

Bejan's Thermodynamics for the heat transfer man, and the law of volume increase

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Abstract

Coming back on Thermodynamics, it is possible to consider the situation corresponding to different fundamental statements made from observations of the earlier power engines. An alternative form of the Kelvin–Planck's statement for the Second Law of Thermodynamics is derived, from which parallel results to those of the well established Thermodynamics can be obtained. Special attention is given to the work transfer interactions undergone by Thermodynamic systems experiencing volume-change instead of heat transfer interactions. It is thus possible the construction of a parallel structure for Thermodynamics, here called Pressodynamics, with the volume-change work transfer interactions, the absolute pressure and the volume playing the roles usually played by the heat transfer interactions, the absolute temperature and entropy in the well established Thermodynamics. The irreversibility associated with the volume-change work transfer interactions gives rise to a volume generation, in a parallel way with the entropy generation in the well established Thermodynamics associated with the heat transfer interactions. This volume generation is associated with the lost available mechanical work related with the volume-change work transfer interactions. The obtained results lead to the expansion of the Universe, in a parallel way with the entropy increase of the Universe as given by the well established Thermodynamics. A natural conclusion of the present work is thus the unification of the Thermodynamic and Cosmological time arrows. Some simple application examples are presented. Implications over the usual relations used in Thermodynamics are presented in a companion paper.

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1. Introduction

Our present understanding of Thermodynamics, and especially of the First and Second Laws of Thermodynamics, is a direct consequence of the statements made by the pioneers from their basic observations of the earlier thermal engines. The principle of energy conservation, embodied by the First Law of Thermodynamics, sounds something familiar, and it is easily accepted on the teaching/learning process. On the other hand, some statements of the Second Law of Thermodynamics, as well as the concept of entropy, sound alien. That some processes cannot occur spontaneously is obvious from our everyday basic observations, but the statement of the possible processes in terms of changes of entropy is not so obvious.

Looking back, it can be seen that the property entropy was introduced in Thermodynamics as a need from the statements of the basic observations made by the pioneers. If the statements of these observations were somewhat different, the role of entropy in the well established Thermodynamics were played by volume, a much more familiar property than entropy, for systems experiencing volume-change work transfer interactions. The implications of this different formulation extend from the analysis of simple engineering systems to our better understanding of the Universe.

In the work presented by Bejan [1,2], imagining a people familiar with properties temperature and entropy, and with the field of heat transfer, the normal development of Thermodynamics leads to the volume as a *new* property, similarly to what happens with entropy in the well established Thermodynamics. It is also presented an equivalent Kelvin–Planck's statement of the Second Law of Thermodynamics,

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Nomenclature

A, B	systems
E	energy
f	function
N	number of Pressure Reservoirs
P	absolute pressure
Q	heat transfer interaction
S	entropy
t	time
T	absolute temperature
V	volume
W	work transfer interaction

Greek symbols

η	efficiency
π	empirical pressure
ϕ	function
Φ	function

Subscripts

A, B	subsystems
C	Carnot's or Carnot's alternative cycle
e	environment
gen	generation
n	Pressure Reservoir's number
P	pressure
R	reservoir
rev	reversible
T	temperature
0	reference state; environment

Superscript

d	deformation (volume-change)
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and a two axioms condensation of the First and Second Laws, in a form similar to that proposed by Carathéodory for the well established Thermodynamics. However, this alternative approach was not explored in order to obtain general statements similar to those of the well established Thermodynamics.

In this work, the statements derived from the basic observations of the power engines are different from the well established ones, the volume emerging as the property from which are stated the possible processes undergone by closed systems experiencing volume-change work transfer interactions. The volume generation resulting from irreversibility in the volume-change work is easily interpreted as being associated with the lost available mechanical work, both in work producing or work absorbing systems. The volume is thus, in the presented formulation, the counterpart of entropy in the well established Thermodynamics for systems experiencing volume-change work transfer interactions.

The developments are made in a form similar to that of recent textbooks on Engineering Thermodynamics [2–4], the volume-change work transfer interactions and the absolute pressure replacing, respectively, the heat transfer interactions and the absolute temperature. Even without the complete development of a parallel structure relative to that of the well established Thermodynamics, the dual (work transfer interaction, absolute pressure) is still being used in order to thermodynamically optimize some pressure-driven engineering devices [5].

A very important result is that irreversibility associated with the volume-change work transfer interactions leads to a volume generation, and thus to a volume increase of the Universe. This result is obtained from Thermodynamic arguments only, what was confirmed from Cosmological

analysis and arguments [6]. In this way, the Thermodynamic and the Cosmological time arrows are unified, what is one of the most important results of the present work. Based on this result, to the Clausius statement saying that the entropy of the Universe is increasing can be added the one saying that the volume of the Universe is also increasing.

Another important aspect is that the parallel structure developed in this work involves volume instead entropy, volume being a much more familiar and ease to interpret variable. This is an advantage when compared with property entropy, many times taken as an *obscure* quantifiable property, the presented developments and interpretations corresponding to an effective added value towards a better understanding of many aspects related with the Second Law of Thermodynamics and entropy. This parallel structure represents thus an effectively added pedagogical value for a better understanding of Thermodynamics. No any of the presented arguments are in contradiction with the well established Thermodynamics, but an effective addition is made to the well established Thermodynamics.

The developments presented in this work are restricted to an alternative form of the Second Law of Thermodynamics that applies to closed systems experiencing volume-change work transfer interactions, and to the presentation of some simple example problems including volume generation analysis. Additional developments, to incorporate the volume generation concept into the well established Thermodynamics are presented in a companion paper [7]. In this companion paper it is also presented, for the first time, the demonstration why the Fundamental Relation of Thermodynamics for simple Thermodynamic systems applies both for reversible and irreversible processes.

2. The First Law of Thermodynamics for closed systems

The energy conservation principle embodied by the First Law of Thermodynamics, in the form of an equation for an infinitesimal process experienced by a closed system, reads

$$dE = \delta Q + \delta W \quad (1)$$

where E is the energy (a property) of the system under analysis, and δQ and δW are, respectively, the heat and work energy transfer interactions of the system with its surroundings. The work transfer interaction is assumed to be positive when it is an energy incoming to the system and negative when it is an energy outcome from the system (rational sign convention).

The volume-change work transfer interaction involved when the system's boundary moves reversibly, against or driven by the system's pressure, is evaluated as

$$\delta W_{\text{rev}} = -PdV \quad (2)$$

where P is the absolute pressure at the system boundary where the work transfer interaction takes place, and dV is the volume-change experienced by the system, associated with this volume-change work transfer interaction. Work given to the system ($\delta W > 0$) compresses the system ($dV < 0$), and work given by the system ($\delta W < 0$) expands the system ($dV > 0$).

A reversible process, in what concerns the volume-change work transfer interactions, means that the process is slow enough so that the pressure is uniform through the overall system (a mass of fluid), and the state of the system, at any instant in time, is described by a single and well defined point in a PV diagram [2]. If, instead, the pressure cannot be taken as uniform, it is said to be an irreversible process in what concerns the volume-change work transfer interactions. This is the case of many actual volume-change processes, which are markedly unsteady and with associated non-uniformities on the Thermodynamic variables, and in particular on pressure.

3. Thermodynamics and Pressodynamics

In the well established Thermodynamics, the heat transfer interactions and the temperature are essential in the Carnot's cycle statement, as well as the concept of absolute Temperature (or Heat) Reservoir. The property entropy, derived from these concepts, emerges as the adequate one to state the possible and impossible processes and thus the one-way behavior of the Universe, whose entropy is increasing.

The primary concepts of Carathéodory's axiomatic formulation are *work transfer* and *adiabatic boundary*, with the heat transfer interaction being a derived concept, evaluated as $dE - \delta W$. The absolute temperature and entropy are also derived properties. In the well established

Thermodynamics, these derived concepts are of greatest significance. Evaluating the entropy generation in a process it is possible quantify how *perfect* (reversible) it is, taking into account all the possible irreversibilities, the entropy generation being closely related to the concept of lost available work due to irreversibility (of any nature) [8], and to the statement if a process is possible or not.

We can imagine the pioneers searching for mechanical work from power engines, from the motion of a device driven by a pressure difference. The work transfer interaction in volume-changing systems can be understood as a direct consequence of a pressure difference and not of the heat supply to (or heat subtraction from) the power engine. This heat addition (or subtraction) is a mere way to change the temperature of the operating fluid and thus its specific volume, making possible to have higher and lower pressures where and when desired. The work transfer interaction in volume-changing systems can be understood as a direct consequence of a pressure difference (similarly to what happens with the heat transfer interaction as a direct consequence of a temperature difference) and not of the heat supply to the power engine. Obviously, for an energetic analysis, it is of primary importance the relation between the heat needed to feed a thermal engine for a given work supply. However, for the present purposes, it suffices to consider the work transfer interaction as the volume-change work associated with a pressure difference.

An alternative form of the Second Law of Thermodynamics can be obtained with the volume-change work transfer interactions and the absolute pressure replacing the heat transfer interactions and the absolute temperature, the volume emerging as the adequate property to play the role played by entropy in the well established Thermodynamics. We can thus speak about *Pressodynamics* instead of Thermodynamics, even if Pressodynamics is relevant for systems experiencing volume-change work transfer interactions only, and the volume generation is related with irreversibilities associated with the volume-change work transfer interactions only.

The parallel structures of Thermodynamics and of the here proposed Pressodynamics are sketched in Table 1, some rows appearing from the developments presented in what follows.

4. Alternative form of the Second Law of Thermodynamics for a closed system experiencing volume-change work transfer interactions

Following the usual structure, the developments are made from a cycle executed by a closed system while in communication with only one Pressure Reservoir to a cycle executed while in communication with any number of Pressure Reservoirs, ending with a process executed while in communication with any number of Pressure Reservoirs.

Table 1
Parallel structures of Thermodynamics and Pressodynamics

Structure	Thermodynamics	Pressodynamics
Fundamental concepts	Heat transfer interaction Absolute temperature	Volume-change work transfer interaction Absolute pressure
Second Law for a closed system executing an integral number of cycles while in communication with no more than one reservoir	$(\oint \delta Q)_{IRT} \leq 0$ or $(\oint \delta W)_{IRT} \geq 0$	$(\oint \delta Q)_{IRP} \leq 0$ or $(\oint \delta W)_{IRP} \geq 0^a$
Type of reservoir	Temperature ^a	Pressure ^a
Fundamental reversible cycle	Rectangular cycle on a <i>TS</i> diagram (Carnot's cycle)	Rectangular cycle on a <i>PV</i> diagram (alternative Carnot's cycle) ^a
Statement of Second Law for an arbitrary closed system executing a cycle while in communication with two reservoirs	$\left(\frac{-Q_2}{Q_1}\right) \geq \left(\frac{-Q_2}{Q_1}\right)_{\text{rev}}$	$\left(\frac{W_2}{-W_1}\right) \geq \left(\frac{W_2}{-W_1}\right)_{\text{rev}}$
Efficiency of the fundamental reversible cycle	$\eta_{T,\text{rev}} = 1 - \frac{T_2}{T_1}$	$\eta_{P,\text{rev}} = 1 - \frac{P_2}{P_1}$
Efficiency of reversible and irreversible cycles	$\eta_T \leq \eta_{T,\text{rev}}$	$\eta_P \leq \eta_{P,\text{rev}}$
Absolute scale	$T = 273.16 \left(-\frac{Q}{Q_{(273.16\text{K})}}\right)_{\text{rev}}$	$P = 611.3 \left(-\frac{W}{W_{(611.3 \text{ Pa})}}\right)_{\text{rev}}$ ^a
Statements of Second Law for an arbitrary closed system executing a cycle while in communication with any number of reservoirs	$\sum_{n=1}^N \frac{Q_n}{T_n} \leq 0$	$\sum_{n=1}^N \frac{W_n}{P_n} \geq 0$
Clausius inequality	$\oint \frac{\delta Q}{T} \leq 0$	$\oint -\frac{\delta W}{P} \leq 0$
Derived property from Second Law	$dS = \frac{\delta Q_{\text{rev}}}{T}$	$dV = -\frac{\delta W_{\text{rev}}}{P}$
Strength of irreversibility	$S_{\text{gen}} = (S_2 - S_1) - \int_1^2 \frac{\delta Q}{T} \geq 0$	$V_{\text{gen}} = (V_2 - V_1) - \int_1^2 -\frac{\delta W}{P} \geq 0$

^a Entries found also in Bejan [1,2].

4.1. Cycle in communication with only one Pressure Reservoir

The Kelvin–Planck’s statement of the Second Law of Thermodynamics reads “It is impossible for any system to operate in a Thermodynamic cycle and deliver a net amount of work to its surroundings while in contact with only one Thermal Reservoir” or, in symbols

$$\left(\oint \delta W\right)_{IRT} \geq 0 \tag{3}$$

From the First Law of Thermodynamics, Eq. (1), $Q_{\text{cycle}} = -W_{\text{cycle}}$, and for any reversible power cycle ($W_{\text{cycle}} < 0$) $Q_{\text{cycle}} > 0$, $Q_{\text{cycle}} > 0$ being given by the enclosed area of the (clockwise) cycle in a *TS* diagram, owing $\delta Q_{\text{rev}} = TdS$. On a *PV* diagram we search also a positive area owing, for systems experiencing reversible volume-change work transfer interactions, $\delta W_{\text{rev}} = -PdV$.

Travelling from points 1 to 2 in Fig. 1a, the closed system is in contact with only the (*T*) Thermal Reservoir while the system and the Thermal Reservoir exchange heat. Trav-

elling now from 2 to 3, the temperature of the system varies but it is not in contact with any Thermal Reservoir because there is no any heat transfer interaction. To proceed from 3 to 1, in order to close the cycle, and searching an enclosed (positive) area on the *TS* diagram, the system should contact with, at the least, another Thermal Reservoir.

A similar conclusion can be obtained for a closed system experiencing volume-change work transfer interactions that executes a cycle while in communication with only one Pressure Reservoir, situation presented in Fig. 1b. A Pressure Reservoir means to an external system that imposes a pressure on the system’s boundary while the two systems exchange work. The closed system is always assumed to be in communication with a Pressure Reservoir if the volume-change work transfer interaction is not equal to zero. A process with a continuously varying pressure should be understood as made in communication with an infinite sequence of Pressure Reservoirs.

Travelling from points 1 to 2 in Fig. 1b, the closed system is in contact with only the (*P*) Pressure Reservoir, while the system and the Pressure Reservoir exchange work. Travelling now from 2 to 3, the system’s pressure varies but it is not in communication with any Pressure Reservoir because there is no any work transfer interaction. To proceed from 3 to 1 in order to close the cycle, and searching an enclosed (positive) area on the *PV* diagram, the system should communicate with, at the least, another Pressure Reservoir. The alternative Kelvin–Planck’s statement reads then “It is impossible for any system to operate in a Thermodynamic cycle and deliver a net amount of work to its surroundings while in communication with only one Pressure Reservoir” or, in symbols

$$\left(\oint \delta W\right)_{IRP} \geq 0 \tag{4}$$

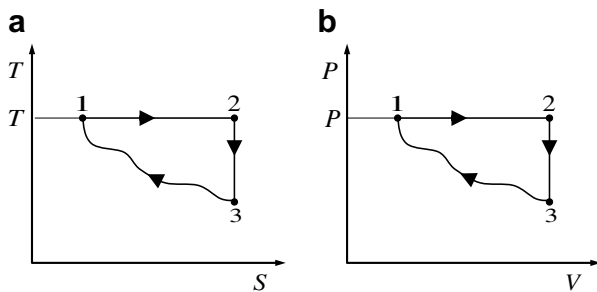


Fig. 1. The Kelvin–Planck’s statement of the Second Law of Thermodynamics: (a) For the well established Thermodynamics; and (b) for the here proposed Pressodynamics.

Thus, (unfortunately) it cannot exist a power engine operating in communication with only the atmospheric Pressure Reservoir and extract mechanical work from it. It should be noted that relations (3) and (4) are only apparently equal, each referring to a different type of Reservoir.

At this stage, the normal way is, similarly to what happens with the well established Thermodynamics, to proceed for a cycle executed by a closed system while in communication with two Pressure Reservoirs.

4.2. Cycle in communication with two Pressure Reservoirs

The analysis of a closed system in contact with two Heat Reservoirs is usually made through the introduction of Carnot’s cycle, which is shown in Fig. 2a for any operating substance and in Fig. 2b for an Ideal Gas. In the present alternative approach, the reversible cycle under analysis is the one that is rectangular on a *PV* diagram, as presented in Fig. 2c, being referred to as the *alternative Carnot’s cycle*, and consists of a sequence of four reversible processes: reversible isometric depressurization 1 → 2 (by cooling); reversible isobaric contraction 2 → 3 with cooling (the operating substance is a fluid that contracts upon cooling at constant pressure) while communicating with the (*P*₂) Pressure Reservoir; reversible isometric pressurization 3 → 4 (by heating); and reversible isobaric expansion 4 → 1, with heating, while communicating with the (*P*₁) Pressure Reservoir. This cycle is presented in Fig. 2d for an Ideal Gas.

The parallel between the fundamental cycles in the well established Thermodynamics and in the here proposed

Pressodynamics is presented in Fig. 2a and b, presented only for comparison purposes with Fig. 2c and d, because the property entropy is not needed in Pressodynamics. As the system under analysis possesses only the (volume-change) *−PdV* mode of reversible work transfer, processes 1 → 2 and 3 → 4 in Fig. 2c are zero-work processes.

As the cycle in Fig. 2c is executed reversibly, the system under analysis can execute the same cycle in the reverse sense, visiting the same sequence of equilibrium states in the reverse order. Thus, if *Q*_C is the net heat transfer given to the system in a cycle, and if *W*_{1C} and *W*_{2C} are the respective work transfer interactions with the Pressure Reservoirs (*P*₁) and (*P*₂), respectively, then the energy transfer interactions of the direct and reversed reversible cycles are symmetric, that is

$$(W_{1C}, W_{2C}, Q_C)_{\text{direct}} = -(W_{1C}, W_{2C}, Q_C)_{\text{reverse}} \tag{5}$$

We proceed now extending the conclusion stated by the Kelvin–Planck’s alternative form for the Second Law of Thermodynamics for a closed system executing a cycle while communicating with two Pressure Reservoirs. The development considers only the power engine situation, for which the searched work transfer interaction is negative, that is, there is a net work transfer interaction *from* the system. Similar conclusions can be obtained for the reverse (work absorbing) engine.

For any *unspecified* power cycle similar to that of Fig. 2c executed by system (*A*) in Fig. 3, it can be written from the First Law of Thermodynamics

$$-Q = W = W_1 + W_2 \tag{6}$$

We search now the implications of the alternative Kelvin–Planck’s statement over the *W*₁ and *W*₂ work transfer interactions. From Eq. (6) it is clear that *W*₁ > 0 and *W*₂ > 0 leads to *W* > 0, situation that doesn’t correspond to the power cycle under analysis. The signs of *W*₁ and *W*₂ compatible with Eq. (6) and *W* < 0 (power engine) are: (i) *W*₁ < 0 and *W*₂ < 0; or (ii) *W*₁ and *W*₂ with opposite signs, but verifying (*W*₁ + *W*₂) < 0.

The hypothesis (i) is analyzed with aid of Fig. 3a, in which is represented a closed system (*A*) executing an unspecified cycle while in communication with the Pressure Reservoirs (*P*₁) and (*P*₂), with *P*₁ ≠ *P*₂, and an auxiliary

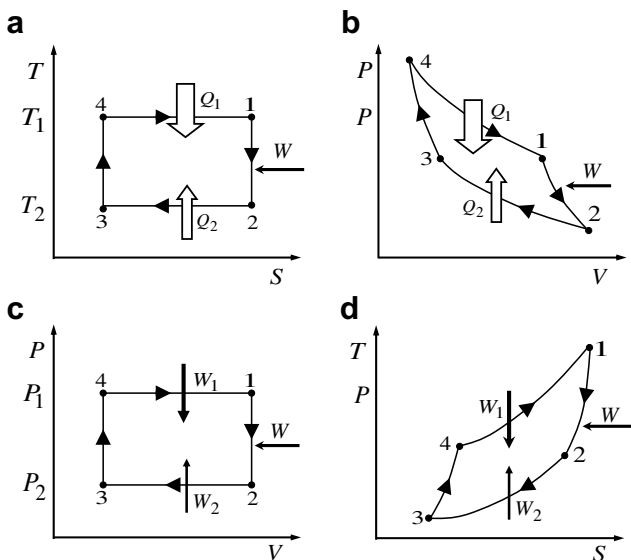


Fig. 2. The fundamental cycles in Thermodynamics and in Pressodynamics: (a) The Carnot’s cycle on a *TS* diagram for any operating substance. (b) The Carnot’s cycle in a *PV* diagram for an Ideal Gas. (c) The alternative Carnot’s cycle in Pressodynamics on a *PV* diagram for any operating substance. (d) The alternative Carnot’s cycle in Pressodynamics on a *TS* diagram for an Ideal Gas.

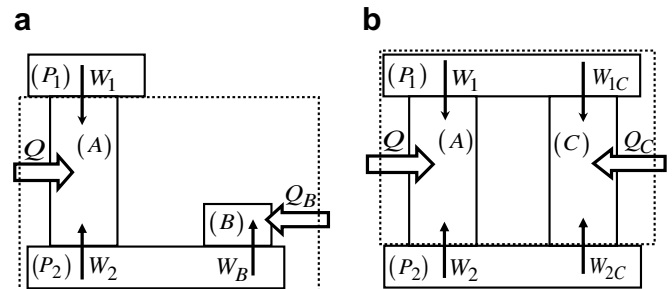


Fig. 3. Implication of the alternative Kelvin–Planck’s statement for a closed system executing a cycle while in communication with two Pressure Reservoirs: (a) For hypothesis (i); and (b) for irreversibility accounting.

system (B) that executes a cycle while in communication with only one Pressure Reservoir, say (P₂). The alternative Kelvin–Planck’s statement applied to system (B) requires that

$$W_B \geq 0 \tag{7}$$

Systems (A) and (B) can be sized such that W₂ = -W_B, situation that is compatible with the assumed negativity of W₂ in hypothesis (i). Thus, it follows that the (P₂) Pressure Reservoir also executes a cycle at the end of the cycles executed by systems (A) and (B). As systems (A) and (B) and the (P₂) Pressure Reservoir execute a cycle, also the composite system ((A) + (B) + (P₂)) executes a cycle while in communication with only the (P₁) Pressure Reservoir. For the composite system, the alternative Kelvin–Planck’s statement requires that W₁ ≥ 0, situation that is incompatible with the negativity of W₁ assumed in (i). A similar conclusion, indicating that W₁ and W₂ cannot have the same sign, can be obtained considering the system (B) in communication with the (P₁) Pressure Reservoir.

The only situation compatible with both the First and Second Laws is that assumed in hypothesis (ii), that is, W₁ and W₂ must have opposite signs. For further discussions we assume that W₁ < 0 (strictly negative) and that W₂ > 0 (strictly positive), being the situation of W₁ = 0 not allowed because W₁ ≠ 0 for a power engine.

To obtain the relation between the work transfer interactions of reversible and irreversible cycles operating while in communication with the same two Pressure Reservoirs, consider Fig. 3b, where the unspecified cycle (A) and the alternative Carnot’s cycle (C) share the two Pressure Reservoirs (P₁) and (P₂). The alternative Carnot’s cycle is sized and its sense selected such that

$$W_1 + W_{1C} = 0 \tag{8}$$

Under these conditions, the (P₁) Pressure Reservoir executes a cycle, with a null net work transfer interaction, and the composite system ((A) + (C) + (P₁)) also executes a cycle while in communication with only the (P₂) Pressure Reservoir. Applying again the alternative form of the Kelvin–Planck’s statement one obtains, for the composite system,

$$W_2 + W_{2C} \geq 0 \tag{9}$$

relation that is equivalent to

$$\left(\frac{W_2}{-W_1}\right) \geq \left(\frac{-W_{2C}}{W_{1C}}\right) \tag{10}$$

noting that -W₁ > 0 due to the assumed strict negativity of W₁, and W_{1C} > 0 by Eq. (8).

The relation present in (10) is the alternative inequality that represents the Second Law of Thermodynamics for a cycle executed by a closed system while in communication with two Pressure Reservoirs. In the limiting situation of equality

$$\left(\frac{W_2}{-W_1}\right) = \left(\frac{-W_{2C}}{W_{1C}}\right) \tag{11}$$

From Eq. (8), from the First Law statements -Q = W₁ + W₂ [for cycle (A)] and -Q_C = W_{1C} + W_{2C} [for the alternative Carnot’s cycle (C)], and from Eq. (11) it can be formed the system of equations

$$\begin{cases} W_{1C} = -W_1 \\ -Q = W_1 + W_2 \\ -Q_C = W_{1C} + W_{2C} \\ \frac{W_2}{-W_1} = \frac{-W_{2C}}{W_{1C}} \end{cases} \tag{12}$$

from which, assuming known W₁ and W₂, one obtains

$$(W_{1C}, W_{2C}, Q_C) = -(W_1, W_2, Q) \tag{13}$$

Comparing Eqs. (13) and (5) one concludes that in the limiting equality situation of relation (10) the corresponding cycle (A) is the reverse of the alternative Carnot’s cycle (C), and vice versa. As the alternative Carnot’s cycle is a reversible cycle, the limiting situation of equality in relation (10) corresponds to a reversible cycle executed by the unspecified system (A) while in communication with the two Pressure Reservoirs (P₁) and (P₂). The alternative Carnot’s cycle can be abandoned, by noting that (-W_{2C}/W_{1C}) = (W₂/-W₁)_{rev}, where the subscript rev stands for a reversible cycle, executed by a system experiencing volume-change work transfer interactions, and relation (10) reads

$$\left(\frac{W_2}{-W_1}\right) \geq \left(\frac{W_2}{-W_1}\right)_{\text{rev}} \tag{14}$$

This relation is the inequality that represents the alternative form for the Second Law of Thermodynamics, for a cycle executed by a closed system while in communication with two Pressure Reservoirs. Defining the *Pressodynamic efficiency* of the cycle as

$$\eta_P = \frac{\text{net work done by the system}}{\text{work done to the system}} \tag{15}$$

one obtains

$$\eta_P = \frac{-(W_1 + W_2)}{-W_1} = 1 + \frac{W_2}{W_1} \tag{16}$$

For the reversible cycle in Fig. 2c it can be concluded that

$$W_1 = -P_1(V_1 - V_4) \tag{17a}$$

$$W_2 = -P_2(V_4 - V_1) \tag{17b}$$

and, after division

$$\left(\frac{W_2}{W_1}\right)_{\text{rev}} = -\frac{P_2}{P_1} \tag{18}$$

The Pressodynamic efficiency of the alternative Carnot’s cycle can then be obtained as

$$\eta_{P,\text{rev}} = 1 - \frac{P_2}{P_1} \tag{19}$$

what is the parallel result for the Thermodynamic efficiency of the Carnot’s cycle in the well established Thermodynamics.

It must be noted that the pressures mentioned here are the pressures at the boundaries of the system where volume-change work transfer interactions take place, remembering that, as stated in Section 4.1, it is the pressure imposed at the boundary while the two systems exchange volume-change work.

Relation (14) can be rewritten as

$$\left(1 + \frac{W_2}{W_1}\right) \leq \left(1 + \frac{W_2}{W_1}\right)_{\text{rev}} \tag{20}$$

which is equivalent to

$$\eta_P \leq \eta_{P,\text{rev}} \tag{21}$$

As expected, the Pressodynamic efficiency is a maximum when the executed cycle is reversible.

The sequence of processes forming the cycle executed by system (A) was unspecified, being thus $(W_2 / -W_1)_{\text{rev}}$ independent of the working fluid and of the sequence of processes that form the cycle. Under such conditions, the lower limit value $(W_2 / -W_1)_{\text{rev}}$ should be a function of only P_1 and P_2 given the assumed existence of two different Pressure Reservoirs.

It can be written that

$$\left(\frac{W_2}{-W_1}\right)_{\text{rev}} = f(\pi_1, \pi_2) \tag{22}$$

where f is an unknown function and π_1 and π_2 are two different numbers indicated by the scale of one manometer, being thus the *empirical pressure* corresponding to the pressure of the Pressure Reservoirs. Considering a reversible cycle executed by a closed system while in communication with the Pressure Reservoirs (π_1) and (π_3) as a cascade of two reversible cycles executed while in communication with, respectively, the Pressure Reservoirs (π_1) and (π_2) ,

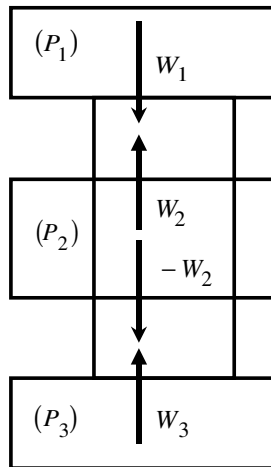


Fig. 4. The cycle executed in communication with the (P_1) and (P_3) Pressure Reservoirs as a cascade of two cycles executed while in communication with the *auxiliary* Pressure Reservoir (P_2) .

and (π_2) and (π_3) ($\pi_1 > \pi_2 > \pi_3$), as illustrated in Fig. 4, it can be written that

$$\left(\frac{W_3}{-W_1}\right)_{\text{rev}} = f(\pi_1, \pi_3) \tag{23a}$$

$$\left(\frac{W_3}{-(-W_2)}\right)_{\text{rev}} = f(\pi_2, \pi_3) \tag{23b}$$

Dividing Eqs. (23a) and (23b), and using Eq. (22) to the ratio $(W_2 / -W_1)_{\text{rev}}$ it can be concluded that

$$f(\pi_1, \pi_2) = \frac{f(\pi_1, \pi_3)}{f(\pi_2, \pi_3)} \tag{24}$$

As the left side of Eq. (24) is independent of π_3 , it must be

$$\frac{f(\pi_1, \pi_3)}{f(\pi_2, \pi_3)} = \frac{\phi(\pi_1)/\phi(\pi_3)}{\phi(\pi_2)/\phi(\pi_3)} = \frac{\phi(\pi_1)}{\phi(\pi_2)} = f(\pi_1, \pi_2) \tag{25}$$

Making $\Phi(\pi) = 1/\phi(\pi)$, Eq. (22) can be rewritten as

$$\left(\frac{W_2}{-W_1}\right)_{\text{rev}} = \frac{\Phi(\pi_2)}{\Phi(\pi_1)} \tag{26}$$

a result that can be generalized to obtain the work transfer interaction W , exchanged while in communication with the arbitrary (π) Pressure Reservoir, from the work transfer interaction W_0 exchanged while in communication with the (π_0) reference Pressure Reservoir, as

$$\left(\frac{W_0}{-W}\right)_{\text{rev}} = \frac{\Phi(\pi_0)}{\Phi(\pi)} \tag{27}$$

The measurement of the ratio between the work transfer interactions in any reversible cycle while communicating with the (π) and (π_0) Pressure Reservoirs leads to $\Phi(\pi) = P$, the absolute Thermodynamic pressure, and Eq. (27) reads

$$P = P_0 \left(\frac{-W}{W_0}\right)_{\text{rev}} \tag{28}$$

relation that defines the *Pressodynamic pressure scale*, or the Thermodynamic pressure scale, in the basis of only one constant fiducial point. Chosen the triple point of water, an invariant, as the fiducial point, $P_0 = 611.3$ Pa, Eq. (28) gives

$$P = 611.3 \left(-\frac{W}{W_{(611.3 \text{ Pa})}}\right)_{\text{rev}} \tag{29}$$

and the Pressodynamic (or Thermodynamic) absolute pressure scale is sketched in Fig. 5. This same absolute scale was derived also by Bejan [1,2]. Eq. (29) is the alternative to the Thermodynamic temperature scale in the well established Thermodynamics. At this point it can be questioned if pressure involved in the evaluation of the volume-change work transfer interactions, with a strong mechanical meaning, can be taken as the Thermodynamic pressure. This point has been worked out by Reynolds and Perkins [9], where a demonstration is given in what concerns the equivalence of the mechanical and the Thermodynamic

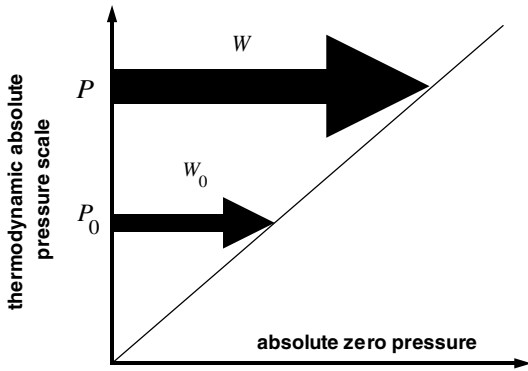


Fig. 5. The Pressodynamic (or Thermodynamic) absolute pressure scale.

pressures, based on well established Thermodynamics' arguments.

Introduction of the result given by Eq. (26) in relation (14), noting that $\Phi(\pi) = P$, leads to an alternative form of this last relation that reads

$$\frac{W_1}{P_1} + \frac{W_2}{P_2} \geq 0 \tag{30}$$

which is the most useful result for a cycle executed by a closed system while in communication with two Pressure Reservoirs.

4.3. Cycle in communication with any number of pressure reservoirs

The preceding developments begin with the alternative Kelvin–Planck's statement for a cycle executed by a closed system while communicating with only one Pressure Reservoir, and follows to a cycle executed by the same closed system while communicating with two Pressure Reservoirs. The next step is to obtain the equivalent expression of (30) for a closed system executing a cycle while in communication with any number of Pressure Reservoirs, which is made following the method of mathematical induction, as proposed by Bejan [2] to the well established Thermodynamics.

For the cycle executed while in communication with only the (P_1) Pressure Reservoir, the alternative Kelvin–Planck's statement [relation (4)] gives

$$W_1 \geq 0 \tag{31}$$

or, dividing by P_1

$$\frac{W_1}{P_1} \geq 0 \tag{32}$$

For the cycle executed while in communication with the two Pressure Reservoirs (P_1) and (P_2) we have relation (30).

For the cycle executed while in communication with the N Pressure Reservoirs (P_n) , $n = 1, 2, \dots, N$, it is assumed that

$$\sum_{n=1}^N \frac{W_n}{P_n} \geq 0 \tag{33}$$

expression from which it remains to be proved that

$$\sum_{n=1}^{N+1} \frac{W_n}{P_n} \geq 0 \tag{34}$$

To test the validity of expression (34) consider a closed system (A) that executes a cycle while in communication with $N + 1$ Pressure Reservoirs $(P_1), (P_2), \dots, (P_N), (P_{N+1})$, as sketched in Fig. 6. To apply the relation (33), assumed valid for a cycle executed while in communication with N Pressure Reservoirs, the Pressure Reservoir (P_{N+1}) is made to go to its original state by communication with the reversible cycle (C) sized such that

$$W_{N+1} + W_{(N+1)C} = 0 \tag{35}$$

The composite system $((A) + (P_{N+1}) + (C))$, enclosed by a dashed line in Fig. 6, executes thus a cycle while in communication with N Pressure Reservoirs, and application of relations (30) and (33) lead to

$$\sum_{n=1}^N \frac{W_n}{P_n} + \frac{W_{NC}}{P_N} \geq 0 \tag{36}$$

For the reversible cycle (C) , which is executed while in communication with the two Pressure Reservoirs (P_N) and (P_{N+1}) it can be written from the equality situation of relation (30) that

$$\frac{W_{NC}}{P_N} + \frac{W_{(N+1)C}}{P_{N+1}} = 0 \tag{37}$$

Relation (36) can now be rewritten as

$$\sum_{n=1}^N \frac{W_n}{P_n} - \frac{W_{(N+1)C}}{P_{N+1}} \geq 0 \tag{38}$$

and then, invoking Eq. (35) to obtain $W_{(N+1)C}$, one arrives to the searched result stated by relation (34). Relation (33) is thus valid for any $N \geq 1$.

Relation (33) was deduced considering a stepwise variation of the system's boundary pressure as imposed by the discrete Pressure Reservoirs. One can now extend this result by considering the situation of a continuous variation of the system's boundary pressure as the cycle is executed while in

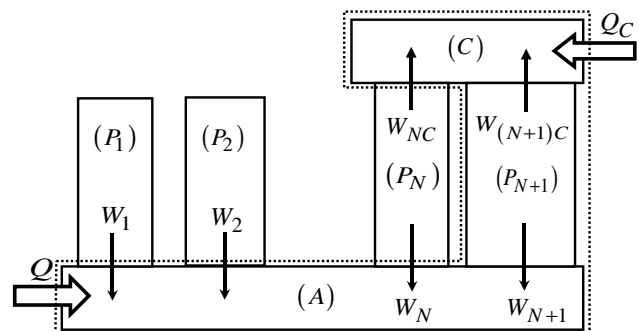


Fig. 6. The Second Law extended to a closed system executing a cycle while in communication with any number of Pressure Reservoirs.

communication with an infinite sequence of Pressure Reservoirs, each contributing with a infinitesimal work transfer interaction δW while maintaining the system’s boundary pressure at P . The sum of relation (33) is, in this case, replaced by one cyclic integral to give

$$\oint \frac{\delta W}{P} \geq 0 \tag{39}$$

or then

$$\oint -\frac{\delta W}{P} \leq 0 \tag{40}$$

remembering, once again, that the involved pressure is the pressure at the boundary where the volume-change work transfers have place. This result can be seen as an alternative form of the Clausius inequality for a system exchanging volume-change work with its neighborings.

The limiting situation of equality in Eq. (40) refers to a reversible cycle, for which

$$\oint -\frac{\delta W_{rev}}{P} = 0 \tag{41}$$

If the cyclic integral of Eq. (41) is null, $\delta W_{rev}/P$ represents a change in a property of the system. Examining Eq. (2) it can be concluded that this property is the volume V , that is

$$dV = -\frac{\delta W_{rev}}{P} \tag{42}$$

It will be reinforced further that subscript rev refers not only to a reversible process but to a process that is internally reversible, that is, in which interior there are no irreversibilities associated with the volume-change work transfer interactions.

The reversible work transfer interaction $-\delta W_{rev}$ is not an exact differential but a Pfaffian, acting the absolute pressure at the boundary P as an integrating denominator to $-\delta W_{rev}$ in order to make the relation $-\delta W_{rev}/P$ an exact differential.

4.4. Process in communication with any number of pressure reservoirs

The preceding results refer to cycles, following the discussion to arbitrary processes between the arbitrary states 1 and 2.

Integration of Eq. (42) over the reversible path linking states 1 and 2 leads to

$$V_2 - V_1 = \int_1^2 -\frac{\delta W_{rev}}{P} \tag{43}$$

The arbitrary process $1 \rightarrow 2$ can be taken as a part of the cycle $1 \rightarrow 2 \rightarrow 1$, where the $2 \rightarrow 1$ process is reversible and the $1 \rightarrow 2$ process is arbitrary in terms of reversibility. For the entire cycle, relation (40) applies to give

$$\int_1^2 -\frac{\delta W}{P} + \int_2^1 -\frac{\delta W_{rev}}{P} \leq 0 \tag{44}$$

or then

$$\underbrace{\int_1^2 -\frac{\delta W}{P}}_{\substack{\text{volume transfer} \\ \text{(non-property)}}} \leq \underbrace{V_2 - V_1}_{\substack{\text{volume-change} \\ \text{(property)}}} \tag{45}$$

The alternative form of the Second Law of Thermodynamics of the here proposed Pressodynamics states thus that the volume transfer never exceeds the volume-change. The difference between the left and the right hand sides of relation (45) gives

$$\underbrace{V_{gen}}_{\substack{\text{volume generation} \\ \text{(non-property)}}} = \underbrace{V_2 - V_1}_{\substack{\text{volume-change} \\ \text{(property)}}} - \underbrace{\int_1^2 -\frac{\delta W}{P}}_{\substack{\text{volume transfer} \\ \text{(non-property)}}} \geq 0 \tag{46}$$

where $V_{gen} \geq 0$ is the *volume generation* or *volume production*, which has never a negative value and leads to the one-way behavior of the Universe, similar to that stated by the entropy increase of the Universe in the well established Thermodynamics. This volume generation is not so strange as it sounds at first contact, as it is seen in the following examples and also verified from Cosmological arguments and analysis [6].

It is based on this result that the Thermodynamic and the Cosmological time arrows are unified, and to the Clausius statement saying that the entropy of the Universe is increasing can be added the one saying that the volume of the Universe is also increasing.

The volume generation concept has also been taken into account in some recent studies on Thermodynamics conducted by Gaggioli [10,11].

5. Evaluation of the volume generation

5.1. Preliminary notes

Before analyzing two elucidative examples including the evaluation of the volume generation, some aspects need to be highlighted in order to conduct the analysis of the systems.

Similarly to what is made in the well established Thermodynamics, a balance equation for volume can be established for a closed system. From Eq. (46), taking present that pressure involved in the integral is the pressure at the boundary where the volume-change work transfer interaction takes place, one can write in a differential form that

$$\delta V_{gen} = dV + \sum_{j=0}^M \frac{\delta W_j^d}{P_j} \geq 0 \tag{47}$$

or, in a time rate basis

$$\dot{V}_{gen} = \frac{dV}{dt} + \sum_{j=0}^M \frac{\dot{W}_j^d}{P_j} \geq 0 \tag{48}$$

where the summation extends to all the N portions of the boundary through which system exchanges energy in the form of volume-change work transfer interactions. Superscript d in Eqs. (47) and (48) reinforces that we are dealing with the energy transfer in the form of deformation (volume-change) work transfer interactions.

The alternative form of the Clausius' inequality can be easily understood using Eq. (47). If this equation is integrated for a cycle, noting that along the portions of such a cycle it is $\delta V_{\text{gen}} \geq 0$ and that it is thus $\oint \delta V_{\text{gen}} \geq 0$, and that the cyclic integral of volume (a property) is null, one arrives to Eq. (40). Thus, another way to see the alternative form of the Clausius' inequality is to say that the integral of δV_{gen} over a cycle can only be positive. Only for a reversible cycle it is $\delta V_{\text{gen}} = 0$ for any portion of the cycle and $\oint \delta V_{\text{gen}} = 0$. This same treatment can be given to the physical interpretation of the original Clausius' inequality of the well established Thermodynamics in terms of heat transfer interactions and absolute temperature.

It is to be stressed that a boundary is a zero thickness surface, such as pointed out by Bejan [2], and that no discontinuities can exist in temperature or pressure across a boundary. Both sides of the boundary share the same temperature or pressure values. A wall, separating parts of a system, is not a boundary but itself a system, through which temperature and pressure discontinuities can take place. This is a fundamental aspect to take into account, in order to correctly conduct the analysis of Thermodynamic systems. It is highlighted in Bejan [2] that the entropy generation takes place at the walls. However, due to the intrinsic character of the irreversibilities associated with the volume-change work transfer interactions, which are related with the non-uniformities of pressure inside the system (a volume-changing mass of fluid), the volume generation takes place inside the system itself.

Also extremely important is the fact that the work transfer interactions represent *net* energy transferred *from* or *to* the system. In this way, any kind of losses (irreversibilities) we are accounting for are internal irreversibilities, an aspect that was pointed out in Eq. (42). If external irreversibilities exist, they must be taken into account when evaluating the net energy transfers experienced by the system, in the form of heat or work transfer interactions, but they are not internal irreversibilities of the system. The choice of the boundary enclosing the system is the obvious and appropriate way to consider what are external irreversibilities and what are internal irreversibilities.

5.2. Filling of an initially evacuated container

Consider the rigid and initially evacuated container of inner volume V represented in Fig. 7. The container is surrounded by the environment at temperature T_0 and pressure P_0 . After a given instant in time the valve represented in Fig. 7a is maintained slightly open, and air slowly enters the container just to the moment when the pressure of the air in the interior of the container equals the ambient pres-

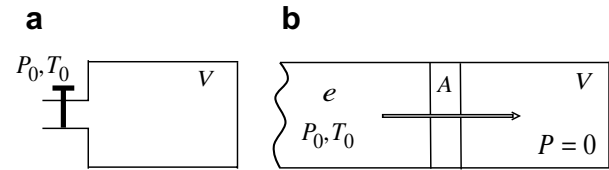


Fig. 7. Filling of an initially evacuated container: (a) Schematic view of the container; and (b) modeling of the filling process.

sure, P_0 . The walls of the container are sufficiently thin or conductive such that the temperature of the air entered inside the container, after some time, equals the temperature of the ambient air, T_0 . Even if this system can be treated as an open system, it can be also treated as a closed system, what was made also by Bejan [2]. This same system is treated as an open system in the companion paper [7]. The most important step to treat this system as a closed system is to take into account that as the air entered inside the container reaches the (T_0, P_0) conditions, the volume V occupied by air inside the container equals the volume of the same mass of air when, initially, outside the container, was incorporated into the ambient air.

This system can be schematically represented as given in Fig. 7b. Environment exerts pressure P_0 over the auxiliary separating piston A of negligible mass and thickness. This separating piston moves and enters inside the initially evacuated container, thus giving rise to the filling process. It must be noted that environment e is a closed system. Volume balance for the environment gives

$$dV_e = -\frac{\delta W_e^d}{P_0} + \delta V_{\text{gen},e} \quad (49)$$

The work transfer δW_e^d is null as pressure is null on the right-hand side of the auxiliary piston, and no work transfer can be absorbed by the evacuated right-hand side of the container. Irreversibility of this process is associated with this lack of mechanical equilibrium [12]. It is thus $\delta V_{\text{gen}} = dV$, and at the end of the filling process it is

$$V_{\text{gen}} = (V_2 - V_1) = V \quad (50)$$

It is interesting to note that the volume generation can be seen as the volume increase of the Universe, which expanded to fill the initially evacuated container.

The maximum available work that can be given by the environment during its expansion against the zero pressure of the initially evacuated container is

$$W_{\text{lost}}^d = -P_0 V_{\text{gen}} = -P_0 V \quad (51)$$

which is a lost available work as no devices are available to extract and deliver it as useful work.

Analysis of the entropy generation for this system using the well established Thermodynamics gives that [2]

$$S_{\text{gen}} = \frac{P_0 V}{T_0} \quad (52)$$

and that

$$W_{\text{lost}} = -T_0 S_{\text{gen}} = -P_0 V_{\text{gen}} = -P_0 V \tag{53}$$

and surprisingly it is obtained that, for this system,

$$P_0 V_{\text{gen}} - T_0 S_{\text{gen}} = 0 \tag{54}$$

It will be explored that this equality is valid for some kinds of systems experiencing some particular processes in the companion paper [7], a key result in what concerns the Fundamental Relation of Thermodynamics.

5.3. Motion of a piston driven by a pressure difference

This problem is analyzed in parallel with a system commonly analyzed in the well established Thermodynamics, in order to continue the parallel developments of Thermodynamics and Pressodynamics. It must be stressed that entropy generation takes place at the walls, and that it occurs even in steady-state processes. By its own turn, volume generation takes place inside the systems, and it is associated with the unsteady (and mechanical non-equilibrium) processes experienced by the systems in which volume-change work transfer interactions occur.

Consider the wall in Fig. 8a, whose left vertical surface is at absolute temperature T_A and whose right vertical wall is at absolute temperature T_B , with $T_A > T_B$. A small amount of heat δQ flows from left to right. From the well established Thermodynamics one obtains that the entropy balance for the wall gives [2]

$$\delta S_{\text{gen}} = -\frac{\delta Q}{T_A} + \frac{\delta Q}{T_B} = \delta Q \frac{(T_A - T_B)}{T_A T_B} = \frac{\delta Q}{T_B} \left(1 - \frac{T_B}{T_A}\right) \tag{55}$$

If a reversible (Carnot) thermal engine was working based on absolute temperatures T_A and T_B , the work transfer interaction of such an engine with its neighborings would be

$$\delta W_{\text{rev}} = -\delta Q \eta_C = -\delta Q \left(1 - \frac{T_B}{T_A}\right) \tag{56}$$

Eq. (56) gives the maximum available work that can be obtained from the absolute temperatures T_A and T_B . No such a Carnot engine is present to deliver this work, which is lost. Combination of Eqs. (55) and (56) give us that

$$\delta W_{\text{lost}} = -T_B \delta S_{\text{gen}} \tag{57}$$

Consider now the system presented in Fig. 8b, which consists on the assembly of a frictionless and negligible mass piston in a cylinder. Left hand side chamber is maintained at absolute pressure P_A and the right-hand side chamber is maintained at absolute pressure P_B , with $P_A > P_B$. Chambers are separated by the piston. Initially the piston is locked, and it is suddenly unlocked, moving from left to right driven by the pressure difference $P_A - P_B$.

Volume balance equations for sub-systems A and B give, respectively

$$dV_A = -\frac{\delta W_A^d}{P_A} + \delta V_{\text{gen},A} \tag{58a}$$

$$dV_B = \frac{\delta W_B^d}{P_B} + \delta V_{\text{gen},B} \tag{58b}$$

which can be added to give, for the overall system under analysis, noting that $dV_A + dV_B = 0$

$$\begin{aligned} \delta V_{\text{gen}} &= \delta V_{\text{gen},A} + \delta V_{\text{gen},B} = \frac{\delta W_A^d}{P_A} - \frac{\delta W_B^d}{P_B} \\ &= -\delta W_A^d \frac{(P_A - P_B)}{P_A P_B} = -\frac{\delta W_A^d}{P_B} \left(1 - \frac{P_B}{P_A}\right) \end{aligned} \tag{59}$$

where it is to be noted that Pressure Reservoir A is releasing volume-change work to the piston, with $\delta W_A^d = -P_A dV_A < 0$, and that the piston is given volume-change work $-\delta W_A^d$ to Pressure Reservoir B . No work is lost in the piston-cylinder assembly, as the piston is a frictionless and has negligible mass. If mechanical equilibrium would exist, the volume-change deformation work transfer interaction would be lower than $|\delta W_A^d|$, as it is $P_B < P_A$. Once again, irreversibility of the process is associated with the lack of mechanical equilibrium [12]. It is clear the parallel between Eqs. (59) and (55), even if they refer to very different situations and processes.

If a reversible engine was working, based on absolute pressures P_A and P_B , the volume-change work transfer interaction of such an engine with its neighborings would be

$$\delta W_{\text{rev}}^d = \delta W_A \eta_{P,\text{rev}} = \delta W_A \left(1 - \frac{P_B}{P_A}\right) \tag{60}$$

where $\eta_{P,\text{rev}}$ is the reversible Pressodynamic efficiency. Eq. (60) gives the maximum available work that can be obtained from the absolute pressures P_A and P_B . Note once again the parallel between Eqs. (60) and (56). No such a reversible engine is present to deliver this work, which is lost. Combination of Eqs. (59) and (60) gives us that

$$\delta W_{\text{lost}}^d = -P_B \delta V_{\text{gen}} \tag{61}$$

where, once again, we can see the parallel between Eqs. (61) and (57).

Insertion of the main developments made in this work in the framework of the well established Thermodynamics is presented in the companion paper [7], where some new

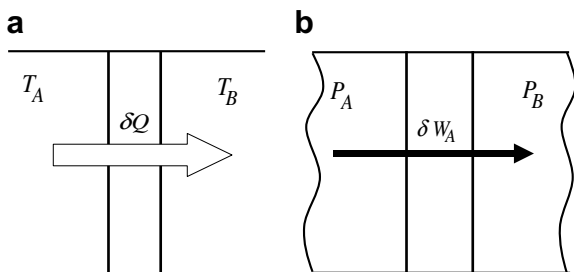


Fig. 8. Irreversible processes: (a) Steady heat transfer through a conductive wall; and (b) unsteady volume-change work transfer through a moving piston.

and interesting Thermodynamic results are obtained and discussed.

6. Conclusions

A parallel structure of the well established Thermodynamics, here called Pressodynamics, is presented, and results are derived that become very similar and make parallel the two different structures. The fundamental difference is the property volume as the adequate one to quantify the irreversibility of the processes undergone by Thermodynamic systems experiencing volume-change work transfer interactions. It is obtained a conclusion very similar to the principle of entropy increase of the Universe, but stated for the volume increase of the Universe. This result is in accordance with the well established expansion of the Universe, which precludes a gravitational collapse [6].

As shown by Bejan [5], the parallelism existing between Thermodynamics and Pressodynamics is also observed when irreversible engines driven by Temperature Reservoirs and irreversible engines driven by Pressure Reservoirs are analyzed from the viewpoint of the well established Thermodynamics.

It should be clarified that the volume is, in our today experience, a geometrical property, that results from the composition of some elementary lengths and forms (geometry) of a body. The obtained results, from which the property volume emerges as the adequate one to quantify irreversibility associated with deformation work, consider the volume as a property evaluated from energetic considerations, in a way similar to what happens with entropy in the well established Thermodynamics. Thus, a better understanding of these results probably needs some abstraction and avoid of geometrical considerations when manipulating and evaluating the volume generation.

The rational sign convention adopted for the work transfer interactions shows to be the adequate one that leads to an increase of the volume of the Universe, similarly

to what happens in the well established Thermodynamics, with the heat transfer interaction sign convention and the increase of the entropy of the Universe.

At the present time, there are essentially two ways to define the sense of the time arrow: the Thermodynamic time arrow (the time elapses in such a way that the entropy of the Universe can only increase), and the Cosmological time arrow (the time elapses in such a way that the volume of the Universe can only increase). The obtained results lead to a unification of these arrows, emerging the expansion of the Universe as a natural Thermodynamic result.

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