"DEFINING ENTROPY BEFORE HEAT, NOT VICEVERSA" IN INTRODUCTORY THERMODYNAMICS: TWENTYFIVE-YEAR TEACHING EXPERIENCE IN ENGINEERING PROGRAMS

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ABSTRACT

As well as many other people, we have felt, both as students and as teachers, that some traditional approaches present ambiguities and logical inconsistencies in the exposition of the basics of thermodynamics. Since the late '80s we have adopted an approach developed over thirty years of course and research work at M.I.T.: rooted in the work of Hatsopoulos and Keenan [1], it has been presented in a systematic and detailed way by Gyftopoulos and Beretta [2]. On the basis of our teaching experience we believe that this approach is particularly suited for students attending engineering programs and our goal here is to underline the most important reasons of its success. In the paper we summarize and discuss how we have adapted the sequence of arguments proposed in [2, Chaps. 2-14] to meet the needs of undergraduate engineering students.

INTRODUCTION

A large variety of expositions of the foundations of thermodynamics are available in textbooks and scientific literature. Roughly, two groups of approaches can be identified. The concise exposition by Fermi [3] or the popular textbook by Zemansky [4] are among the best examples of the first group of approaches, that could be called traditional. Heat and empirical temperature are usually introduced at the outset of the logical development. Sometimes they are assumed as primitive concepts, sometimes the authors try to explain the difference between heat and work in terms of mechanical illustrations, mostly based on statistical arguments. As well as many other students or teachers, we have felt discomfort with some of these expositions because of ambiguities and logical inconsistencies. Moreover, we think that any confused reference to microscopic physics or statistical mechanics, which do not belong to the background of most engineering students, should be avoided when teaching thermodynamics in engineering programs.

The second group is based on an axiomatic approach. Examples can be traced back to the work of Carathéodory [5] and include textbooks as the one by Giles [6], or the popular one by Callen [7], or the recent work by Lieb and Yngvason [8]. These expositions are rigorous, but rather abstract, and do not seem a suitable choice for engineering students. As a matter of fact, Giles in the Preface of his book identifies his potential readers among "physicists who are not entirely satisfied with the logical basis of their subject, [...] mathematicians who may be interested to discover a novel application of pure mathematics, and [...] phylosophers" [6, p. XII], without any mention of engineers.

As a result of long-time conversations and discussions with our friend and colleague G.P. Beretta, since the late '80s we have adopted an approach developed over thirty years of course and research work at M.I.T.: rooted in the work of Hatsopoulos and Keenan [1], it has been presented in a systematic and detailed way by Gyftopoulos and Beretta [2]. The exposition follows an axiomatic approach which is characterized by a two-fold goal. On one hand the basic concepts are introduced and developed trying to avoid equivocal definitions and logical short-circuits. On the other hand, the operational approach typical of the best traditional expositions is preserved. Particular attention is paid to fundamental questions of important practical consequences, like the amount of energy of a system that can be used to perform a useful task. Here "to perform a useful task" means to produce mechanical effects such as rise weights, compress springs, moving electrical charges. Ideally most engineering applications can be reduced or described in terms of a set of useful tasks to be performed. Studying mechanics a student is led to think that all the energy of a system can be used to perform a useful task, whereas exposition to thermodynamics conveys the fundamental idea that, in general, only part of the energy can be exploited. In some case (systems in stable equilibrium states) energy is not available at all. Starting from the question: "how much energy can be extracted from a system to perform work?" two properties are introduced, the adiabatic availability and the available energy. They are defined for any system in any state. Then, entropy is defined as a linear combination of energy and available energy differences. The definition is operational and describe an ideal way to measure entropy. Moreover entropy results to be a property of systems in any state, just like energy, momentum, mass, etc. Another key feature of this approach, particularly important for engineering students, is that it naturally leads to the physical interpretation of entropy as a measure of the energy of a system that cannot be used to perform work and underlines the strong interrelation between entropy generation by irreversibility and loss of potential to perform work.

Following Gyftopoulos and Beretta [2; 9; 10], in our courses we introduce the basic concepts according to the following order: system; properties; state; energy and energy balance; classification of states and existence of stable equilibrium states; available energy; entropy (both for equilibrium and non-equilibrium states) and entropy balance; properties of stable equilibrium states; temperature in terms of energy and entropy; pressure; work and heat. In this paper we discuss how we have adapted the sequence of arguments proposed in [2, Chaps. 2-14] to meet the needs of engineering students with different background (mechanical, industrial, civil, etc.), attending the course either during their 2nd or their 3rd year of program. On the basis of our teaching experience we believe that this approach is particularly suited for students attending engineering programs and our goal here is to underline the most important reason of its success.

UNIT 1: SYSTEMS, PROPERTIES, AND STATES

The first course hour is devoted to the introduction of the concepts of system, property and state.

A set or collection of constituents is called a *system* when it is clearly specified what follows.

1. Type of each constituent and allowed range of values of the corresponding amount.
2. Type and allowed range of values of the parameters that fully characterize any external forces exerted on the constituents by bodies other than the constituents. The external forces may depend on coordinates of the constituents of the system only.
3. The internal forces among constituents, such as intermolecular forces.

A force parameter can be a quantity that appears in the equation describing an external force field like g in the uniform gravitational field near the Earth ground, or like the charge q in the electrical field that it generates. In some cases the force field expression is not even necessary to describe its effects on the constituents: for many applications the effects of the walls of a container that confines a gas are fully described by the volume V of the enclosure, and we do not need to specify its actual geometry. Furthermore, point 2. expresses the fundamental request of *separability* of constituents of a system from other bodies. Constituents that are not separable cannot be considered a system: as an illustrative example from mechanics, consider a set A of material points subject to a force potential depending on coordinates of other material points external to A: in this case it is not possible to define the corresponding potential energy of A and, as a consequence, to determine the value of A's energy.

Everything that is not included in the system is the *environment*, which is thought as a system itself.

For a system with r constituents, we denote their amounts by the vector $\mathbf{n} = (n_1,\ n_2, \ldots,\ n_r)$. For a system with external forces described by s parameters we denote the parameters by the vector $\boldsymbol{\beta} = (\beta_1,\ \beta_2, \ldots,\ \beta_s)$. For most systems studied in the course, volume is the only parameter, $s = 1$ and $\beta_1 = V$.

The notion of system can be suitably illustrated with examples from mechanics and electromagnetism: like a set of material points of different masses (type of constituents), in a uniform gravitational field characterized by the parameter g and subject to internal elastic forces.

At any instant of time, the amount of each constituent and the parameters of each external force have specific values, but these do not suffice to characterize completely the condition of the system: we need to know the values of a larger, specific set of properties. For example, referring to systems of material points, we need to specify position and velocity of each particle.

A *property* is a system attribute that can be quantitatively evaluated at any given instant of time by means of a set of well-defined measurements and operations provided that the value is independent of the measuring devices, other systems in the environment and other instants of time. The difference of instantenous velocity and average velocity can be used to illustrate the difference among properties and other physical observables.

Two properties are said to be *independent* if the value of one can be varied without affecting the value of the other. The characterization of the condition of a system at an instant of time is given by the values of a *complete* set of independent properties: this set of values is called the *state* of the system. The expression complete set denotes a set of properties which are sufficient to determine the values of all other properties: the existence of complete sets of independent properties is implicitly assumed here. As a final remark, we underline that the amounts of constituents and the force parameters are system properties.

As already mentioned, we try to follow a gradual approach from mechanics to thermodynamics. Definitions and results we are teaching must encompass as a special cases the ones known from introductory physics courses. This is the case, for example, with the definitions of system, property, and state which are valid without change in any physical theory.

UNIT 2: CHANGES OF STATE, PROCESSES

The second course unit takes into consideration the time evolution of systems and how it can be described. Roughly, it takes one hour.

It is self-evident that the state of a system may change in time. Two or more systems interact among them, when correlated changes of their properties can be observed. Through examples from mechanics (elastic collisions) or electromagnetism (contact between charged conductors) it is underlined that some property changes can be thought of as due to an exchange between interacting systems (momentum, electric charge), while other properties are not exchanged (velocity, electric potential). *Interactions* among systems are classified in terms of properties exchanged and modes of exchange.

In mechanics students learn that to describe the time evolution of a system, one has to solve an equation of motion to find a trajectory in a proper phase space. For more general systems such an equation is not available, thus we are content with a less strong description of motion. A collision experiment can be used to illustrate the concept. Even if we do not know exactly the internal forces acting during the collision, and therefore we are not able to reconstruct the particles motion, we do know that collision will results in an exchange of momentum and energy: both momentum and energy (kinetic plus internal potential energy) are conserved. In some cases one measures masses and velocities before and after the collision, to evaluate the amount of properties which have been exchanged. In other cases, one takes advantage of the conservation principles to determine properties of the initial or the final states that have not been measured.

As well as a collision among particles can be fully described in terms of values of properties before and after the collision, to describe system evolutions we introduce the concept of *process* that is the specification of the initial and the final states plus the interactions active during the change of state.

Different types of processes can be identified. A class of processes of particular importance for the subsequent development of the exposure are the so-called *mechanical processes*. A process is denoted mechanical if the only net effect in the environment is a mechanical one. By mechanical effect we mean the change of elevation of a weight in a uniform gravitational field, the change of momentum of a material point, the change of distance of two masses or two electrical charges, the change of length of a spring etc. As taught in introductory physics courses all these examples are perfectly equivalent: it is always possible, for example, to modify the elevation of a weight without any other net effect but a change of the distance between two electrical charges. Without loss of generality, the change of elevation of a weight is taken as representative of all mechanical effects. The processes studied in mechanics and electromagnetism are all of this type.

A type of process which does not pertain to mechanics is the spontaneous process. Upon studying real systems one realizes that some changes of state are not induced by other systems nor produce a non-zero effect in the environment. Several examples from everyday life can be successfully used to exemplify this concept: some milk carefully poured into a cup of coffee will slowly change into white coffee even without any stirring or shaking from the environment; the battery of a cell phone left off for a few weeks will not supply enough charge to operate the phone. In some cases it is clear, in others it may require prolonged and careful observations, but one has to conclude that some changes of properties of a system are uncorrelated to any change of properties of any other system: these are called *spontaneous* changes of state. Systems which undergo only to spontaneous changes of state are said *isolated*. Consideration and analysis of spontaneous processes is a distinct feature of thermodynamics with respect to mechanics.

Finally, we introduce the concept of steady processes (when the state of the system does not vary in time, in spite of active interactions with other systems) and of reversible processes (when it is possibile to perform a second process that restores the initial state of both the system and its environment).

UNIT 3: FIRST LAW, ENERGY, ENERGY BALANCE

This unit requires two hours at most to introduce the First Law of Thermodynamics and its main consequences, first of all the existence of a property, energy, which is defined for all states of any system. The First Law is stated as follows:

Any two states of a system may always be the end states of a mechanical process. Moreover, for a given weight m, the value of the product mgΔz is fixed by the end states of the system, and independent of the details of the mechanical process.

Here m is the mass of the weight, g the gravitational acceleration and Δz the weight elevation change.

Commenting on this statement in class, it is important to underline that although any pair of states can be connected through a mechanical process, nothing can be said about the direction of the process. It is not guaranteed that each of the two states can be either the initial or the final state: in general, therefore, the mechanical process can be either reversible or irreversible.

The main consequence of the First Law is that every system A in any state A_1 has a property called *energy*, with a value denoted by E_1^A. If one chooses a reference state A_0 to which is assigned an arbitrary reference value E_0^A, then the energy E_1^A can be evaluated performing a mechanical process that connnects A_0 and A_1,

$$E_1^A = E_0^A - mg(z_1 - z_0) \tag{1}$$

Next we introduce the concept of composite system, that is a set of two or more systems, which can be considered a system itself. On the other hand, a partition of a system does not guarantee that the single parts are systems themselves.

A series of important results for energy are proved. Conservation: energy is conserved in any spontaneous process (a spontaneous process is a zero-net-effect mechanical process, $mg\Delta z = 0$). Additivity: the energy of a composite system is the sum of the energies of its subsystems. Transferability: considering spontaneous processes of a composite system, it is shown that energy is a property that can be exchanged among systems when they interact. Energy balance: for any process of any system A it holds,

$$E_2^A - E_1^A = E^{A\leftarrow} \tag{2}$$

Here $E^{A\leftarrow}$ denotes the net energy transferred to A from all the other interacting systems during the process that changes the state of A from A_1 to A_2. The energy gained by a system A must be accounted for by the energy transferred across the boundary of the system, because energy neither can be generated nor destroyed in A.

UNIT 4: EQUILIBRIUM STATES

This unit requires about one hour and is a necessary introduction to the Second Law statement. It should be illustrated to classes with examples from mechanics.

For most systems the number of possible states is infinite. Among these infinite states there are some that have important characteristics. We introduce a classification of states based on their time evolution in spontaneous processes.

A *non-equilibrium* state is one that changes spontaneously as a function of time. An *equilibrium* state is one that does not change as a function of time while the system cannot interact with other systems: it is a state that does not change spontaneously.

Equilibrium states can be divided further in non-stable equilibrium states and stable equilibrium states. Is it possible to perform a process that starts with the system in a non-stable equilibrium state and ends in a different state, with non-zero exchange of properties during the process, but without net final effects in the environment. A stable equilibrium state is an equilibrium state that can be altered to a different state only by interactions that leave net effects in the environment of the system. These definitions are equivalent to the ones presented in mechanics in introductory physics courses, but encompass a larger set of states than those encountered in mechanics. The motion of a material point in a force field with potential energy with relative minima (metastable states) and maxima (unstable states) and an absolute minimum (stable state) can be used to illustrate the concept.

UNIT 5: SECOND LAW, AVAILABLE ENERGY

This unit which takes about two hours, starts with the presentation of the Second Law of Thermodynamics, formulated as a statement about the existence of stable equilibrium states.

Among all the states of a system with given values of the energy, the amounts of constituents, and the parameters, there ex-

ists one and only one stable equilibrium state. Moreover, starting from any state of a system it is always possible to reach a stable equilibrium state with arbitrarily specified values of amount of constituents and parameters by means of a reversible mechanical process.

In this exposition the crucial difference between systems as studied in mechanics and electromagnetism, and systems as studied in thermodynamics, is the existence of a moltitudo of stable equilibrium states of a system, as experience and experimental evidence show. In mechanics and in electromagnetism a system has only one stable equilibrium state (ground state). At ground state the energy of the sistems attains its minimum value: thus it is usually chosen as reference state and its energy is set equal to zero. In thermodynamics, it is stated that for fixed values of amounts of constituents and parameters, there exist one stable equilibrium state for each energy value and not for the ground energy value only. Moreover the stable equilibrium state corresponding to a value of E is unique.

Let's turn to what we could call a fundamental engineering problem: given a system with energy E, which fraction of it could we extract to perform useful tasks such as rise weights, compress springs, moving electrical charges?

In a mechanical process starting either from a non-equilibrium or a non-stable equilibrium state, a system can transfer energy out. In mechanics, the maximum transfer of energy to the environment occurs in a process ending in the ground state. If ground energy is set equal to zero, we convey the idea that all the energy of a system can be extracted in a mechanical process.

Therefore, in mechanics the answer to the previous question is "all", while, upon introduction of the Second Law, the answer is "only a fraction of it": furthemore, if the initial state is a stable equilibrium one the answer is "none". The latter conclusion is known as the *impossibility of the perpetual motion machine of the second kind*.

At this point a new property defined for any state of any system is introduced: the *adiabatic availability* Ψ. The adiabatic availability of system A in state A_1 represents the maximum energy that can be extracted from A by a mechanical process starting from state A_1, without changing amounts of constituents and parameters. Let's consider all conceivable mechanical processes starting from state A_1 that do not change the amounts of constituents and the parameters, and compare the values of the energy extracted from A: the maximum value of the energy extracted satisfies all the independence requirements for a physical observable to be a property. The adiabatic availability is the maximum energy that can be extracted from a system in a given state to perform useful tasks (without vary amounts of constituents and parameters): it is equal to zero for any stable equilibrium state and it is positive for any other state. It allows to state a criterion for reversibility of a mechanical process: given two states A_1 and A_2 with the same amounts of the constituents and parameters, a mechanical process from A_1 to A_2 can be performed if and only if $\Psi_1^A - \Psi_2^A \geq E_1^A - E_2^A$. If the two differences are equal, the process is reversible. Unlike energy, adiabatic availability is not additive and does not satisfy a balance equation.

UNIT 6: THE ROUTE TO ENTROPY

This unit is the longest one and it may take up to three hours of lecturing. However it is possible to skip some minor points or proofs and save about an hour.

The fact that adiabatic availability is not additive represents a limitation to its extended use. In this unit we restrict to consider systems which are composed by a generic system and a special reference system, called *reservoir*. Upon studying the mechanical processes of the composite of a system and a reservoir, we are lead to introduce a new property which captures the important features of adiabatic availability and is additive: the *available energy*.

More than one property, available energies form a class of properties that differ by the reservoir taken as reference. So we speak of *available energy with respect to the reservoir R* and denote it as Ω^R. Each available energy is a property defined for any system in any state: $(\Omega^R)_1^A$ is the available energy with respect to R of system A in state A_1.

In class we spend some time explaining with examples that in Nature many systems behave like a reservoir and, in particular, that the natural environment acts like a reservoir: the composite of a system and a reservoir is a realistic model of most engineering systems. As a consequence, it is of great practical importance to investigate how much energy can be extracted out of such a composite system in a mechanical process.

Let's consider all conceivable mechanical processes for AR – the composite of sytem A with reservoir R, that do not change the amounts of constituents and the parameters of both A and R and start with system A in state A_1, and compare the values of the energy extracted from AR: the maximum value of the energy extracted satisfies all the independence requirements for a physical observable to be a property of A. We call it available energy of A in state A_1 (with respect to R).

As a matter of fact $(\Omega^R)^A$ is the energy extracted from AR in a reversible, mechanical process of AR that ends with A and R in mutual stable equilibrium without changes in amounts of constituents and parameters of A and R. It follows that the available energy $(\Omega^R)_1^A$ of system A coincides with the adiabatic availability Ψ_1^{AR} of composite system AR, whereas it is larger or equal to the adiabatic availability Ψ_1^A of system A.

The criterion for reversibility of a mechanical process of A can be stated in terms of $(\Omega^R)^A$ also: given two states A_1 and A_2 with the same amounts of the constituents and parameters, a mechanical process from A_1 to A_2 can be performed if and only if $(\Omega^R)_1^A - (\Omega^R)_2^A \geq E_1^A - E_2^A$. If the two differences are equal, the process is reversible. Unlike adiabatic availability, available energy is additive.

The energy E and the available energy with respect to a reference reservoir R, Ω^R determine a third property that is called entropy and denoted as S. In [2] is described the measurement procedure that allows to determine the value of S for any state A_1 of any system A. It is needed the auxiliary reservoir R, a reference state A_0 with energy E_0 and available energy $(\Omega^R)_0^A$, to which is assigned a reference value S_0, then S_1 is evaluated by the expression

$$S_1^A = S_0^A + \frac{1}{c_R}\left\{(E_1^A - E_0^A) - \left[(\Omega^R)_1^A - (\Omega^R)_0^A\right]\right\} \tag{3}$$

where c_R is a well-defined positive constant that depends on the auxiliary reservoir R only. Entropy S is shown to be independent of the reservoir, which is introduced only because it facilitates the definition of S. It is also shown that the reference value S_0^A can be chosen in such a way that S is always non-negative.

The proof of the independence of S from the particular reservoir chosen as reference is given in Par. 7.4 of [2], but in our experience is too abstract to be proposed in a ten-twenty hours introductory course to Engineering Thermodynamics.

The points that we underline and stress in class are the following. Entropy is a property in the same sense that energy, momentum, electric charge are properties. Entropy is not restricted to equilibrium states: it is defined for both equilibrium and non-equilibrium states because energy and available energy are defined for all states. Being defined in terms of energy and available energy, its measure requires only energy difference measurements which, in principle, can be determined upon measurement of the changes of elevation of weights which occur in mechanical processes. Entropy definition does not involve the concepts of heat and temperature which have not yet been defined.

Entropy is an additive property being a linear combination of additive properties: energy and available energy[1].

Next, the reversibility criterion established for available energy, yields the following series of results.

Criterion for reversibility of a mechanical process: given two states A_1 and A_2 a mechanical process from A_1 to A_2 can be performed if and only if $S_2^A - S_1^A \geq 0$, moreover if $S_2^A = S_1^A$, the process is reversible.

Entropy increases in any irreversible spontaneous process (which is a zero-net-effect mechanical process): a phenomenon which is due to creation of entropy. Any process of any system may always be regarded as a process of a composite isolated system consisting of all the systems interacting with the first one. If the process of the composite system is irreversible, its entropy does increase. It is natural to think that it is the sum of the entropy created inside the single interacting systems. The entropy created in an irreversible process is called *entropy generated by irreversibility* and denoted by S_{irr}.

Analysis of a reversible process of a composite system shows that entropy is a property that can be exchanged among systems when they interact. Therefore, the entropy gained by a system A can be accounted for by the entropy transferred across the boundary of the system and by the entropy created inside the system. Entropy does satisfy a balance equation: for any process of any system A it holds,

$$S_2^A - S_1^A = S^{A\leftarrow} + S_{\mathrm{irr}}, \qquad S_{\mathrm{irr}} \geq 0 \tag{4}$$

At this point, in class, we usually make two comments. First, the combined use of energy and entropy balance is the key to the solution of almost every thermodynamics problem. Second, the entropy of a system can even decrease in an irreversible process: it is sufficient that the entropy transferred out of the system be larger than the entropy created. Although this statement may seem obvious, many students tend to confuse the source term S_{irr} with the entropy system change $S_2^A - S_1^A$, perhaps they are confused by high-school reminiscences like “Entropy is always increasing”.

The dimensions of S depend on the dimensions of both energy and c_R. It turns out that the dimensions of c_R are independent of mechanical dimensions, and are the same as those of temperature (defined later).

UNIT 7: STABLE EQUILIBRIUM STATES

Also this unit is quite long, taking about three hours of lecturing.

One of the most important consequence of the Second Law statement is the existence of strong interrelations among the properties of the system when in stable equilibrium states.

For given values of E, $\mathbf{n}$, and $\boldsymbol{\beta}$ there exists one and only one stable equilibrium state, that implies the existence of a bijective relation between the set of E, $\mathbf{n}$, and $\boldsymbol{\beta}$ and the stable equilibrium states of A. Recalling that state is the set of values of all the system properties, the value of any property P at equilibrium can be expressed as

$$P = P(E, \mathbf{n}, \boldsymbol{\beta}) \tag{5}$$

this result will be referred to as the *state principle* and functions as Eq. 5 will be called *state equations*.

Borrowing the concept of basis from Vector Algebra, we say that $(E, \mathbf{n}, \boldsymbol{\beta})$ form a convenient basis to represent any other property of stable equilibrium states. As in Algebra the choice of a basis is not unique, in Thermodynamics any other set of $(1+r+s)$ independent properties can be used to determine stable equilibrium states: $(S, \mathbf{n}, \boldsymbol{\beta})$ is another useful choice. Among the state equations a special role is played by the *fundamental relation*:

$$S = S(E, \mathbf{n}, \boldsymbol{\beta}), \quad \text{entropy form} \tag{6}$$

$$E = E(S, \mathbf{n}, \boldsymbol{\beta}), \quad \text{energy form} \tag{7}$$

Both $S(E, \mathbf{n}, \boldsymbol{\beta})$ and $E(S, \mathbf{n}, \boldsymbol{\beta})$ are almost everywhere analytic funtions.

The first derivatives of the fundamental relations will play an important role in the subsequent developments of the subject presented in class. They are: the absolute temperature $T = \partial E/\partial S$; the $i-$th total potential $\mu_i = \partial E/\partial n_i$, $i = 1, 2, \ldots, r$; the force conjugated to the $j-$th parameter $f_j = \partial E/\partial \beta_j$, $j = 1, 2, \ldots, s$. In particular, the force conjugated to the parameter V, volume, is the opposite of pressure, $p = -(\partial E/\partial V)$.

By a simple argument we make the student understand that the abstract and somehow obscure quantity $-(\partial E/\partial V)$ does coincide with the idea of pressure introduced in mechanics, that is the ratio between normal force and the surface area on which it acts. After this proof it is easier for them to accept to call temperature the partial derivative of energy with respect to entropy!

At this point we introduce and prove the *highest-entropy principle* – among all the states with the same energy and given values of $(\mathbf{n}, \boldsymbol{\beta})$ the state of stable equilibrium has maximum entropy – and the *lowest-energy principle* – among all the states with the same entropy and given values of $(\mathbf{n}, \boldsymbol{\beta})$ the state of stable equilibrium has minimum energy. The highest-entropy principle is the basis to derive necessary conditions for mutual equilibrium between interacting systems. We usually prove explicitly that when two systems may exchange energy a necessary condition for mutual equilibrium is equality of temperature, then by analogy we simply state other conditions like equality of i-th total potential (for systems that may exchange i-th constituent) or equality of pressure (for systems that may exchange volume). Further developments of the last proof, allow to obtain the following results: temperature is a positive quantity; temperature is a non-decreasing function of energy (and entropy); entropy fundamental relation $S(E, \mathbf{n}, \boldsymbol{\beta})$ is concave with respect to energy, whereas energy fundamental relation $E(S, \mathbf{n}, \boldsymbol{\beta})$ is convex with respect to entropy; the constant c_R

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[1] Both adiabatic availability and available energy have been defined in terms of mechanical processes that do not change amounts of constituents and parameters of the system A. It is possible to consider also mechanical processes that end in states of A with assigned values of $\mathbf{n}'$ and $\boldsymbol{\beta}'$ different from those of the initial state. That yields to the so-called *generalized* adiabatic availability and available energy. These properties share the same features of adiabatic availability and available energy, but can assume negative values also. Actually, entropy is defined in terms of energy and generalized available energy.

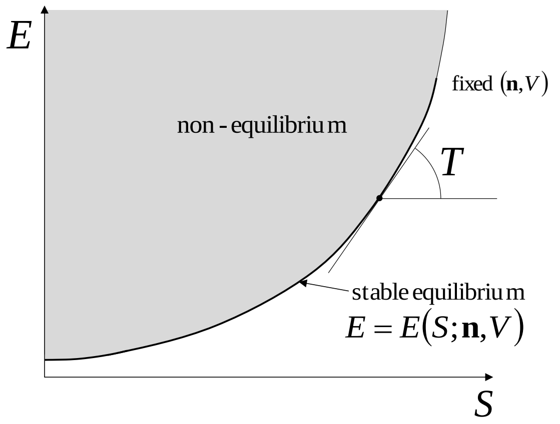

Figure 1. Energy vs. entropy graph for assigned values of $\mathbf{n}$ and V.

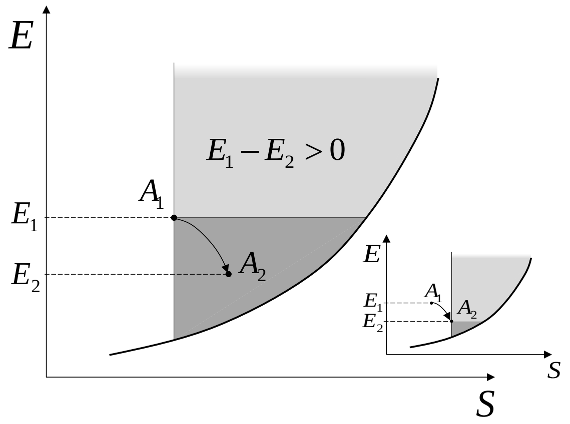

Figure 2. Allowed end states of a mechanical process starting from A_1: energy is extracted out of the system in processes ending in the darker region. Small graph: the darker region collapses as the starting state approaches stable equilibrium.

of a reservoir coincides with its temperature; last, but not least, in a spontaneous interaction between systems (without changes of $\mathbf{n}$ and $\boldsymbol{\beta}$) initially at different temperatures energy and entropy are transferred from the hotter to the colder (which is the Second Law formulation due to Clausius).

To conclude this unit, relative temperature scales are introduced and illustrated. We point out that temperature measurement procedures require mutual equilibrium between two systems that can exchange energy, but neither constituents nor volume: the system whose temperature has to be measured and the thermometer. These remarks should remove any residual doubt about the identification of $\partial E/\partial S$ with temperature.

UNIT 8: WORK AND HEAT

This is a quite short unit which takes one hour at most.

Eventually the concepts of work and heat are introduced: both are modes of energy transfer. In UNIT 2 we said that it is possible to classify interactions on the basis of property exchanged and mode of exchange: the first criterion adopted is the transfer of entropy. Any interaction that results in a net exchange of energy, but no exchange of entropy is called a *work interaction*. The energy exchanged during a work interaction is called work.

Any interaction that results in entropy exchange is called *non-work interaction*. Any process that involves at least one non-work interaction is said *diabatic*.

Consider a diabatic process for systems A and B that do not experience change of constituents or parameters. It can be reproduced as a sequence of a diabatic process that ends with one of the two system, say A, in the final state A_2, followed by a mechanical process of the second system B that ends in final state B_2. For this reason we say that the non-work interaction can be regarded as partly non-work and partly work. It is proved – but usually we do not do it in class – that if the initial states A_1 and B_1 are stable equilibrium states, in the limit $(T_1^A - T_1^B)$ tending to zero, the work transferred in the mechanical process vanishes: it can be said that in this limit the non-work interaction is totally distinguishable from work and it will be called heat interaction. Moreover, in the limit $(T_1^A - T_1^B)$ tending to zero the ratio between the energy and the entropy exchanged between A and B tends to the almost common value of the initial temperatures $T_1^A \cong T_1^B$.

Thus, we define heat interaction an interaction that results in a net exchange of energy and entropy but no constituents between two systems that are in stable equilibrium states at almost the same temperature T_Q, and such that the ratio of the amount of energy transferred to the amount of entropy transferred is equal to T_Q. The energy transferred is called heat.

The heat definition – we may called it, *strong* definition – just cited appears to many students rather puzzling. Why the interacting systems must be initially in stable equilibrium states with temperatures almost equal? Isn't it too a special case? After all when one thinks of heat, he thinks of systems whose temperatures are rather different. To answer to these objections a *weak* definition is introduced: in general, we talk of heat interaction between systems A and B which are not even in stable equilibrium states, if the interaction is localized into two subsystems A' and B' that satisfy the strong definition. We conclude quoting or anticipating that in conductive and convective heat transfer, the interaction between media always occurs through layers adjacent to the media interface that are almost at the same temperature.

We underline that the interacting systems must be almost at the same temperature because only in this case heat is entirely distinguishable from work. If it were not, one could not write

$$E_2^A - E_1^A = Q^{A\leftarrow} - W^{A\rightarrow} \tag{8}$$

$$S_2^A - S_1^A = S^{A\leftarrow} + S_{\text{irr}} \tag{9}$$

where $Q^{A\leftarrow}$ is the total energy transferred into A by heat interactions and $W^{A\rightarrow}$ is the total energy transferred out of A by work interactions. $S^{A\leftarrow}$ is the total entropy transferred into A: $S^{A\leftarrow} = Q_1^{A\leftarrow}/T_{Q_1}$ if there is only one heat interaction at temperature T_{Q_1}; $S^{A\leftarrow} = Q_1^{A\leftarrow}/T_{Q_1} + Q_2^{A\leftarrow}/T_{Q_2}$ if there are two heat interactions at temperatures T_{Q_1} and T_{Q_2}, respectively; etc. Equations 8 and 9 hold for processes that do not involve changes of constituents. We conclude quoting [10, p. 215]: "Work and heat are ingenious concepts. For given end states of a system, they allow the quantitative distinction between entropy generated by irreversibility and entropy exchanged via interactions with other systems. As such, these two concepts provide practical means for identifying opportunities to reduce the entropy generation by irreversibility and, hence, improve the performance of the system. The identification of these opportunities would be missed if heat were defined as just any interaction that is not work, i.e., any non-work interaction."

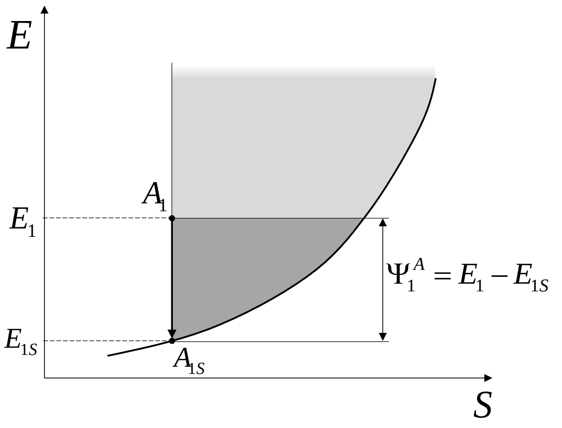

Figure 3. Graphical representation of adiabatic availability.

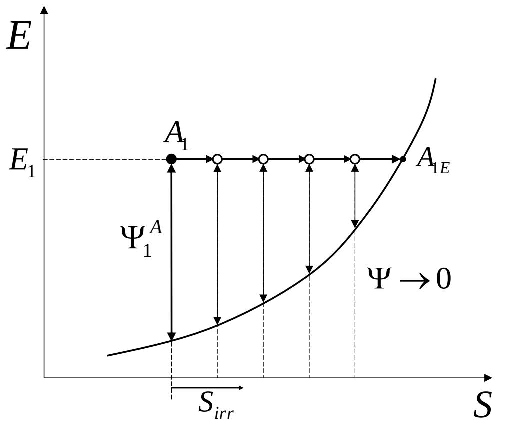

Figure 4. Graphical representation of a spontaneous process. As system state tends towards stable equilibrium, entropy increases by internal generation, whereas adiabatic availability is lost.

UNIT 9: ENERGY-ENTROPY GRAPHS

As a conclusion of this series of lessons we introduce the energy-entropy graphs. Although their use is not widespread, we consider them a very powerful educational tool. In particular, they are a simple mean to review and to put on firm basis the material presented in the preceding units. The graphs supply a clear and suggestive illustration of many concepts and make it easier for the student to grasp and retain the fundamental ideas. The material can be presented in about two hours.

For simplicity, but without loss of generality, we restrict ourselves to consider systems with one parameter only, the volume V. Then we represent on the plane S-E all the states of the system with prescribed values of $\mathbf{n}$ and V (see Fig. 1). Only points in the gray region and on its boundary correspond to possible states of the system. The boundary of the gray region is called the *curve of the stable equilibrium states*. It is the graph of the fundamental relation $E(S,\mathbf{n},V)$: each point of it corresponds to a single state of stable equilibrium and viceversa. Each point in the gray area represents several – usually infinite – non-equilibrium or non-stable equilibrium states. Points outside would have a combination of entropy and energy values that is not compatible with the assigned pair $(\mathbf{n},V)$: it is a consequence of either the highest-entropy principle or lowest-energy principle.

The slope of the stable equilibrium state curve, $\partial E/\partial S = T$ is the geometric representation of the temperature. The curve is convex, since $\partial^2 E/\partial S^2 \geq 0$, therefore its slope T increases (better, non-decreases) with both S and E.

Mechanical process end states: the grey regions in Fig. 2 show which states can be end states of a mechanical process starting in state A_1, without changes of $\mathbf{n}$ and V. System entropy can not diminish in such a process. Furthermore, in processes ending in the light grey region energy is transferred into the system, in processes ending in the dark grey region energy is extracted out of the system. The latter processes are those "performing a useful task". Considering a sequence of states approaching the stable equilibrium state curve, it is readily seen that the dark grey region quickly reduces, until collapsing in a state of stable equilibrium: that is the graphical representation of the impossibility of PMM2.

Adiabatic availability: it is the maximum energy that can be extracted from a system in a given state to perform useful tasks (without vary $\mathbf{n}$ and V), a glance at Fig. 3 shows that is the energy extracted in the reversible, mechanical process from state A_1 to the stable equilibrium state A_{1s} with the same values of S, $\mathbf{n}$ and V.

Spontaneous process: Fig. 4 represents a spontaneous process starting from non-equilibrium state A_1. As time proceeds the system state approaches the stable equilibrium state curve along a horizontal path (neither E, nor V, nor $\mathbf{n}$ can vary) while its entropy increases due to production by irreversibility. At the end the system will reach the stable equilibrium state A_{1e}: it is possible to determine a relaxation time, τ_s, characteristic of the internal spontaneous mechanisms that drive the system towards equilibrium. In a spontaneous process like the one in Fig. 4, system energy does not change, but as system entropy increases by irreversibility, adiabatic availability decreases. The potential of extracting energy from the system to perform a useful task is progressively lost. It reduces to zero when stable equilibrium is attained: we do think that this graph is an important tool for students to understand the strict relation between entropy creation by irreversibility and destruction of capability of performing work.

Another remark that we consider enlightener, is the following. The internal spontaneous mechanisms towards stable equilibrium are always active causing entropy generation and destruction of adiabatic availability. If one wants to extract as much energy as possible from a non-equilibrium state by a mechanical process, it has to do it fast: in order to minimize entropy production the characteristic time scale of the mechanical process, τ_m, must be much shorter than the relaxation time, $\tau_m << \tau_s$. Some students have the wrong idea that a process close to be reversible can be performed only proceeding slowly, through a quasi-steady evolution. Here it is shown that quasi-reversible processes can be obtained operating fast, much faster than spontaneous mechanisms towards equilibrium.

Sound propagation is an interesting illustration of this concept. The time period of the sequence of reversible compression and rarefaction induced by a sound wave in gas through which it propagates, is much shorter than the time scale of dissipative heat exchange between hot, compressed layers of gas and the adjacent, colder, rarefied layers: thus sound attenuation is a secondary effect, which has to be taken into consideration only over long distance propagation.

Available energy: Fig. 5 illustrates the graphical representation of available energy of system A and shows in the small diagram the stable equilibrium state curve for a reservoir (a straight

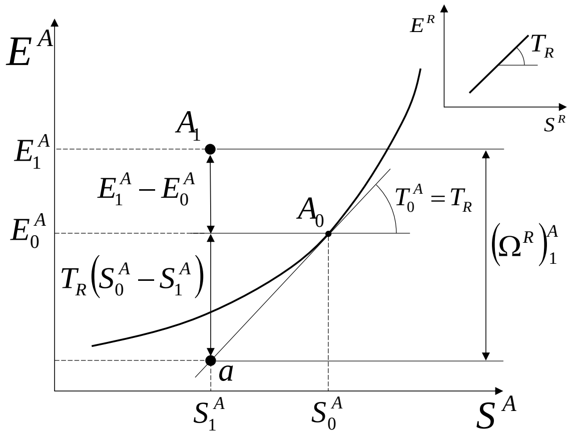

Figure 5. Graphical representation of available energy with respect to reservoir R. Small graph: the E vs. S graph for R.

line). In the energy-entropy graph of system A, state A_0 is the state of mutual equilibrium with reservoir R, that is the stable equilibrium state at $T_0^A = T_R$. Usually we show in class that available energy of state A_1 can be obtained as follows. Draw the tangent line at the stable equilibrium state curve through A_0, draw the vertical line through A_1, find the intersection a of the two lines: $(\Omega^R)_1^A$ is equal to the difference between the energy E_1^A and the energy level corresponding to point a.

CONCLUSIONS

After these lectures devoted to the foundations of thermodynamics, we proceed practicing the use of energy and entropy balances on heat engines and refrigeration units, introducing the concept of simple systems, i.e. systems whose behavior is somehow independent of the amounts of constituents, and deriving Gibbs, Maxwell, Euler and Gibbs-Duhem relations, presenting heterogeneous states and the phase-rule. Then, we address processes that result in exchanges of constituents and, upon introduction of the bulk-flow interaction, we extend balance equations of mass, energy, and entropy to these processes also. Eventually energy conversion devices and other standard applications are considered.

In our experience this exposition is particularly suited to undergraduate students of engineering programs. Its key points are the following.

It starts from concepts studied in mechanics and that are familiar to students, and try to use them to investigate a larger set of phenomena without resorting to empirical ideas of heat and temperature.

Spontaneous processes, easily recognizable in everyday life, and the existence of stable equilibrium states for any set of values of energy, amounts of constituents, and parameters are distinct features of thermodynamics with respect to mechanics: in any system in a non-equilibrium state are active internal mechanisms that spontaneously drive the system towards equilibrium.

Energy does not coincide with the possibility of performing work. Due to spontaneous evolution towards stable equilibrium, energy is conserved, but at the same time the possibility of extracting energy to perform work decreases reaching zero at stable equilibrium.

The maximum energy that can be extracted from a system and from the composite of a system and a reservoir, to perform work, are identified as system properties: adiabatic availability and available energy. They are defined for any state of any system and they can be measured in terms of the change of elevation of a weight in a gravitational field. They are progressively destroyed in spontaneous evolution towards equilibrium. The engineering student faces here one of the challenges of his profession: devices, machines, and systems that perform work efficiently must be designed to operate on time scales much shorter than the relaxation time scales of spontaneous irreversible processes.

Entropy is defined in terms of energy and available energy, for both equilibrium and non-equilibrium states. The definition is operational, i.e. it is expressed in terms of a sequence of operations and measurements: this feature is usually missing in axiomatic exposition of thermodynamics.

Balance equations of energy and entropy are derived and extensively used as powerful tools to analyse processes and to improve their efficiency.

Last, but not least, the use of energy vs. entropy diagrams as an effective educational tool to illustrate in a graphical way most of the concepts presented in these lectures. In particular, they show in a clear way the close relation between the creation of entropy by irreversibility and the destruction of the possibility of performing useful task.

ACKNOWLEDGMENT

The authors thank Prof. Gian Paolo Beretta for the uncountable hours spent in fruitful discussion on thermodynamics.

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