Thermodynamics super efficiency

Jose Iraides Belandria

Escuela de Ingeniería Química, Universidad de Los Andes, Mérida, Venezuela

Abstract

This article shows a surprising prediction of the global formulation of the second law of thermodynamics that suggests the hypothetical existence of super-efficient thermodynamics processes. Such processes, according to the local formulation of the second law of thermodynamics, may occur as a consequence of an internal entropy coupling between the different systems that make up the universe of the process. In this way, the heuristic combination of the aforementioned formulations predicts the theoretical existence of an operation zone where thermodynamic processes can produce more mechanical work than conventional reversible operations.

Keywords: thermodynamics super efficiency, global formulation, local formulation, second law, entropic coupling.

Introduction

The global formulation of the second law of classical thermodynamics postulated in the nineteenth century from the works of Clausius and others [1-4] states that the differential variation of the entropy of the universe dSu is equal to the additive contribution of the differential of the entropy of the system dS and the differential variation of the entropy of the surroundings dSs. Additionally dSu is greater than or equal to zero. It is greater than zero in the case of irreversible processes and is equal to zero if the processes are reversible, that is,

$$dSu = dS + dSs \geq 0 \quad (1)$$

Regarding the local formulation of the second law of thermodynamics proposed by Prigogine in the mid-twentieth century, the differential variation of the entropy of the system dS is equal to the sum of the differential variation of the entropy flow related to the interactions of the system with the surroundings dSe plus the differential variation of the entropy associated with the internal irreversibility of the system dSi [4].

$$dS = dSe + dSi \quad (2)$$

dSi is greater than zero in the case of irreversible processes, and is equal to zero when the processes are reversible, that is,

$$dSi \geq 0 \quad (3)$$

Based on a combination of the aforementioned formulations, the objective of this paper is to present the theoretical existence of a region of operation in which thermodynamic processes are more efficient than known reversible transformations, suggesting the hypothetical possibility of thermodynamics super efficiency.

Thermodynamics model

To analyze the predictions of the global and local formulation of the second law of thermodynamics on the hypothetical possibility of thermodynamic super efficiency, I will use a simple example in which we estimate the work done during the irreversible isothermal expansion of an ideal monatomic gas in a piston-cylinder. In this example, we will assume that 1 mol of ideal gas expands from an initial pressure P_1 of 2 bar to a final pressure P_2 of 1 bar at the constant temperature of 300 K.

Here, we will consider the ideal gas as an isothermal closed system whose surroundings are constituted by a heat reservoir at a constant temperature equal to 600 K. Also, to simplify the calculations we will neglect the effects of potential and kinetic energy, and we will assume that the cylinder and the piston do not absorb or transmit heat.

Also, for the gas contained in the cylinder-piston, the ideal gas equation is valid [1]

$$PV = n\,RT \qquad (4)$$

Where n, P, V, T and R represent the number of moles, the pressure, volume, temperature and the ideal gas constant, respectively. R equals 8.314 J mol^{-1} K^{-1}.

Results and Discussion

Work estimation according to the global formulation of the second law of thermodynamics

Under the conditions assumed in the previous model, the entropy variation of the system constituted by the ideal gas is given by the following equation [2,3].

$$dS = -n\,R\,dP / P \qquad (5)$$

Also, since the surroundings are constituted by an isothermal heat reservoir operating at constant temperature Ts, then by definition [3] results

$$dSs = dQs / Ts \qquad (6)$$

In this expression dQs is the heat differential transferred through the boundaries of the surroundings.

From an energy balance it is possible to infer that

$$dQs = - dQ \tag{7}$$

In this equation dQ is the heat differential transferred through the system boundaries.

Also, from the first law of thermodynamics [2,3].

$$dU = dQ - dW \tag{8}$$

Where dU is the differential variation of the internal energy of the system and dW is the work differential done by the system. Here, it is considered that the work done by the system is positive. Also, the heat that enters to the system is assumed positive. On the other hand, in the case of the isothermal expansion of an ideal gas dU = 0, which implies that [2,3].

$$dQ = dW \tag{9}$$

Now, combining and integrating equations (1), (5), (6), (7) and (9) we find that the global formulation of the second law of thermodynamics suggests that the irreversible work W performed during the proposed irreversible isothermal expansion is given by the following equation

$$\Delta Su = - n R \, Ln (P_2 / P_1) - W / Ts > 0 \tag{10}$$

That is

$$W < - n R \, Ts \, Ln (P_2 / P_1) \tag{11}$$

After integrating this equation and substituting values, we get

$$W < 3457.69 \text{ J} \tag{12}$$

Work estimation according to the local formulation of the second law of thermodynamics

Similarly, considering the local formulation of the second law of thermodynamics given by equation (2), and noting that in this case the differential variation of the entropy flow associated with the interactions of the system with the surroundings is related only to the heat flow through the system boundaries results [4].

$$dSe = dQ / T \tag{13}$$

In this way, introducing equations (5), (9) and (13) into (2) and integrating we find that for the proposed irreversible transformation

$$\Delta Si = - n R \, Ln (P_2 / P_1) - W / T > 0 \tag{14}$$

Where ΔSi is the internal entropy production of the ideal gas.

From equation (14) we get

$$W < - nR\,T\,Ln\,(P_2 / P_1) \qquad (15)$$

According to this equation, we appreciate that the local formulation of the second law of thermodynamics indicates that the irreversible work W performed during the irreversible isothermal expansion of the ideal gas is

$$W < 1728.85\ J \qquad (16)$$

Comparison of the work estimated by the global and local formulation of the second law of thermodynamics

In principle, we observe that the predictions about the maximum work done by the system are different according to both formulations. Notably, the global formulation (equation 12) predicts that the system can perform a greater amount of work than the value predicted by the local formulation (equation 16) of the second law of thermodynamics.

In this sense, in order to understand and to have a greater clarity about the meaning of the differences observed in the estimated work values, we will evaluate, using the local formulation of the second law of thermodynamics, the entropy production in the different systems that make up the universe of the process.

Estimation of internal entropy production in the different systems of the universe

By doing a thermodynamic analysis in the universe of the process it is possible to detect that there is an internal entropy production ΔSi associated with the irreversible expansion of the ideal gas in the piston -cylinder which is given by equation (14). Also, there is an entropy production ΔSc caused by the transfer of heat from the thermal reservoir whose temperature is Ts to the ideal gas that is at temperature T. This entropy production can be estimated [4] with equation (17).

$$\Delta Sc = Q\,[(1 / T) - (1 / Ts)] \qquad (17)$$

Likewise, it is possible to infer that the production of internal entropy inside the heat reservoir is zero, because by definition of thermal reservoir [3] the changes that occur within an isothermal reservoir during the heat transfer are reversible.

On the other hand, thermodynamics deductions suggest [2] that when a system produces internal entropy dSi, then the potential of the system to perform work decreases and, consequently, there is a lost work Wp whose differential variation is given by the following equation

$$dWp = T\,dSi \qquad (18)$$

Integrating this equation at the constant temperature of the system results

$$Wp = T\,\Delta Si \qquad (19)$$

Alike, it is possible to deduce that the relation between the reversible work Wr, the irreversible work W and the lost work Wp is defined by the following expression [2].

$$Wp = Wr - W \tag{20}$$

Where Wr and W are the reversible work and the irreversible work, respectively, done by the system between the same initial and final states.

For the proposed case, the reversible work Wr performed between the same initial and final state of the irreversible system can be estimated [2] by integrating the following equation.

$$dWr = PdV \tag{21}$$

Combining equations (4) and (21) and integrating it is found that if the gas is reversibly expanded at the temperature of 300 K from 2 bar to 1 bar, the reversible work Wr is

$$Wr = 1728.85 \text{ J} \tag{22}$$

Also, combining the expressions (19), (20) and (22), it is found that the irreversible work W obtained when the ideal gas expands irreversibly at 300 K is given by the following expression.

$$W = 1728.85 \text{ (J)} - 300 \text{ (K)} \, \Delta Si \text{ (J / K)} \tag{23}$$

Estimation of the internal entropy production in the range W <1728.85 J predicted by the local formulation of the second law of thermodynamics. Lost work

Integrating equations (10), (14) and (17) we observe that in the range where W is less than 1728.85 J, the internal entropy production ΔSi during the expansion of the ideal gas in the piston-cylinder is greater than zero. Also, the internal entropy production associated with the transfer of heat from the thermal reservoir to the ideal gas contained in the piston-cylinder ΔSc is greater than zero. Likewise, the variation of the entropy of the universe ΔSu is greater than zero.

Here, we also appreciate that as the work W produced increases from 0 J to 1728.87J, the internal entropy production in the piston-cylinder ΔSi decreases gradually from a value of 5.766 J / K to a value tending to 0 J / K, respectively. That is, as the system performs more mechanical work ΔSi decreases. In the same way, the production of internal entropy associated with the transfer of heat from the heat reservoir to the ideal gas ΔSc progressively increases from 0 J / K and tends to 2,881 J / K, respectively. Analogously, the variation of the entropy of the universe ΔSu decreases from 5.766J / K and tends to 2.881 J / K in the aforementioned range.

Likewise, considering the application of equation (19) we see that there is a lost work Wp associated with the positive production of internal entropy of the system ΔSi. As a consequence[2], the system loses its capacity to perform work with respect to the reversible work executed between the same initial and final states whose value is equal to Wr = 1728.85J. In the mentioned range, the lost work Wp decreases from 1728.85 J and tends to 0 J.

Under these conditions, according to equation (23) the work done by the irreversible process is less than 1728.85 J, and its value decreases as the production of internal entropy ΔSi increases due to the internal irreversibility of the system.

Estimation of the internal entropy production in the range W <3457.69 J predicted by the global formulation of the second law of thermodynamics. Lost work and gained work . Entropic coupling. Thermodynamics super efficiency.

To facilitate the interpretation of the results we can divide into two intervals the range where W is less than 3457.69 J. The first interval corresponds to the range where W is less than 1728.85 J. The second interval corresponds to the case where W is less than 3457.69 J, but greater than or equal to 1728.85 J

The analysis on the production of internal entropy in the first interval where W is less than 1728.85 J, coincides with the analysis previously made on the local formulation of the second law of thermodynamics in which we appreciate that the production of internal entropy ΔSi during the expansion of the ideal gas in the piston-cylinder is greater than zero. Likewise, the production of internal entropy related to the transfer of heat from the thermal reservoir to the ideal gas contained in the piston-cylinder ΔSc is greater than zero. In the same way, the variation of the entropy of the universe ΔSu is greater than zero. Now, considering the application of equation (19) we detect that there is a lost work Wp accompanying the positive production of internal entropy of the system ΔSi; as a consequence [2] , the system loses its ability to perform work. In these circumstances, the work done by the irreversible process according to equation (23) is less than 1728.85 J.

Following an approach similar to that previously illustrated, we see that in the second interval where W is less than 3457.69 J, but greater than or equal to 1728. 85J, the internal entropy production of the ideal gas contained in the piston-cylinder is zero or negative. However, the entropy production associated with the heat transfer ΔSc from the thermal reservoir to the ideal gas contained in the piston-cylinder is positive and compensates sufficiently the negative entropy production ΔSi detected within the ideal gas process expansion. In the same way, the variation of the entropy of the universe is greater than zero. Also, we detect that when W equals 1728. 85J, the internal entropy production ΔSi during the expansion of the ideal gas is 0 J / K; the entropy production linked to the heat transfer ΔSc from the thermal reservoir to the ideal gas contained in the piston-cylinder is 2881 J / K; and the variation of the entropy of the universe ΔSu is 2881 J / K. As well, we notice that as W increases from 1728. 85J to values lower than 3457.69 J, the internal entropy production of the ideal gas ΔSi becomes more negative and ranges from 0 J / K to -5.763 J / K. In compensation, the production of internal entropy associated with the transfer of heat from the thermal reservoir to the ideal gas ΔSc grows from 2.881J / K and tends to 5.763 J / K. Also, the variation of the entropy of the universe ΔSu, is positive and approaches 0 J / K, from an initial value of 2881 J / K. On the other hand, in this interval we observed, notoriously, that the lost work Wp predicted by equation (19) is zero or negative because the entropy production ΔSi is zero or negative. Consequently, the work done by the system W according to equation (23) is equal to or greater than the reversible work Wr performed by the system operating isothermally at 300 K. In the mentioned range Wp decreases from 0 J to -1728.85 J. This is a surprising result that can be interpreted assuming that in this range the system gains a certain amount of work Wg because the work lost Wp is negative as a consequence of the production of negative entropy. In this sense, equation (24) can be inferred using equation (19)

$$Wg = - Wp = -T \Delta Si \quad (24)$$

As previously mentioned, when the lost work Wp is positive the system loses its capacity or its potential to perform mechanical work [2] . Then, by analogy, when the lost work Wp is negative, the potential of the system to perform work increases thanks to the work gained Wg due to the negative entropy production. Combining equations (20) and (24) follows that in these circumstances the work W performed by the system is greater than the reversible work and it is given by equation (25)

$$W = Wr + Wg \quad (25)$$

Under these conditions, the system is thermodynamically super efficient, since it is capable of producing a greater amount of work than the corresponding reversible operation.

Internal entropy coupling

The existence of this process in the second interval where W is less than 3457.69 J, but greater than or equal to 1728. 85J can be explained by arguing the possibility of an internal entropy coupling between the process that produces positive entropy and the process that simultaneously produces negative entropy. Such entropic coupling has been observed in some processes such as thermo diffusion where a temperature gradient produces enough positive entropy to induce a concentration gradient that produces negative entropy [4]. In our case, the positive entropy producing process is associated with the temperature gradient between the thermal reservoir and the ideal gas which produces sufficient internal entropy ΔSc to induce the negative entropy producing process represented by the isothermal expansion of the ideal gas in the piston-cylinder which produces negative entropy ΔSi. Under these conditions, the positive entropy producing process induces the occurrence of the negative entropy producing process. In this context, the total production of entropy must be positive [4], that is,

$$\Delta Sc + \Delta Si > 0 \quad (26)$$

It is convenient to point out that the predictions observed in this simple example have been detected in other cases [5] where we perceive that the global formulation of the second law of thermodynamics predicts a hypothetical operating region in which conventional processes can operate super efficiently using an irreversible trajectory as in the illustrated case.

Conclusion

The combination of the global and local formulation of the second law of thermodynamics suggests the hypothetical existence of a set of conditions where thermodynamic processes can operate more efficiently than conventional reversible operations. Such a prediction theoretically suggests the possibility of thermodynamics super efficiency that may be achieved thanks to an internal entropy coupling between the different systems that make up the universe of the process.

References

1. De Voe H. A Comparison of local and global formulations of thermodynamics. J. Chem. Educ., 2013, 90 (5).

2. Smith JM, Van Ness HC, Abbot MM. Introduction to Chemical engineering Thermodynamics, Sixth edition, McGraw-Hill, Inc. New York, 2001

3. Zemansky M W, Van Ness H C. Basic engineering thermodynamics. McGraw Hill, Inc. New York, 1966

4. Prigogine I. Thermodynamic of Irreversible process, Third Edition, Interscience publishers, New York, 1955.

5. Belandria JI. J. Chem. Educ., 1995.72, 116-118 .