PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 44, NO. 1, PP. 17–27 (2000)

THERMODYNAMICS OF GYULA FARKAS – A NEW (OLD) APPROACH TO ENTROPY

Katalin MARTINAS* and Ildikó BRODSZKY**

*Department of Atomic Physics
Loránd Eötvös University
H–1117 Budapest, Pázmány sétány 1, Hungary
** AUTOKUT RT, Budapest, 1115 Csóka u. 7., Hungary

Received: April 8, 2001

Abstract

Caratheodory's postulate system is regarded as a milestone in the history of foundation of thermodynamics and as one of the most elegant constructions. Entropy is introduced via the adiabatic inaccessibility postulate. The main statement is the existence of an integrating factor for the heat element of the first law independently of the number of variables.

The early history is nearly forgotten. Ideas leading to Caratheodory's principle have developed slowly from the very moment that Clausius proved his famous integral formula. Gyula Farkas, a Hungarian physicist has already in 1895 formulated a version of the adiabatic inaccessibility postulate.

Keywords: thermodynamics, entropy.

1. Introduction

Gyula Farkas (or as his name is used in his German publications according to the contemporary fashion in a translated form: Julius Farkas), a Hungarian physicist and mathematician (1847–1930), was the professor of theoretical physics in the University of Kolozsvár. In 1886 he published a paper in which he opened the way of mathematically rigorous introduction of entropy.

Farkas lemma: In reversible processes no body or system of bodies can go adiabatically into a state to which it can go by means of pure heat exchange, i.e. by changing only the temperature by supplying or abstracting heat.

That lemma is a consequence of Clausius postulate of Second Law.

Farkas theorem: In reversible processes the heat elements absorbed by the bodies always have integrating divisors, and one of them is for each body an identical function of the empirical temperature

$$dS = Q/T, \tag{1}$$

that is there exist an absolute entropy and absolute temperature scale (up to a constant multiplier).

The Farkas method is not only earlier than the Caratheodory approach to integrating multiplier, but it is superior. The Lebesgue–Riesz theorem says that the

Farkas lemma is sufficient to prove the global existence of the absolute temperature, as integrating multiplier – compared to the local proof of Caratheodory.

2. Integrating Factor

Caratheodory's postulate system is one of the most elegant constructions of thermodynamics. It shows that the so called adiabatic inaccessibility postulate is sufficient to ensure the existence of an integrating factor for the heat element of the first law independently of the number of variables. It means that $đQ$ can always be written in the form: $d'Q = t\,ds$, where t and s are functions not yet specified. It suffices to postulate the existence of thermal equilibrium and to introduce the concept of empirical temperature to show, that one of the possible t functions depends only on the temperature.

Caratheodory's postulate system is a so called deductive system (in its time it was even thought to be a complete one), where a most general theorem is postulated first, and its consequences can be directly tested. This most general theorem is the adiabatic inaccessibility. To prove the existence of entropy it is sufficient to postulate the adiabatic inaccessibility principle for quasi-static processes (that is: in whatever small neighbourhood of a state there are states which are inaccessible by quasi-static adiabatic processes). To show the increasing nature of entropy one has to consider a stronger form of the postulate (that is there are states, which are inaccessible even by non-static processes.)

One of the most fascinating aspects of Caratheodory's construction is that he always makes a very clear distinction between mathematical principles and pieces of physical experience. Being acquainted with it makes easier to understand in retrospect the earlier discussions and judging their merits.

2.1. A Reminder of the Mathematical Tools

A differential equation of the following form is called a Pfaffian expression:

$$d'w = A_1(x_1, x_2, \dots, x_n)\,dx_1 + A_2(x_1, x_2, \dots, x_n)\,dx_2 + \cdots + A_n(x_1 + x_2 + \dots x_n)\,dx_n. \quad (2)$$

If dw is a total differential then the integral of dw is independent of the path and the Pfaffian equation has a solution:

$$\eta(x_1 \dots x_n) = c, \quad (3)$$

where c is a constant. If $d'w$ is not a total differential, in certain cases a λ integrating factor can be found, such that

$$\lambda\,dw = d\eta = \lambda A_1(x_1 \dots x_n)\,dx_1 + \lambda A_2(x_1 \dots x_n)\,dx_2 + \cdots + \lambda A_n(x_1 \dots x_n)\,dx_n, \quad (4)$$

where dη is a total differential.

Johann Friedrich Pfaff (1765–1825) proved that for two variables a Pfaffian expression always has an integrating factor. In the case of three or more variables certain conditions must be satisfied (given relationships between the second order partial derivatives).

In thermodynamics heat is a Pfaffian. Caratheodory has shown that the condition for the existence of an integrating factor for heat can be formulated topologically. A Pfaffian in three or more variables has an integrating factor if and only if there exist points in the neighbourhood of a given point that cannot be reached along curves representing solutions of the Pfaffian equation.

3. Beginnings

When Clausius formulated the integral form of the Second Law, he based his reasoning entirely on physical considerations. One of his mainly acknowledged merits is that he has given the law a clear mathematical form. The result can be read so that absolute temperature is an integrating factor of the heat [5].

$$dS = dQ/T. \tag{5}$$

That inspired other physicists to start with heat as a Pfaffian expression. To look for an integrating divisor to show this way the existence of a conserved entropy for reversible processes, that the integrating divisor can be identified with the absolute temperature. This endeavour was motivated partly by the fact that they felt that the mathematically precise use of temperature requires a bit closer examination.

The idea – to introduce temperature as an integrating factor – came at first from ZEUNER [4]. We know his priority from Clausius, since he discussed in detail in his book every early reaction on his own work ([5] Abschnitt XIII.). Zeuner has shown that when the state can be specified by two variables the existence of entropy is the consequence of the First Law. Zeuner had two main aims:

1. To deduce both the First and Second Law from the principle of the equivalence of heat and work without using any other principle.
2. Not to use the absolute temperature as a primary concept at the beginning, rather to define it as a result.

> “Clapeyron hat naemlich, wie auch Clausius, von Anfang an die Grösse S [1] als eine Funktion der Temperatur allein dargestellt. Ich habe aber vorgezogen, zu zeigen, dass man bei der Entwickelung beider Hauptgleichungen keine andern Grundsaetze aufzustellen braucht, als den der Aequivalenz von Waerme und Arbeit, und halte es für zweckmaessig, den Begriff ‘Temperatur eines Körpers’, der sich nur schwer mathematisch scharf definieren laesst, so

[1] Zeuner denoted by S the integrating divisor.

> lange als möglich den vorliegenden mathematischen Entwickelungen fern zu halten.” ([4] p. 42).
> ‘. . . ist dann . . . durch die mathematisch scharf gestellte Definition der Funktion *S* zugleich eine klare Definition des Temperaturmaasses gegeben.’ (p. 74).

Zeuner’s argumentation however was not convincing enough for Clausius. He objected that Zeuner used a hypothesis:

> ‘Es ergiebt sich hieraus, dass in den Betrachtungen, welche Zeuner in der zweiten Auflage seines Buches zur Begründung des zweiten Hauptsatzes anstellt, als wesentliche Grundlage nur die Analogie zwischen der Arbeitsleistung durch die Schwerkraft und durch die Waerme dient, und im Uebrigen dasjenige, was bewiesen werden müsste, teils stillschweigend vorausgesetzt, teils *ausdrücklich als Hypothese angenommen wird*. . .’ ([5] p. 369).

At first glance he is right, since Zeuner has written:

> ‘Wir sind daher berechtigt, den weitern Untersuchungen die *Hypothese* zu Grunde legen: dass die Funktion *S* das wahre Temperaturmaass darstellt.’ (p. 74).

Zeuner however continued the following way:

> ‘und mit dieser Hypothese ist dann, *wenn alle weiteren auf ihr ruhenden Schlüsse in Übereinstimmung mit den Erfahrungen stehen*, durch die mathematisch scharf gestellte Definition der Funktion *S* zugleich eine klare Definition des Temperaturmaasses gegeben.’

Zeuner claimed to build a deductive system where the consequences of a hypothesis are to be justified by experience. Zeuner did not notice that his result was valid only for the case of two variables, neither Clausius objected it in his criticism, they both just discussed a given differential expression of two variables. So we do not know whether Zeuner hoped to generalize it or not. (Pfaff’s results were already known by the time). We can suppose that Clausius assigned Zeuner’s surprising result to some lack of precision (or fault) in the discussion and not to the limited validity of the statement.

A statement about the existence of entropy in the case of two variables though limited in its scope is not without usefulness. It is interesting to note at this point that the construction developed by PLANCK and HAUSEN (1934) actually uses in its proof as a tool a system of bodies characterized with two variables [8], [9]. For completing the proof they naturally had to use another principle (the nonexistence of perpetual motion engines of the second kind).

4. Discussion of the *n*-Dimensional Case

W. VOIGT, professor of Göttingen, in his book ([3] Vol. I) examined the expression of elementary heat in the case of *n* variables. He realized that the existence of an (not specified) integrating divisor for the heat is mathematically equivalent with the existence of $n-1$ dimensional adiabatic surfaces (which are the geometrical place of all those states that are adiabatically accessible from a given state).

> 'Jede dieser Flaechen ist der geometrische Ort aller derjenigen Zustaende, die man von einem auf ihr liegenden Anfangzustand ohne thermische, durch alleinige mechanische Einwirkung erreichen kann; man nennt sie kalorische oder adiabatische Flaechen.' (p. 502).

The isothermic surfaces are introduced as well:

> 'Wenn naemlich die Variabeln $a, b, c, \ldots$ den Zustand eines homogenen Körpers vollstaendig angeben, *so müssen sie auch seine Temperatur eindeutig bestimmen*, und daraus folgt, dass durch konstantes t ein geometrischer Ort, eine Flaeche im n-dimensionalen Raume, eine Kurve in der Ebene, gegeben ist. *Wir können also auch t als eine der neu eingeführten Unabhaengigen betrachten.*' (p. 503).

The Clausius principle, applied in a gedanken experiment identifies the originally unspecified integrating factor with the absolute temperature. However, in Voigt's approach, the existence of the adiabatic surfaces is only an assumption. Originally he wanted to make it plausible by statistical mechanical considerations, but he did not succeed. It was left out. Gyula Farkas, a Hungarian physicist, noticed that deficiency.

He called the Pfaffian result, and further he gave the missing proof. Voigt in the second volume of his book, which was published later, referred to Farkas' article. (Ergaenzungen und Berichtigungen zum I. Band. p. 803.),

> 'fehlt eine Überlegung, welche begründet, dass die Gleichung $\mathrm{d}E' = \mathrm{d}A'$ stets einen integrierenden Faktor hat. Es war ursprünglich meine Absicht, dies als eine Annahme einzuführen, welche durch die Entwickelungen von S. 89 plausibel gemacht werden kann; durch ein Versehen ist die Ausführung dieser Absicht unterblieben. Die Herren Beltrami und Farkas haben mich auf die so entstandene Lücke aufmerksam gemacht; der letztere hat auch einen Weg zu dem Carnot-Clausius'schen Satze angegeben, der jene Hypothese vermeidet.' (p. 502).

5. Contribution of Gyula Farkas

Upon reading Voigt's book, Gyula Farkas published a paper in which he outlined his own construction [1], [2]. He showed that the Clausius postulate (and the equivalent Kelvin postulate) requires that the adiabatic processes on are surfaces. The existence of adiabatic surface implies the existence of an integrating factor. To develop it, he first introduced a new impossibility principle (Farkas Lemma), namely that it is impossible that in a reversible adiabatic process only the temperature changes.

He considered a system undergoing reversible changes. The state of a system is defined by n independent state variables, one of them being the empirical temperature, ϑ:

$$\vartheta, a, b, c, \ldots$$

The heat expressed with these state variables is

$$d'Q = \theta \, d\vartheta + A \, da + B \, db + \ldots, \tag{6}$$

where θ is the heat capacity at constant a, b, c. For this system he proved the following special form of the inaccessibility principle:

Farkas Lemma

> 'In reversible processes no body or system of bodies can go adiabatically into a state to which it can go by means of pure heat exchange, i.e. by changing only the temperature by supplying or abstracting heat.'

That is the following process

$$\vartheta, a, b, c \ldots \rightarrow \vartheta^*, a, b, c \ldots \tag{7}$$

must not be a reversible adiabatic process.

Proof If the lemma were not true, a cyclic process could be constructed, where the result would be that heat is transferred from a source of lower temperature to a body of higher temperature.

Farkas formulated the following corollary of his lemma:

Corollary 1 *In a quasi-static adiabatic process the temperature is always entirely defined by the momentary values of the other state variables and it is independent of the path.*

That corollary implies the existence of the integrating factor. In quasi-static adiabatic processes one of the independently chosen n state variables (namely the temperature) is completely defined by the other $n - 1$ variables. So for adiabatic processes the n dimensional space reduces to an $n - 1$ dimensional one. That is the adiabatic process takes place on a surface.

In adiabatic changes the functional relationship of the variables is an equation of a surface:

$$s(\vartheta, a, b, \ldots) = \text{const}. \tag{8}$$

or for a system of bodies:

$$S(\vartheta, a_1, b_1, \ldots, a_i, b_i, \ldots) = \text{const}. \tag{9}$$

That is equivalent with the statement that in adiabatic changes the Pfaffian equations:

$$\theta\,\mathrm{d}\vartheta + A\,\mathrm{d}a + B\,\mathrm{d}b + \ldots = 0, \tag{10}$$

$$\sum_i \theta_i\,\mathrm{d}\vartheta + \sum (A_i\,\mathrm{d}a_i + B_i\,\mathrm{d}b_i + \ldots) = 0 \tag{11}$$

are integrable and the integrated forms are as follows.

for a simple system

$$s(\vartheta, a, b, \ldots) = 0, \tag{12}$$

for a composite system

$$S(\vartheta, a_i, b_i \ldots) = \text{const}. \tag{13}$$

In adiabatic changes both $\mathrm{d}s$ and $\mathrm{d}'Q$ disappears. Since $\mathrm{d}'Q$ is not a total differential, it must be of the form:

$$\mathrm{d}Q = \varphi\,\mathrm{d}s; \qquad \mathrm{d}Q = \phi\,\mathrm{d}S \tag{14}$$

that is there exists an integrating factor, which is defined for a simple system in the form:

$$\varphi = \theta/(\mathrm{d}s/\,\mathrm{d}\vartheta). \tag{15}$$

That approach not only proves the existence of the integrating factor, but it also constructs it. Nevertheless the integrating factor is not unique, as all s functions in the form $s^* = f(s)$ can be used as an adiabatic constant, and the new integrating factor will be

$$\phi^* = \phi\,\mathrm{d}s^*/\,\mathrm{d}s. \tag{16}$$

6. Absolute Entropy and Temperature Scales

As the last step Farkas proved that the integrating factor can be identified with the absolute temperature.

The theorem is proved simply by applying the former result upon a system of two bodies. Similarly as later Caratheodory did it, he considered two bodies in thermal equilibrium. Regarding the two bodies separately, for each of them the heat can be written as

$$\delta Q_1 = \theta_1\,\mathrm{d}\vartheta + A_1\,\mathrm{d}a_1 + B_1\,\mathrm{d}b_1 + \ldots = \varphi_1\,\mathrm{d}s_1, \tag{17}$$

$$\delta Q_2 = \theta_2\,\mathrm{d}\vartheta + A_2\,\mathrm{d}a_2 + B_2\,\mathrm{d}b_2 + \ldots = \varphi_2\,\mathrm{d}s_2, \tag{18}$$

and for the united system the total heat flow is the sum of the individual flows:

$$\delta Q = \delta Q_1 + \delta Q_2 = \varphi_1\,\mathrm{d}s_1 + \varphi_2\,\mathrm{d}s_2 = \Phi\,\mathrm{d}S. \tag{19}$$

Substituting s_1 and s_2 for a_1 and a_2 and expanding dS according to the new variables, we get:

$$\mathrm{d}S = \frac{\partial S}{\partial s_1}\,\mathrm{d}s_1 + \frac{\partial S}{\partial s_2}\,\mathrm{d}s_2 + \frac{\partial S}{\partial \vartheta}\,\mathrm{d}\vartheta + \frac{\partial S}{\partial b_1}\,\mathrm{d}b_1 + \frac{\partial S}{\partial b_2}\,\mathrm{d}b_2 + \dots . \tag{20}$$

Comparing the two expressions for dS and taking into consideration that s_1, s_2, ϑ, b_1, b_2 etc. are independent variables, we can see that:

$$\frac{\partial S}{\partial \vartheta} = 0; \quad \frac{\partial S}{\partial b_1} = 0; \quad \frac{\partial S}{\partial b_2} = 0. \tag{21}$$

That means that S depends only upon s_1 and s_2, and on the other hand φ_1 and φ_2 depend on s_1 and s_2, as well as on ϑ.

$$\varphi_1 = \varphi_1(s_1, \vartheta, b_1, c_1 \dots), \tag{22}$$

and

$$\varphi_2 = \varphi_2(s_2, \vartheta, b_2, c_2 \dots), \tag{23}$$

Their quotient must be independent of ϑ, as

$$\varphi_1 = \phi \frac{\partial S}{\partial s_1}; \qquad \varphi_2 = \phi \frac{\partial S}{\partial s_2} \tag{24}$$

so

$$\varphi_1/\varphi_2 = \frac{\partial S}{\partial s_1}\Big/\frac{\partial S}{\partial s_2} = g(s_1, s_2). \tag{25}$$

It requires that ϕ is a separable function of ϑ and s, namely:

$$\varphi_1 = f(\vartheta)\Psi(s_1), \tag{26}$$

and

$$\varphi_2 = f(\vartheta)\Psi(s_2). \tag{27}$$

Selecting now a new S, $\mathrm{d}S_1^* = f_1(s_1)\,\mathrm{d}s_1$ and $\mathrm{d}S_2^* = f_2(s_2)\,\mathrm{d}s_2$ the resulting (new) integrating factor will be the same function of the empirical temperature for both systems.

Selecting now a new S in the form

$$\mathrm{d}\vec{S}_1 = \Psi_1(s_1)\,\mathrm{d}s_1 \tag{28}$$

and

$$\mathrm{d}\vec{S}_2 = \Psi_2(s_2)\,\mathrm{d}s_2. \tag{29}$$

The new integrating factor will be a universal function of the empirical temperature for both systems.

$$\varphi_1 = \varphi_2 = f(\vartheta). \tag{30}$$

That is, there is a universal temperature scale defined for all systems with the property

$$\delta Q = f(\vartheta)\,\mathrm{d}S. \tag{31}$$

The final form of the Farkas theorem states:

> 'In reversible processes the heat elements absorbed by the bodies always have integrating divisors, and one of them is for each body an identical function of the empirical temperature.'

Farkas' construction seems to lead in the shortest way from Clausius' postulate or from Kelvin's postulate to the exact proof of the existence of an integrating divisor and its identification with the absolute temperature and to the definition of an entropy function. After he proved his lemma from the Clausius principle everything else is shown to be mere mathematical consequence. It is interesting to note that this construction does not exclude the negative absolute temperature.

Farkas' paper remained unnoticed because of its extraordinary terseness.

7. Later Developments

Caratheodory's system was regarded at its time as a complete deductive system. P.T LANDSBERG writes about it [7]:

> 'Caratheodory's work is often referred to as furnishing a treatment which is axiomatic in the rigorous sense of the mathematician. However, it is clear that his discussion is no longer satisfying because the various forms of the third law of thermodynamics were put forward after his paper was written.'

Landsberg gives a conceptual and also a mathematical extension of Caratheodory's method. His more rigorous treatment provides tools for the discussion of the states near the absolute zero of temperature. He did not attempt a complete separation between mathematical and physical ideas and does not regard it possible at the present stage. However, he suggests a possible path which might be followed in order to accomplish this separation and to create a more rigorous axiomatization.

Caratheodory's treatment offers an abstract mathematical model of which thermodynamics is only one of the possible interpretations.

8. Example of an Ideal Gas

Here the entropy function of an ideal gas system is derived by the method of Farkas. For an ideal gas system we change the notations of Farkas for the common notations in the present textbooks. The empirical temperature ϑ will be T (ideal gas temperature), and a is V (volume), b is n (mole number).

The Poisson formula of elementary heat theorem states

$$\delta Q = nc_v \,\mathrm{d}T + \frac{nRT}{V}\,\mathrm{d}V, \tag{32}$$

where $\Theta = c_V$, it is the heat capacity, and R is the gas constant. In an adiabatic process $\delta Q = 0$, that is

$$0 = nc_v \,\mathrm{d}T + \frac{nRT}{V}\,\mathrm{d}V. \tag{33}$$

Assuming that $c_V > 0$, and $n > 0$

$$\frac{\mathrm{d}T}{\mathrm{d}V} = -\frac{RT}{c_v V}. \tag{34}$$

Dividing both sides by T (assuming $T > 0$)

$$\frac{\mathrm{d}T}{T\,\mathrm{d}V} = -\frac{R}{c_v V}. \tag{35}$$

Integration yields the equation of adiabatic curves

$$\ln T = \ln kV^{-\frac{R}{C_v}}, \tag{36}$$

or

$$TV^{\frac{R}{c_v}} = T_0 V_0^{\frac{R}{c_v}} \tag{37}$$

T_0 is a constant on an adiabatic surface. (It characterizes the adiabatic surface, as it gives the temperature on the surface belonging to N_0 and V_0.) In the following N_0 and V_0 are fixed parameters, so

$$T_0 = TV^{\frac{R}{c_v}} / V_0^{\frac{R}{c_v}}. \tag{38}$$

The left hand side, that is T_0 will be the s-function, then

$$\frac{\partial s}{\partial T} = \frac{\partial T_0}{\partial T} = (V/V_0)^{\frac{R}{c_v}} \tag{39}$$

and

$$\frac{\partial s}{\partial V} = \frac{\partial T_0}{\partial V} = \frac{R}{c_v} TV^{\left(\frac{R}{c_v}-1\right)} V_0^{-\frac{R}{c_v}}. \tag{40}$$

Now the integrating factor is

$$\varphi = \frac{\Theta}{\dfrac{\partial s}{\partial T}} = \frac{nc_v}{V^{\frac{R}{c_v}}}. \tag{41}$$

Expressing it with s and T one gets

$$\varphi = \frac{nc_v}{V^{\frac{R}{c_v}}} = T\frac{nc_v}{TV^{\frac{R}{c_v}}} = T\frac{nc_v}{s}. \tag{42}$$

Comparing it with *Eq.* (22) the results show that the integrating factor is the ideal gas temperature.

$$f(\vartheta) = T \tag{43}$$

and

$$\psi(s) = \frac{nc_v}{s}. \tag{44}$$

That is $\mathrm{d}S = \phi(s)\,\mathrm{d}s$.

The entropy function is

$$S = \int \psi\,\mathrm{d}s = nc_v \ln s = nc_v \ln TV^{\frac{R}{c_v}} + g(n), \tag{45}$$

where $g(n)$ is function of n. The demand for homogeneous linearity of S defines the functional form of $g(n)$, and the final form of entropy is

$$S = nc_v \ln TV^{\frac{R}{c_v}} - nc_v \ln n^{\frac{R}{c_v}} = nc_v \ln T\left(\frac{V}{n}\right)^{\frac{R}{c_v}}. \tag{46}$$

References

[1] FARKAS, Gy., A Carnot-Clausius féle tétel egyszerűsített levezetése, *Mathematikai és Physikai Lapok* **IV** (1895), pp. 7–11.
[2] FARKAS, J., Vereinfachte Ableitung des Carnot-Clausius'schen Satzes, *Mathematische und Naturwissenschaftliche Berichte aus Ungarn*, **XII**. (1895), pp. 282–286.
[3] VOIGT, W., *Kompendium der theoretischen Physik*, Verlag von Veit u. Comp., Leipzig. I. Band. 1895. II. Band. 1896.
[4] ZEUNER, G., *Grundzüge der mechanischen Waermetheorie*, Zweite Auflage 1866. Neuer Abdruck, Leipzig, 1877.
[5] CLAUSIUS, R., *Abhandlungen über die mechanische Waermetheorie I.*, Vieweg und Sohn, Braunschweig. 1864.
[6] LANDÉ, A., Axiomatische Begründung der Thermodynamik durch Caratheodory, *Handb. Phys.*, **IX** (1926), pp. 281–300.
[7] LANDSBERG, P. T., *Thermodynamics*, Interscience Publishers, New York, London, 1961.
[8] FÉNYES, I., *Termosztatika és termodinamika*, Műszaki Könyvkiadó, Budapest, 1968.
[9] HAUSEN, H., Über die Begründung des zweiten Hauptsatzes der Thermodynamik durch Kreisprozesse, *Z. Phys.*, **35** (1934), pp. 517–524.