BASIS OF THE ENTROPY EXISTENCE PRINCIPLE IN THERMODYNAMICS*

E. T. Bartosh, N. F. Volkov, and B. A. Romanov

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Prior to the beginning of the 20th century, the second law of classical thermodynamics was formulated as a unified principle of the existence and increase of entropy

$$dS \geqslant \delta Q^*/T,$$

where T is the absolute temperature of the body (equilibrium thermodynamic system), and δQ^* is the heat supplied to the body externally (external heat exchange).

In the expression of the second law the equality sign refers to reversible processes, and the inequality sign—to real processes.

Classical thermodynamics operates with the idea of external heat exchange δQ^*, to which corresponds the only possible expression under these conditions of the first law of thermodynamics relating to the external balance $\delta Q^* = dU + \delta L^*$. Hence it follows directly that the mathematical expression of the entropy existence principle (i.e., the equality) within the bounds of classical thermodynamics can be given only for reversible processes, $(\delta Q^*_{\text{rev.}} = TdS_{\text{rev.}})$.

The role of the second law in various fields of knowledge—from heat engineering calculations to the philosophy of natural science—is very great, and therefore in the construction of this principle there are very great requirements of generality, visualization, and mathematical rigor. This explains the unceasing, though not always fruitful and soundly based attempts to revise the already known constructions, mainly concerning the problem of the foundation and the mathematical expression of the entropy existence principle.

The first widely known critical investigation of ways of justifying the entropy existence principle was made in an article by T. A. Afanas'eva-Erenfest [4]. In this paper three methods of constructing the entropy existence principle for reversible processes were examined: the method of Clausius, which is currently the most widely disseminated, the first method of M. Planck, as described in his well-known course "Thermodynamics," and the method of Caratheodory. Without touching upon the mathematical side of the question, Afanas'eva-Erenfest made the valid comment that in the methods of Clausius and Planck the entropy existence principle was in fact postulated. Of the method of Caratheodory, based on the theorem of Caratheodory concerning conditions of holonomy of differential polynomials of type $\delta Q_{\text{rev.}} = \sum Y_i\, dx_i$ (i.e., concerning conditions of existence of the integrating divisors of these polynomials $\delta Q_{\text{rev.}} = \tau dz_{\text{rev.}}$), and in the well-known postulate of Caratheodory concerning adiabatic inaccessibility, Afanas'eva-Erenfest states: "From the single fact of holonomy Caratheodory derives that the integrating divisor of the expression dQ is the absolute temperature T." It is evident that Afanas'eva-Erenfest's final conclusion has been a source of numerous errors in the development and appraisal of methods of constructing the entropy existence principle.

A comprehensive physical and mathematical analysis of the large number of methods of construction of the second law of classical thermodynamics has been given by Belokon in the monograph "Thermodynamics" [6]. A considerable part of the monograph is devoted to the construction of a new principle of the second law of thermostatics, i.e., of the mathematical expression of the principle of existence of entropy and of absolute temperature for real processes of any thermodynamic systems, whose state may be described by the values of a finite number of coordinates $(x_1, x_2, \ldots, x_\nu)$, and to the analysis of the methods of R. Clausius, Clausius-Kirchhoff-Duhem, N. Schiller, K. Caratheodory, M. Planck (two methods), M. A. Leontovich, and others.

The main theses of this investigation [6] may be formulated in the following terms:

1. The coincidence of the principles of existence and production of entropy within the framework of the second law of thermodynamics results from erroneous derivations (methods of Clausius, Planck, and others); the two principles should be based on independent postulates.

2. The correct construction of the entropy existence principle may be accomplished only on the basis of the definition of temperature as a unique function of state characterizing the direction of heat exchange and the state of thermal equilibrium, and of the symmetric postulate, equivalent to the assertion that it is impossible to accomplish complete conversion of work into heat and heat into work simultaneously.

*Apropos the articles of Ya. Z. Kazavchinskii [1] and S. M. Volosov [2, 3].

The most important consequences of these premises are the following three theorems: the theorem of incompatibility of adiabatic and isotherm, the theorem of Carnot, and the theorem of thermal equilibrium. The incompatibility theorem has been given in two forms: the general, equivalent to the expression $dz \neq \lambda dt$, and the limited $\delta Q_t \neq 0$ for the working media of cyclic processes ($L \neq 0$).

3. Mathematical analysis of the above-mentioned schemes for the basis of the entropy existence principle for reversible processes leads to the conclusion that the incompatibility theorem is used implicitly in all these schemes.

In particular, Caratheodory examines two parts of the system $\delta Q_1 = \tau_1 dz_1$ and $\delta Q_{11} = \tau_{11} dz_{11}$ and the system as a whole $\delta Q_{\text{rev}} = \delta Q_1 + \delta Q_{11} = \tau_1 dz_1 + \tau_{11} dz_{11} = \tau dz$, and replaces the three coordinates x_1, x_2, and x_3 in the expression $\tau = \tau(x_1, x_2, \ldots, x_\nu)$ by the coordinates t, z_1 and z_{11}, which is equivalent to the implicit use of the incompatibility theorem in its general form ($dz_i \neq \lambda_i dt$). This derivation is subjected to mathematical investigation (§ 24) regarding the difference in the number of conditions which are equivalent to the assertion that the polynomials are holonomic, and the number of conditions for existence of the primary integrating divisor—the absolute temperature ($N - N_1 = \nu - 1$). Therefore, the Caratheodory postulate is sufficient only to establish the holonomy of the polynomials $\delta Q_{\text{rev}} = \Sigma\, Y dx_i$, but insufficient as a basis for the entropy existence principle; this means, moreover, that as soon as it proves necessary to use the incompatibility theorem, and hence the original symmetric postulate (thesis 2), inclusion of the Caratheodory postulate proves unnecessary, and the above-mentioned final thesis of Afanas'eva-Erenfest must be recognized as erroneous.

In all the other familiar constructions of the entropy existence principle (Clausius, Clausius-Kirchhoff-Duhem, and others), the incompatibility theorem is also used implicitly, and in the limiting form ($\delta Q_t \neq 0$), which appreciably lowers the degree of generality of the basis and the content of this principle.

4. On the basis of the definition of temperature and use of the symmetric postulate, the author obtains first a mathematical expression of the entropy existence principle for the working media of cyclic processes ($\delta Q_t \neq 0$), and then extends this result, using the theorem of thermal equilibrium, to the level of a new principle of thermodynamics—the second law of thermostatics, i.e., to the level of a mathematical expression of the principle of existence of entropy and of absolute temperature in the real processes of any equilibrium and nonequilibrium system ($dS = \Sigma \delta Q_i / T_i$; $\delta Q_i = \delta Q_i^* + \delta Q_i^{**}$). This final result was achieved by introducing and defining the concept of internal heat exchange δQ^{**} and by expressing the first law of thermodynamics according to the balance of the working medium, or system of media, in the general case of any change (dE_{cz}) in the energy of the external state of the system ($\delta Q = \delta Q^* + \delta Q^{**} = dU + \delta L = dU + \Sigma F_i dx_i$; $\delta L^* = \delta L_{cz}^* + dE_{cz}$).

It is of considerable importance to note that in the contemporary development of negative absolute temperatures [9] there is full confirmation of the important statement that it is necessary to include the symmetric postulates in all schemes on which the entropy existence principle may be based.

The basis of the second law of thermodynamics, in conformity with reference [2], starts from the following assertion: "The new feature here is that the proposed basis does not include postulates specifically showing some characteristics or other of thermal phenomena," and ends with the conclusion: "Since the proof given does not contain a specific postulate for the thermal action, it may be asserted that the proposition concerning the existence of entropy does not go beyond the limits of the law of conservation and conversion of energy." This means that the numerous differential relations of thermodynamics, for example, $\left(\frac{\partial c_p}{\partial p}\right)_t = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$, describing the properties of a substance and deriving from juxtaposition of the first law of thermodynamics and the entropy existence principle, are nothing other than consequences of the first law, and this in turn is equivalent to the statement that the differential relations of thermodynamics may be obtained directly from the postulate of conservation of energy of isolated systems.

Work and energy in reference [2] have the same name "work," and accordingly have the same symbol δQ_i, but to avoid the possibility of confusion, we shall use the symbols and definitions of classical thermodynamics in parallel, and restrict the problem to the limits, implied in reference [2], of reversible processes ($\delta Q = \delta Q_{\text{rev}}$):

$$\delta Q = dU + \delta L, \tag{a}$$

or

$$dU = \sum_{j=1}^{m} \frac{\partial U}{\partial x_j} dx_j = \delta Q - \delta L = \sum_{i=1}^{n} \delta Q_i. \tag{b}$$

Later on, Volosov writes: "This leads to the possibility of examining each of the work values δQ_i of some action or other as a sum of Pfaffian form":

$$\delta Q_i = \sum_{j=1}^{m} M_{i,j} dx_j; \quad i = 1, 2 \ldots n. \tag{c}$$

We need not proceed further, since Volosov, in the above statement, either postulates the existence of entropy or reduces the matter to a trivial identity (tautology).

The heat δQ and the work $\delta L = \Sigma \delta L_i$ has been selected as independent components only because all forms of work δL_i allow in principle the possibility of complete mutual conversion and are therefore equivalent to mechanical work [4]; following the laws of mechanics, we can simplify the problem and write

$$\delta L = \sum_{j=1}^{n-1} F_j \, dx_j. \tag{d}$$

Comparing (a), (b), and (c), we obtain an expression for the amount of heat δQ as a symbol of the differential polynomial

$$\delta Q = dU + \delta L = \sum_{j=1}^{n-1} \left(\frac{\partial U}{\partial x_j} + F_j \right) dx_j + \\ + \sum_{j=n}^{m} \frac{\partial U}{\partial x_j} dx_j = \sum_{j=1}^{m} Y_j \, dx_j, \tag{e}$$

we shall continue the comparison of (c) and (e):

$$\delta Q_n = \delta Q = \sum_{j=1}^{m} M_{n,j} \, dx_j = \sum_{j=1}^{m} Y_j \, dx_j. \tag{f}$$

From this we obtain the uninformative identity

$$Y_j = M_{n,j}. \tag{g}$$

While Volosov did not have this identity in mind, the only possible statement may be written in the form of the Caratheodory relation $\delta Q = \tau dz$, but for this it is necessary to include a postulate equivalent to the conditions (N_j) of holonomy of the polynomial $\delta Q = \Sigma Y_j \, dx_j$ (for example, the Caratheodory postulate); in addition, even after obtaining the relation $\delta Q = \tau \, dz$, the set objective—the basis of the entropy existence principle—has not been attained since for transition from $\delta Q = \tau \, dz$ to $\delta Q = TdS$ it is necessary to include the incompatibility theorem $(dz \neq \lambda \, dt)$, or the supplementary postulate equivalent to this theorem (thesis 3, above).

It should also be noted that the title of the Volosov article [2] "A new basis for the second law of thermodynamics" does not fully correspond to its content: the author assumes [2] that "the name 'second law' should be reserved only for increase of entropy of an isolated system," but this problem is not examined at all in the article.

"A new basis for the second law of thermodynamics," as proposed by Ya. Z. Kazavchinskii [1], relates mainly to the justification of the entropy existence principle under reversible process conditions and is fully described by the postulate: "It is impossible to realize a perpetual motor of the second kind, for the reason that it is impossible to achieve by reversible means an effect identical with the friction process."

The author assumes that this postulate corresponds to the objective that he has set himself, namely, "to use classical concepts" in conditions of 20th-century thermodynamics, but this is not the case. In the first place, he is at variance with the spirit of thermodynamics and, moreover, of the classical case: the postulates of thermodynamics describe the flow features of real processes, and therefore it must be judged erroneous to include in the postulates statements referring to reversible processes.

It should be added that the postulates previously proposed are much more convincing and correspond fully to the spirit of thermodynamics and to the task of providing a basis for the entropy existence principle, not only within the limits of reversible processes, but also at the level of the second law of thermostatics. For instance, the symmetric postulate regarding the impossibility of simultaneous achievement of total conversion of work into heat and heat into work, proposed in 1954 [6] and verified in 1956 [9], is a postulate of this kind. Secondly, the above postulate is completely inapplicable in the thermodynamics of negative absolute temperatures, i.e., it does not conform to the level of development of contemporary thermodynamics. Thirdly, it is an unsuccessful imitation of the symmetric postulates: it contains an indication of the observable direction of the irreversible phenomena, but this premise is superfluous as regards a basis for the entropy existence principle and contradicts the already proved and generally recognized thesis of the independence of the principles of existence and increase of entropy [7].

Subsequent use of the proposed postulate has been directed along the path of "a new basis" for already well-known truths—the Caratheodory postulate and the theorem of thermal equilibrium—and hence also to the "development" of the corresponding two schemes for the basis of the entropy existence principle for reversible processes.

In his first scheme Kazavchinskii began by obtaining from his postulate the known Caratheodory postulate, and then asserted that from this, without including any kind of physical premises, "the existence of temperature and entropy may be proved by the method of Caratheodory, and thus a more general and rigorous basis for the second law of thermodynamics may be obtained." Regarding this scheme the following should be noted: firstly, the derivation of the Caratheodory postulate from the Thomson-Planck postulate, or from the above-mentioned symmetric postulate has already been effected [5, 8]; secondly, the postulate and the theorem of Caratheodory do not suffice as a basis for the entropy existence principle, as has been shown with sufficient rigor by mathematical analysis of conditions of holonomy of the differential polynomials and of the entropy existence conditions (thesis 3 above).

In order to facilitate analysis of the second scheme, it is first necessary to become familiar with the known general solution of the problem, which plays a very important part in the contemporary theory of cyclic processes [6]: cyclic processes are examined for two thermally coupled bodies forming an adiabatically isolated system, the existence of entropy having previously been established for the first body (the standard or control body); applying the theorem of thermal equilibrium to this body (in equilibrium cyclic processes of two thermally coupled bodies forming an adiabatically isolated system, both bodies return simultaneously to the original state), we immediately reach the conclusion that the entropy existence principle must extend also to the second body (which is any thermodynamic system under study); the control body is in general taken to be the working media of the cyclic processes, and in illustrative arrangements—perfect gases or simple substances to which known properties may be assigned "by definition" (for simple substances the coordinates p, v and t, v are independent). With the aid of this scheme the widest generalizations of the entropy existence principle are achieved, up to and including the second law of thermostatics.

In fact, Kazavchinskii repeats this scheme in its illustrative form, but further complicates it and supplements it with errors not found in the original. In the first place, he proves the entropy existence principle for simple substances on the basis of the identical inadequate premise of incompatibility of variables t and v, using a transformation of type $\delta Q = \lambda(t, \sigma)\, d\sigma$, which is equivalent to the implied use of the incompatibility theorem $d\sigma \neq \mu dt$; the correct construction of the entropy existence principle for simple substances is known, but Kazavchinskii ignores this. Secondly, he complicates the theorem of thermal equilibrium by introducing the concept of "adiabatic-isotherms", unnecessary in the theory of cyclic processes. It is known that cyclic processes are quite controllable, and can be arrested by compulsory return to the original state of all the altered coordinates, and by supply of heat in the final state, by which the temperature t of the working substance may be restored to the original level. Hence the above-mentioned thermal equilibrium theorem follows directly [6], which avoids the need to include the "adiabatic-isotherm" concept, extraneous both in the classical and in the contemporary theory of cyclic processes; in the light of these considerations Volosov's comment [3] about lack of proof of Kazavchinskii's first theorem should be considered valid.

It is known that the entropy increase principle $(TdS > \delta Q^*)$, within the limits of methods of classical thermodynamics, may be based without impediment on the entropy existence principle $(TdS_{\text{rev.}} = \delta Q^*_{\text{rev.}})$ and one single postulate concerning the impossibility of complete conversion of heat into work. Nevertheless, Kazavchinskii brings in one more assertion ("it is impossible by a reversible path to obtain an effect identical to the effect of an irreversible process") that is extraneous to the spirit of thermodynamics, i.e., he commits a double error.

REFERENCES

1. Ya. Z. Kazavchinskii, IFZh, no. 3, 1964.
2. S. M. Volosov, Izv. vuzov, Energetika, no. 12, 1960.
3. S. M. Volosov, IFZh, no. 12, 1964.
4. T. A. Afanas'eva-Erenfest, Prikladnaya fizika, vol. 5, no. 3–4, 1928.
5. M. A. Leontovich, Introduction to Thermodynamics [in Russian], ITTL, 1952.
6. N. I. Belokon, Thermodynamics [in Russian], Gosenergoizdat, 1954.
7. Proc. of the First Scientific Methodology Conference on Thermodynamics [in Russian], Gostoptekhizdat, 1962.
8. Collection: Developments in Contemporary Physics [in Russian], Izd. "Nauka," 1964.
9. N. F. Ramsey, Physical Review, July, 1956