

## Characterizations of entropy in thermodynamics Part I

V. C. DANNON (ATHENS)

FREQUENTLY, the analysis of entropy in thermodynamics is second in priority to the wish of having its existence assured. Missing are characterizations of entropy and, in particular, a quantitative one. Furthermore, the methods of Caratheodory's entropy surfaces and Carnot cycles, used to establish the existence of entropy, are not popular with many authors. Consequently, the existence of entropy is frequently postulated in the literature. We seek here characterizations of entropy and derive them without using either entropy surfaces or Carnot cycles. Our quantitative characterization allows for the checking of the existence of entropy, rather than postulating it. We illustrate its power with some examples and apply it to obtain further characterizations.

Analiza entropii w termodynamice ustępuje często miejsca badaniom dotyczącym problemu jej istnienia; brak jest danych dotyczących charakterystyk entropii, a zwłaszcza odpowiednich danych ilościowych. Ponadto metody powierzchni Caratheodory'ego i cykły Carnota stosowane do rozwiązania problemu istnienia entropii nie cieszą się dużą popularnością wśród wielu autorów. W związku z tym w literaturze często postuluje się istnienie entropii. W pracy poszukuje się i określa charakterystyki entropii bez posługiwania się powierzchniami entropii i cyklami Carnota. Otrzymana charakterystyka ilościowa pozwala raczej sprawdzić niż udowodnić istnienie entropii. Możliwości omawianej metody analizy ilustrują podane przykłady.

Анализ энтропии в термодинамике уступает часто места исследованиям, касающимся проблемы ее существования; отсутствуют данные, касающиеся характеристик энтропии, а особенно соответствующих количественных данных. Кроме этого методы поверхностей Каратеодори и циклов Карно, применяемые для решения проблемы существования энтропии, не имеют большой популярности среди многих авторов. В связи с этим в литературе часто постулируется существование энтропии. В работе ищутся и определяются характеристики энтропии без послуживания поверхностями энтропии и циклами Карно. Полученная количественная характеристика позволяет скорее проверить, чем доказать существование энтропии. Возможности обсуждаемого метода анализа иллюстрируют приведенные примеры.

### List of symbols

$\delta Q$	infinitesimal change of heat,
$s$	specific entropy,
$\tau$	empirical temperature,
$v$	concentration,
$\delta W$	infinitesimal change of work,
$p$	pressure,
$C$	specific heat at constant volume,
$\nu$	latent heat = specific heat at constant temperature,
$u$	specific internal energy,
$\theta$	empirical temperature,
$p_\tau$	$\frac{\partial p}{\partial \tau}$ at constant volume,

$$\theta_\tau \quad \frac{\partial \theta}{\partial \tau} \text{ at constant volume,}$$

$$T \quad \text{absolute temperature,}$$

$$T_\tau \quad \frac{\partial T}{\partial \tau}.$$

## 1. Introduction

THE HEAT absorbed by a system undergoing a process does not depend just on the initial and final temperature and density but on their many intermediate values that appear in the process. Hence an infinitesimal change in the heat added or absorbed is not an exact differential and is denoted by  $\delta Q$ .

The aspiration to relate  $\delta Q$  of an ideal (reversible) process to an exact differential has led to the concept of entropy. Roughly speaking, an entropy is a civilized heat function that does not depend on the process but only on initial and final thermodynamic states.

If there is a nonvanishing function  $\theta$ , so that  $\delta Q/\theta$  is an exact differential  $ds$ , we call  $s$  the specific entropy of the system.  $1/\theta$  is called an integrating factor for  $\delta Q$ . ( $ds = \delta Q/\theta$  is considered the mathematical form of the second law [e.g. [PAULI P. 25]).

For the perfect gas system given by  $pv = T$  where  $T$  is the perfect gas temperature (we shall see that)  $\delta Q/T = ds$ . So  $1/T$  is an integrating factor and the perfect gas system is endowed with an entropy function but, in general, the existence of an integrating factor for  $\delta Q$  (and hence of entropy) of a frictionless system is far from obvious. For instance, the simple form

$$\omega(x, y, z) = xdy + dz$$

does not have an integrating factor (see PIPPARD pp. 32–33).

In spite of that, some introductory books (e.g. CALLEN; BADGER, p. 239; ABBOTT and NESS) tell the reader that entropy always exists (an open question, in fact) and some axiomatic treatments (e.g. DOMINGOS, p. 7; “Critical review of Thermodynamics”, pp. 38, 239; HERMANN, p. 259) start by postulating the existence of an entropy function.

This faulty approach dates back to the 19-th century when the concept of entropy was introduced without a proof into thermodynamics by Clausius’ insight. Clausius’ paper can be found in KESTINE’S source book “The second law of thermodynamics” [28].

A common derivation of the so-called Clausius inequality (see for example ASTRON and FRITZ, p. 61; SEARS, p. 130; FERMI, p. 46) would apply the 2-nd law to Carnot cycles (paths composed exclusively from isothermal and adiabatic segments) and conclude from

$$\sum \frac{AQ_i}{T_i} \leq 0 \quad \text{that} \quad \oint \frac{\delta Q}{T} \leq 0$$

is true for any cyclic process of a thermodynamical system (that obeys the second law). This derivation extends a result proven for a special path, to an arbitrary path, through a limiting process that is seldom explained in detail. The method assumes implicitly that

the limit possesses the properties of the approximations. Generally, this is not true (see also HSIEH, p. 21; DODGE, p. 64; MUNSTER, p. 9; SILVER, p. 73; SOCRATES, p. 74; BUCKINGHAM, p. 24).

This flaw initiated attempts to approach otherwise the concept of entropy. An estimable attempt was made by Caratheodory in 1909. (See “the 2-nd law of thermodynamics”, edited by KESTIN, pp. 229–243). This was interpreted and popularized by BORN [KESTIN, p. 306] and eventually was accepted as THE mathematical treatment of thermodynamics. The Carnot cycles method precedes this treatment sometimes when an author wishes to present an intuitive introduction to the subject, but rarely would the heuristic approach appear alone in the modern texts. Among the many texts that follow Caratheodory’s approach are: Pauli, Pippard, Bazarov, Hsieh, Buchdal, Landsberg, Adkins and Kestin’s Thermodynamics.

For systems depending on two state variables  $\tau$  and  $v$ , Caratheodory’s method considers those satisfying the relation  $\delta Q = Cd\tau + vdv$  and studies the equation  $\delta Q_I + \delta Q_{II} = 0$  of adiabatic cyclic processes of the union of the systems I and II. The state variables here are  $\tau$ ,  $v_I$  and  $v_{II}$ . A process geometrically is represented by curves in the  $(\tau, v_I, v_{II})$  state

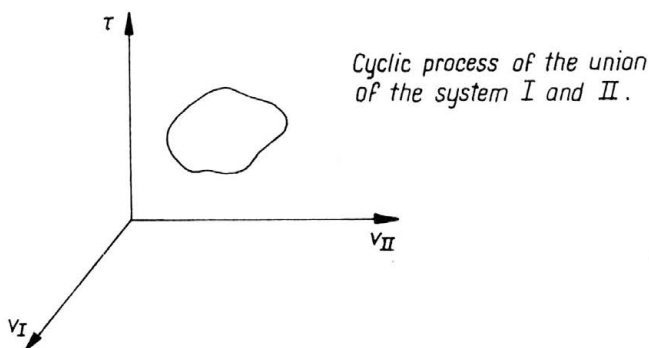


FIG. 1.

space (Fig. 1). Caratheodory’s version of the 2-nd law says that, for a given point  $P$  in this state space, there are points arbitrarily close to  $P$  that cannot be joined to  $P$  by adiabates.

Using this (so-called axiom of adiabatic inaccessibility) he shows, rather intuitively, that the state space is foliated uniquely into a family of surfaces of equal entropy (that do not intersect each other), from which follows the existence of an integrating factor (which is the same for both systems I and II).

While this geometric argument captures one’s imagination, the integrating factor is not explicit and the surfaces of equal entropy do not seem to be a natural product of the problem. We start with two state variables, construct a three-dimensional space and return to our initial two variables. Could this be done without the construction of surfaces?

Furthermore, either approach to entropy (Carnot’s cycles or Caratheodory’s) does not equip us with a quantitative measure allowing us to determine whether entropy exists, nor does it supply us with an explicit intergrating factor.

The above may explain why in texts on irreversible thermodynamics many authors (Yourgrau, Prigogine, DeGroot, Fitts, Lavenda) avoid both approaches and postulate the correctness of the Gibbs equation

$$Tds = du + pdv - \sum_i \mu_i dx_i$$

(where  $T$  is the absolute temperature,  $s$  is the specific entropy,  $u$  the specific internal energy,  $v$  the specific volume,  $p$  is the pressure,  $\mu_i$  chemical potentials and  $x_i$  specific concentrations of the  $i$ -th component). Clearly, this amounts to the implicit assumption that

$$\frac{1}{T} (du + pdv - \sum_i \mu_i dx_i)$$

is a total differential. All of these authors prefer this assumption to a specific reference to any of the existing approaches to entropy.

This is not entirely satisfactory. Either approach is based on the 2-nd law, hence finds the existence of entropy on physical laws. On the other hand postulating the 2-nd law is not logically superior to assuming the Gibbs equation. Moreover, neither assumption enables us to check whether entropy exists.

Thermodynamics contains several derivations of the existence of entropy. If one is ready to accept the 2-nd law, then the existence of entropy can be derived. Missing are characterizations of entropy and, in particular, quantitative ones. The choice of the Gibbs equation as a starting point indicates a clear preference for a quantitative measure.

We pose our question in three parts:

A) Are there characterizations of entropy?

B) If so, can they be derived without using either the not very popular entropy surfaces or the Carnot cycles?

C) In particular, is there a quantitative measure for the existence of entropy?

Our basic result is an affirmative answer to C) [See the abstract in "Notices" of A.M.S. Oct. 79, A-520]. A necessary condition for the existence of entropy is that

$$\frac{p_\tau}{v} \text{ is a function of } \tau \text{ alone.}$$

(Here  $p$  is the pressure,  $v$  is the latent heat and  $\tau$  is the empirical temperature). This was established by the use of entropy surfaces in [44] and in [53, p. 67] by the use of Carnot cycles. Using neither, we establish for systems obeying the first law of thermodynamics, the equivalence of this condition to the existence of entropy. Thus the existence of entropy can be checked instead of being postulated.

In [Abstracts of A.M.S. Aug. 1980, p. 490] we indicated that A) and B) can be answered positively and stated other characterizations of entropy.

The questions that motivate this paper are close to the ones posed so far. Yet they are distinct. Frequently (e.g. [31]) the analysis of entropy is second in priority to the wish to have its existence assured. In this paper we make that analysis our prime concern. We wish to refine the concept, to understand it better and to elaborate on its meaning and on its implications.

Our analysis holds for nonfrictional ideal system in reversible thermodynamics. In a later paper we plan to discuss frictional systems in irreversible thermodynamics that obey an ideal form of the first law of thermodynamics.

Now we turn to a description of non-frictional systems.

## 2. Thermodynamical systems

We start with a system characterized by its empirical temperature  $\tau$  (one to one bicontinuous function) and by a concentration  $v$ . The points in  $\tau \times v$ , range through a domain called the state space of the system. A process of the system is assumed to be represented by a continuous curve of bounded variation.

If the system is ideal (that is frictionless), the infinitesimal work done in any process is assumed to be

$$\delta W = p dv,$$

where  $p = p(\tau, v)$  is the pressure.  $p$  and  $\left[ \frac{\partial p}{\partial \tau} \right]_v = p_\tau$  are continuous functions and  $p_\tau$  is nonvanishing. The infinitesimal heat absorbed in a process is assumed to be

$$\delta Q = C d\tau + v dv,$$

where  $C = C(\tau, v)$  is the specific heat at constant volume and  $v$  is the latent heat.  $C$ ,  $\left[ \frac{\partial C}{\partial v} \right]_\tau = C_v$ ,  $v$ , and  $\left[ \frac{\partial v}{\partial \tau} \right]_v = v_\tau$  are continuous and  $v$  is nonvanishing.

We shall assume the first law of thermodynamics. It states that in any cyclic process (represented by a closed curve  $\gamma$ ), energy is conserved, i.e.

$$\oint \delta Q = \oint \delta W.$$

This is equivalent to the assumption that  $\delta Q - \delta W$  is an exact differential. It is denoted by  $du$ , where  $u$  is called the internal energy. Alternatively,

$$0 = \oint_\gamma du = \oint_\gamma \delta Q - \delta W = \oint_\gamma C d\tau + (v - p) dv = \iint_{(\text{interior of } \gamma)} [(v - p)_\tau - C_v] d\tau dv$$

implies that

$$v_\tau - p_\tau = C_v$$

(since  $\gamma$  is arbitrary). Note that assuming the correctness of the first law is consistent with our assumption that  $\delta Q$  and  $\delta W$  are inexact differentials. The 1-st law with  $\oint_\gamma \delta Q = 0$  or  $\oint_\gamma \delta W = 0$  implies that  $p_\tau = 0$  (clearly, the pressure does depend on temperature).

Observe that

$$du + p dv = C d\tau + v dv.$$

We shall call it the Gibbs (differential) form of the system.

We are now ready to investigate the concept of entropy.

### 3. A quantitative characterization of entropy

Given such a thermodynamical system that satisfies the first law, the following statements are equivalent:

E) The system has an entropy; A state function  $s(\tau, v)$  such that  $ds = \frac{Cd\tau + vdv}{\theta}$ , where  $\theta$  is an empirical temperature.

I) The Gibbs form  $du + pdv$  has an integrating factor  $\frac{1}{\theta}$ .

II)  $\frac{p_\tau}{v}$  is a function of  $\tau$  alone and  $\theta = \exp \int_0^\tau \frac{p_\tau}{v} d\tau$ .

The following direct proof uses no figures and does not employ much more than partial differentiation.

We first show  $I \Rightarrow II$ .

If  $\frac{1}{\theta}$  is an integrating factor, then for an arbitrary cyclic process (described by the closed curve  $\gamma$ ),

$$0 = \oint_\gamma \frac{\delta Q}{\theta} = \oint_\gamma \frac{C}{\theta} d\tau + \frac{v}{\theta} dv = \oint\oint \left( \left[ \frac{v}{\theta} \right]_\tau - \left[ \frac{C}{\theta} \right]_v \right) d\tau dv.$$

Hence

$$\left[ \frac{v}{\theta} \right]_\tau = \left[ \frac{C}{\theta} \right]_v.$$

Performing the differentiation and simplifying, we derive

$$v\theta_\tau - C\theta_v = \theta(v_\tau - C_v).$$

Applying the 1-st law ( $v_\tau - C_v = p_\tau$ ), we have

$$v\theta_\tau - C\theta_v = \theta p_\tau.$$

The solution to this partial differential equation for  $\theta$  is given by

$$\frac{d\tau}{v} = -\frac{dv}{C} = \frac{d\theta}{\theta p_\tau}.$$

Integrating the equation  $\frac{d\tau}{v} = -\frac{dv}{C}$ , we obtain

$$\int C d\tau + v dv = C_1$$

and integrating the equation  $\frac{d\theta}{\theta} = \frac{p_\tau}{v} d\tau$  we derive

$$\theta = \exp \int \frac{p_\tau}{v} d\tau + f(C_1),$$

where  $f$  is an arbitrary function. For an adiabatic process, we have  $C_1 = 0$  and so

$$\theta = \exp \int \frac{p_\tau}{\nu} d\tau + f(0).$$

Hence

$$\theta_\tau = \theta \frac{p_\tau}{\nu}.$$

Substituting this back into  $\nu\theta_\tau - C\theta_\nu = \theta p_\tau$ , we get  $C\theta_\nu = 0$ . Since  $C$  is not identically zero,  $\theta_\nu = 0$ , i.e.  $\theta$  is a function of  $\tau$  alone. Hence  $\frac{\theta_\tau}{\theta} = \frac{p_\tau}{\nu}$  is a function of  $\tau$  alone and  $\theta$  has the form  $\exp \int \frac{p_\tau}{\nu} d\tau$ .

Conversely, to show that II implies I, assume that  $\frac{p_\tau}{\nu}$  is a function of  $\tau$  alone and define  $\theta = \exp \int \frac{p_\tau}{\nu} d\tau$ . Then  $\frac{d\theta}{d\tau} = \theta \frac{p_\tau}{\nu}$ . Hence  $\frac{\nu}{\theta} = \frac{p_\tau}{\theta_\tau} = p_\theta$ . To show that  $\frac{1}{\theta}$  is an integrating factor for  $Cd\tau + \nu dv$ , consider an arbitrary path  $\gamma$  in the  $(\theta, \nu)$  plane (being a monotone increasing function of  $\tau$  alone,  $\theta$  serves here as an empirical temperature). We then have

$$\begin{aligned} \oint \left\{ \frac{C}{\theta} d\tau + \frac{\nu}{\theta} dv \right\} &= \oint \left\{ \frac{C d\tau}{\theta d\theta} d\theta + \frac{\nu}{\theta} dv \right\} = \oiint \left( \left[ \frac{\nu}{\theta} \right]_0 - \left[ \frac{C}{\theta\theta_\tau} \right]_v \right) d\theta dv \\ &= \oiint \left( \frac{\nu_0}{\theta} - \frac{\nu}{\theta^2} - \frac{C_\nu}{\theta\theta_\tau} \right) d\theta dv = \oiint \frac{1}{\theta\theta_\tau} [(v_0 - p_0)\theta_\tau - C_\nu] d\theta dv = 0 \end{aligned}$$

since  $(v_0 - p_0)\theta_\tau - C_\nu = \nu_\tau - p_\tau - C_\nu = 0$ , by the first law.

The integrating factor  $\theta$  is an empirical temperature which is the same for all systems with the same  $\tau$ . We soon identify it with the absolute temperature.

#### 4. Absolute temperature

Our experience says that thermometric materials do not exist for the whole hotness range. Rather we shall assume that each hotness level belongs to the domain of an empirical temperature of some thermometric material. For instance, a mercury glass thermometer serves for up to 850°K, a thermocouple for up to 2000°K and magnetic salts are used for very high temperatures (see Experimental Thermodynamics, P.15).

On the overlap of two hotness ranges we have  $\theta' ds' = \theta ds$ . Hence  $\frac{\partial s'}{\partial \tau} = 0$ . Therefore  $s'$  depends on  $s$  alone. Thus  $\frac{ds'}{ds} = \frac{\theta}{\theta'}$  depends on  $s$  alone. On the other hand  $\frac{\theta}{\theta'}$  depends only on  $\tau$ . So in conclusion both quotients must be constant and  $\theta$  equals  $\theta'$ , i.e. up to

a multiplication by a constant. Thus we can construct a unique temperature scale  $T$  and refer to it as the Absolute Temperature. To fix a more familiar scale for  $T$ , we set

$$T_s = T_i \exp \int_{\tau_i}^{\tau_s} \frac{1}{v} \frac{\partial p}{\partial \tau} d\tau \quad \text{and} \quad T_s - T_i = 100,$$

where  $T_i$  is the temperature of freezing water at atmospheric pressure and  $T_s$  is the temperature of boiling water at atmospheric pressure. Thus we obtain  $T_i = 273.15$  (in the Kelvin scale).

We illustrate the power of our characterization with the following examples.

## 5. Examples

### 5.1. Ideal gas system

This term is used to describe a frictionless system that obeys the relation

$$v = p = \frac{T}{v} \quad (\text{here we denote } \tau = T).$$

By the 1-st law  $C_v = 0$ . Hence  $C = C(T)$  is a function of  $T$  only and the internal energy

is given by  $u(T) = \int C(T) dT$  which is a function of  $T$  only. Now  $\frac{\partial p}{\partial T} = \frac{\partial}{\partial T} \left( \frac{T}{v} \right) = \frac{1}{T}$ .

i.e.  $\frac{p}{T}$  is a function of  $T$  only. Hence  $\theta = T$  and the Entropy is given by

$$s = \int \frac{C(T) dT + p dv}{T} = \int \left\{ \frac{C(T) dT}{T} + d(\log v) \right\}.$$

To comprehend the complexity of an analysis that follows Caratheodory, the reader is referred to Marshall's "Simplified Version of Caratheodory" applied to the same system.

### 5.2. System with no entropy

Consider the system that in the region  $\tau > 0$ ,  $v > 0$  obeys the constitutive equations

$$\begin{aligned} C &= \tau + v, \\ v &= 2(\tau + v), \\ p &= \tau. \end{aligned}$$

This system satisfies the first law since  $v_\tau - p_\tau = C_v$  and has an internal energy function  $u = \frac{1}{2}\tau^2 + v^2 + v\tau$ . However, we have

$$\frac{p_\tau}{v} = \frac{1}{2(\tau + v)}.$$

Hence there does not exist an Entropy function.



## 6. Generalization to higher order systems

In the presence of external force fields (electric, magnetic, etc.) or internal forces (elastic stress, osmotic pressure, etc.), the infinitesimal changes of heat and work are assumed to be given by

$$\delta Q = C d\tau + \sum_i v_i dv_i \quad (i = 1 \dots k),$$

$$\delta W = \sum_i p_i dv_i \quad (i = 1 \dots k),$$

where  $v_1 \dots v_k$  are chemical concentrations (also strains, electric or magnetic moments, etc.),  $v_1 \dots v_k$  are specific heats due to the additional forces and  $p_1 \dots p_k$  are chemical potentials (also mechanical pressures, elastic stress, magnetic or electric forces, etc.). (see CALLEN [9] for a detailed description). The assumptions on  $p_i$ ,  $C$ ,  $v_i$ , are natural extensions of the assumptions given for the 1-st order system.

Assuming the first law, i.e. that  $\delta Q - \delta W$  is an exact differential  $du$  where  $u$  is the internal energy, we have

$$\partial_\tau(v_i - p_i) = \partial_{v_i} C.$$

Then the following statements are equivalent:

- (I) The Gibbs form  $du + \sum_i p_i dv_i = C d\tau + \sum_i v_i dv_i$ , has an integrating factor  $\frac{1}{\theta}$ .
- (II)  $\frac{\partial_\tau p_i}{v_i} = f(\tau)$  for any  $i = 1 \dots k$  and  $\theta = \exp \int_0^\tau f(\tau) d\tau$ .

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MATHEMATICS DEPARTMENT  
OHIO UNIVERSITY, ATHENS, OHIO, USA

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