Entropy change of an ideal gas determination with no reversible process

(Determinação da variação de entropia num gás ideal sem usar um processo reversível)

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As is stressed in literature [1], [2], the entropy change, $\Delta S$, during a given irreversible process is determined through the substitution of the actual process by a reversible one which carries the system between the same equilibrium states. This can be done since entropy is a state function. However this may suggest to the students the idea that this procedure is mandatory. We try to demystify this idea, showing that we can preserve the original process. Another motivation for this paper is to emphasize the relevance of the reservoirs concept, in particular the work reservoir, which is usually neglected in the literature [2]. Starting by exploring briefly the symmetries associated to the first law of Thermodynamics, we obtain an equation which relates both the system and neighborhood variables and allows entropy changes determination without using any auxiliary reversible process. Then, simulations of an irreversible ideal gas process are presented using Mathematica®, which we believe to be of pedagogical value in emphasizing the exposed ideas and clarifying some possible misunderstandings relating to the difficult concept of entropy [4].

**Keywords:** First Law, symmetry, reversible process, entropy.

1. First Law as an interaction

The first law relates the variation of the internal energy of a system, $\Delta U$, to the heat, $Q$, and work, $W$, flows crossing its boundary. Adopting the point of view that both heat and work are positive whenever these energies enter into the system [3], for an infinitesimal process the first law may be written as [1]

$$dU = \delta Q + \delta W, \quad (1)$$

where $dU$ is an exact differential and $\delta Q$ and $\delta W$ are inexact ones.

By considering a hydrostatic system [3] and a reversible process, we can replace $\delta Q$ by $TdS$ and $\delta W$ by $-PdV$, where $T$, $S$, $P$ and $V$ are the temperature, the entropy, the pressure and the volume, respectively. Therefore, Eq. (1) becomes

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2The concept of heat reservoir is indeed required to set up the formalism of Thermodynamics, and this is sufficiently emphasized in textbooks (see Refs. [1] and [2]). In contrast, the concept of work reservoir is not mentioned very often in the literature. However, an important exception is [3].

3Some authors [2] consider $W$ as a positive quantity when energy leaves the system, following the historical development of Thermodynamics. See, for example, [5]. This paper includes a list of references which use different sign conventions for work.

4Elementary work is generally expressed as the product of a generalized force (intensive variable) by differential of a generalized displacement (extensive variable) (see Ref. [1]). However, by considering $\delta W = -PdV$ we maintain the conceptual generality.


\[ dU = TdS - PdV. \] (2)

Analogously, the variation of the energy of the system neighborhood, \( dU_n \), is given by

\[ dU_n = T_n dS_n - P_n dV_n, \] (3)

where the subscript \( n \) means neighborhood\(^5\). The energy conservation requires that \( dU = -dU_n \) and Eqs. (2) and (3) may be related as

\[ TdS - PdV = -T_n dS_n + P_n dV_n. \] (4)

Even though preceding equation had been obtained by imposing the restrictive condition of reversibility, it will be valid also for an irreversible process, because all quantities involved are state variables. This seems to be a contradiction, and we believe, based on our teaching experience, that this issue is an important source of difficulties.

An inspection of Eq. (4) shows its symmetric character: both sides are mathematically similar and expressed by the same thermodynamic quantities, and their values depend only on the initial and final states. This symmetry is related to the conservation of energy\(^6\).

On the other hand, the symmetry expressed by

\[ T = T_n, \quad P = P_n, \quad \text{and} \quad dV = -dV_n, \] (5)

which could be called process symmetry, leads to the conservation of the entropy, \( dS = -dS_n \).

Equations (5) imply that \( \delta Q = TdS = -T_n dS_n \) and \( \delta W = -PdV = P_n dV_n \), and the process is reversible. The use of reservoirs is redundant, since no extra information is obtained from them, and the system variables are quite sufficient to describe the process.

However, when conditions (5) are not simultaneously satisfied, not all terms in Eq. (4) express heat or work exchanges. In this case the process is irreversible. Both the heat and work reservoir concept become not only useful but also essential to describe the process, and accordingly all phenomena in the neighborhood can be considered reversible and therefore the following equations remain valid,

\[ \delta Q = -T_n dS_n, \] (6)

\[ \delta W = P_n dV_n, \] (7)

in spite of \( \delta Q \neq TdS \) and \( \delta W \neq -PdV \). This explains the contradiction mentioned formerly. Interesting enough, is the fact that the elementary work \( \delta W = P_n dV_n \) does not depend on any variable of the system, and assumes a unifying role since it includes all kinds of work exchanged: both the configuration and the dissipative work. This is important to be pointed out, as the work is expressed by thermodynamic variables of special systems – work reservoirs – that never exhibit irreversible phenomena. Finally, from Eq. (4) we have

\[ dS = -\frac{T_n}{T}dS_n + \frac{P_n}{T}dV_n + \frac{P}{T}dV, \] (8)

which permits to obtain the entropy change for any process, even irreversible, as we will see next.

2. **Simulation of a non-quasi-static process of an ideal gas**

Consider the following problem. An monatomic ideal gas, initially at equilibrium with its neighborhood, is characterized by the variables \( V_i = 0.01 \text{ m}^3, P_i = 10^5 \text{ Pa}, \) and \( T_i = 300 \text{ K} \). The gas is in a diathermic container with a piston, as illustrated in Fig. 1. Suddenly, the pressure and the temperature of the neighborhood are changed to \( P_n = 4 \times 10^5 \text{ Pa} \) and \( T_n = 200 \text{ K} \). Find the entropy change when the final equilibrium state \( (V_f, T_f, P_f) \) is reached.

The final equilibrium is attained when \( T_f = T_n \) and \( P_f = P_n \). It is known\(^1\) that the entropy change for a monatomic ideal gas is given by

\[ \Delta S = \frac{3}{2} n R \ln \left( \frac{T_f}{T_i} \right) - n R \ln \left( \frac{P_f}{P_i} \right), \]

where \( R \) is the molar gas constant and \( n \) is the amount of substance. This formula, which was obtained by recurring to a reversible process between the states \( (T_i, P_i) \) and \( (T_f, P_f) \), gives \( \Delta S = -8.000 \text{ J K}^{-1} \).

The neighborhood entropy change is given\(^1\) by

\[ \Delta S_n = -\frac{1}{T_n} \left[ \frac{3}{2} n R (T_f - T_i) + P_n (V_f - V_i) \right], \]

which gives \( \Delta S_n = 19.168 \text{ J K}^{-1} \).

However, our goal is to obtain the entropy change, both for the system and the neighborhood, without recurring to any auxiliary reversible process. From Eq. (8) and using the state equation \( PV = nRT \) we obtain the equations we have to integrate numerically,

\[ dS = \frac{1}{T} \left[ (P_n dV + \frac{3}{2} n R dT) + \frac{nR}{V} \left( 1 - \frac{P_n}{P} \right) dV \right], \] (9)

\[ dS_n = \frac{1}{T_n} \left[ (P - P_n) dV - TdS \right]. \] (10)

The system attains the final state differently depending on the walls thermal conductivity, on the strength of the friction at the piston, and on the relaxation efficiency of turbulent pressure gradients in the gas\(^2\). Nevertheless, the entropy changes are expected to be exactly the same, irrespective to the way the system

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\(^5\)Eqs. (2) and (3) somehow already incorporate the second law due to the presence of the entropy.

\(^6\)The conservation laws in Physics turn out to be closely connected to symmetries; see \([6]\). In field theory, for instance, Noether’s theorem states that, for each invariance of the lagrangian, there is a conservation law, and vice-versa; see \([7]\).

\(^7\)This consideration goes beyond the ideal gas model. See \([8]\).
reaches the final state, because those changes depend only on the initial and final states and on the external constrains.

Figure 1 - An ideal gas in a diathermic container with a piston. By suddenly changing the initial neighborhood pressure and temperature, the system undertakes an irreversible process till a new equilibrium state is attained.

To simulate the process, we consider a series of infinitesimal changes in the thermodynamic variables which carry the system to the final state, as follows:

Let us consider the volume to be divided in $N_V$ infinitesimal parts, each of which has the volume $dV = V/N_V$. Starting at $V = V_i$, a new value $V_{\text{new}} = V \pm dV$ is computed, taking the + sign if $P_n < P$ and the – sign if $P_n > P$. The temperature variation has two contributions: $dT_1 = (T_n - T)/N_T$ (due to the heat exchange) and $dT_2 = -P_n dV/C_V$ (due to the work exchange), where $C_V = \frac{3}{2}nR$ and $N_T$ is an integer like $N_V$. So, starting at $T = T_i$, a new value $T_{\text{new}} = T + dT_1 + dT_2$ is computed. Finally, a new value of the gas pressure is calculated using the state equation. Then, the new values are taken as the current ones and the procedure is repeated till the conditions $|T - T_n| < 0.1$ and $|P - P_n| < 1.0$ were satisfied as the criterion for the final state reaching.

For each infinitesimal change on $P$, $V$ and $T$ we compute the entropy changes, using Eqs. (9) and (10). By adding up all them, from the initial to the final state, we obtain $\Delta S$ and $\Delta S_n$.

Integers $N_V$ and $N_T$ must be large enough to ensure negligible computational errors. We can simulate an isochoric process ($\delta W = 0$) by considering $N_V \rightarrow \infty$, and an adiabatic one ($\delta Q = 0$) by considering $N_T \rightarrow \infty$. Appropriate choices of $N_V$ and $N_T$ simulate different processes, all irreversible, between the former limiting cases.

Figures 2 and 3 show two simulations, labeled as (a) and (b), performed using Mathematica© for $N_V = 6000$ and two different values of $N_T$, $N_T = 2500$, Figure 2, and $N_T = 200$, Figure 3. The graphs show the time evolution of $P$, $V$, $T$ and $S$, where the unit of time corresponds to a calculation step.

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Figure 2 - Simulation (a): $N_V = 6000$, $N_T = 2500$.

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The Mathematica© notebook simulation program can be downloaded at the address http://home.utad.pt/~anacleto/entropy.nb.
In simulation (b) the gas reaches the final equilibrium much faster than in simulation (a). This happens because in case (a) the walls have a lower thermal conductivity than in the case (b), which explains why the temperature rises over 400 K, due to the strong gas compression, before it decreases reaching the thermal equilibrium at 200 K. As a consequence, the system entropy also rises before it decreases till its final value. In case (b), the situation is reverse, the walls are good heat conductors and the pressure starts decreasing, due to the fast drop in temperature, and then it rises to its final equilibrium value. In both cases the overall entropy changes are the same and agree with the values calculated before, within an error less than 0.05%. We can reduce this error as much as we desire, by considering extremely high values for \( N_V \) and \( N_T \), but at an enormous computation time cost. Lots of simulations for different values of \( N_V \) and \( N_T \) were performed and all of them gave the same entropy changes, showing that all processes considered are equivalent.

The simulations showed that entropy change can indeed be calculated without considering any auxiliary reversible process, and they are also of didactical and pedagogical value, since they can be used to follow the evolution of the gas under a variety of different conditions by adequately choosing the variables values in the program.

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**References**