LETTERS TO THE EDITOR

COMMENTS ON THE ARTICLE BY BARTOSH ET AL. "SYSTEMS FOR BASING THE ENTROPY EXISTENCE PRINCIPLE IN THERMODYNAMICS"

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We shall first introduce a number of general arguments which it will be convenient to use in analyzing the article by Bartosh and his co-authors. As is known, in classical thermodynamics the second law is formulated in the form of a postulate expressing the irreversibility of the heat transfer or friction process, and upon this is based a proof of the existence of entropy and of its growth during irreversible processes in an adiabatic system. This conception, which reflects the unity of the second law, was subjected to doubts by many investigators, since, in their opinion, the proof of the existence of entropy, put forward by classical authors, is not fully correct, since a relation valid for reversible processes is obtained from the postulate regarding irreversibility.

We cannot concur with this reasoning, since it loses sight of the following very important fact: when the irreversibility of some process is asserted, it inevitably follows that it is impossible by reversible means to obtain an effect identical or directly opposite to the effect of the irreversible process. Thus, if we take Planck's postulate as a formulation of the second law (the transformation of heat by means of friction is an irreversible process, the immediate consequence is obtained) it is impossible by reversible means to accomplish either the full transformation of heat into work, or of work into heat, i.e., both a perpetual engine of the second kind and its direct opposite are impossible, and these are just what are required for a basis of the second law.

In connection with the thermodynamics of negative absolute temperatures it should be noted that if the postulate of the second law is simply represented in the form "the friction process is irreversible," without indicating specifically what the effects of this process are (i.e., without indicating how the complete transformation of work into heat or indeed of heat into work are carried out), the consequence of such a postulate coincides with that made earlier, since it does not depend on the specific direction of the irreversible process.

Since a criticism was made in the article by Bartosh et al. of the paper "Investigation of the Classical Idea in a New System for the Basis of the Second Law" (IFZh, no. 3, 1964), it is necessary to remark here that the basic objective of our paper was to show how the equality of the second law for reversible processes may be correctly obtained, not on the basis of the postulate of irreversibility, but with the aid of the symmetric consequence resulting from it (in the paper cited it appeared as an expanded formulation of the second law). This postulate of irreversibility should serve to derive the inequality of the second law, relating to irreversible processes. In order not to fasten this to a specific method for the basis, it was shown there that by means of a consequence of the postulate of the second law we may reach a symmetrical position regarding quasi-static adiabatic unattainability (which is connected with the postulate of adiabatic unattainability due to Caratheodory in the same way as the formulation of the second law has been enlarged with Planck's postulate) and that with its aid a fully rigorous and complete basis of the second law could be reached according to the Caratheodory method.

Let us dwell a little more on the statement concerning the incompatability of the adiabat and the isotherm for complex systems (for simple systems their incompatability is not disputed), on which the authors base their criticism. The weakness of the theorem regarding the incompatability of an adiabat and an isotherm was demonstrated in reference [1]. To avoid returning to this question, we shall give a simple example. We shall consider a system composed of two thermally interconnected ideal gases, separated by a rigid and perfectly thermally conducting diaphragm. The state of the system is described by the common temperature T and the independent volumes V_1 and V_2 of the gases. For simplicity we shall assume that we have one mole of each gas. The above system is subject in the general case to a thermal influence and to two independent mechanical influences, characterized by the pressures T_1 and T_2. The equation of the first law for the elementary quasi-static process of this system may be written in the form

$$\delta Q = (C_{V_1} + C_{V_2})\, dT + P_1\, dV_1 + P_2\, dV_2.$$

Making use of the equations of state of the gases, we find

$$\delta Q = (C_{V_1} + C_{V_2})\, dT + RT\left(\frac{dV_1}{V_1} + \frac{dV_2}{V_2}\right).$$

Putting $\delta Q = 0$ and $dT = 0$, we obtain the isotherm-adiabat equation in the form

$$\frac{dV_1}{V_1} + \frac{dV_2}{V_2} = 0, \quad \text{or} \quad V_1 V_2 = \text{const}.$$

The example given illustrates the compatability of the isotherm and adiabat for systems where the number of independent variables exceeds two, and it is sufficient to refute the "theorem" regarding the incompatability of the adiabat and isotherm.

Coming now to an analysis of the article by Bartosh and his co-authors, we turn to the arguments presented there, which, according to the authors' statement, present the basic conclusions from the book "Thermodynamics" by Belokon [2].

Thesis 1 states: "The integration of the principles of existence and increase of entropy in the framework of the second law of thermodynamics results from erroneous derivations (the methods of Clausius, Planck, and others), and independent postulates must lie at the basis of the two principles." The introductory part of the present paper speaks to the incorrectness of this thesis. Moreover, it would be interesting to see how these "independent" postulates of the author of reference [2] would look if we put one behind the other: heat cannot simultaneously pass from a hot body to a cold one, and, conversely, heat passes from a hot to a cold body.

Thesis 2 states: "A correct construction of the principle of existence of entropy may be accomplished on the basis of a determination of temperature ... and of a symmetry postulate, equivalent to a statement that it is impossible to accomplish simultaneously full transformation of work into heat and of heat into work."

It was shown in [1] that Belokon's postulate presented in the thesis is a postulate regarding irreversibility, in which not only the direction of an irreversible process is fixed and either the process of total conversion of work into heat or of total conversion of heat into work are possible. When we make use of this postulate in a system of irreversible processes an error shows up, connected with the fact that in the course of the arguments, as was true also for an irreversible process, it is assumed possible to transform one into the other fully, while for reversible processes total conversion of work into heat or of heat into work is not permissible*. Thus, the method of constructing the entropy and existence principle in this thesis turns out to be unjustifiable.

* The validity of what has been said may easily be verified from examination of the proof in reference [2] of the Carnot theorem by means of the postulate that simultaneous conversion of heat in two directions is impossible.

Later on in the second thesis the comment is made: "Three theorems are an important consequence of these premises: the theorem that the adiabat and isotherm are incompatible, the Carnot theorem, and the theorem of thermal equillibrium." If the premises to which the authors refer lead to an absolutely incorrect consequence regarding the incompatibility of the adiabat and isotherm for complex systems, then it remains only to say that either the premises are incorrect, or they are being used incorrectly.

In Thesis 3 the statement is made: "Mathematical analysis of the above basis for the entropy existence principle for reversible processes (here the authors are referring to the methods of Clausius-Kirchhoff-Duhem, Schiller, Carathéodory, Planck, and Leontovich) leads to the conclusion that in all these schemes the use is implied of the theorem regarding the incompatibility of the adiabat and isotherm.

This thesis, which contains an accusation that classical thermodynamicists and other investigators have made this implicit use of the clearly incorrect statement regarding the incompatibility of the adiabat and isotherm, needs no comment.

In Thesis 4 we read: "As a basis for determining temperature and using the symmetry postulate of Belokon we have first the mathematical expression of the entropy existence principle for the working substances of cyclic processes ($\delta Q_t \neq 0$), and this result is then generalized on the basis of the theorem of thermal equillibrium up to the level of a new principle of thermodynamics—the second law of thermodynamics, i.e., to the level of a mathematical expression of the principle of existence of entropy and of absolute temperature in real processes occurring in any equilibrium and nonequilibrium systems."

This thesis expresses the odd conception that the existence of entropy must also be proved, for greater certainty, by examining real nonequilibrium processes. The incorrectness of this conception is clear from the fact that one speaks of obtaining the equality of the second law for reversible processes, and therefore it should not, and moreover cannot, be obtained by examining real, nonequilibrium processes. But, since the existence of entropy as a function of state has been proved, then it has thereby been proved that its variation does not depend on the kind of process, including also irreversible processes.

The critical comments of Bartosh and his co-authors on the paper "The Use of Classical Ideas ..." is based as a whole on their ideas, expressions, and the four theses. The detailed analysis of these theses given above, together with the part of the article reproduced, in essence responds to all the authors' comments and demonstrates that they are unjustified. Therefore there is no need of a special examination of their comments, the more so because the authors often bring forward the "spirit" of thermodynamics as the only argument for their assertions. We shall dwell only on two comments of a particular nature.

In an attempt to criticize the method that we have put forward as a basis for the second law, the authors show that the "general solution" of this problem has been given by Belokon in terms of several schemes, and apropos of one of these they write: "Kazavchinskii reproduces this scheme in the form illustrated, but in addition complicates it and includes errors which did not exist in the original." In the article "Comments on Belokon's book" [1] a comprehensive criticism was given of all these schemes for the basis of the second law and their complete lack of justification was demonstrated. Therefore there is no sense in the author of this critique repeating any of the above schemes and adding errors to it—there were enough of them in the original even without it.

Further on the authors write: "The correct methods of constructing the entropy existence principle for simple substances are known, but Kazavchinskii says nothing about this." Here they are referring to the methods of construction presented in the book [2], and in order to show how our "silence" appears, we shall quote from reference [1]: Thus, Belokon's theorem of thermal equilibrium for simple substances has not been proved without the postulate of the second law, and a proof of the existence of entropy based on it for these substances must be recognized as incorrect."

Finally, we note that Bartosh and his co-authors criticized Volosov's paper [3] on the basis of the second law, in the course of one and a half pages. Meanwhile it would be sufficient to note that after all his calculations, Volosov arrived at an expression for the "work" of the action

$$\delta Q_i = N_{ii}\, dy_i,$$

in which dy_i is not a total differential of the function with respect to the parameters x_i, but is a Pfaffian form, as is true also of the original expression for δQ_i. Thus, Volosov is back where he started in having to prove that each of the δQ_i has an integrating factor.

REFERENCES

1. Ya. Z. Kazavchinskii, Izv. VUZ. Energetika, no. 2, 1964.
2. N. I. Belokon, Thermodynamics [in Russian], Gosenergoizdat, 1954.
3. S. N. Volosov, Izv. VUZ. Energetika, no. 12, 1960.

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EDITORIAL NOTE

The editors of Journal of Engineering Physics note that discussion of which the above notes are part has been quite unjustifiably prolonged, and they consider it concluded.