VALIDITY OF THE PRIGOGINE THEOREM IN ESTABLISHING A SIGNIFICANTLY NONEQUILIBRIUM STEADY STATE OF A THERMODYNAMIC SYSTEM

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It is concluded that there exists a certain class of thermodynamic systems for which the Prigogine theorem is satisfied in setting up a steady state significantly different from a equilibrium state.

The Prigogine theorem is a theorem of the thermodynamics of irreversible processes. It asserts that a steady (i. e., time-independent) state of a thermodynamic system in which irreversible processes occur is a state corresponding to the minimum possible production of entropy in the given conditions [1, 2]. The Prigogine theorem has been proved for various thermodynamic systems (homogeneous, heterogeneous, continuous) on the assumption that this steady state is close to equilibrium, when it is possible to use a phenomenological or generalized transfer law with constant coefficients, and also the Onsager reciprocity relation [1-3]. It remains to establish the validity of the Prigogine theorem for the setting up, in a thermodynamic system, of steady states that are far from equilibrium, i. e., states in which the production of entropy is finite.

The present work examines an example of the setting up of a steady state that is, on the one hand, significantly different from a quasiequilibrium state and, on the other, is characterized by the minimum possible production of entropy, i. e., satisfies the Prigogine theorem.

We consider the propagation of detonation waves in a brisant gas which is initially at rest, for two cases: plane waves induced at the end of a cylindrical tube with thermally insulated walls and spherical waves induced at some point of space.

According to current ideas [4, 5], the leading edge of the detonation wave is a shock wave in the initial gas. In this wave, the gas is compressed and heated to such a degree that combustion is initiated. As a result, heat is liberated and, in the case of a purely endothermic reaction considered below, the pressure of the gas decreases as long as the reaction continues. In front of the detonation wave, the gas parameters and, in particular, its entropy do not change. In the wave the entropy of the gas increases, since its leading edge is a shock wave and, behind this edge, combustion occurs and heat is liberated. After the detonation wave has passed (at the end of combustion), the gas motion in the cases considered is again isentropic.

Plane and spherical detonation waves may be induced, for example, by a sharp increase in pressure. Directly after they are induced, the plane and spherical detonation waves are nonsteady in the general case. However, after a certain lapse of time, they become steady; i. e., they attain some constant velocity [5, 6].

In other words, the detonation wave is an open thermodynamic system, in which irreversible transformations occur. Setting up steady plane and spherical detonation waves may be considered as an example of the process of establishing a steady state in such a system.

After the considered detonation waves have been induced, the gas velocity at the points of induction (at the closed end of the cylinder and at the center of the spherical wave) becomes zero. In both these cases, moreover, none of the given characteristic parameters has the dimensionality length, and therefore the gas motion arising as a result of the passage of a steady detonation wave should be self-modeling. If this is so, and if it is assumed additionally that the gas velocity in front of the wave is zero, and that the gas in front of and behind the wave is ideal, it is possible to show [7] that the gas velocity behind a steady detonation wave (whether plane or spherical) cannot be subcritical. On the other hand, in accordance with the principle of reversibility

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[8], this velocity cannot be supersonic, since the gas velocity behind the shock wave (that is, the leading edge of the detonation wave) is subcritical, while the combustion in the detonation wave is endothermic. (According to the principle of reversibility, a subcritical flow velocity may be increased by heating only to the velocity of sound.) Hence, the gas velocity behind the steady detonation wave must be equal to the local velocity of sound or, in other words, the wave must be a Chapman–Jouguet wave.

As is known, there have been many successful experimental confirmations of this conclusion [5, 9].

Using the well-known procedure [7] of thermodynamic treatment of a shock wave, we shall show that the velocity v_1^* of the Chapman–Jouguet detonation wave and the entropy s_2^* of unit mass of gas behind the wave are the minimum possible values for the system parameters of the initial gas. However, we must first make the following remark: Chapman [10] calculated the velocity of the detonation wave on the assumption that it was a minimum, whereas Jouguet [11, 12] assumed that the entropy of the gas behind the wave was a minimum; Crussard [13] showed that these assumptions were equivalent, while Zel'dovich [14] was the first to put them on a rigorous basis. Thus, the proof below that v_1^* and s_2^* are minimum values should be considered exclusively as a subsidiary simplifying aspect of the present work.

The condition of continuity of the mass, momentum, and energy flows through the detonation wave implies that

$$w_1 - w_2 + \frac{V_1 + V_2}{2}(p_2 - p_1) = 0, \tag{1}$$

where the subscripts 1 and 2 refer, respectively, to the initial gas and the combustion products behind the detonation wave; w is the enthalpy; V is the specific volume; and p is the pressure.

The dependence $p_2(V_2)$ corresponding to Eq. (1) — called the detonation adiabatic curve — is shown in Fig. 1, together with the point p_1, V_1, which expresses the state of the initial gas. (Of course, p_1, V_1 lies below the detonation adiabatic curve.)

The condition of continuity of single mass and momentum flows through the detonation wave gives another expression, first obtained by Michelson:

$$p_2 = p_1 + j^2(V_1 - V_2), \tag{2}$$

where $j = v_1/V_1$ is the density of the mass flow through the wave.

In the plane (p_2, V_2) in Fig. 1, this relation gives a straight line passing through the point p_1, V_1, since it was derived without assuming continuity of the energy flow, and should therefore be valid for the initial gas in any section within the detonation wave, and also for the combustion products.

For the sake of brevity, let us say that the Chapman–Jouguet point in the plane (p_2, V_2) is the point of intersection of the detonation adiabatic curve and the Michelson straight line. Thus, taking into account the above remark on the gas velocity behind the detonation wave, we must show that at the point p_2^*, V_2^* in Fig. 1 the velocity v_1^* and the entropy s_2^* are minimal, and that v_2^* is the velocity of sound.

Using Eqs. (1) and (2), it is not difficult to show that

$$w_1 + \frac{j^2V_1^2}{2} = w_2 + \frac{j^2V_2^2}{2}. \tag{3}$$

For given constant values of w_1 and V_1, it follows that

$$\frac{V_1^2}{2}d(j^2) = dw_2 + \frac{V_2^2}{2}d(j^2) + j^2V_2dV_2.$$

In accordance with well-known thermodynamic relations, the differential dw_2 may be written in the form $dw_2 = T_2ds_2 + V_2dp_2$, after which we obtain

$$dp_2 = \frac{V_1^2 - V_2^2}{2V_2}d(j^2) - \frac{T_2}{V_2}ds_2 - j^2dV_2.$$

On the other hand, differentiating Eq. (2) and solving it with respect to dp_2 gives

$$dp_2 = (V_1 - V_2)d(j^2) - j^2dV_2. \tag{4}$$

After equating the two expressions for dp_2, we obtain

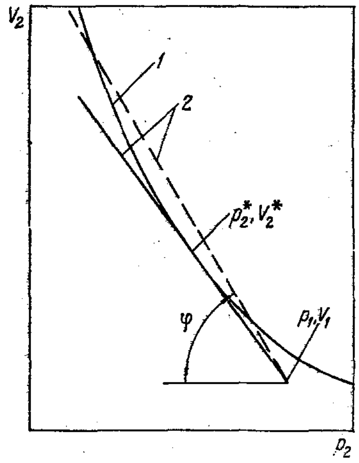

Fig. 1. Detonation adiabatic curve (1) and Michelson straight lines (2); φ is the angle between the Michelson straight line and the p_2 axis.

$$T_2 ds_2 = \frac{(V_1 - V_2)^2}{2} d(j^2) \tag{5}$$

or

$$\frac{ds_2}{d(j^2)} = \frac{(V_1 - V_2)^2}{2} \frac{1}{T_2} > 0. \tag{6}$$

Thus, it follows from Eq. (6) that increase in j^2 is associated with increase in s_2.

Consider again Fig. 1 for the angle φ:

$$\operatorname{tg} \varphi = \frac{p_2 - p_1}{V_1 - V_2}$$

and in accordance with Eq. (2)

$$\operatorname{tg} \varphi = j^2.$$

In the case of a straight line joining the points p_1, V_1 and p_2^*, V_2^*, the values of φ and $\tan\varphi$ are the minimum possible. Hence, in view of the definition of j ($j = v_1/V_1$) the values of the velocity v_1 and, according to Eq. (6), the entropy s_2 corresponding to this straight line are the minimum possible.

Hence we now show that at the point p_2^*, V_2^*, v_2 is equal to the velocity of the sound.

We again use Eq. (4), substituting into it the identity

$$dV_2 = \left(\frac{\partial V_2}{\partial p_2}\right)_{s_2} dp_2 + \left(\frac{\partial V_2}{\partial s_2}\right)_{p_2} ds_2,$$

and also the expression for ds_2 from Eq. (5). We then divide by dp_2 and take into account that at the point p_2^*, V_2^*, since j is a minimum,

$$\left[\frac{d(j^2)}{dp_2}\right]^* = 0.$$

As a result, we find that at the point p_2^*, V_2^*,

$$1 + j^2 \left(\frac{\partial V_2}{\partial p_2}\right)_{s_2} = 1 - \frac{v_2^2}{c_2^2} = 0$$

or

$$v_2 = c_2,$$

since

$$c = \sqrt{\left[\frac{\partial p}{\partial (1/V)}\right]_s} \text{ and } \left(\frac{\partial V_2}{\partial p_2}\right)_{s_2} = -\frac{V_2^2}{c_2^2}.$$

Since v_1^* and s_2^* are minimal, the production of entropy P* in the Chapman–Jouguet detonation wave is also a minimum. In fact, the production of entropy in the thermodynamic system [1, 2] is the increase in unit time of that part of the entropy which arises in the system itself. Accordingly, the production of entropy P over unit area of any plane or spherical detonation wave is

$$P = \frac{1}{V_1} v_1 (s_2 - s_1),$$

and

$$P^* = \frac{1}{V_1} v_1^* (s_2^* - s_1)$$

is the minimum possible value.

Moreover, P* is finite for given parameters of very large amplitude, for example, in the case of a strong detonation wave, when the specific heat of reaction q is much larger than the internal thermal energy $c_{V1}T_1$ of the initial gas

$$v_1^* = \sqrt{2(\varkappa_2^2 - 1) q},$$

and

$$s_2^* - s_1 = \int_0^{T_2} \frac{c_{p2}(p_2, T)}{T} dT - \int_0^{T_1} \frac{c_{p1}(p_1, T)}{T} dT,$$

where c_p and c_V are the specific heat of unit mass of gas for constant pressure and volume, respectively, and $\varkappa = c_p/c_V$, while

$$T_2 = \frac{2\varkappa_2}{\varkappa_2 + 1} \frac{q}{c_{v2}}$$

and

$$p_2 = p_1 \frac{2(\varkappa_2 - 1)}{\varkappa_1 - 1} \frac{q}{c_{v1} T_1}.$$

Thus, in fact, the example given here may be considered as an example of the establishment in a thermodynamic system of a steady state, on the one hand, significantly different from quasiequilibrium and, on the other, characterized (in agreement with the Prigogine theorem) with the minimum possible production of entropy.

On this basis, it may evidently be assumed that there exists a certain class of thermodynamic systems, and irreversible processes occurring in them, for which the Prigogine theorem, although as yet unproved, is satisfied in establishing significantly nonequilibrium states.

An analogous assertion — admittedly in implicit form — was made in the second part of [15], when a gas consisting of molecules with quantized energy was considered.

The next step, as we see it, is to subject this conclusion to detailed scrutiny and, if possible, to provide a statistical basis for it. Actually, nonequilibrium states are at present studied using the evolution condition rather than the Prigogine theorem [16]. However, "the existence of the evolution condition is a direct consequence of the condition of stable equilibrium, and therefore an indirect consequence of the second law of thermodynamics" [16]. Accordingly, the Prigogine theorem provides significantly more information than the evolution condition, as is evident at once on considering that the Prigogine theorem is obtained from the evolution condition only on the assumption that the transfer law with constant coefficients and the Onsager reciprocity relation are true [16].

It remains to point out that there has already been positive experience of the use of the Prigogine theorem in considering nonequilibrium steady states of fairly diverse thermodynamic systems [17, 18].

In conclusion, we note that considerations similar to those above are also possible for spin detonation waves [19], since, as shown in [20], the average over the cross section and time of the pressure at the front of a spin detonation wave coincides with the pressure behind a shock wave moving at the Chapman–Jouguet velocity.

NOTATION

v_1, velocity of detonation wave; v_2, gas velocity behind wave; s, entropy of unit mass of gas; w, enthalpy; V, specific volume; p, pressure; j, density of mass flow through wave; T, temperature; c, velocity of sound; P, production of entropy; q, specific heat of reaction; c_p, c_V, specific heats of unit mass of gas at constant pressure and volume, respectively. Indices: 1, initial gas; 2, combustion products; *, Chapman–Jouguet point.

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