Analysis of entropy production in some enclosed subsystems where spontaneous processes take place

Marius BREBENEL*

*Corresponding author
"POLITEHNICA" University of Bucharest, Faculty of Aerospace Engineering,
Department "Elie Carafoli" Aerospace Science
Polizu Street 1-7, postal code 011061, sector 1, Bucharest, Romania
mariusbreb@yahoo.com

Abstract: *It is well-known that every spontaneous process occurring in an isolated system is accompanied by increasing entropy. The goal of this paper is to show that if the system is made of several subsystems, the entropy production of some subsystems can be negative, without violating the 2nd law. An analysis of the instantaneous entropy generation is presented, considering two simple cases of spontaneous processes, namely heat and mass transfer between two volumes of gases. The calculations show that, in the case of mass transfer, it is possible one subsystem to exhibit a negative entropy production, although the total entropy production of the whole system is positive, according to 2nd law.*

Key Words: *entropy production, spontaneous process, non-equilibrium, order.*

1. INTRODUCTION

The basic transport phenomena like heat conduction, diffusion or viscous friction are irreversible processes characterized by entropy rise, which is of type "generated entropy".

According to 2nd law, in the case of isolated systems, the entropy variation during a process toward the equilibrium is positive and can be calculated using the tools of classical *Thermodynamics*. In exchange, if there are several open subsystems included in an isolated system, the entropy variation at the level of each subsystem can be computed using equations which are specific to irreversible *Thermodynamics*.

Such models include the general equation of transport (or balance) for the entropy with respect to a given control volume:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sum_k \frac{\dot{Q}_e^{(k)}}{T_k} + \dot{S}_{in} - \dot{S}_{out} + \frac{\mathrm{d}S_i}{\mathrm{d}t} \qquad (1)$$

where $\mathrm{d}S/\mathrm{d}t$ = total entropy variation rate, $\mathrm{d}S_i/\mathrm{d}t$ = entropy production rate, $\dot{S}_{in}$, $\dot{S}_{out}$ = rate of transported entropy along the fluid mass in/out of system, $\dot{Q}_e^{(k)}$ = flux of heat exchanged with surroundings at some fixed temperatures T_k. The above equation can be expressed briefly:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}S_e}{\mathrm{d}t} + \frac{\mathrm{d}S_i}{\mathrm{d}t} \tag{2}$$

where $\mathrm{d}S_e/\mathrm{d}t$ = rate of entropy exchanged with the surroundings.

It is important to point out that in the case of closed and isolated systems, the entropy production rate $\mathrm{d}S_i/\mathrm{d}t$ must be positive, in order to satisfy the 2nd law of *Thermodynamics* ([1], [4], [5], [6]). Many authors extend this condition for the case of open systems too, but we will show by calculation that this is not always mandatory.

For the sake of simplicity let's consider an isolated system made of two subsystems denoted as [ ]$^{(1)}$ and [ ]$^{(2)}$. Initially, those subsystems are out of equilibrium, so that a spontaneous process toward the equilibrium will occur. According to (2), the equations of entropy balance for each subsystem will be:

$$\mathrm{d}S^{(1)} = \mathrm{d}S_e^{(1)} + \mathrm{d}S_i^{(1)}, \quad \mathrm{d}S^{(2)} = \mathrm{d}S_e^{(2)} + \mathrm{d}S_i^{(2)} \tag{3}$$

Since the whole system is isolated, the following constraint applies:

$$\mathrm{d}S_e^{(1)} + \mathrm{d}S_e^{(2)} = 0, \quad \mathrm{d}S_e^{(2)} = -\mathrm{d}S_e^{(1)} \tag{4}$$

As a consequence, by adding the equalities (3), the instantaneous entropy variation of whole system will be found, which has to be a positive quantity, according to 2nd law:

$$\mathrm{d}S_{syst} = \mathrm{d}S^{(1)} + \mathrm{d}S^{(2)} = \mathrm{d}S_i^{(1)} + \mathrm{d}S_i^{(2)} > 0 \tag{5}$$

For example, there are situations when the subsystem [ ]$^{(2)}$ can have a negative variation of entropy, such that

$$\mathrm{d}S^{(2)} < 0 \quad \text{where} \quad \left|\mathrm{d}S^{(2)}\right| < \mathrm{d}S^{(1)}, \ \mathrm{d}S^{(1)} > 0 \tag{6}$$

without violating the 2nd law, since the total entropy variation of the system remains positive. This happens when, according to eq. (1):

$$\dot{S}_{out} > \sum_k \frac{\dot{Q}_e^{(k)}}{T_k} + \dot{S}_{in} + \frac{\mathrm{d}S_i}{\mathrm{d}t} \tag{7}$$

In general, the biological systems enjoy this property.

The following analysis shows that for some subsystems it is also possible to have a negative entropy production (i.e. $\mathrm{d}S_i < 0$) satisfying a similar condition as in (6):

$$\mathrm{d}S_i^{(2)} < 0 \quad \text{where} \quad \left|\mathrm{d}S_i^{(2)}\right| < \mathrm{d}S_i^{(1)}, \ \mathrm{d}S_i^{(1)} > 0 \tag{8}$$

It is already known ([2], [3]) that in the case of coupled irreversible processed, some of them can yield a negative source of entropy, which is also a local source of order. We will show that even in the case of simple irreversible processes involving mass transfer, a negative entropy production is also possible to occur. In the next paragraphs, two cases of basic irreversible processes will be analyzed, in which the evolution of each kind of entropy variation (internal and external) during the process will be described. These processes are:
(1) Heat transfer between two volumes of the same gas, completely isolated from surroundings;
(2) Mass transfer during pressure balancing between two volumes of the same gas, completely isolated from surroundings.

2. HEAT TRANSFER

Two volumes of the same gas are enclosed in an isolated box, having two different temperatures and pressures, according to fig.1:
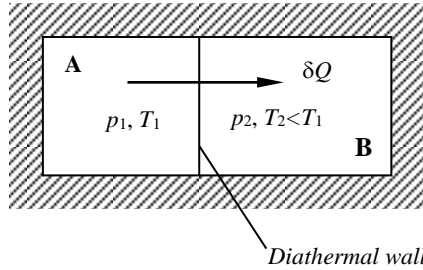

Fig. 1 Model of analysis for the heat transfer between two volumes of the same gas

The initial temperatures of the gas in subsystems denoted as A and B are T_1 and T_2 respectively, where $T_1 > T_2$. The separating wall is a diathermal one, permitting only the heat transfer between the subsystems. Since the whole system is out of equilibrium, a heat transfer will occur until the temperatures in both subsystems will be the same. Let's denote the equilibrium temperature as T_f (final).

The process of heat transfer in an irreversible one since it is spontaneous, so that it obeys the 2nd law, which means that the entropy of the system increases continuously until it gets a maximum value when the equilibrium is reached.

The equilibrium temperature can be found easily by means of classical *Thermodynamics*, using the balance of internal energy. It is given by the formula:

$$T_f = \frac{M_1 T_1 + M_2 T_2}{M_1 + M_2} \tag{9}$$

where M_1, M_2 denote the masses of each volume of gas.

The classical *Thermodynamics* permits also to compute the entropy variation of the whole system until the equilibrium is reached. Using constant specific heats on the temperature range $[T_1, T_2]$ and considering the isochoric processes of each volume, this entropy variation is given by the expression:

$$\Delta S_{syst} = c_v \left(M_1 \ln \frac{T_f}{T_1} + M_2 \ln \frac{T_f}{T_2} \right) \tag{10}$$

where c_v = specific heat at constant volume.
By denoting

$$x = \frac{M_1}{M_1 + M_2}, \quad 1 - x = \frac{M_2}{M_1 + M_2} \tag{11}$$

and using the formula (9), the expression of entropy variation (10) can be re-written as:

$$\left(\Delta S \right)_{syst} = \left(M_1 + M_2 \right) c_v \left\{ \ln \left[x + \left(1 - x \right) \frac{T_2}{T_1} \right] - \left(1 - x \right) \ln \frac{T_2}{T_1} \right\} \tag{12}$$

It can be shown that the above quantity is always positive as $x \in [0, 1]$.
It is worth to note that the calculation of entropy variation during each isochoric process has

used the hypothesis of reversible (quasistatic) path, although the whole spontaneous process is irreversible.

In the next, the heat transfer from subsystem A to B will be analyzed using the equation of entropy balance, which considers the entropy flux and the entropy production. For the subsystem A, this equation reads:

$$dS_A = (dS_e)_A + (dS_i)_A \tag{13}$$

where, under the assumption of local equilibrium:

$$dS_A = \frac{(\delta Q_e)_A}{T_A}, \quad (dS_e)_A = \frac{(\delta Q_e)_A}{T_{ref}} \tag{14}$$

The temperature T_A is the actual temperature of the gas in subsystem A at a given instant, while T_{ref} is a reference temperature needed to estimate the entropy flow from A to B. This temperature needs to be the same for A and B subsystems and independent of the actual temperatures T_A and T_B.

Since near equilibrium $T_{ref} = T_{eq} = T_f$, we will consider this temperature to be constant and having the value T_f. With this remark, the entropy balance gets the form:

$$(dS_i)_A = \left(\frac{1}{T_A} - \frac{1}{T_f} \right)(\delta Q_e)_A \tag{15}$$

The initial temperatures are $T_1 > T_2$, so that the heat flow will be only from A to B, the actual heat transferred being denoted as $(\delta Q_e)_A$.

According to the sign convention, a heat which is released has a "minus" sign:

$$(\delta Q_e)_A < 0 \tag{16}$$

On the other hand, the actual temperature in A subsystem will be always higher than the equilibrium temperature:

$$T_A > T_f, \quad \frac{1}{T_A} < \frac{1}{T_f} \tag{17}$$

As a result, the entropy production expressed by eq. (15) will be a positive quantity along the whole process toward the equilibrium.

A similar analysis can be done for the subsystem B. The corresponding equations are:

$$dS_B = \frac{(\delta Q_e)_B}{T_B} = \frac{(\delta Q_e)_B}{T_f} + (dS_i)_B \tag{18}$$

$$(dS_i)_B = \left(\frac{1}{T_B} - \frac{1}{T_f} \right)(\delta Q_e)_B \tag{19}$$

It can be observed that

$$(\delta Q_e)_B = -(\delta Q_e)_A, \quad (\delta Q_e)_B > 0 \tag{20}$$

and also

$$T_B < T_f , \quad \frac{1}{T_B} > \frac{1}{T_f} \tag{21}$$

Finally, the entropy production in subsystem B given by eq. (19) is also a positive quantity as in the case of subsystem A.

Thus, we have shown that in the case of heat transfer between two subsystems enclosed in an isolated system, each subsystem exhibits at every instant a positive entropy production which yields a positive global entropy variation.

More than that, the analysis of entropy variation using irreversible *Thermodynamics* allows computing the components of instantaneous entropy variation (internal and external) and, by integration, the cumulated values of these components for each subsystem, which classical *Thermodynamics* doesn't permit.

If we refer to the subsystem A, by applying the 1st law to an isochoric process, one can write:

$$(\delta Q_e)_A = M_1 c_v \cdot dT_A \tag{22}$$

and introducing in (15), one yields:

$$(dS_i)_A = M_1 c_v \left(\frac{1}{T_A} - \frac{1}{T_f} \right) \cdot dT_A \tag{23}$$

By integrating this equation between the limits T_1 and T_f, the total entropy production for the subsystem A is obtained:

$$(\Delta S_i)_A = \int_{T_1}^{T_f} (dS_i)_A = M_1 c_v \left(\frac{T_1}{T_f} - 1 - \ln \frac{T_1}{T_f} \right) \tag{24}$$

A similar expression can be found for the subsystem B:

$$(\Delta S_i)_B = \int_{T_2}^{T_f} (dS_i)_B = M_2 c_v \left(\frac{T_2}{T_f} - 1 - \ln \frac{T_2}{T_f} \right) \tag{25}$$

These quantities are both positive, based on the algebraic inequality:

$$\ln x \leq x - 1 \quad (\forall) x > 0 \tag{26}$$

The total entropy production for the whole system A + B can be computed by adding the last results.

Since the internal energy of the system remains unchanged, the following equation is satisfied:

$$M_1 c_v (T_f - T_1) + M_2 c_v (T_f - T_2) = 0 \tag{27}$$

so that

$$(\Delta S_e)_A + (\Delta S_e)_B = 0 \tag{28}$$

and

$$\left(\Delta S_i\right)_{syst} = \left(\Delta S_i\right)_A + \left(\Delta S_i\right)_B = c_v\left(M_1 \ln\frac{T_f}{T_1} + M_2 \ln\frac{T_f}{T_2}\right) \tag{29}$$

This is the same expression as the total entropy variation for the whole system till the equilibrium is reached.

The above result was expected, since the process of heat transfer in an isolated system exhibits an entropy variation which is only of "internal" type (no entropy exchange with the surroundings take place).

By integrating the equations (14), the external component of total entropy variation for either subsystem A or B can be determined. The overall picture of entropy variation looks like below:

$$\left(\Delta S_i\right)_A = M_1 c_v\left(\frac{T_1}{T_f} - 1 - \ln\frac{T_1}{T_f}\right), \quad \left(\Delta S_e\right)_A = M_1 c_v\left(1 - \frac{T_1}{T_f}\right) \tag{30}$$

$$\left(\Delta S_i\right)_B = M_2 c_v\left(\frac{T_2}{T_f} - 1 - \ln\frac{T_2}{T_f}\right), \quad \left(\Delta S_e\right)_B = M_2 c_v\left(1 - \frac{T_2}{T_f}\right) \tag{31}$$

$$\Delta S_A = -M_1 c_v \ln\frac{T_1}{T_f} < 0, \quad \Delta S_B = -M_2 c_v \ln\frac{T_2}{T_f} > 0, \quad \Delta S_A + \Delta S_B > 0 \tag{32}$$

One can see that the total entropy variation for subsystem A is negative, since the entropy flux is negative due to heat release and it is higher than the entropy production (which is positive).

However, the entropy rise in subsystem B is higher, so that the entropy variation for the isolated system A + B is positive, according to the 2nd law.

The above formulas allow us to give also a graphical representation of the evolution of both kinds of entropy for each subsystem (fig. 2, 3 and 4).
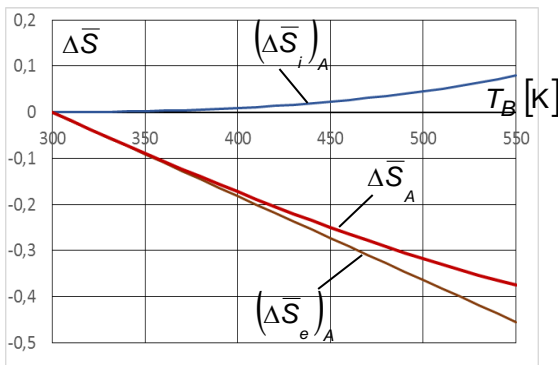

Fig. 2 Variation of entropy components in the subsystem A during the heat transfer
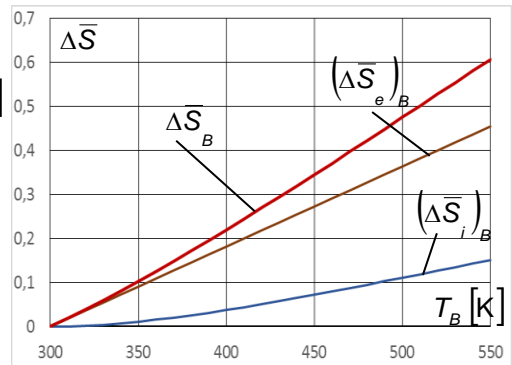
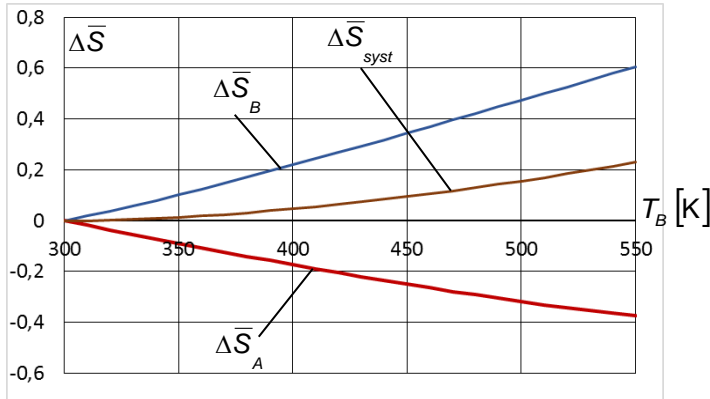Fig. 3 Variation of entropy components in the subsystem B during the heat transfer

Fig. 4 Variation of entropy for whole system (A + B) during the heat transfer

The graphs were plotted based on following data: $x = 1/2$ $(M_1 = M_2)$, $T_1 = 800$ K, $T_2 = 300$ K, $T_f = 550$ K, using the notation $\Delta \overline{S} = \Delta S / M c_v$.

3. MASS TRANSFER

The second irreversible process to be analyzed consists of a mass transfer between two volumes of the same kind of gas, with the same temperature but different pressures. Let $p_1 > p_2$ be the initial pressures. These volumes are supposed to be separated by a porous wall, which allows the mass transfer between the rooms denoted as previously with A and B. One neglects the other dissipations while transferring the gas from A to B (fig. 5).

Assuming that initially the mass transfer is blocked and suddenly it is allowed, the process of mass transfer from the higher pressure room A to the lower pressure room B will be analyzed, till the pressure becomes uniform throughout the whole system.
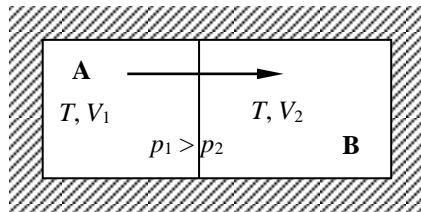

Fig. 5 Model of analysis for the mass transfer between two volumes of the same gas

Like in the case of heat transfer, the overall entropy variation during the process of reaching the equilibrium will be calculated first. This will be done using the classical *Thermodynamics*, namely by considering the evolution of each mass of gas enclosed initially in rooms A and B (control mass method).

By applying the equation of mass balance along with the law of ideal gas, the final (equilibrium) pressure can be found:

$$M_1 + M_2 = \frac{p_1 V_1}{RT} + \frac{p_2 V_2}{RT} = \frac{p_f (V_1 + V_2)}{RT} \tag{33}$$

where M_1, M_2 are the initial masses of gas, R = gas constant, V_1 and V_2 are the geometric volumes of the rooms A and B and p_f is the final pressure (at equilibrium). It follows that:

$$p_f = \frac{p_1 V_1 + p_2 V_2}{V_1 + V_2} \tag{34}$$

For the isothermal evolution of each gas mass from the initial pressure to the final one, the corresponding entropy variation will be given by the classical formulas:

$$\Delta S_1 = -M_1 \text{R} \ln \frac{p_f}{p_1}, \quad \Delta S_2 = -M_2 \text{R} \ln \frac{p_f}{p_2} \tag{35}$$

Hence, the entropy variation for the whole system will be:

$$\left(\Delta S \right)_{syst} = \Delta S_1 + \Delta S_2 = -\text{R} \left(M_1 \ln \frac{p_f}{p_1} + M_2 \ln \frac{p_f}{p_2} \right) \tag{36}$$

and it can be shown that the above expression is always positive. This confirms that the process of pressure balancing is irreversible and since the system is isolated, the entropy rise is of "generated entropy" type.

However, since $p_2 < p_f < p_1$, the entropy variation for the individual masses M_1 and M_2 will have opposite signs:

$$\Delta S_1 > 0, \quad \Delta S_2 < 0 \tag{37}$$

In the next, the instantaneous entropy variation for each subsystem will be analyzed, by using this time the tools of irreversible *Thermodynamics*. The subsystems will be defined as the actual contents in each room A and B, so that one works with M_A, M_B, ΔS_A, ΔS_B rather than M_1, M_2, ΔS_1, ΔS_2 (control volume method). Only at the beginning of the process, the equalities $M_A = M_1$, $M_B = M_2$ are satisfied.

Using the equation of entropy balance (1) for each subsystem, the following relations can be written, under the assumption of local equilibrium:

$$dS_A = s_A \cdot dM_A + \left(dS_i \right)_A \tag{38}$$

$$dS_B = -s_A \cdot dM_A + \left(dS_i \right)_B \tag{39}$$

where an entropy flux from A to B is transferred along with the mass of gas which flows from the higher pressure to the lower one. The actual specific entropy of the gas in subsystem A was denoted by s_A.

The instantaneous entropy variation for the subsystem A can be computed using formula

$$dS_A = s_A \cdot dM_A + M_A \cdot ds_A \tag{40}$$

where

$$s_A = s(p_1, T) - \text{R} \cdot \ln \frac{p_A}{p_1} = s_1 - \text{R} \cdot \ln \frac{p_A}{p_1}, \quad ds_A = -\text{R} \cdot \frac{dp_A}{p_A} \tag{41}$$

$$M_A = \frac{p_A V_1}{\text{R}T}, \quad dM_A = \frac{V_1}{\text{R}T} \cdot dp_A \tag{42}$$

Introducing in (40), one yields:

$$dS_A = \frac{V_1}{T}\left(\frac{s_1}{R} - \ln\frac{p_A}{p_1} - 1\right) \cdot dp_A \tag{43}$$

It is important to note that the parenthesis is positive ($p_A < p_1$, $s_1 > R$) while the pressure is decreasing ($dp_A < 0$), so that the instantaneous entropy variation in A is always negative. On the other hand, by comparing equations (38) and (40) which contain the term $(dS_e)_A = s_A \cdot dM_A$, the expression of the internal entropy variation can be derived:

$$(dS_i)_A = M_A \cdot ds_A = -\frac{V_1}{T} \cdot dp_A \tag{44}$$

Since $dp_A < 0$ along the whole process, it follows that the entropy production rate in subsystem A is always positive, as expected for an irreversible process.

Similarly, the instantaneous entropy variation in subsystem B is described by the equation:

$$dS_B = s_B \cdot dM_B + M_B \cdot ds_B \tag{45}$$

where s_B is the actual specific entropy (per unit of mass) of the gas in subsystem B:

$$s_B = s(p_1, T) - R \cdot \ln\frac{p_B}{p_1} = s_1 - R \cdot \ln\frac{p_B}{p_1}, \quad ds_B = -R \cdot \frac{dp_B}{p_B} \tag{46}$$

and M_B is the actual gas mass in room B:

$$M_B = \frac{p_B V_2}{RT}, \quad dM_B = \frac{V_2}{RT} \cdot dp_B \tag{47}$$

The equation of mass balance yields:

$$M_A + M_B = \text{const.}, \quad dM_A + dM_B = 0 \tag{48}$$

and from (42) and (47), the following equation is derived:

$$V_1 \cdot dp_A + V_2 \cdot dp_B = 0 \tag{49}$$

By replacing this in (47), one finds:

$$dM_B = -\frac{V_1}{RT} \cdot dp_A \tag{50}$$

Introducing all these in (45), the equation of instantaneous entropy variation of subsystem B becomes:

$$dS_B = -\frac{V_1}{T}\left(\frac{s_1}{R} - \ln\frac{p_B}{p_1} - 1\right) \cdot dp_A \tag{51}$$

A brief overview on the signs of the terms in above equation shows that $dS_B > 0$. The rate of entropy production in subsystem B can be determined using the equation (39):

$$(dS_i)_B = dS_B + s_A \cdot dM_A \tag{52}$$

which, after some algebra, yields:

$$(dS_i)_B = \frac{V_1}{T}\left(\ln\frac{p_B}{p_A} + 1\right) \cdot dp_A \tag{53}$$

This is an interesting result, since the parenthesis can be either positive or negative, depending on the pressure ratio in subsystems A and B. Thus, the following cases arise:

(i) $$\frac{p_B}{p_A} < \frac{1}{e} \quad \Rightarrow \quad \ln\frac{p_B}{p_A} < -1 \quad \Rightarrow \quad (dS_i)_B > 0 \tag{54}$$

(ii) $$\frac{1}{e} < \frac{p_B}{p_A} < 1 \quad \Rightarrow \quad -1 < \ln\frac{p_B}{p_A} < 0 \quad \Rightarrow \quad (dS_i)_B < 0 \tag{55}$$

It has to be noted that first case appears only if $\frac{p_1}{p_2} < \frac{1}{e}$, which means that for slight

pressure differences between the rooms A and B, the entropy production rate in B is negative along all the process.

We will check now the entropy production rate for the whole system:

$$(dS_i)_{syst} = (dS_i)_A + (dS_i)_B \tag{56}$$

Replacing with the results (44) and (53), the following formula is found for the entropy production rate of the system:

$$(dS_i)_{syst} = \frac{V_1}{T}\ln\frac{p_B}{p_A} \cdot dp_A \tag{57}$$

It can be seen that $dp_A < 0$, $p_B < p_A \Rightarrow (dS_i)_{syst} > 0$, so that the 2nd law is satisfied for the whole system along the entire irreversible process of pressure balancing.

One has determined so far that a negative entropy production can occur in a process where a mass transfer is present, the same way as happens in the coupled processes where a stronger thermodynamic flux with positive entropy production can trigger another flux with negative entropy production, going apparently "against the nature".

However, the process analyzed hereby shows only one flux of matter, yet affecting two subsystems.

In order to plot the entropy variation for each control volume A and B, the finite entropy variation will be computed by integrating the expressions (43), (44), (51) and (53). Thus, by integrating (43), the cumulated entropy variation in the control volume A at any given instant is found:

$$\Delta S_A = \frac{V_1}{RT}\int_{p_1}^{p_A}\left(s_1 - R\ln\frac{p_A}{p_1} - R\right) \cdot dp_A = -\frac{p_1 V_1}{T}\left[\frac{s_1}{R}\left(1 - \frac{p_A}{p_1}\right) + \frac{p_A}{p_1}\ln\frac{p_A}{p_1}\right] \tag{58}$$

The final entropy variation will be determined by replacing p_A with p_f:

$$(\Delta S_A)_f = -\frac{p_1 V_1}{T}\left[\frac{s_1}{R}\left(1 - \frac{p_f}{p_1}\right) + \frac{p_f}{p_1}\ln\frac{p_f}{p_1}\right] \tag{59}$$

Similarly, the equation (44) yields:

$$\left(\Delta S_i\right)_A = -\frac{V_1}{T}\int\limits_{p_1}^{p_A} \cdot \mathrm{d}p_A = \frac{p_1 V_1}{T}\left(1 - \frac{p_A}{p_1}\right), \quad p_1 \geq p_A \geq p_f \tag{60}$$

and

$$\left(\Delta S_i\right)_{A,f} = \frac{p_1 V_1}{T}\left(1 - \frac{p_f}{p_1}\right) \tag{61}$$

For the control volume B, the calculations yield:

$$\Delta S_B = \frac{V_2}{\mathrm{R}T}\int\limits_{p_2}^{p_B}\left(s_1 - \mathrm{R}\ln\frac{p_B}{p_1} - \mathrm{R}\right)\cdot \mathrm{d}p_B = \frac{p_2 V_2}{T}\left[\frac{s_1}{\mathrm{R}}\left(\frac{p_B}{p_2} - 1\right) - \frac{p_B}{p_2}\ln\frac{p_B}{p_1} + \ln\frac{p_2}{p_1}\right] \tag{62}$$

and

$$\left(\Delta S_B\right)_f = \frac{p_2 V_2}{T}\left[\frac{s_1}{\mathrm{R}}\left(\frac{p_f}{p_2} - 1\right) - \frac{p_f}{p_2}\ln\frac{p_f}{p_1} + \ln\frac{p_2}{p_1}\right] \tag{63}$$

$$\left(\Delta S_i\right)_B = -\frac{V_2}{T}\int\limits_{p_2}^{p_B}\ln p_B \cdot \mathrm{d}p_B + \frac{V_1}{T}\int\limits_{p_1}^{p_A}\left(1 - \ln p_A\right)\cdot \mathrm{d}p_A \tag{64}$$

$$\left(\Delta S_i\right)_B = -\frac{p_2 V_2}{T}\left[\frac{p_B}{p_2}\ln\frac{p_B}{p_2} + \left(\frac{p_B}{p_2} - 1\right)\left(\ln\frac{p_2}{p_1} - 1\right)\right] + \frac{p_1 V_1}{T}\left[2\left(\frac{p_A}{p_1} - 1\right) - \frac{p_A}{p_1}\ln\frac{p_A}{p_1}\right] \tag{65}$$

$$\left(\Delta S_i\right)_{B,f} = \frac{p_2 V_2}{T}\ln\frac{p_2}{p_f} + \frac{p_1 V_1}{T}\left(\ln\frac{p_1}{p_f} + \frac{p_f}{p_1} - 1\right) \tag{66}$$

It can be checked that the total entropy production of the whole system is positive and has the same expression as given by equation (36):

$$\left(\Delta S_i\right)_{A,f} + \left(\Delta S_i\right)_{B,f} = \left(\Delta S\right)_{syst} = -\mathrm{R}\left(M_1\ln\frac{p_f}{p_1} + M_2\ln\frac{p_f}{p_2}\right) \tag{67}$$

The graphical representation of the evolution of entropy for each subsystem during the process of pressure balancing is presented in figs. 6, 7, 8 and 9.

The system consists of two equal volumes of nitrogen (N2), having $p_1 = 5$ bar, $p_2 = 1$ bar and $T = 298$ K. The process extent is described by increasing pressure in subsystem B.

In the following figures, the notation $\Delta \bar{S} = T \cdot \Delta S /(p_1 V_1)$ was used as a dimensionless entropy variation.

For the sake of comparison, the diagram from fig.8 was repeated for two other cases: p_1=5 bar, p_2=0.2 bar (fig. 10) and p_1=5 bar, p_2=3 bar (fig. 11).
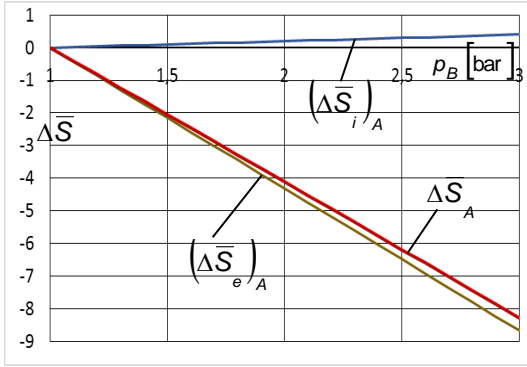
Fig. 6 Variation of entropy components in the subsystem A during the mass transfer
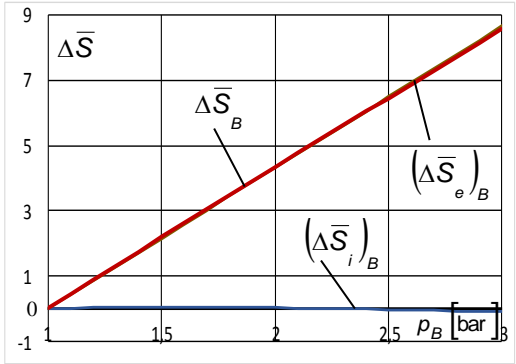

Fig. 7 Variation of entropy components in the subsystem B during the mass transfer
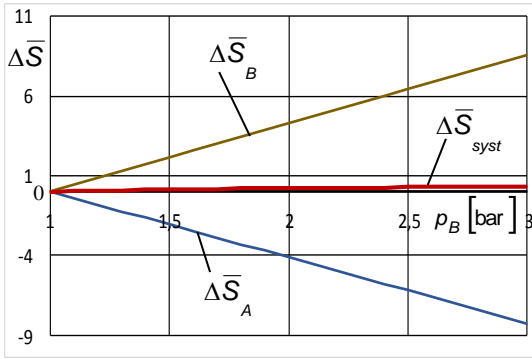

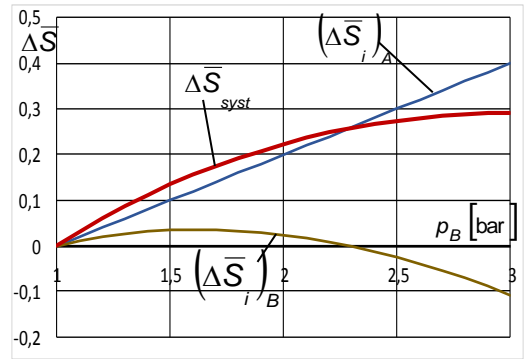Fig. 8 Variation of entropy for whole system (A + B) during the mass transfer

Fig. 9 Variation of entropy production for the whole system during the mass transfer
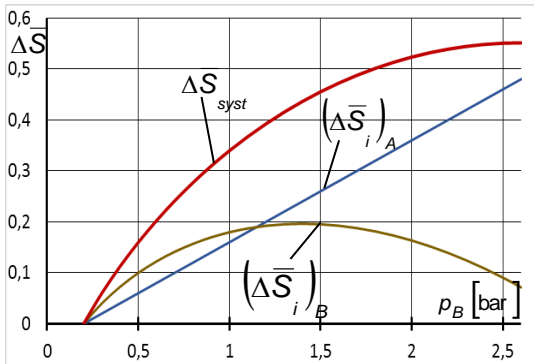(p_1=5bar, p_2=1bar)

Fig. 10 Variation of entropy production for the whole system during the mass transfer
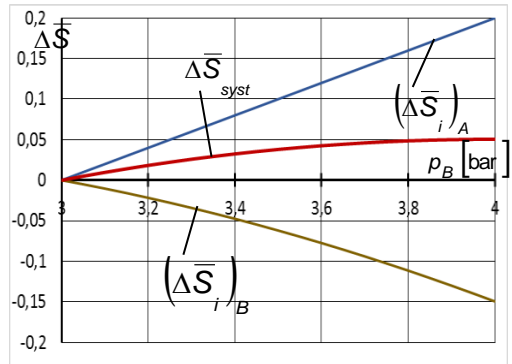(p_1=5bar, p_2=0.2bar)

Fig. 11 Variation of entropy production for the whole system during the mass transfer
(p_1=5bar, p_2=3bar)

It can be observed that while in the case where p_2=0.2 bar the entropy production in subsystem B remains positive along all the process, in the last case (p_2=3 bar), the entropy production in subsystem B in only negative.

In the first case analyzed (fig. 9), the instantaneous entropy production in subsystem B is positive at the beginning and becomes negative during the last part of the process, so that the

final entropy production is negative. As such, one can conclude that the sign of entropy production in subsystem B depends on the initial pressure ratio of the given subsystems. On the other hand, in all cases, the entropy production for the whole system (A + B) is positive, as the 2nd / law requires.

4. CONCLUSIONS

(i)   In the case of irreversible heat transfer, two closed subsystems were considered; the law of positive entropy production rate applies for each subsystem at any given instant.

(ii)   For the case of irreversible mass transfer, the considered subsystems are open and it was proved by calculation that the subsystem which exhibits a mass addiction yields an entropy production rate which can be negative as well, while the entropy production rate for the entire system is positive according to the 2nd law.

(iii)   Negative entropy production is possible not only in the case of coupled processes, but also in the case of some subsystems between which a mass exchange occurs.

(iv)   If the subsystems consist of a given system and the surroundings, only positive entropy production is possible for that system, since the entropy of the universe cannot decrease during natural processes; however, some systems can exhibit a negative entropy variation (this was observed at biological systems).

(v)   Negative entropy production during natural processes is possible for a system only if it is open and another system (with which matter and energy is exchanged) provides a higher positive entropy production. In other words, an order can be induced in a system only when interacting with another system wherein more disorder occurs, so that the 2nd law gets satisfied when both systems are considered.

(vi)   For the open systems, the postulate stating that "the entropy production must be positive during spontaneous processes" is not always necessary. Specifically, some unsteady spontaneous processes involving a mass addiction can exhibit a negative entropy production. However, for the steady processes, the condition of positive entropy production always applies.

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