoniot adiabat intersects the abscissa axis, the first limiting case is reached. In Fig. 1 it corresponds to the Michelson straight line 1—2P—3P. At the intersection point 3P the pressure goes to zero, and the entropy of the strong deflagration goes to $-\infty$. This occurs when

$$\sigma_{3P} = q + \varkappa, \quad (4)$$

$$\operatorname{tg} \theta = \frac{1}{q + \varkappa - 1}. \quad (5)$$

The specific volume at the point of intersection of the Michelson line with the branch of weak deflagrations is related to the specific volume at the point of intersection of the same line with the branch of strong deflagrations by the relation

$$\sigma_2 = \frac{2\gamma}{\gamma + 1} \frac{1 + \operatorname{tg} \theta}{\operatorname{tg} \theta} - \sigma_3. \quad (6)$$

From (6), (5), and (4) we find

$$\sigma_{2P} = \frac{1}{\chi} q + 1, \quad (7)$$

whence we determine the entropy on the branch of weak deflagrations at the point 2P

$$\frac{S_{2P}}{c_v} \lg e = \lg \pi_{2P} \sigma_{2P}^\gamma = \lg \frac{\left(\frac{1}{\chi} q + 1\right)^{\gamma+1}}{\frac{\gamma-1}{2} q - 1}. \quad (8)$$

It is equal to a finite quantity. Consequently, the difference in entropies in the first limiting case reaches infinity. Specific volumes exceeding $q + \chi$ need not

be considered, since for them the pressure becomes negative. In the other limiting case, when the deflagration velocity increases and approaches the Jouguet deflagration velocity, point 2 shifts toward point K in Fig. 2, and points 2₁ and 3 are drawn together there as well. The difference in entropies decreases and at point K becomes zero. From the limiting cases it is evident that the entropy of a weak deflagration is always greater than the entropy of a strong deflagration propagating with the same velocity (lying on the same Michelson line). The intermediate cases, lying between the limiting ones, have no analytic solution. Therefore the quantitative value of the difference in entropies has to be determined by numerical solution of the problem. The graphs in Figs. 1 and 2 were constructed for $\gamma = 1.4$ and $q = 20$. Calculations give similar results for other values of γ and q .

The impossibility of strong deflagrations has exactly the same physical basis as the nonrealizability of rarefaction shock waves. But the impossibility of rarefaction shock waves is absolute in character: the entropy of the shock-expanded gas is always below the entropy of the initial state 1. In deflagration, a decrease in entropy occurs only relative to a weak deflagration moving with the same velocity as the strong one. Relative to the initial state 1 in Fig. 1, strong deflagrations have a higher entropy, except for states lying to the right of point 4, which represents the intersection of the Hugoniot adiabat with the Poisson isentrope π_1 passing through point 1. Therefore strong deflagrations are impossible if the gas cannot pass point 2, i.e., if it first enters a state on the branch of weak deflagrations corresponding to a real physical process. In chemical combustion reactions this is always so. But one may imagine (we do not undertake to judge their possibility) exothermic reactions of condensation type, with a strong temperature dependence: such reactions do not occur under the conditions of point 2, but proceed instantaneously in states described by point 3. The state of the gas then, bypassing point 2, passes directly—by a jump—to 3. Under the condition $\sigma_3 < \sigma_4$, nothing prevents the realization of a strong deflagration of this kind: neither the conservation laws nor the second law of thermodynamics.

In a strong deflagration the gas velocity passes from subsonic to supersonic—a phenomenon that at first glance seems impossible. Indeed, for isentropic processes a transition through the speed of sound without removal of heat or mass, performance of work, or expansion of the stream is impossible. But deflagration is a nonisentropic process; therefore the transition from subsonic to supersonic velocity becomes possible.

4. The impossibility of weak detonations holds only so long as a mechanism of ignition of the gas by a shock wave is valid. Strictly speaking, in this case there is no detonation as such. There is a deflagration for which the initial state is a gas compressed by a shock wave running ahead of it. The entropy on the Hugoniot adiabat for the Zel'dovich-Neumann mechanism has a maximum at the Jouguet point, whereas on the detonation branch at the Jouguet point J , as is seen in Fig. 2, it has a minimum.

The literature discusses a mechanism for the propagation of detonation in con-

densed explosives by means of electron diffusion ⁽³⁾. Its propagation by means of light is also conceivable. If in any cases the validity of diffusional propagation of detonation is established, this will be a weak detonation. The velocity will be determined not by the Jouguet selection rule, but by a relation which, on dimensional grounds, has the form

$$D \simeq \sqrt{\frac{lv}{\tau}}, \quad (9)$$

where l is the mean free path of the electrons or quanta, v is their velocity, and τ is the time of the chemical decomposition reaction of the explosive under the action of the electrons or quanta.

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Note: Figure translations are in progress. See original paper for figures.

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