

Equation (15) can be compared to the local equation (per unit actual volume) of *entropy balance* in a continuum without exchange of mass ( $dM_k/dt = 0, \forall k$ ) which can be written as [8–9]

$$\rho \frac{d}{dt}(S^t/\rho) = -\nabla \cdot \mathbf{s} + \rho \hat{\eta} + \rho \tilde{\eta} \quad (16)$$

where  $\rho$  is the mass density at time  $t$ ,  $S^t$  is the entropy per unit volume (hence,  $S^t/\rho$  is intensive) at time  $t$ ,  $\mathbf{s}$  is the (in)flux of entropy,  $\hat{\eta}$  is the entropy source per unit mass, and  $\tilde{\eta}$  is the entropy generated per unit mass at material point  $\mathbf{X}$  in the body. The first two terms in the right-hand side of this equation play the role of the term  $\dot{Q}/T$  of (15), while the last term plays the role of  $\dot{S}_i$ . In standard continuum thermodynamics (cf. [8–9]),

$$\mathbf{s} = \mathbf{q}/\theta, \quad \hat{\eta} = h/\theta \quad (17)$$

where  $\mathbf{q}$  is the (in)flux of heat and  $h$  is the energy source per unit mass in the body. The fact that

$$\tilde{\eta} \geq 0 \quad (18)$$

reflects the second law of thermodynamics (dissipation is positive). It is the aim of irreversible thermodynamics to relate the entropy production  $\tilde{\eta}$  to the various irreversible phenomena which may occur inside the system (see [5, 9] for this aspect).

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## Entropy: The Classical View

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## Overview

The thermodynamic interpretation of entropy concept, consistent with the classical thermodynamics, is presented and discussed in this entry. One can distinguish between two concepts of entropy promoted by famous theorists and scientists of the past times. Their efforts and researches have helped to create the entropy concept for both reversible and irreversible processes. In the first concept (reversible processes), the entropy plays the role of the state parameter and is responsible for the reversible part of the thermal phenomena. The keynote of this group is the thesis of Rankine, which say that “the entropy of the Universe is constant.” Besides Rankine, the researchers such as Carnot, Gibbs, Maxwell, Kestin, and Sieniutycz contributed to the development of this concept of entropy. The second concept of entropy (irreversible processes) was developed by researchers such as Fourier, Clausius, Zeuner, Okatov, Mach, Planck, Ostwald, and Smoluchowski. Ideological keynote of this group was the thesis of Clausius saying that “the entropy of Universe is a half-preserved, it cannot decrease or be constant, can only increase.” The details of these concepts of entropy, both Carnot and Rankine, as well as the concept of entropy created by Clausius are discussed here. Both definitions of entropy are presented in mathematical notation. The main attention is paid to the Clausius entropy, which immediately became inviolable paradigm

of continuum physics, but the line of reasoning of Carnot and Rankine had been forgotten. The semi-conservation law of Clausius entropy was also developed by researchers such as Planck, Duhem, Natanson, Onsager, and Eckart. Finally, Clifford Truesdell decided to define this law in the form of inequality and to name it as the “Clausius–Duhem inequality.”

### Three Concepts of Entropy

Entropy is an abstract concept, occurring in many disciplines and in everyday life. Three main sciences that use it are the thermomechanics (in the British Isles called thermodynamics), statistical physics, and computer science (information science). Therefore, there are at least three, little consistent with each other, definitions of entropy: thermodynamic, statistical, and informational [1, 2]. Although all of these entropies have the same physical dimensions – i.e., (J/kg°K) – they are not related to each other, and, frankly speaking, they share only a common name.

Fortunately, all three sciences use different mathematical symbols for its determination. Historically speaking, the statistical entropy was intended to generalize the thermodynamic entropy to nonequilibrium states, while the information entropy was created to generalize the notion of statistical entropy on information nonmaterial objects. The consequences of these borrowings are three different concepts that are the foundation of three different disciplines.

It should be emphasized that simultaneously mixing and defining these three concepts, which takes place in textbooks and encyclopedias, is wrong from teaching point of view and harmfully contributes to the understanding of fundamental laws of physics. The fundamental laws of physics in the face of the enormous quantity of facts provided to us every day by advanced measuring tools should be rebuilt again and again in such a way that the concept of entropy found in them their adequate place. If we are to explain, justify, and understand the direction of the processes taking place on all scales of our observations that is not sufficient classical relationship

between entropy and the second law of thermodynamics. What is needed is a continuous change in our paradigm of thinking. However, there is no revision of our views without a clear statement of the reasons and goals which guided us in the past and which perhaps in a hidden manner guiding us today. Hence, it is believed that the history of the evolution of the concept of entropy is implicitly present in the whole process of teaching, application, and understanding. Therefore, the scientific foundations about entropy are presented here in a historical mode, because the main goal of that is to present the essence of this abstract concept to all readers of this encyclopedia. For instance, the readers should know that before Clausius introduced his concept of entropy, he studied the work of Rankine and his concept of entropy. Rankine’s action is not without significance in the further shaping of scientific concepts of entropy, because in the field of basic and fundamental concepts, human knowledge is accumulated and only later transformed into a new quality. This quality could be the concept of Rankine entropy.

Herein, the concept of entropy is confined only to its thermodynamic explanation. It is present with original point of view, which enables numerous attempts describing the problem and the associated second law of thermodynamics to divide into two main groups of reasoning, definition and practical use of this concept.

The first group – reversible process – which includes concepts of entropies of such scientist as follows: Carnot (1824), Rankine (1851), Reech (1853), Gibbs (1873), Thurston (1878), Maxwell (1878), Natanson (1890), Duhem (1901), Kestin (1971), Bejan (1990), and Sieniutycz (1999). These entropies played the role of the state parameter and were responsible for the reversible part of the thermal phenomena. The keynote of this group is the thesis of Rankine (1856) which say that “*the entropy of the Universe is constant*” [3]. Today’s technical thermodynamics and the thermodynamics of reversible processes just grow out of this group of reasoning (endoreversible thermodynamics) [4–6].

The second group – irreversible processes – starting with Fourier (1824), Clausius (1865), Zeuner (1868), Okatov (1855), Mach (1896),



Planck (1900), Ostwald (1896), and Smoluchowski (1914) was further developed, for instance, in the work of Onsager (1931), Eckart (1941), Prigogine (1947), Meisner (1954), Mushik (1960), Müller (1967), Lebon (1980), and Grmela (1999). Ideological keynote of this group was the thesis of Clausius (1865) saying that “*the entropy of Universe is a half-preserved, it cannot decrease or be constant, can only increase.*” There were many works belonged to this group that have attempted to estimate both the growth rate of entropy per 1 year and the limiting value of entropy causing the thermal death of the universe. Extended nonequilibrium thermodynamics (extended irreversible thermodynamics) [7] and nonequilibrium thermodynamics (thermodynamics of irreversible processes) [8, 9] stem from this line of reasoning, in which the primary task is to study irreversible phenomena and calculating the “entropy production.”

These two groups of reasoning are distinguished between each other by mathematical signs. The specific entropy and total entropy are denoted in the first group as  $\eta$  and  $H$ , respectively. In the second group, entropies are indicated as  $s$  and  $S$ , respectively.

### Idea of Carnot Entropy

Sadi Carnot was the first researcher, who set himself the task of creation a theory of heat engines based on the primary laws [10]. He was inspired by the Lagrange’s analytic mechanics, which was developed by his father – Lazare Carnot. However, Carnot did not accept Ampere’s thermal equations of motion, and he reached for a different pattern, i.e., Volta’s weightless electric fluid that in the solid state contains the conservative quantity called a charge. In analogy to this, Carnot proposed to describe the heat phenomenon by means of “the thermal charge” characterized by invariant scalar motion which is induced by both heating and cooling processes. Therefore, if the difference of voltage (temperature) determines the driving force of movement, the amount of thermal fluid

characterizes the stream carrying the charge per unit of time. That the driving force and the topological charge of heat motion is called “temperature” and “entropy” by Carnot, respectively. The working substance is a material carrier of thermal fluid. Hence, scientists often say: the gas entropy.

Carnot forms his theorems concerning thermal engines based on the law of conservation of entropy, which says that *after summing up all entropy changes that occur during the engine cycle due to heating and working processes, the entropy of the working body returns to the initial point.* This spoken law can be mathematically written as follows:

$$\oint \left( \frac{d}{dt} H \right) d\tau = \oint \left( \frac{d}{dt} \iiint_V \rho \eta dv \right) d\tau = 0. \quad (1)$$

Although, it refers to the conservation of the total entropy  $H$ , which is located in the working body (solid, fluid)  $B$  having a volume  $V$ , but it can be easily determined by the specific entropy  $\eta$  contained in a unit mass of the working fluid  $B$ . In this equation, the time  $\tau$  means the integration parameter. Hence, it differs from the local time  $\tau$  (Kestin 1966).

It is known that Carnot took into account only two processes of working fluid  $B$  in all five of his considered engines. The first process is the most essential to the concept of the ideal heat engine working without “unnecessary entropy losses.” It is based on specific and impossible to realize simultaneous processes of heating and working. It is important that these processes, specified by the mechanical energy flux  $\vec{F}_{work}$  and thermal energy flux  $\vec{F}_{heat}$ , took place on two disjoint surfaces limiting the volume  $V$  occupied by the agent  $B$ , i.e.,  $\partial V = A = A_{work} \cup A_{heat}$ . Ideality of the process lies in the fact that a reserve of agent internal energy during this process remains constant but the energy supplied as heat to the surface  $A_{heat}$  is instantaneously (elastically) converted to work as form of outgoing energy on the surface  $A_{work}$ . Therefore, it is a transformation with a constant internal energy of working fluid  $B$ . Presentation of this process is more complicated

from the standpoint of “thermal fluid.” Agent  $B$  touches the heat reservoir on its surface, so as result it has the same temperature which has a heat reservoir ( $\theta = \text{const}$ ), but the amount of agent entropy simultaneously increases. Weightless thermal fluid interacts with its carrier, i.e., working fluid in which it causes the changes in pressure and volume (or the stress and deformation – in the solid state). This allows on the induction of mechanical energy flux on the surface  $A_{\text{work}}$ , called “working” by Carnot (*in French: puissance motrice*). This “iso-energetic” transformation is named by Carnot as “drawing entropy” (heating) or “returning entropy” (cooling).

The amount of drawing entropy or on the other hand, its growth during the iso-energetic process taking place from time  $\tau_1$  to  $\tau_2$  is defined by Carnot by means of the first in the history, constitutive equations of thermoelasticity, who say about it as the “geometric formula” [10]:

$$d_{1,2}\eta = \eta_2 - \eta_1 = R \ln\left(\frac{v_2}{v_1}\right) \quad (2)$$

A unit of Carnot entropy is  $1.228 \text{ [kJ/(kg}^\circ\text{K)]}$ , but  $R = 0.3 = c_p - c_v$  is a constant elastic value discovered by him and always the same for all analyzed gases. In their calculations of ideal thermal cycles, Carnot uses the law of conservation of entropy (1) for the thermal cycle having only two iso-energetic transformations using the equation (2):

$$\oint (d\eta) d\tau = (\eta_2 - \eta_1) + (\eta_4 - \eta_3) = 0 \quad (3)$$

which can be interpreted in the following manner: *Drawing entropy during the process 1–2 is returned in the process 3–4.*

The entropy flux is another basic concept that Carnot verbally introduces. He stresses that the process of heating takes place at the interface of solid body (heater) and the working fluid  $B$ . The influx of thermal fluid and simultaneous thermal charge transfer happen even though both bodies have the same temperature. This charge is the entropy. The charge per unit area and per second

is called the entropy flux, and it is a vector indicated as  $\vec{h}$ , because the entropy itself is a scalar.

Mathematically speaking, we are interested in the influx that is only the component of the vector  $\vec{h}$  that is normal to the influx surface, i.e.,  $h_n = \vec{h} \cdot \vec{n}$ . Entropy flux cannot act in any quantities, because after passing the whole engine cycle, the entropy of working body returns to base level. Therefore, the total entropy flux, drawing and returning, in all processes have to be equal to zero:

$$\oint \left( \iint_{A_{\text{heat}}} \vec{h} \cdot \vec{n} dA \right) d\tau = 0 \quad (4)$$

The entropy flux is realized in Carnot engine only when the agent touches a heater surface at area  $A_{\text{hot}}$  or a cooler surface at area  $A_{\text{cold}}$ , then the whole area is equal to  $A_{\text{heat}} = A_{\text{hot}} \cup A_{\text{cold}}$ . Hence, (4) can be rewritten as follows:

$$\begin{aligned} \int_1^2 \left( \iint_{A_{\text{hot}}} \vec{h} \cdot \vec{n} dA \right) d\tau + \int_3^4 \left( \iint_{A_{\text{cold}}} \vec{h} \cdot \vec{n} dA \right) d\tau \\ = H_{1,2} + H_{3,4} = 0 \end{aligned} \quad (5)$$

and this equation can be interpreted in the following manner: *Drawing entropy flux in the upper heat source (hot) is entirely returned to the bottom heat source (cold).* The indexes 1, 2, 3, 4 mean starting and ending time point of interaction between agent and entropy source.

Carnot, speaking of the concept of entropy sources, several times recalls enigmatically about the inevitable losses of entropy, the incomplete reduction of entropy or entropy leaks, etc. using verbs relevant to irreversible processes. If the thermal fluid would have unknown origin internal sources of entropy, say  $\sigma_\eta$  they would result in a loss of entropy in one place and simultaneously a gain of entropy elsewhere. Nevertheless, if the entropy of agent  $B$  is to be invariant of engine cycle, the sources have to compensate each other, i.e.,

$$\oint \left( \iiint_V \rho \sigma_\eta dv \right) d\tau = 0 \quad (6)$$



In summary, (1), (4), and (6) describe the primary law of the engine cycle for which Carnot considers and proposes integrated laws. Hence, there are no statements about the local entropy balance in his work. It can be anticipated as a local law both in time and space that will be the equivalent of integral conservation laws of entropy (1), entropy flux (4), and entropy sources (6):

$$\iiint_V \left( \rho \frac{d}{dt} \eta = \text{div } \vec{h} + \rho \sigma_n \right) dv \quad (7)$$

which is a combination of three integral terms of Carnot. There will be no exaggeration to say that Sadi Carnot is the author of the law of conservation of entropy, sometimes identified with the second law of thermodynamics. It was established before the law of conservation of energy, which is the first principle of thermodynamics.

Carnot also considers engine cycles on the basis of the another thermodynamic transformation, in which entropy fluxes are equal to zero, but the agent  $B$  still works using the accumulated internal energy decreasing simultaneously its potential. This second process is characterized by a constancy of entropy. Hence, this transformation is called by Carnot a constant entropy process. In its calculations for infinitesimal cycles, he used his second constitutive law expressing the specific volume as a function of pressure  $p$  and absolute temperature,  $\theta = c + 267$  [10]:

$$pv = R(c + 267) \quad (8)$$

where  $c$  is an empirical Celsius temperature.

This means that the two constitutive laws, i.e., (2) and (8) are only needed to calculate both the work cycle and heat cycle per mass unit of substance  $B$ . Nowadays, these laws are known as caloric and thermal equations of state. However, the Carnot cycle has to consist of two processes with constant entropy and two additional transformations with constant internal energy. In all of these four transformations, the mechanical energy fluxes occur on the area  $A_{work}$ .

Their sum leads to an integral quantity defined as the work cycle:

$$\mathcal{F}_{work}^{cycle} = \oint_{1U2U3U4} \left( \iint_{A_{work}} \vec{\mathcal{F}}_{work} \cdot \vec{n} dA \right) d\tau \quad (9)$$

Carnot's successors asked each other how to determine the work cycle. Finally, the work cycle was calculated based on the available thermal energy of fuel supplied by heater, as follows:

$$\begin{aligned} \mathcal{F}_{work}^{cycle} &= C \mathcal{F}_{heat}^{1,2} \\ \mathcal{F}_{heat}^{1,2} &= \int_1^2 \left( \iint_{A_{hot}} \vec{\mathcal{F}}_{heat} \cdot \vec{n} dA \right) d\tau \end{aligned} \quad (10)$$

where the main task is to find the proper expression for the Carnot function  $C$  in (10).

## Idea of Rankine Entropy

Carnot's laws of conservation of entropy, its flux and source, as well as his multiplicative constitutive equations (2) and (8) have not been accepted by successors. Therefore, a new concept of entropy, constructed by Rankine (1849), has been not referred to the Carnot cycle. Only in 1851, vaguely in the commentary to the Carnot cycle, Rankine gives a set of mathematical formulas used for his calculations with the apparent participation of entropy, which is called the thermodynamic function and is marked out as a letter  $\phi$  [11]. Rankine presents also the first time in the literature the visual diagram  $p - v$  of processes taking place in Carnot engine. Referring to the Stokes work (1851) concerning the heat flux  $\vec{\mathcal{F}}_{heat}$ , Rankine proposes to join the flux of thermal energy with the entropy flux by the following relationship:

$$\vec{\mathcal{F}}_{heat} = (\theta + \kappa) \vec{h} \quad (11)$$

This allowed him to rewrite the formula (5) as the formula expressed rather than flux of thermal energy or entropy flux [11]:

$$\int_1^2 \left( \iint_{A_{hot}} \frac{\vec{\mathcal{F}}_{heat} \cdot \vec{n}}{(\theta_{hot} + \kappa)} dA \right) d\tau + \int_3^4 \left( \iint_{A_{cold}} \frac{\vec{\mathcal{F}}_{heat} \cdot \vec{n}}{(\theta_{cold} + \kappa)} dA \right) d\tau = 0 \quad (12)$$

This equation talks nothing about equality of the heat collected in heater and devoted in the cooler. It is essentially a different conclusion than the one which concluded by Clapeyron (1834), Kelland (1937), Thompson (1849), Poggendorff (1843), Clausius (1850), Reech [12], and Zeuner [13]. In the above-mentioned formulas, there is Rankine absolute temperature  $\theta$  heightened by a constant temperature of the background  $\kappa$  – nowadays identified with the temperature vacuum of space.

The researchers regards to the problem of the relationship of thermal energy flux and entropy flux by dichotomous way [14]. For instance, when more general cases of working fluid are considered and when the reserve of internal energy depends not only on the entropy but entropy gradients, i.e., time or spatial, then Rankine formula (11) is not in force, and new formula of thermal energy flux  $\vec{\mathcal{F}}_{heat}^{inter}$  should be used. This new quantity is called “interstitial heating” [9]. The researchers belonging to the first group, i.e., reversible processes, use the following formula:  $\vec{\mathcal{F}}_{heat} = \theta \vec{h} + \vec{\mathcal{F}}_{heat}^{inter}$ , whereas authors representing the second group, i.e., irreversible processes and entropy of nonequilibrium (Müller 1971, [7]), employ the formula with an extra entropy flux defined as follows:  $\vec{h} = \frac{\vec{\mathcal{F}}_{heat}}{\theta} + \vec{k}$ . This means that both lines of approach to the problem of the definition of entropy differ not only in interpretation but in the mathematical formulation.

It should be emphasized that the concept of Rankine entropy in his pictorial presentation was not referred to Carnot’s “thermal charge” and was based on the idea of “vortex atom” in which the Rankine anticipates spinning electron carries circulating movement around the nucleus. Entropy was here a function of velocity vortex (spin), and the temperature was a function of the angle of the spin axis relative to the plane of the circulating movement. Using such a mental model can

explain what the internal energy is. Additionally, it can be shown that the conversion of thermal flux into the mechanical flux takes place at the level of “vortex atom.”

Reech [12] took over and developed the concept of Rankine entropy, proposing its designation by the letter, first as  $u$  and later as  $n$ . He proposed a systematization of the elastic constitutive equations – thermal:  $v = f(p, \theta)$  and caloric:  $\eta = f(p, \theta)$  [12], determining the specific volume and entropy as a function of the pressure and temperature and more importantly showed the relationship of these equations with the internal energy (so-called hyperelasticity) and the rate representation of these equations (hypoelasticity). In addition, he also correctly defined the free energy, enthalpy, and free enthalpy.

Gibbs (1873) put down entropy the same role of state parameter and marked it finally by the letter  $\eta$ . He finally made possible including of entropy balance in the overall energy balance writing the material increase in the internal energy through the parameters of the state [4]. At the same time, Gibbs develops Rankine’s geometric thermodynamics enriching it with the basic graphs and diagrams, because he wants to give thermodynamics a good geometric representation. He represents the surface of the internal energy as a function of volume and specific entropy and a temperature–entropy diagram for the Carnot cycle and also shows a geometric explanation of way to increase the efficiency of thermal cycle.

## Idea of Clausius Entropy

Conception of Clausius is the foundation of the second line of reasoning – assuming that the entropy is a certain invariant which measures human anthropocentric attitude to the surroundings. It is possible to observe and measure only irreversible phenomena occurring in it. The researchers of this group adopted from of everyday life many verbs denoting unidirectional natural phenomena: viscosity, resistance, friction, diffusion, dissolution, dispersion, mixing, etc.



Clausius had no great problems of interpretation – he already announced in the titles of his works that explores “the mechanical theory of heat,” which today is the view that the phenomenon of heat can be reduced to mechanical phenomenon, and these are described by a universal law of Newton. In the paper “On some extended form of the second law of thermodynamics,” Clausius (1854) acknowledges that the mechanical laws of heat motion have to be limited to a certain subclass of movements creating irreversible effects. Nevertheless, Clausius accepts Rankine’s equation (12) of entropy flux fading in engine cycle, writing it in the following form [15]:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad \text{or} \quad \oint \frac{dQ}{T} d\tau = 0 \quad (13)$$

appropriate respectively to the Carnot cycle or any cycle. The entropy flux is called “compensated heat transformation” by Clausius (*kompensierte Verwandlung*). At this stage of consideration, it does not appear even the concept of entropy, although there is the notion of “uncompensated heat transformation”:  $N = \int \int \int_V \rho n_s dv$ . In 1862, when Clausius was working in parallel on the foundations of the kinetic theory of gases, he made an unsuccessful attempt to define entropy. The entropy was called “disgregation” and marked with the letter  $Z$ . Clausius rejects “disgregation” and introduces the concept of entropy until the next paper from 1865:

$$S = \int \int \int_V \rho s dv \quad (14)$$

Unfortunately, it comes here to write unfortunate and unintended mathematical notion, because the author’s intention was to deepen understanding of the abstract concept. In fact, Clausius contributed to the largest-ever study of ambiguity concerning a manner of definition of entropy [15]:

$$dS = \frac{dQ}{T} \quad (15)$$

This formula should be treated as a local in time but global in space (in the entire volume of the body) balance of Carnot entropy (7) restricted to the thermodynamic processes in which the uncompensated heat is equal to zero:  $N = 0$ .

Herein, saying such a radical statement one can cite earlier thesis of Clausius spoken as follows (1854): “*The sum of the compensated heat transformation of any thermal cycle is equal to the uncompensated heat transformation*,” which can be written as [15]

$$N + \oint \frac{dQ}{T} = 0 \quad (16)$$

Therefore, it is a prototype of semi-conservation law of entropy, but that does not appear explicitly in the entropy itself, because Clausius following the Carnot and Rankine, tacitly assumes that all entropy changes in the engine cycle are compensated:  $\oint dS d\tau = 0$ . Definition (15) made a lot of trouble to mathematicians. They developed a special formalism “differential forms” in which temperature played the role of “an integrating factor” (factor of proportionality, integrating factor, etc.) or any function dependent on temperature, which Müller (1970, [7]) called the “coldness.” Combining the growth of entropy, entropy fluxes, and uncompensated entropy source together, Clausius receives the semi-conservation law of entropy in the time interval  $\tau_0 - \tau$  (1865) [15]:

$$S - S_0 = \int_{\tau_0}^{\tau} \frac{dQ}{T} d\tau + N_{0-\tau} \quad (17)$$

In the sense of form, it is a law integral in both time and space. Nevertheless, in the sense of mathematical content, it is identical with the local conservation law of Carnot entropy. The only distinguishing element in this equation is a postulate independently spoken by Clausius, that “uncompensated heat transformation is always positive  $N > 0$ .” In the case of the Universe, modeled as a “perfect rarefied gas,” which instead of molecules has solar systems, entropy fluxes on its corners should be zero. Hence, it results from Equation (17) that the

entropy of the Universe continues to grow from some initial entropy  $S_0$ . Needless to say, that the last statement, terminating the famous work of Clausius, is still a source of new discussions, especially among the newly educated philosophers of nature.

### Clausius–Duhem Inequality

This above-mentioned semi-conservation law of Clausius entropy immediately became inviolable paradigm of continuum physics, but the line of reasoning of Carnot, Rankine, Reech, or Gibbs had been forgotten. Although, semi-conservation law of entropy, until the formation of the foundations of the kinetic theory of gases, was operated mainly for the development of the statistical approach introduced by Boltzmann, Hirn, Meyer, Stephen, Warburg, and others. It was used by a few researchers such as Planck (1899, [14]) and Duhem [16–18] on phenomenological basis. There was a need to define precisely this law only after the works of Natanson [8], Onsager (1931), Eckart [19] and others, because they gave the foundation for nonequilibrium thermodynamics (see, Sieniutycz [6]). In 1952, Truesdell decided to give it a form of inequality and to name the “inequality of Clausius–Duhem” [20]:

$$\frac{d}{dt}H > \iint_{A_{heat}} \frac{1}{\theta} \vec{\mathcal{F}}_{heat} \cdot \vec{n} dA + \iiint_V \rho \frac{r}{\theta} dv; \quad (18)$$

where  $H = \iiint_V \rho \eta dv$

This inequality can easily be written in the local form as follows:

$$\rho \frac{d}{dt} \eta > \text{div} \left( \frac{\vec{\mathcal{F}}_{heat}}{\theta} \right) + \rho \frac{r}{\theta} \quad (19)$$

Unfortunately, Truesdell – the founder of the analytical form of semi-conservation law of entropy – speaking by means of his pictorial language, saddled this inequality to some “the original sin.” He was the only one of the few

modern researchers who was aware that there are two entropy definitions in thermodynamics, i.e.,  $\eta$  and  $S$ . They are associated with the two approaches: reversible and irreversible, but Truesdell when speaking of the Clausius inequality, he did not use his original designation:  $S$  or  $s$ , which even today is clearly associated with nonequilibrium thermodynamics of Onsager. He probably had already called to pierce the soap bubble of the Onsager theory. Taking this into account, the removal of Clausius  $S$  from the formula and inserting competitive Gibbs marking  $\eta$  instead of it should be acclaimed in the science as a cardinal error. The next two errors of Truesdell, which contains the inequality (18), is that he uses thermal energy flux  $\vec{\mathcal{F}}_{heat}$  and sources of internal energy  $r$  in the entropy balance equation. Instead of it, he should use the entropy flux  $\vec{h}$  and uncompensated heat transformation  $n_s$ . Especially, the internal energy source, appearing *ex cathedra*, is an illegal extension of Clausius concept of heat to all other forms of energy.

Nowadays, Clausius–Duhem inequality (19) plays a special role in continuum thermodynamics, and it is the basis for determining the restrictions on the constitutive constants appearing in the describing equations. In practice, this equation is used in the manner outlined by Eckart [19] and Truesdell [20]. The first method was developed by Liu and Müller and is called “the procedure of Liu multipliers,” while the second one, based on the elimination of the internal energy source, was developed by Coleman and Noll (1963) and is called “Coleman–Noll procedure” [9]. There are also many papers showing the relationship of inequality (19) with the second law of thermodynamics [1, 5].

In summary, there are two distinct lines of reasoning in the phenomenological approach, which lead to the conservation or semi-conservation laws of entropy. The semi-conservation law of entropy has become a starting point for statistical and computer recognition of the problem [1]. Therefore, common understanding of entropy as a parameter measuring the degree of chaos is opposed to used by professionals the concept of Carnot entropy, reflecting the highest order of thermal motion.



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## Equation of Heat Conduction

► [Constitutive and Geometrical Equations for the Thermomechanical Analysis of Shells](#)

## Equation of Motion: Scalar Formalisms and Theory

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## Overview

The derivations of strong and weak forms of Cauchy's first equation of motion in the sense of the scalar formalisms, namely, from Hamilton's principle and from the principle of balance of total energy for an isothermal continuum body, are briefly summarized. In the scalar formalisms, unlike the vector formalism, we mainly deal with the scalar-valued functions, that is, the autonomous Lagrangian function and the autonomous total energy function of an isothermal continuum body, which is sometimes called the autonomous mechanical energy in the literature, and the autonomous Hamiltonian function, which is equivalent to the autonomous mechanical energy function. Both Hamilton's principle and the principle of balance of mechanical energy are consequences of Cauchy's first equation of motion. Once the Cauchy's first equation of motion in the Lagrangian and Hamiltonian mechanics is derived, the spatially discrete forms are readily obtained following the Galerkin finite element method.

## Hamilton's Principle and the Principle of Balance of Mechanical Energy

In this section, we derive the strong form of the initial boundary-value problem and its weak form for isothermal elastodynamical systems from Hamilton's principle and the principle balance of mechanical energy (in the Lagrangian and Hamiltonian mechanics frameworks).