

# An Exceptional Theoretical Process with Internal Entropy Coupling

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The laws of thermodynamics regulate the existence of processes in the real world and for any process to be possible it must fit the requirements of these laws (1, 2).

The second law of thermodynamics postulates that in all permitted processes the total entropy change of the universe is equal to or greater than zero (1-4). If the processes are reversible such variation is zero and when the processes are irreversible the total change of entropy of the universe is greater than zero. This happens because in all irreversible transformations there is a creation of entropy while in a reversible process the creation of entropy is null (3-6). The second law also implies that the created entropy accumulates in the universe and never can be destroyed in any part of a one-component closed system (5). However, in open systems entropy can be created in some regions and destroyed in other regions and the process occurs by means of an entropy coupling as seen in some biological processes or in thermo diffusion (5). A similar situation may occur in multicomponent systems with coupled chemical reactions (5).

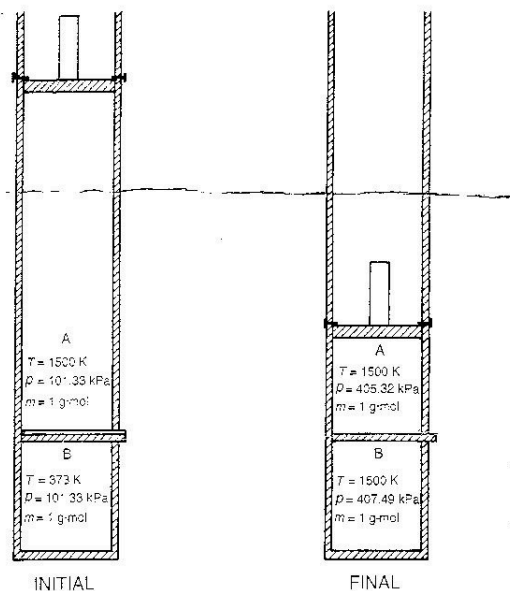
In this article there is proposed a closed theoretical process, permitted by thermodynamic laws, in which there is a set of conditions where internal entropy is created and destroyed during the operation. In this region the process is more efficient than a reversible process carried out between the same change of state, and it may be suggested that the process takes place by means of an entropy coupling between the systems involved.

## The Process

The equipment shown in the figure consists of two adiabatic tanks, A and B, separated by a partition composed of a good heat-conducting metal covered with an adiabatic film. The adiabatic film of the partition can be removed or put back in place during process operation if desired. Tank A is fitted with a piston and tank B is a rigid box. In both tanks there is 1 g-mol of a monoatomic ideal gas.

Initially the metal partition is covered with the adiabatic film. Then, the ideal gas in A is set at 1500 K and 101.33 kPa and the ideal gas in B is set at 373 K and 101.33 kPa. When these conditions are reached in both tanks the adiabatic film is removed and the following process starts. In tank A the gas is compressed isothermally in a nonreversible way at 1500 K from 101.33 kPa to 405.32 kPa, and work is done on the ideal gas, and heat is transferred through the metal partition to the ideal gas in tank B. The gas temperature of B increases; when the compression is stopped the temperature in B is 1500 K. Then, the process is finished and the adiabatic film of the partition is put back in place again. Since tank B is rigid and there is no piston, then no work is involved in the process occurring in this tank.

During the process heat is transferred only between gases and there are no heat losses to the surroundings because the boundaries of the tanks in contact with the surroundings are adiabatic.



The theoretical process discussed in this paper.

## Application of the First and Second Law of Thermodynamics

For a process to be possible it must meet the requirements of the first and second laws of thermodynamics, which can be expressed in the following way for the process under discussion.

The universe of the process can be assumed to be formed by system A, system B, system M, and the surroundings S. System A is a closed system formed by tank A, the gas inside, and the piston enclosed in this tank. System B is also closed and consists of tank B and the gas inside this tank. System M is the dividing metal partition located between the tanks, which is also a closed system.

### First Law of Thermodynamics

Neglecting the changes of kinetic and potential energy the first law can be expressed in the following way for each of the above closed systems. In these equations heat transferred to the system is considered positive and work done on the system is negative.

System A

$$Q_A - W_A = \Delta U_A$$

(1)

where  $Q_A$  and  $W_A$  are the heat and work transferred through the boundaries of system A during the change of state and  $\Delta U_A$  is the internal energy change of the process. If the mass of the walls of tank A and the mass of the piston are neglectable, then

$$\Delta U_A = M_A C_{VA} (T_{2A} - T_{1A}) \quad (2)$$

where  $M_A$  is the mass of the ideal gas in tank A,  $C_{VA}$  is the constant volume ideal gas heat capacity, and  $T_{1A}$  and  $T_{2A}$  are the initial and final temperature in tank A.

Tank A is isothermal, therefore

$$\Delta U_A = 0 \text{ J} \quad (3)$$

and

$$Q_A = W_A \quad (4)$$

Since the process in tank A is nonreversible,  $W_A$  cannot be calculated from the usual  $P$ - $V$  work relationship employed for reversible closed systems and should be obtained from the interrelation of the energy balances between the systems.

*System B*

$$Q_B - W_B = \Delta U_B \quad (5)$$

where  $Q_B$  and  $W_B$  are the heat and work transferred through the boundaries of tank B and  $\Delta U$  is the change of internal energy in tank B during the change of state.

The process in tank B takes place at constant volume so

$$W_B = 0 \text{ J} \quad (6)$$

and

$$Q_B = \Delta U_B \quad (7)$$

If the mass of the walls of tank B are neglected then

$$\Delta U_B = M_B C_{VB} (T_{2B} - T_{1B}) \quad (8)$$

where  $M_B$  is the mass of the ideal gas in tank B,  $C_{VB}$  is the ideal gas heat capacity at constant volume and  $T_{1B}$  and  $T_{2B}$  are the initial and final temperature of tank B.

For the conditions given in the figure

$$\begin{aligned} \Delta U_B &= 1 \text{ g-mol} (12.47 \text{ J g-mol}^{-1} \text{ K}^{-1}) (1500 - 373) \text{ K} \\ &= 14,053.69 \text{ J} \end{aligned} \quad (9)$$

and

$$Q_B = 14,053.69 \text{ J} \quad (10)$$

*System M*

The metal partition can be assumed as a film of negligible mass that receives heat from tank A and transfers it to tank B without accumulation of energy, then

$$Q_A = -Q_B \quad (11)$$

and from eq 4

$$W_A = -M_B C_{VB} (T_{2B} - T_{1B}) \quad (12)$$

For the process in the figure and from eqs 11 and 12,

$$Q_A = -14,053.69 \text{ J} \quad (13)$$

and

$$W_A = -14,053.69 \text{ J} \quad (14)$$

*Second Law of Thermodynamics*

The second law of classical thermodynamics postulates that the total entropy change of the universe is equal or greater than zero in all thermodynamically permitted processes.

$$\Delta S_{\text{univ}} \geq 0 \quad (15)$$

where  $S_{\text{univ}}$  is the total entropy change of the universe.

In this case,

$$\Delta S_{\text{univ}} = \Delta S_A + \Delta S_B + \Delta S_M + \Delta S_S \quad (16)$$

where,  $\Delta S_A$ ,  $\Delta S_B$ ,  $\Delta S_M$ , and  $\Delta S_S$  are the change of entropy of systems A, B, M, and surroundings S during the change of state.

Since A, B, M, and S are closed systems, the change of entropy in each of the above systems can be estimated by the following equation

$$\Delta S = \int \frac{\partial Q}{T} + \Delta S_g \quad (17)$$

where  $\Delta S$  is the entropy change of the system,  $Q$  is the heat transferred through the system boundaries during the process,  $T$  is the system temperature, and  $\Delta S_g$  is the internal entropy created by the irreversibilities.

*System A*

$$\Delta S_A = \int_{T_{1A}}^{T_{2A}} M_A C_{PA} \frac{dT}{T} - \int_{P_{1A}}^{P_{2A}} M_A R \frac{dP}{P} \quad (18)$$

where  $C_{PA}$  is the ideal gas heat capacity at constant pressure,  $R$  is the gas constant,  $P$  is the gas pressure and  $P_{1A}$  and  $P_{2A}$  are the initial and final pressure in tank A.

The creation of entropy in tank A can then be evaluated with eq 17

$$\Delta S_{gA} = \Delta S_A - \int \frac{\partial Q_A}{T_A} \quad (19)$$

where  $\Delta S_{gA}$  is the internal entropy created in tank A during the change of state and  $T_A$  is the temperature in tank A.

Using the conditions presented in the figure,

$$\begin{aligned} \Delta S_A &= -1 \text{ g-mol} (8.314 \text{ J g-mol}^{-1} \text{ K}^{-1}) \ln \frac{405.32 \text{ kPa}}{101.33 \text{ kPa}} \\ &= -11.53 \text{ J K}^{-1} \end{aligned} \quad (20)$$

and

$$\Delta S_{gA} = -11.53 \text{ J K}^{-1} + \frac{14,053.69 \text{ J}}{1500 \text{ K}} = -2.16 \text{ J K}^{-1} \quad (21)$$

then there is a destruction of entropy in tank A during the change of state depicted in the figure.

*System B*

$$\Delta S_B = \int_{T_{1B}}^{T_{2B}} M_B C_{VB} \frac{dT}{T} + \int_{V_{1B}}^{V_{2B}} M_B R \frac{dV}{V} \quad (22)$$

where  $V$  is the gas volume and  $V_{1B}$  and  $V_{2B}$  are the initial and final volume in tank B.

$$\Delta S_{gB} = \Delta S_B - \int \frac{\partial Q_B}{T_B} \quad (23)$$

where  $\Delta S_{gB}$  is the internal entropy created during the change of state in tank B and  $T_B$  is the temperature in B.

Applying the above equations for the process in the figure gives

$$\Delta S_B = 1 \text{ g-mol} (12.47 \text{ J g-mol}^{-1} \text{ K}^{-1}) \ln \frac{1500 \text{ K}}{373 \text{ K}} = 17.36 \text{ J K}^{-1} \quad (24)$$

and

$$\begin{aligned} \Delta S_{gB} &= 17.36 \text{ J K}^{-1} - 1 \text{ g-mol} (12.47 \text{ J g-mol}^{-1} \text{ K}^{-1}) \ln \frac{1500 \text{ K}}{373 \text{ K}} \\ &= 0 \text{ J K}^{-1} \end{aligned} \quad (25)$$

Therefore there is neither creation nor destruction of entropy in tank B.

### System M

To simplify the solution, the metal partition can be considered as a metallic film of negligible mass that receives heat from tank A and transfers it to tank B without accumulation of heat and entropy. Under this consideration

$$\Delta S_M = 0 \text{ J K}^{-1} \quad (26)$$

and

$$\Delta S_{gM} = \Delta S_M - \left( \int \frac{\partial Q_A}{T_A} + \int \frac{\partial Q_B}{T_B} \right) \quad (27)$$

where  $\Delta S_{gM}$  is the entropy created in the metal partition during the change of state.

For the process described in the figure

$$\Delta S_M = 0 \text{ J K}^{-1} \quad (28)$$

and

$$\begin{aligned} \Delta S_{gM} &= 1 \text{ g-mol} (12.47 \text{ J g-mol}^{-1} \text{ K}^{-1}) \\ &\times \left[ -\frac{(1500 - 373) \text{ K}}{1500 \text{ K}} + \ln \frac{1500 \text{ K}}{373 \text{ K}} \right] \\ &= 7.99 \text{ J K}^{-1} \end{aligned} \quad (29)$$

The calculation shows that there is a creation of entropy in the metal partition M during the process.

### Surroundings S

Since the piston and the tank walls are externally adiabatic then there are no heat losses to the surroundings. Also, it can be assumed, to simplify the solution, that there are no irreversible processes happening in the surroundings and, therefore, the internal entropy created in the surroundings during the change of state is negligible. Under these assumptions,

$$\Delta S_S = 0 \text{ JK}^{-1} \quad (30)$$

and

$$\Delta S_{gS} = 0 \text{ JK}^{-1} \quad (31)$$

where  $S_{gS}$  is the internal entropy change of the surroundings.

Therefore, for the process represented in the figure the total entropy change of the universe will be, according to eq 17

$$\Delta S_{\text{univ}} = 5.83 \text{ J K}^{-1} \quad (32)$$

This result suggests that the process depicted in the figure is permitted by thermodynamics and there is a destruction of entropy in tank A and a creation of entropy in the metal partition M. In tank B there is neither creation nor destruction of entropy.

### Discussion

In order to generalize the results and understand better the behavior of the process above, equations can be expressed in terms of the initial temperature in tank A.

Given the initial and final pressure in tank A and the trajectory of the process in this tank and given the initial and final conditions in tank B as shown in the figure, it is possible to demonstrate that the above equations can be expressed in terms of the initial temperature in tank A in the following way:

$$\Delta U_A = 0 \quad (33)$$

$$\Delta U_B = 12.47T_{1A} - 4651.31 \quad (34)$$

$$Q_B = 12.47T_{1A} - 4651.31 \quad (35)$$

$$Q_A = -12.47T_{1A} + 4651.31 \quad (36)$$

$$W_B = 0 \quad (37)$$

$$W_A = -12.47T_{1A} + 4651.31 \quad (38)$$

$$\Delta S_{\text{univ}} = -85.36 + 12.47 \ln T_{1A} \quad (39)$$

$$\Delta S_{gA} = \frac{0.94T_{1A} - 4651.31}{T_{1A}} \quad (40)$$

$$\Delta S_{gB} = 0 \quad (41)$$

$$\Delta S_{gM} = -86.31 + \frac{4651.31}{T_{1A}} + 12.47 \ln T_{1A} \quad (42)$$

From these equations it is possible to see that, for initial temperatures in tank A greater than 4948.20 K, the process is permitted by thermodynamics, and there is a creation of entropy in system A and system M. In system B there is neither creation nor destruction of entropy.

The equations also show that, if the initial temperature in tank A is between 940.14 K and 4948.20 K, the process is permitted by thermodynamics since the total entropy change of the universe is greater than zero, but there is a destruction of entropy in tank A and creation of entropy in the metal partition M. In system B there is neither creation nor destruction of entropy.

Analyzing the process, it can be seen that the destruction of entropy in tank A is compensated by a sufficient generation of entropy in the metal partition M, and the process may occur with an internal entropy coupling between the systems involved.

Under these conditions the compression process occurring in tank A is more efficient than a reversible compression process for the same change of state. For the conditions given in the figure the work required by the compression process under entropy coupling can be calculated with eq 12 and the value is -14,053.69 J. By comparison, the reversible work required for the same isothermal compression process is -17,288.48 J. These values suggest that a compression system similar to the one in the figure operating in the region of entropy coupling will be thermodynamically more efficient than a reversible compression process between the same change of state. This behavior is exceptional in its nature and takes place because of the internal entropy coupling suggested in this one-component closed system.

For temperatures below 940.14 K the process is not permitted by thermodynamics because the total entropy change of the universe is less than zero.

### Conclusion

In this work a theoretical process that meets the requisites of the first and second law of thermodynamics was demonstrated to have a set of conditions where there is a destruction of entropy in one region of the universe and a creation entropy in another part of the universe. Under such conditions the process may take place with internal entropy coupling and the compression process is more efficient than a reversible compression taking place for the same change of state. This kind of behavior is uncommon and has not been observed in similar one-component closed systems.

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