ON THE ARTICLE "USE OF CLASSICAL CONCEPTS AS PART OF A NEW BASIS FOR THE SECOND LAW OF THERMODYNAMICS"**

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Inzhenerno-Fizicheskii Zhurnal, Vol. 9, No. 3, pp. 409–412, 1965

In his objections to the above article, S. M. Volosov (IFZh, No. 12, 1964) begins with the fact that Theorem 1 was not proved by the author. It is easy to establish the absolute rigor of the conclusions by a thoughtful analysis of the whole course of the argument that accompanied the proof of Theorem 1.

Theorem 1 states: "If a compound system, consisting of two composite subsystems, undergoes a reversible adiabatic process, in which subsystem 1 returns to its original state, then subsystem 2 goes to a state located on the same isotherm-adiabatic as its original state." We shall denote by the letter a the original state of subsystem 2 at the beginning of the adiabatic process of the whole compound system, and by b the state reached by subsystem 2 after subsystem 1 has completed the cycle. Since the two subsystems are thermally coupled, the original state a and the final state b of subsystem 2 lie on the same isotherm. Thereafter, subsystem 2, being separate from subsystem 1, is brought in contact with a heat source whose temperature is the same as the initial temperature of the whole compound system, and therefore undergoes the isothermal process b$-a$. The remarks of S. M. Volosov to the effect that "it is not even necessary to require that the temperature be constant in this process. Here it is only necessary to satisfy equality of initial temperature t_2 and final temperature t_1 when t = variable," are not evidence of a profound understanding of the problem.

In fact, in the proof of Theorem 1, the object of the whole argument is not concern as to how subsystem 2 returns to its original state, but the reaching of conclusions relating to the basis of the second law. For this we must of necessity choose an isothermal process from the multitude of processes by which subsystem 2 might return to its original state.

On the basis of the postulate of the second law in Theorem 1, it is proved with full rigor that in the isothermal process b$-a$ of subsystem 2, the heat $Q_t = 0$. Apropos this S. M. Volosov writes: "The equality $Q_t = 0$ referred to by the author does not designate only an adiabat, since when $Q_t = 0$ it is not necessary that $\delta Q = 0$. According to the sense of the author's argument the total amount of heat supplied here must equal zero, but the elementary amount δQ of heat supplied may be shown not to equal zero (neutral thermal process)."

The assumption made in Theorem 1 to the effect that when one subsystem returns to its initial state, the second subsystem may not return to its original state means that the work in the adiabatic process of the whole compound system differs from zero. It is clear that for a fixed initial state of the whole compound system (and, therefore, of its subsystems), the state b, which the second subsystem may reach, depends on the nature of the cyclic process of the first subsystem and finally on the work Z, which may have the most varied values in amplitude and sign, depending on the mode of action in the two subsystems.

For this reason, states b of the second subsystem prove to be different, and include possible states which coincide and are infinitely close to state a, and, in general, also states which are infinitely close one to another. The totality of all possible states lies on a single isotherm, and for each of the isotherms of the process b$-a$, the heat $Q_t = 0$. This also means that the process b$-a$ is isothermal and adiabatic in the sense that in any elementary section of the process $\delta Q = 0$. This shows that the word "adiabatic" appearing in the formulation of Theorem 1 was used there absolutely correctly.

We shall deal further with Volosov's two remarks, and then return to his conclusions apropos Theorem 1. Looking at the special case when subsystem 2 is described by three independent variables t, a_1, a_2, and when the equation of the first law, as applied to an isothermal and adiabatic process, gives

$$\left(\frac{\partial U}{\partial a_1} + A_1\right)da_1 + \left(\frac{\partial U}{\partial a_2} + A_2\right)da_2 = 0,$$

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*In view of the fact that the discussion of Ya. Z. Kazavchinskii's articles (IFZh, Nos. 3 and 12, 1964; Vol. 9, 3, 1965) led to a debate on fundamental questions of thermodynamics, which have been repeatedly argued at specialized conferences on thermodynamics and in the pages of a number of scientific journals, the Editors consider that further discussion would be inappropriate.

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he writes: "This means that in an isothermal and adiabatic process there exists a quite definite relation between parameters a_1 and a_2, which does not allow state 1 to be reached from state 2" (in the notation adopted here we should read: state a to be reached from state b).

Volosov's error may be most simply exposed by examining an adiabatic process with a perfect gas, since such a process is analogous to the isothermal-adiabatic process of a system with three independent variables, in the sense that in both cases a quite definite relation exists between two parameters. Thus, if it is shown that the two states 1 and 2 of the perfect gas are located on a single adiabatic, then the result, according to Volosov, is that the relation between the parameters "does not allow state 1 to be reached from state 2."

His next remark is this. He states: "Furthermore, one cannot agree with the author that in the special case (for a simple subsystem) an isotherm-adiabatic degenerates to a point." We may as well disagree with the equation of the first law as applied to a simple system, which when $Q_{b-a}=0$ gives the isotherm-adiabatics degenerating to a point, i.e., coincidence of points b and a.

Indeed, choosing the parameters t and v as independent variables of the simple system, and applying the first law to the process for this system, we obtain

$$Q_{b-a} = Q_t = \int_{U_b}^{U_a} \left[\left(\frac{\partial U}{\partial v} \right)_t + p \right] dv = 0.$$

For the simple system the expression $\left[\left(\frac{\partial U}{\partial v} \right)_t + p \right]$ keeps its sign, and therefore the integral may vanish only when the limits of integration coincide, i.e., when states b and a coincide. Thus, if the second subsystem is simple, then, according to Theorem 1, it returns to its original state at the same time as the first. The most important point, however, is that for the whole of the postulated system the justification of the second law is not required at all, in order for the process b−a to be isothermal-adiabatic in the sense that, in any part of the process, when t = const, $\delta Q_t = 0$ but it is sufficient to take the word "adiabatic" to mean that, when t = const, the total $Q_t = 0$. In fact, in the proof of the second Theorem, use was made of Theorem 1 in the part where it was stated that when subsystem 2 is simple, it returns to the original state at the same time as the first. As has just been shown, this is also obtained when $Q_t = 0$.

In an exactly similar way, in the proof of the third Theorem, it is required only that in an isothermal process b−a of a composite system $Q_t = 0$. However, Volosov, assuming that he has disproved Theorem 1, writes: "It may be asserted from the foregoing that neither the second nor the third Theorems have been proved by the author, since for their proof it was required to use the first Theorem."

Not restricting himself to this, Volosov decided to show further that from the extended formulation of the postulate of the second law one should not obtain the Caratheodory postulate regarding adiabatic (quasistatic) inaccessibility, and for this reason he asserted: "While the author, in the proof of his theorems, makes use of the finite concepts ($Q=0$, $t_1=t_2$), and incorrectly attributes to them the differential relations ($\delta Q=0$; $dt=0$), here, on the other hand, he commits the opposite error—in examining the elementary processes, he attributes to them properties which are characteristic of finite changes of state." It would be interesting to know what are these properties that are characteristic of finite and not characteristic of elementary processes.

Later on, Volosov continues: "In fact an elementary cycle is obtained. Here the work δL of the cycle, which is calculated for a simple substance according to the formula $\delta L = Ada$, represents the A−a an area which is an infinitely small number of higher order in comparison with the elementary quantity of heat. Therefore it cannot be a question of a perpetual engine of type II or of an effect identical to friction". To begin with, we are concerned here with a simple substance, and is not Caratheodory's postulate derived from a compound system? It is likewise interesting, as Volosov was able to show with the aid of the A−a diagram, that the work δL of the elementary cycle is an infinitely small quantity of higher order in comparison with the elementary quantity of heat: in fact, the heat supplied cannot in the general case be represented in the A−a diagram. In spite of this, he reached the unexpected conclusion that the work of the elementary cycle, being a difference between infinitely small quantities of heat of the first order (this is a requirement deriving from both laws), is in general a quantity of higher order of smallness compared to them.

Passing now to A. L. Ashkinazi's paper (IFZh, No. 12, 1964) "The question of the foundation of the second law of thermodynamics," it should be noted that the author does not criticize the original article which has excited discussion, but puts forward his own concept of the foundation of the second law of thermodynamics, starting from the following proposition: "The amounts of heat required for isothermal transitions at each temperature, from states of one adiabatic process to states of another adiabatic process, are the same for all substances (if they are the same at some initial temperature)."

It is not hard to show that the arguments which Ashkinazi puts forward in defense of the above assertion are completely invalid. However, this is unnecessary, bearing in mind his final conclusion: "Thus it is shown that for reversible processes all the statements of the second law derive from the first law," which speaks for itself.

In conclusion, we note that although the statements of Volosov and Ashkinazi differ from one another in nature, the authors share a single erroneous point of view, since each in turn "derives" the second law of thermodynamics from the first (see S. M. Volosov "New foundation of the second law of thermodynamics," Izv. vuzov, Energetika, No. 12, 1960).