Volume balance equation, availability analysis and the fundamental relation in the thermodynamics for the heat transfer man

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Abstract

An alternative form of the Second Law of Thermodynamics for systems experiencing volume-change work transfer interactions has been presented in a companion paper, from which the volume generation concept emerges in a similar way with what happens with entropy generation in the well established thermodynamics. The volume balance equation and the new concept of volume generation are introduced into the framework of thermodynamics in the present work. A volume balance equation is developed to apply to closed or open systems. Thermomechanical availability is evaluated taking into account these new developments and emphasis is given to the physical meaning of volume generation, which is closely related with the lost available work associated with irreversibilities of volume-change work transfer interactions. Special attention is given to the fundamental relation of thermodynamics, the volume generation concept being of crucial importance to set the conditions under which this relation applies to reversible or/and to irreversible processes.
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1. Introduction

The volume generation concept and the volume balance equation for a closed system were presented in the companion paper [1]. They are introduced in the structure of thermodynamics in this work, following a form similar to that of some recent treatises on engineering thermodynamics [2–4].

A volume balance equation is developed for closed systems and for open systems, which is essentially the same balance equation for both types of systems as the mass inflow and outflow have no direct influence on the volume of the open systems. It is highlighted that the usual treatment of the flow work, at the inlets and outlets of open systems, assumes that it results from contributions of reversible volume-change work transfer interactions. Emphasis is given to the existing similarity between the volume balance equation and the well established entropy balance equation, even if they refer to different situations and processes.

Availability definition and evaluation can be made considering the volume balance equation and the volume generation concept from the first steps of development. The main result is the same as in the well established thermodynamics, but clearer expressions emerge for the work transfer interactions, and especially for the volume-change work transfer interactions. It is obtained that the volume generation is closely related with the lost available work associated with the irreversibilities of the volume-change work transfer interactions. For work-producing systems this results on a reduction of the volume-change work produced, and for work-absorbing systems this results in an increase of the volume-change work needed. It is also highlighted that the entropy generation is related with all the irreversibilities present in the system, and that volume generation is only related with irreversibilities associated with volume-change work transfer interactions.

The fundamental relation of thermodynamics is obtained taking into account the volume balance equation and the volume generation concept. This equation includes, in a quantitative basis, irreversibilities associated with the volume-change work transfer interactions. It is shown that

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Nomenclature

e	specific (total) energy	W	work transfer interaction
E	energy	$\dot{W}$	work flow rate
h	specific enthalpy		
m	mass	*Subscripts*	
$\dot{m}$	mass flow rate	b	boundary
M	mass	cv	control volume
P	absolute pressure	e	environment
Q	heat transfer interaction	gen	generation
$\dot{Q}$	heat flow rate	i	chemical species i
s	specific entropy	irr	irreversible
S	entropy	rev	reversible
t	time	0	reference state (environment)
T	absolute temperature		
v	specific volume	*Superscript*	
U	internal energy	d	deformation (volume-change)
V	volume		

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if the unique source of irreversibility is that associated with the volume-change work transfer interactions the entropy generation term balances the volume generation term, and that they cancel each other.

2. The volume balance equation

The volume balance equation established for closed systems in the companion paper [1] can be written on a differential basis as

$$dV = -\frac{\delta W^{\mathrm{d}}}{P_{\mathrm{b}}} + \delta V_{\mathrm{gen}} \tag{1}$$

where superscript d reinforces that the work transfer interaction δW^{d} is a volume-change (deformation) work transfer interaction. 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). If the system under analysis exchanges work through $N + 1$ locations of its boundary, the volume balance equation can be stated as

$$dV = \sum_{j=0}^{N} -\frac{\delta W_j^{\mathrm{d}}}{P_j} + \delta V_{\mathrm{gen}} \tag{2}$$

where P_j is the absolute pressure at the portion j of the boundary of the closed system through which the volume-change work transfer interaction δW_j^{d} takes place. On a time rate basis, this equation comes

$$\frac{dV}{dt} = \sum_{j=0}^{N} -\frac{\dot{W}_j^{\mathrm{d}}}{P_j} + \dot{V}_{\mathrm{gen}} \tag{3}$$

At this point it is interesting to note that the entropy balance equation for a closed system which exchanges heat through $M + 1$ locations of its boundary can be expressed as

$$dS = \sum_{i=0}^{M} \frac{\delta Q_i}{T_i} + \delta S_{\mathrm{gen}} \tag{4}$$

where T_i is the absolute temperature at the portion i of the boundary of the closed system through which the heat transfer interaction δQ_i takes place. On a time rate basis, this equation comes

$$\frac{dS}{dt} = \sum_{i=0}^{M} \frac{\dot{Q}_i}{T_i} + \dot{S}_{\mathrm{gen}} \tag{5}$$

From Eqs. (2)–(5) it can be seen the parallel structure of Pressodynamics and of the well established thermodynamics.

For open systems, work transfer interactions exist in the form of flow work [2–4]. For such systems the volume balance equation can the be written as

$$dV = \underbrace{\sum_{j=0}^{N_1} -\frac{\delta W_{\mathrm{cv},j}^{\mathrm{d}}}{P_j}}_{\text{closed boundary}} + \underbrace{\sum_{n=1}^{N_2} -\frac{\delta W_n^{\mathrm{d}}}{P_n}}_{\substack{\text{open boundary} \\ \text{(flow work)}}} + \sum_{\text{in}} dmv - \sum_{\text{out}} dmv + \delta V_{\mathrm{gen}} \tag{6}$$

where mass fluxes at the inlet and outlet ports are $dm > 0$. In this equation, $\delta W_{\mathrm{cv}}^{\mathrm{d}}$ means for the volume-change work other than the flow work. Open systems can even to have other forms of work transfer interactions, like shaft work, electrical work or magnetic work, but they have no direct contribution to the volume balance equation.

Entropy balance equation for an open system needs to take into account the entropy entering and leaving the system accompanying the mass flow, and it reads

$$dS = \sum_{i=0}^{M} \frac{\delta Q_i}{T_i} + \sum_{in} dms - \sum_{out} dms + \delta S_{gen} \qquad (7)$$

or, on a time rate basis

$$\frac{dS}{dt} = \sum_{i=0}^{M} \frac{\dot{Q}_i}{T_i} + \sum_{in} \dot{m}s - \sum_{out} \dot{m}s + \dot{S}_{gen} \qquad (8)$$

At this point, from Eqs. (6) and (7) it can be seen the parallel structure between the well established thermodynamics and of Pressodynamics.

If the flow work can be evaluated as reversible volume-change work it is

$$\delta W_n^d = -P_n dV_n = \begin{cases} P_n dm_n v_n & \text{at the inlets} \\ -P_n dm_n v_n & \text{at the outlets} \end{cases} \qquad (9)$$

taking into account that flow entering the system compresses the system and work is given to the system, and flow leaving the system expands the system and work is given by the system. In this way, the summation present in Eq. (6) relative to the open boundary can be written as

$$\underbrace{\sum_{n=1}^{N_2} -\frac{\delta W_n^d}{P_n}}_{\substack{\text{open boundary} \\ \text{(flow work)}}} = -\sum_{in} dmv + \sum_{out} dmv \qquad (10)$$

and the volume balance equation, Eq. (6), can be written as

$$dV = \sum_{j=0}^{N_1} -\frac{\delta W_{cv,j}^d}{P_j} + \delta V_{gen} \qquad (11)$$

The physical meaning of the foregoing developments is as follows. Mass flowing into the system compresses the system, and its volume decreases. However, the mass entering into the system exactly compensates this compression, and thus the mass entering the system has no contribution to the volume balance equation. In a similar way, mass flowing out of the system expands the system, and its volume increases. However, the mass leaving the system exactly compensates this expansion, and thus the mass leaving the system has no contribution to the volume balance equation. Thus, Eq. (2) applies also for an open system, taking into account that the volume-change work taken into account in it does not include the flow work.

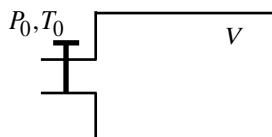At this point, the problem relative to the filling of the container presented in Fig. 1 and analyzed in the compan-

Fig. 1. Filling of an initially evacuated container: application of the open system volume balance equation.

ion paper [1] considering the system as a closed system can now be solved taken the system as the open system that it is in reality. Application of the volume balance Eq. (11) to the open system that is the environment, taking into account that there is no work transfer interaction other than flow work, gives that

$$dV_e = \delta V_{gen} \qquad (12)$$

which, integrated between the initial state, when the container is evacuated (with null volume filled by air), to the final state when the container, of volume V, is filled with air at the ambient pressure P_0 gives

$$V_{gen} = V \qquad (13)$$

the same result as obtained in the companion paper [1] considering the system as a closed system.

3. Availability analysis

The amount of mechanical work that can be extracted from a system, when it evolves in a process, is a very important concept, as it allows the evaluation of this system as a source of mechanical work, and also to identify and to quantify the irreversibilities present in the system. Particularly important is the situation when the system evolves from a given original state to reach the equilibrium conditions with the environment. The maximum amount of mechanical work that can be extracted from the system, in this extreme process, is obtained in the limit situation of no irreversibilities, and it is usually referred to as availability, or exergy [2–4]. In the present treatment availability analysis is limited to the thermomechanical availability, and the chemical availability is not considered [2,4]. Developments are presented for open systems, the closed systems being the (simpler) limit situation of open systems without mass crossing their boundaries.

The First Law of Thermodynamics for an open system, if the flow work can be evaluated as reversible volume-change work, can be written in a differential basis as [2,4]

$$dE = \sum_{i=0}^{M} \delta Q_i + \sum_{j=0}^{N_1} \delta W_{cv,j}^d + \sum_{k=1}^{K} \delta W_{cv,k}^{other} + \sum_{in} dme^o$$
$$- \sum_{out} dme^o \qquad (14)$$

where

$$e^o = e + Pv \qquad (15)$$

In this equation $\delta W_{cv,j}^d$ refers to the j portion of volume-change work other than flow work, and $\delta W_{cv,k}^{other}$ refers to the k portion of other forms of work transfer interactions than volume-change work, like shaft work transfer, electrical work transfer or magnetic work transfer. Summations in Eq. (14) for heat transfer interactions and for volume-change work transfer interactions other than flow work extend from 0 to M and from 0 to N_1, respectively, the 0

index referring to the environment. That is, we are considering an open system that can exchange heat and volume-change work also with the environment, whose temperature and pressure conditions are T_0 and P_0, respectively.

Heat transfer interaction δQ_0 can be extracted from Eq. (7) as

$$\delta Q_0 = T_0 dS - \sum_{i=1}^{M} \delta Q_i \frac{T_0}{T_i} - \sum_{\text{in}} dm T_0 s + \sum_{\text{out}} dm T_0 s - T_0 \delta S_{\text{gen}} \tag{16}$$

and work transfer interaction $\delta W_{\text{cv},0}^{d}$ can be extracted from Eq. (11) as

$$\delta W_{\text{cv},0}^{d} = -P_0 dV - \sum_{j=1}^{N_1} \delta W_{\text{cv},j}^{d} \frac{P_0}{P_j} + P_0 \delta V_{\text{gen}} \tag{17}$$

Results given by Eqs. (16) and (17) can be introduced in Eq. (14), which becomes

$$dE = T_0 dS - P_0 dV + \sum_{i=1}^{M} \delta Q_i \left(1 - \frac{T_0}{T_i}\right)$$
$$+ \sum_{j=1}^{N_1} \delta W_{\text{cv},j}^{d} \left(1 - \frac{P_0}{P_j}\right) + \sum_{k=1}^{K} \delta W_{\text{cv},k}^{other}$$
$$+ \sum_{\text{in}} dm(e^{\circ} - T_0 s) - \sum_{\text{out}} dm(e^{\circ} - T_0 s)$$
$$- T_0 \delta S_{\text{gen}} + P_0 \delta V_{\text{gen}} \tag{18}$$

This equation can be rewritten as

where $-\delta W_{\text{cv}}$ is the total amount of work given by the system, as illustrated in Fig. 2. On a time rate basis this equation becomes

$$-\dot{W}_{\text{cv}} = -\left[\sum_{j=1}^{N_1} \dot{W}_{\text{cv},j}^{d} \left(1 - \frac{P_0}{P_j}\right) + \sum_{k=1}^{K} \dot{W}_{\text{cv},k}^{other} + P_0 \dot{V}_{\text{gen}}\right]$$
$$= -\frac{d}{dt}(E - T_0 S + P_0 V) + \sum_{i=1}^{M} \dot{Q}_i \left(1 - \frac{T_0}{T_i}\right)$$
$$+ \sum_{\text{in}} \dot{m}(e^{\circ} - T_0 s) - \sum_{\text{out}} \dot{m}(e^{\circ} - T_0 s) - T_0 \dot{S}_{\text{gen}} \tag{20}$$

When no irreversibilities are present the limit amount of work given by the system or to the system is thus, from Eq. (19)

$$(-\delta W_{\text{cv}})_{\text{rev}} = -\left[\sum_{j=1}^{N} \delta W_{\text{cv},j}^{d} \left(1 - \frac{P_0}{P_j}\right) + \sum_{k=1}^{K} \delta W_{\text{cv},k}^{other}\right]$$
$$= -(dE - T_0 dS + P_0 dV)$$
$$+ \sum_{i=1}^{M} \delta Q_i \left(1 - \frac{T_0}{T_i}\right) + \sum_{\text{in}} dm(e^{\circ} - T_0 s)$$
$$- \sum_{\text{out}} dm(e^{\circ} - T_0 s) \tag{21}$$

It is interesting to note that the evaluation of the thermo-mechanical availability as conducted above automatically takes into account the volume-change work transfer interaction with the environment pressure reservoir, at pressure P_0. This is not the case in the usual textbooks on engineering thermodynamics [2–4], where some specific considerations are needed in order to take into account this volume-change work transfer interaction.

For work-producing systems Eq. (19) can be interpreted as

$$\underbrace{-\delta W_{\text{cv}}}_{>0} = -\left[\underbrace{\overbrace{\sum_{j=1}^{N_1} \delta W_{\text{cv},j}^{d} \left(1 - \frac{P_0}{P_j}\right)}^{<0} + \sum_{k=1}^{K} \delta W_{\text{cv},k}^{other}}_{\left(\delta W_{\text{cv}}^{d}\right)_{\text{rev}}} + \underbrace{P_0 \delta V_{\text{gen}}}_{-\delta W_{\text{lost}}^{d} > 0}\right]$$
$$= \underbrace{-(dE - T_0 dS + P_0 dV) + \sum_{i=1}^{M} \delta Q_i \left(1 - \frac{T_0}{T_i}\right) + \sum_{\text{in}} dm(e^{\circ} - T_0 s) - \sum_{\text{out}} dm(e^{\circ} - T_0 s)}_{-(\delta W_{\text{cv}})_{\text{rev}} > 0} - \underbrace{T_0 \delta S_{\text{gen}}}_{-\delta W_{\text{lost}} > 0} \tag{22}$$

$$-\delta W_{\text{cv}} = -\left[\sum_{j=1}^{N_1} \delta W_{\text{cv},j}^{d} \left(1 - \frac{P_0}{P_j}\right) + \sum_{k=1}^{K} \delta W_{\text{cv},k}^{other} + P_0 \delta V_{\text{gen}}\right]$$
$$= -(dE - T_0 dS + P_0 dV) + \sum_{i=1}^{M} \delta Q_i \left(1 - \frac{T_0}{T_i}\right)$$
$$+ \sum_{\text{in}} dm(e^{\circ} - T_0 s) - \sum_{\text{out}} dm(e^{\circ} - T_0 s) - T_0 \delta S_{\text{gen}} \tag{19}$$

thus informing us that the amount of mechanical work that can be extracted from the system is reduced in the amount of $|\delta W_{\text{lost}}|$ due to irreversibility. However, taking into account the volume-change work transfer interactions only, the work reduction (work lost) is $|\delta W_{\text{lost}}^{d}|$. For work-absorbing systems Eq. (19) can be interpreted as
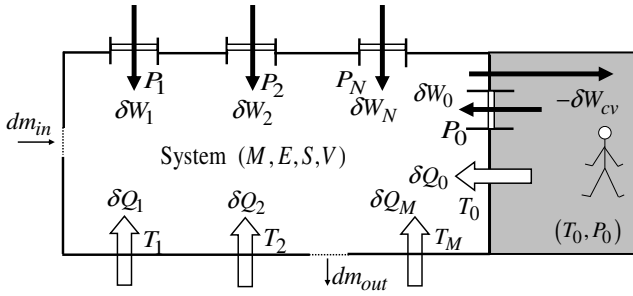
Fig. 2. Schematic representation of an open system in contact with $N+1$ pressure reservoirs and with $M+1$ temperature reservoirs, for the evaluation of the work delivered to the user placed in the environment.

in the form of volume-change work transfer interactions. Detailed description about what is a simple thermodynamic system is given by Bejan [2]. If the simple system exchanges heat and work with only the T_0 temperature and P_0 pressure reservoirs, Eq. (18) can be written as

$$dU = T_0 dS - P_0 dV + \sum_{i=1}^{N} dM_i(h_{0,i} - T_0 s_{0,i})$$
$$- T_0 \delta S_{gen} + P_0 \delta V_{gen} \qquad (25)$$

where the system can receive mass of each chemical species i, coming from mass reservoirs at the T_0, P_0 conditions, as illustrated in Fig. 3. It is to be noted that $dM_i = dm_i$, for each

$$\underbrace{-\delta W_{cv}}_{<0} = -\left[\underbrace{\overbrace{\sum_{j=1}^{N_1} \delta W_{cv,j}^{d}\left(1 - \frac{P_0}{P_j}\right)}^{>0} + \sum_{k=1}^{K} \delta W_{cv,k}^{other}}_{(\delta W_{cv}^{d})_{rev}} + \underbrace{P_0 \delta V_{gen}}_{-\delta W_{lost}^{d} > 0}\right]$$
$$= \underbrace{-(dE - T_0 dS + P_0 dV) + \sum_{i=1}^{M} \delta Q_i\left(1 - \frac{T_0}{T_i}\right) + \sum_{in} dm(e^{o} - T_0 s) - \sum_{out} dm(e^{o} - T_0 s)}_{-(\delta W_{cv})_{rev} < 0} - \underbrace{T_0 \delta S_{gen}}_{-\delta W_{lost} > 0} \qquad (23)$$

thus informing that the amount of mechanical work that is given to the system is increased in the amount of $|\delta W_{lost}|$ due to irreversibility. However, taking into account the volume-change work transfer interactions only, the work increase (work lost) is $|\delta W_{lost}^{d}|$.

It must be noted that the term

$$\underbrace{\sum_{j=1}^{N_1} \delta W_{cv,j}^{d}\left(1 - \frac{P_0}{P_j}\right)}_{(\delta W_{cv}^{d})_{rev}} + \underbrace{P_0 \delta V_{gen}}_{-\delta W_{lost}^{d}}$$

represents the subtraction of the lost work associated with the volume-change work transfer interactions from the reversible overall volume-change work transfer interactions. It is also to be stressed that the term $P_0 \delta V_{gen}$ represents the work lost due to irreversibilities associated with volume-change work transfer interactions only (where the flow work transfer interactions are not included as they were assumed to be reversible, Eq. (9)), and that the term $T_0 \delta S_{gen}$ represents the work lost due to all the irreversibilities present in the system, including those associated with the volume-change work transfer interactions. It is thus

$$T_0 \delta S_{gen} \geqslant P_0 \delta V_{gen} \qquad (24)$$

4. The fundamental relation

A simple thermodynamic system is taken as the one for which the only component of energy E that is relevant is the internal energy, U, and that can only exchange work

particular chemical species i, where M_i refers to the mass of chemical species i contained into the system and dm_i to the differential mass of chemical species i entering the system. For the simple systems, we are especially interested on the irreversibility term, $-T_0 \delta S_{gen} + P_0 \delta V_{gen}$.

If there are irreversibilities other than the ones associated with the volume-change work transfer interactions, it is $T_0 \delta S_{gen} > P_0 \delta V_{gen}$ and the term $(-T_0 \delta S_{gen} + P_0 \delta V_{gen})$ < 0 cannot be deleted from Eq. (25). Another aspect that needs to be taken into account is that irreversibilities associated with the volume-change work transfer interactions give rise to heat generation and to heat transfer interactions. However, the source of such irreversibilities is in the volume-change work transfer interactions.

If the unique irreversibilities present are those associated with the volume-change work transfer interactions it is $T_0 \delta S_{gen} = P_0 \delta V_{gen}$ and the term $(-T_0 \delta S_{gen} + P_0 \delta V_{gen}) = 0$ can be deleted from Eq. (25). This is the case of the filling of an initially evacuated container problem analyzed in the companion paper [1]. The unique primary source of
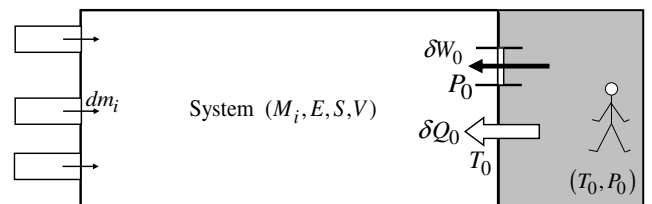

Fig. 3. Open system in communication with mass reservoirs of N particular chemical species and the atmosphere at (T_0, P_0).

irreversibility present in that problem is the one associated with the volume-change work transfer interaction, which gives rise to heat generation that is transferred to the environment in order to maintain the temperature of the air in the container equal to T_0. In this case the irreversibility term can be interpreted as

$$-T_0 \delta S_{\text{gen}} + P_0 \delta V_{\text{gen}} = - \underbrace{\delta Q_{\text{irr}}}_{>0} - \underbrace{\delta W_{\text{irr}}}_{<0} = 0 \qquad (26)$$

saying us that, for simple thermodynamic systems, and under the aforementioned conditions, the lost of available volume-change work in the system always results in a heat release inside the system, which balance each other.

The general case needs to be treated using Eq. (25), the irreversibility term being null or depending on the nature of the particular process undergone by the system. Obviously if the process undergone by the system is reversible the irreversibility term $-T_0 \delta S_{\text{gen}} + P_0 \delta V_{\text{gen}}$ is null. Thus, only if the process is reversible or if the unique primary sources of irreversibility are those associated with the volume-change work transfer interactions the irreversibility term can be taken as equal to zero. This is in contrast to what is usually assumed in thermodynamics, the irreversibility term being taken as zero for both reversible and irreversible processes, without questioning its particular nature [5], the used equation being

$$\mathrm{d}U = T_0 \mathrm{d}S - P_0 \mathrm{d}V + \sum_{i=1}^{N} \mathrm{d}M_i (h_{0,i} - T_0 s_{0,i}) \qquad (27)$$

The usual way is to start considering an internally reversible process, for which $\delta Q_{\text{rev}} = T_0 \mathrm{d}S$ and $\delta W_{\text{rev}} = -P_0 \mathrm{d}V$, and obtain Eq. (27). As this equation involves only thermodynamic properties, its applicability range is extrapolated to both reversible and irreversible processes [4]. Some word explanations are given [5], but no any mathematical evidence is given about what is involved. Hatsopoulos and Keenan [5] claim, using words, that it is always $T_0 \delta S_{\text{gen}} = P_0 \delta V_{\text{gen}}$, but no demonstration is given for that. The developments presented above show that Eq. (27) applies to reversible processes or to irreversible processes if the unique primary sources of irreversibility are those associated with the volume-change work transfer interactions. If other kinds of irreversibility are present the general expression that must be used is Eq. (25), with $(-T_0 \delta S_{\text{gen}} + P_0 \delta V_{\text{gen}}) < 0$. To the best authors' knowledge this is the first time this point is discussed in detail, and that are detailed the conditions under which Eq. (27) can be applied. It is to be noted that the volume generation concept is crucial to that.

If the process undergone by the simple thermodynamic system takes place under equilibrium conditions, for which the temperature T_b at the boundary equals the temperature T of the system and of its boundaries, and for which the pressure P_b at the boundary equals the pressure P of the system and of its boundaries, no irreversibilities exist in the system, $\delta S_{\text{gen}} = \delta V_{\text{gen}} = 0$ and Eq. (25) becomes

$$\mathrm{d}U = T \mathrm{d}S - P \mathrm{d}V + \sum_{i=1}^{N} \mathrm{d}M_i (h_i - T s_i) \qquad (28)$$

This equation involves only values of thermodynamic properties, and thus applies both to irreversible or to reversible processes connecting a sequence of equilibrium states of simple thermodynamic systems [5].

5. Conclusions

Consideration of the volume balance equation and of the volume generation concept into the framework of the well established thermodynamics is made in this work. The volume balance equation has its own physical insight, and it is essentially the same for closed systems or to open systems, as mass entering or leaving the system has no direct influence on then system's volume.

Evaluation of the thermomechanical availability automatically takes into account the volume-change work transfer interaction with the environment pressure reservoir. It appears, explicitly, how the irreversibilities associated with the volume-change work transfer interactions must be subtracted from the reversible volume-change work transfer interactions. These irreversibilities result on a reduction of the work released by work-producing devices, and on an increase of the work received by work-absorbing devices. It is also highlighted that entropy generation is related with all irreversibilities present, and that the volume generation is related with irreversibilities associated with volume-change work transfer interactions only.

The fundamental relation of thermodynamics is worked out taking into account the volume balance equation and the volume generation concept, and a general result is obtained that applies to both reversible or to irreversible processes. It is demonstrated that the irreversibility term of the fundamental relation is null only if the process is reversible or if the unique primary source of irreversibility is on the volume-change work transfer interactions.

The volume balance equation and the volume generation concept are new subjects in thermodynamics, and further work needs to be conducted towards their complete understanding and integration in the framework of thermodynamics.

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