EXTROPY – REFORMULATION OF THE ENTROPY PRINCIPLE

Katalin MARTINÁS* and Marek FRANKOWICZ**

*Department of Atomic Physics
Loránd Eötvös University
H–1117 Budapest, Pázmány Péter sétány 1, Hungary
**Department of Chemistry
Jagiellonian University
30-060 Kraków, Ingardena 3, Poland

Abstract

A quantitative measure of order, called extropy is introduced.

Keywords: non-equilibrium thermodynamics, entropy.

1. Introduction

The entropy principle is the product of a long attempt to find an adequate quantitative expression defining the directional properties of natural processes. Time arrow can be formulated so that entropy within an isolated system never decreases. A great success of the entropy approach is classical thermodynamics, a theory describing systems in equilibrium or undergoing quasi-static processes. But the entropy defined by the Clausius inequality is an abstract concept. Mainly its increasing nature is used.

Classical thermodynamics introduces entropy via the concept of heat. The result is a unique absolute entropy function. Nevertheless there are other approaches, namely statistical physics, or constructive thermodynamics (TISZA [1]; CALLEN [2]), which allow for a broader class of functions expressing the unidirectionality of processes. FOWLER [3] noticed that the statistical physical definition of entropy, logically founded on its increasing property, is not unique. 'The identification of S and $k \log W$ is based on an analogy, correct enough so far as it goes, but insufficiently deep. For it is tacitly assumed that the entropy is the only function of the state of the assembly which has this increasing property.' Fowler showed that any function defined by

$$P = k \log W + K U, \tag{1}$$

where W is the thermodynamic probability, K is an arbitrary constant, and U is the internal energy, has the same increasing property, and a maximum at the same position, as statistical entropy. We have no a priori reason for preferring one value of K to any other. He called P 'ekaentropy', and concluded that one needs an

additional postulate in statistical physics to arrive at the thermodynamic entropy. This additional postulate can be in the form

$$\mathrm{d}S = \frac{\Delta Q}{T},\tag{2}$$

that is, we have to demand in the statistical derivation of the entropy that 'in a quasi-static adiabatic process the entropy does not change'.

Fowler's conclusion was: 'the use of functions with the increasing property can apparently never lead to precise results without an appeal to δQ. If this appeal has to be made in any case, the method of approach by the increasing property loses any possible advantage over the classical method.'

There are other techniques to eliminate the arbitrariness, that is to fix the required value for constants. These constants define the position of absolute maximum for entropy [8]. A further postulate, which fixes the position of the absolute maximum of entropy is sufficient. The statement in the form, that temperature goes to infinity when the energy density tends to infinity, has the same effect as the Clausius postulate. Instead of the Clausius postulate, it is sufficient to prescribe that

$$\lim_{U/V \to \infty} \frac{\partial S}{\partial E} = 0.$$

The use of functions with the increasing property leads to precise results without an appeal to δQ. The method of approach by the increasing property has some advantage over the classical method. There is no need for the concept of quasi-static process during the construction of the theory. Similarly, the concept of heat is not needed as a basic quantity. Further, these free constants open a way to find new functions to describe the irreversible nature of processes.

It will be shown below that there is another 'physically sound' set for the free constants, which lead us to a new formulation of the Second Law, fitted for systems in a uniform environment (reservoir). There is one function from the 'ekaentropy' family, called by us 'extropy', which on the one hand has the same mathematical properties as the entropy, on the other hand, it has an important conceptual advantage, namely it quantifies the colloquial notions of 'close to equilibrium' and 'far from equilibrium'. Time arrow can be formulated so that in a uniform environment the extropy of any system never increases.

Extropy was introduced first for environmental investigations [4]; originally, it was called 'Π – potential'. The name was changed later to extropy [5] to emphasize the close relation to exergy. In the Appendix a short introduction to exergy concept is presented.

2. Entropy

In classical thermodynamics entropy is introduced via the concept of heat. The word *entropy* was introduced by CLAUSIUS [6]. Its root is the Greek word $\tau\rho o\pi\eta$

meaning 'transformation'. Entropy change is defined as being equal to the reversible flow of heat into the system, divided by the temperature of the system, i.e.,

$$\Delta S = \int_{\text{rev}} \frac{\delta Q}{T}, \tag{3}$$

where δQ is the heat transferred to the system at temperature T in a reversible process.

In natural processes the entropy increase is always higher than the thermal term, i.e.,

$$\Delta S \geq \int \frac{\delta Q}{T} \tag{4}$$

and the equality sign is valid only for reversible processes.

Entropy has the following properties:

i) As $\delta Q = dU - p \, dV - \sum_i \mu_i \, dN_i$ from this we get

$$dS = \frac{1}{T} dU + \frac{p}{T} dV + \sum_i \frac{\mu_i}{T} dN_i. \tag{5}$$

It means that the entropy depends on extensive variables. S can be written as a function of extensive variables:

$$S = S(U, V, N) = S(X_1, \ldots, X_n), \tag{6}$$

where X_i are extensive variables, and

$$\frac{\partial S}{\partial X_i} = Y_i, \tag{7}$$

where Y_i are the intensive variables.

ii) Entropy can be written as a sum of bilinear products of extensive and intensive variables,

$$S = \frac{1}{T} U + \frac{p}{T} V + \sum_i \frac{\mu_i}{T} N_i. \tag{8}$$

iii) The entropy of a system is the sum of entropies of its parts. In this respect entropy is similar to mass, volume and energy. Entropy is an extensive variable.

iv) In isolated systems entropy never decreases.

From properties iii and iv follows, that if systems A and B are in equilibrium then

$$Y_i^A = Y_i^B \tag{9}$$

that in equilibrium the intensive variables have the same value in all subsystems. The stability of equilibrium state is defined by the positive definitivity of the entropy matrix,

$$g_{ik} = -\frac{\partial^2 s}{\partial x_i \partial x_k}, \tag{10}$$

where $s = S/V$ and $x_i = X_i/V$.

The above listed properties are almost sufficient to define the entropy function. Herbert CALLEN in his book, first published in 1961 [2], gave a constructive approach to thermodynamics without the concept of heat and the concept of adiabatic processes. His postulates are as follows:

Postulate I. There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U, the volume V, and the mole numbers $N_1, N_2, \ldots, N_r$ of the chemical components.

Postulate II. There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

Postulate III. The entropy of a composite system is additive over the constituent subsystems. The entropy is a continuous and differentiable function and is a monotonically increasing function of the energy.

Postulate IV. The entropy of any system vanishes in the state for which

$$\frac{\mathrm{d}U}{\mathrm{d}S} = 0. \tag{11}$$

It is easy to show that the Clausius entropy fulfils the requirements of the postulates. However, as it was shown [7, 8], these postulates are not sufficient to yield a unique entropy function. They define only a family of functions, and one member of that family is the entropy. We call members of that function family 'ekaentropies' (like in statistical physical case treated by FOWLER [3]).

Properties of an ekaentropy function:

a. From Postulate I it follows that P is a function of extensive variables:

$$P = P(U, V, N). \tag{12}$$

b. the additivity property states that P of a composite system is merely the sum of the ekaentropies P^α of the constituent subsystems.

$$P = \sum_\alpha P^\alpha. \tag{13}$$

The ekaentropy of each subsystem is a function of the extensive variables of that subsystem alone. The additivity property requires the following property: The ekaentropy of a simple system is a homogeneous first order function of extensive parameters. That is, if all the extensive parameters of a system are multiplied by a constant λ, the ekaentropy is multiplied by the same constant.

$$P(\lambda U, \lambda V, \lambda N) = \lambda P(U, V, N). \tag{14}$$

The differentiability property implies that the differentials exist. Differentiating by λ, and taking the value at $\lambda = 1$ we get.

$$P = \sum_i \frac{\partial P}{\partial X_i} X_i \tag{15}$$

and

$$\mathrm{d}P = \sum_i \frac{\partial P}{\partial X_i} \, \mathrm{d}X_i. \tag{16}$$

The first partial derivatives are

$$\frac{\partial P}{\partial X_i} = \Gamma_i, \tag{17}$$

where Γ_i are ekaentropic intensive parameters. They are zero-th order functions of the extensives. Postulates II and III demand that the ekaentropic intensive variables for systems A and B are equal if and only if they are in equilibrium.

In equilibrium state $P(A + B) = P(A) + P(B)$, that is

$$\Gamma_i^{A+B} X_i^{A+B} = \Gamma_i^A X_i^A + \Gamma_i^B X_i^B. \tag{18}$$

In equilibrium state $\Gamma_i^{A+B} = \Gamma_i^A = \Gamma_i^B$; all the ekaentropic intensive parameters are homogeneous. Ekaentropic intensive parameters must be strictly monotonous functions of the entropic ones, Y_i,

$$\Gamma_i = \Gamma_i(Y_1, Y_2, \ldots, Y_{n-1}). \tag{19}$$

Every strictly monotonous function of the entropic intensive parameters is an 'empirical intensive' parameter, but not all of them are ekaentropic intensive variables. Γ_i is an ekaentropic intensive variable if it is the first derivative of ekaentropy, so the second derivative matrix of ekaentropy must be a symmetric one.

$$P_{ik} = \frac{\partial^2 P}{\partial X_i \partial X_k} = \frac{\partial \Gamma_i}{\partial X_k} = P_{ki}. \tag{20}$$

P_{ik} can be expressed by the help of the entropy matrix:

$$P_{ik} = \sum_l \frac{\partial \Gamma_i}{\partial Y_l} \frac{\partial Y_l}{\partial X_k} = -\sum_l \Gamma_{il} S_{lk}, \tag{21}$$

where

$$S_{ik} = -\frac{\partial^2 S}{\partial X_i \partial X_k} \tag{22}$$

is the entropy matrix, and

$$\Gamma_{il} = \frac{\partial \Gamma_i}{\partial Y_l} \tag{23}$$

is the transformation matrix. We get, that all the functions of the form

$$\Gamma_i = \int \sum_k \Gamma_{ik}\, dY_k + \Gamma_{i0} \tag{24}$$

are ekaentropic intensive variables, if Γ_{ik} satisfy the condition:

$$\sum_l \Gamma_{il} S_{lk} = \sum_l \Gamma_{kl} S_{li}. \tag{25}$$

When one investigates only one type of systems, then there may be several solutions. In case of an ideal gas the entropy matrix elements are:

$$S_{11} = -\frac{c_v}{T^2},$$
$$S_{12} = s_{21} = 0,$$
$$S_{22} = -\frac{1}{R}(p/T)^2.$$

Every $\Gamma_1 = \Gamma_1(T)$, where $d\Gamma(x)/dx < 0$ and $\Gamma_2 = \Gamma_2(p/T)$, where $d\Gamma(x)/dx > 0$ leads to a valid ekaentropy. Nevertheless, if we require it for any composite system, then

$$\sum_l \Gamma_{il} S_{lk}^\alpha = \sum_l \Gamma_{kl} S_{li}^\alpha \tag{26}$$

for every subsystem ($\alpha = 1, \ldots, r$) r is the number of different subsystems. That property, after a lengthy calculation [10], leads to a more restricted Γ function. If $r \geq 3$, then

$$\Gamma_i = KY_i + K_i, \tag{27}$$

where constant K defines the unit of ekaentropy. K_i transforms the zero point of intensive variables, if $K_i \neq 0$, then the ekaentropy does not coincide with entropy. Let us assume that only $K_1 \neq 0$, then

$$dP = dS + K_1 dU, \tag{28}$$

that is in a quasistatic adiabatic process the ekaentropy will change, while the entropy remains constant. To eliminate that discrepancy a further postulate is needed. One of the possibilities, as it was proposed by GUGGENHEIM [7] is to add that 'in

a quasistatic adiabatic process P does not change'. There are two problems with that addition.

First, that postulate assumes a clear distinction between heat and work. Nevertheless, it is not always the case. As MALLINCKRODT and LEFF [11] have shown, it can be difficult to make a clear distinction between heat transfer and mechanical work at a surface.

On the other hand that addition destroys the logic of Callen's system, refraining from the notion of heat as a primary concept.

Another possibility is to set the position of the maximum of P to the same values of extensive variables, as in case of entropy. Entropy as a function of energy tends to maximum for $U, T \to \infty$. The postulate, which gives $K_1 = 0$, and is in harmony with other Callen postulates is:

$$\lim_{U/V \to \infty} \frac{\partial P}{\partial U} = 0. \tag{29}$$

It expresses the inaccessibility of infinite temperature for systems without upper bound on energy density.

It is worthwhile to mention, that in case of upper bound, as for nuclear spin systems, the above postulate allows the appearance of negative temperatures. In postulate III Callen demanded the positivity of temperature, but that property was not needed in the derivation. It can be eliminated from the postulate. The price of it will be, that the entropy-energy function can be inverted separately in the positive and in the negative temperature regime.

Entropy as a function of volume tends to maximum for $V \to \infty$ and $p \to 0$. The postulate, which gives $K_2 = 0$, and is in harmony with other Callen postulates is as follows:

$$\lim_{V/U \to \infty} \partial P / \partial V = 0. \tag{30}$$

This postulate states the inaccessibility of zero pressure state for systems without upper bound on volume. This postulate allows for the appearance of negative absolute pressure states in systems with upper bound on volume. They were observed in liquids and in the quark matter. (For the literature on systems with upper bound on energy and volume see [12, 13]).

3. Extropy

Besides entropy, we can choose another function from the ekaentropy family with great physical significance. As in physics equilibrium states are of special interest, we may look for such ekaentropy, whose maximum corresponds to the equilibrium state of the system. If we select

$$K_i = -Y_{io}, \tag{31}$$

then

$$P = \sum (Y_i - Y_{io}) X_i \tag{32}$$

and

$$\partial P / \partial X_i = Y_i - Y_{io}. \tag{33}$$

It will be zero, when $Y_i = Y_{io}$, that is extropy will take its extremum value in the equilibrium state.

There are two classes of systems which can attain equilibrium:

- isolated systems,
- systems embedded in a reservoir with fixed values of intensive parameters. In the first case, the initial values of state variables define the equilibrium values of the intensive parameters

$$P = S - S_o, \tag{34}$$

that is the difference of the initial and final (equilibrium) entropy. P is just the negative of the Brillouin negentropy, N [16].

In case of systems in a reservoir, the equilibrium values of intensive variables of the system will be equal to those of the reservoir, Y_{io}. In that case P can be interpreted as the total entropy increase during the equilibration process. As the reservoir's entropy is $S_r = \sum Y_{io} X_{ir}$, P can be written as

$$P = \sum Y_i X_i + \sum Y_{io} X_{ir} - \sum Y_{io}(X_i + X_{ir}). \tag{35}$$

The first two terms give the initial entropy of the system and reservoir. The third term is the final (equilibrium) entropy. The system and its reservoir together constitute an isolated system, so ekaentropy never decreases, and in equilibrium it is zero. The ekaentropy is negative. To avoid the problems arising from the handling of negative quantities, we introduce extropy as the negative of ekaentropy,

$$\Pi = -P, \tag{36}$$

$$\Pi = \sum (Y_{io} - Y_i) X_i. \tag{37}$$

Extropy has the following properties:

1. $\Pi \geq 0$, it is non-negative; it is zero in the equilibrium state.
2. Extropy depends on extensive variables

$$\Pi = \Pi(U, V, N) = \Pi(X_1, \ldots, X_n), \tag{38}$$

where X_i are extensive variables, and

$$\frac{\partial \Pi}{\partial X_i} = (Y_{io} - Y_i), \tag{39}$$

where $Y_{io} - Y_i$ are the extropic intensive variables.

3. Extropy can be written as a sum of bilinear products of extensive and intensive variables,

$$\Pi = \left(\frac{1}{T_0} - \frac{1}{T} \right) U + \left(\frac{p_0}{T_0} - \frac{p}{T} \right) V + \sum_i \left(\frac{\mu_{io}}{T_o} - \frac{\mu_i}{T} \right) N_i. \qquad (40)$$

4. The extropy of a system is the sum of extropies of its parts. In this respect extropy is similar to mass, volume and energy and entropy. Extropy is an extensive variable. When systems A and B are in the same reservoir, then $\Pi_A + \Pi_B \leq \Pi_{A+B}$.

5. In isolated systems and in systems embedded into a reservoir extropy never increases.

6. Extropy is a measure of disorder. Peter LANDSBERG [18] proposed a measure for the degree of disorder. This measure is defined only for isolated systems,

$$\eta = \frac{S_0 - S}{S_0}, \qquad (41)$$

$\eta = 0$ in equilibrium systems. In a totally ordered state ($S = 0$) $\eta = 1$. In isolated systems the relation of extropy and Landsberg's measure is:

$$\Pi = S_o \eta$$

while η is an intensive characteristic of order, Π is an extensive, additive measure. A more important difference is, that Landsberg's measure does not reflect the order appearing in the difference from the equilibrium. A golden ring has $\eta = 0$, but it is not considered as a disordered system. Extropy resolves that problem.

4. Appendix: Exergy

The name exergy (German: 'Exergie') arose first among German power station and refrigeration plant engineers. A Slovenian engineer, Z. Rant proposed the word 'Exergie' in 1953 in LINDAU [19]. Exergy is widely used in the engineering practice as a very useful tool for investigating the plants for efficiency [20]. Szargut gave the following definition for exergy: 'Exergy is the amount of work obtainable when some matter is brought in a state of thermodynamic equilibrium with the common components of the natural surroundings by means of reversible processes, involving interactions only with the above mentioned components of nature.' Exergy is the theoretical maximum useful work that is obtainable from a well-defined quantity of matter by bringing it to thermodynamic equilibrium with its surroundings. In this definition, it is assumed that the surroundings are capable of supplying or absorbing unlimited amounts of heat at temperature T_0 and of doing or receiving unlimited amounts of expansion work at pressure P_0. The maximum available work is calculated by comparing the initial and final equilibrium states [21].

5. Conclusions

The extropy decrease principle is equivalent to the entropy increase principle formulation of the Second Law. In the definition of extropy we take into account the reservoir variables; we lose universality (the environment appears in the characterization of our system), but we can quantify colloquial notions of 'close to equilibrium' and 'far from equilibrium'. Therefore the extropic approach can be viewed as an 'operational' tool to deal with real non-equilibrium natural systems.

Acknowledgement

References

[1] TISZA, L., *Generalized Thermodynamics*, MIT Press, Cambridge, MA, 1966.
[2] CALLEN, H., *Thermodynamics*, Wiley and Sons, N.Y., 1960.
[3] FOWLER, R., *Statistical Mechanics*, 1936.
[4] AYRES, R. U. – MARTINAS, K., Waste Potential Entropy: The Ultimate Ecotoxic, *Economie Appliquée* XLVIII 2, (1995), p. 95120.
[5] MARTINAS, K.: Entropy and Information, *World Futures*, **50** (1997), p. 483.
[6] CLAUSIUS, R., *Abhandlungen über die mechanische Wärmetheorie I.*, Vieweg und Sohn, Braunschweig. 1864.
[7] GUGGENHEIM, E. A., *Proc. Phys. Soc. (B)* **79** (1962), p. 1079.
[8] MARTINAS, K., The Completion of the Callen's Postulate System, *Acta Phys. Hung.*, **50** (1981), pp. 121–124.
[9] MARTINAS, K., On the Callen's Postulate System, *Atti Accademia Peloritana dei Pericolanti*, Messina, **60** (1992), pp. 169–182.
[10] LUKÁCS, B. – MARTINÁS, K., The Callen's Postulates Define the Riemann Metric, *Phys. Letts.*, **114A** (1986), p. 306.
[11] MALLINCKRODT, A. J. – LEFF, H., S., All about Work, *Am. J. Phys.*, **60**, pp. 356–365.
[12] LUKÁCS, B. – MARTINÁS, K., *Acta Physica Polonica*, **B21** (1990), p. 177.
[13] IMRE, A. – Van HOOK, W. A., *J. Polym. Sci. B*, **32** (1994), p. 2283;
[14] HOLBROOK, N. M. – BURNS, M. J. – FILED, C. B., *Science*, **270**, p. 1193; SCHERER, G. W. – SMITH, D. M., *J. Non-Cryst. Solids*, **189** (1995), p. 197; STEUDLE, E., *Nature*, **378** (1995), p. 663;
[15] IMRE, A. – Van HOOK, W. A., *J. Pol. Sci. B*, **37** (1997), p. 1251.
[16] BRILLOUIN, L., *Science and Information Theory*, Academic Press, New York, 1956.
[17] LEBON, G. – JOU, D. – CASAS-VAZQUEZ, J., Questions and Answers about a Thermodynamic Theory of Third Type, *Contemporary Physics*, **33** (1992), pp. 41–51.
[18] LANDSBERG, P. T., Can Entropy and 'Order' Increase Together?, *Phys. Lett.*, **102A** (1984), p. 171.
[19] SZARGUT, J. – MORRIS, D. R. – STEWARD, Frank R., *Exergy Analysis of Thermal, Chemical, and Metallurgical Processes*, Hemisphere Publishing Corporation, NY, 1988.
[20] MALASKA, P. – KAIVO-OJA, J., Science and Technology for Sustainable Development, *Int. Congress of Engineers and Scientists, Challenges of Sustainable Development*, Amsterdam, 1996. 22-25 August.
[21] EVANS, R. B., A Proof that Essergy is the Only Consistent Measure of Potential Work, Ph.D. Thesis, Dartmouth College. University Microfilms, Ann Arbor, Michigan.