

## Revisiting an exceptional theoretical process with internal entropy coupling

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A few years ago, I published in the Journal of Chemical Education an article titled "An Exceptional Theoretical Process with Internal Entropy Coupling" (1) that generated a discussion and a collective reply by Robert Freeman and other critics (2).

Because of the considerations expressed in the mentioned reply, I would like to respond some questions they ask in the collective response to which I did not have the opportunity to answer, and to argument that I used a legitimate thermodynamic procedure to find the final pressure in tank A. Therefore, I am going to demonstrate with new arguments, that the process described in the mentioned article, although difficult to prove or to set up experimentally, is theoretically correct, and not wrong as they said in that response.

To start, they say that "eq. 27 for  $\Delta S_{gM}$  is logically inconsistent, and it is arithmetically incompatible with eq. 29. If a minus sign is inserted these difficulties are eliminated". Indeed, as they say, and I detected, there is a transcription error ( besides of this error, there are other minor transcriptions errors in some words) and a minus sign is required before each integral sign in eq. 27 of my original article (1). However, I used the right sign when I did the calculations with eq. 29 which is logically and arithmetically correct. They add "eq. 42b has the needed signs before the integral signs.....Olivares and Colmenares (2)

provide a detailed discussion of the errors in JB's eq 42b". Almost, at the end of their reply, they refer to the same questioning by indicating: " Finally, Olivares and Colmenares(3) have argued persuasively that JB's application ( entropy " creation and destruction) of Prigogine's formulation of entropy production is not valid". To this regard, I would like to say that eq. 27 (with the required minus sign), eq.29 and eq. 42b are logically consistent and there are not errors in their derivation. That equation describes the entropy production due to heat flow through a partition, and it is similar to equation (3. 16) derived by Prigogine in his book "Thermodynamics of Irreversible Processes " (3), for the heat flow through a partition with negligible mass, located between two regions at uniform temperature  $T'$  and  $T''$ . The only difference with Prigogine's model, is that in my case, one region is at a uniform temperature  $T_A$  and the other is at a variable temperature  $T_B$ . With this consideration I got eq.29. or eq.42b for the production of internal entropy due to heat flow through a metal partition with negligible mass. Therefore, if we believe in Prigogine, Nobel Prize of chemistry and one of the most remarkable non classical thermodynamicists of the world, all of the equations in my original article (1) are logically consistent, and the deductions of Olivares et al.(2) related to eq.27, eq. 29 and eq.42b are wrong.

Other question that the critics focused was related to the procedure for getting the final pressure in tank A. The referees wonder " ¿ How can we get that value? . From what is given above, one cannot. To obtain the correct value for the final pressure in A one must ( i ) measure it, or ( ii) specify the compression process in sufficient detail that the final pressure maybe determined . JB's specification (1) of the compression process as isothermally in a nonreversible way is not sufficient ". It seems to me, that the referees did not realize that

besides the specification of "isothermal in a nonreversible way", in other words, besides knowing the final temperature, I defined the path to reach the given final state by specifying its total entropy change that measure the degree of irreversibility of the trajectory. At this point, I would like to mention that any trajectory of a process can be specified, directly, by its mathematical equation in terms of pressure, temperature and volume, or , indirectly, by the degree of irreversibility of the path, defined by its total entropy change and its temperature or pressure. I have used this last alternative to design my process, in the range of allowed thermodynamic paths. Now, I am going to explain the details of the procedure to get the final pressure in tank A . The first thing I did was to find the final pressure values admitted by thermodynamics using eq. 39b. Since, we know the final temperature we can determine easily what final pressure values gives a total entropy change of the universe equal or greater than zero. For the "connected tanks case", I find that for final pressures below 6.55 bars, the total entropy change of the universe is equal or greater than zero. Therefore, these final pressure values are allowed by second law of thermodynamics. It is evident that each final state is reached by a specific path characterized by a certain degree of irreversibility defined by the total entropy change of the universe of each path and its final temperature. The value of the final pressure attained by the system is not a matter of chance , as the critics wonder. Nature knows what final pressure value to reach according to the final temperature and the degree of irreversibility of each path, defined by its total entropy change . Also, using eq.39b, combined with eq.40b and eq.42b, we can see that for any value greater than 2.92 bar and less than 6.55 bar ,  $\Delta S_u$  is positive,  $\Delta S_{gA}$  is negative ( entropy is destroyed or absorpted) and  $\Delta S_{gM}$  is positive ( entropy is created or produced). In this range of pressures, internal entropy coupling takes

place. For pressures below 2.92 bar,  $\Delta S_u$  is positive,  $\Delta S_gA$  is positive and  $\Delta S_gM$  is positive. In this region the process behaves according to classical thermodynamics expectations. Above 6.55 bar, the process is not allowed by thermodynamic laws.

As I said, each final state is reached by a trajectory characterized by its total entropy change which I know from above equations, in terms of the final pressure of tank A. Therefore, in order to make a thermodynamic model or a prediction, I do not need to know the mathematical equation of the trajectory in a P-V scheme, because I already know the total entropy change of each path as a function of the final pressure of tank A. With this in mind, we can choose any specific trajectory allowed by thermodynamics. For example, let us to select a path defined by a total entropy change,  $\Delta S_u$  equal to 9.57 J/K. From above equations, this path is allowed by thermodynamics and may reach a final state at 2.07 bar and 1400K, located in the classical region, where entropy is created in all of the systems of the universe. To carry out this transformation the compression work required is - 12.47 kJ . If the process were carried out reversibly it would require - 8.47 kJ of work, in agreement with classical thermodynamic expectations. Now , we can try to find a trajectory to carry out the indicated change of state. In order to do that, we need to develop a trial and error procedure, which starts by assuming a possible equation for the path in terms of P, V, T variables. Then we test if the equation fits the specification of the change of state and the work requirement. If the assumed equation fits these requirements then we have found a possible trajectory for the process, but if the equation does not fit the requirements, we have to choose other path, and repeat the procedure. For example, one possible trajectory to carry out the above change of state is an isothermal path with a constant external pressure equal to

2.07 bar. In this case is relatively easy to find the trajectory, but in other cases we need a trial and error procedure that may take a long time to get a solution. What I try to point out with this example, is that, if we know the total entropy change of the trajectory and the final temperature, the final state is completely defined, to such an extent that we may be able to find its trajectory by a trial and error procedure. Other path that we can analyze is the one in which the total entropy change,  $\Delta S_u$ , is 6.71 J/k. This trajectory is permitted by thermodynamics and may arrive at a final state at 2.92 bar and 1400K. For this trajectory  $\Delta S_{gA}$  is zero and  $\Delta S_{gM}$  is 6.71 J/K. By inspection, we find that this state may be reached by an isothermal path, where the external pressure is equal to the gas pressure. This trajectory requires -12.47 kJ of compression work, which is the same amount of work required for a conventional reversible isothermal compression. Now, let us to analyze a path characterized by a total entropy change of the universe,  $\Delta S_u$ , equal to 5 J/K. According to above equations, this path is permitted by thermodynamics and may reach a final state at 3.59 bars and 1400 K, located in the internal entropy coupling region. The compression work required by this transformation is -12.47 kJ. If the same change of state is conducted by a reversible isothermal compression it requires a work equal to -14.87 kJ. Therefore, the irreversible isothermal compression under internal entropy coupling conditions is more efficient than a conventional isothermal reversible compression between the same initial and final states. This behavior, may be due to the internal entropy coupling that allows the possibility of converting the internal entropy destruction in tank A into useful compression work. As, I communicated to Freeman et al., there are infinite final pressure values in that region that show an exceptional behavior and may be reached by an specific trajectory, according to

second law expectations. Now, by using a similar procedure, I found the final pressure in my original article ( 1 ). I said, let us take a trajectory allowed by thermodynamics, defined by a total entropy change of the universe,  $\Delta S_u$ , equal to 5.83 J / K and a final temperature of 1500K. Then, by using eq. 16 of my original article (1) and by employing a similar modus operandi, I found that a final pressure of 405.32 kPa may be reached in the internal entropy coupling zone, and according to thermodynamics laws, it may exist a path to reach such a final state at 405.32 kPa and 1500K, with a compression work equal to -14,053.69J. Afterwards, I predicted what would happen if the process reach this state. To analyze this prediction and to make a thermodynamic model of the indicated process, I only need to know the relationship between the total entropy change of the possible path, used to reach each final state, and the final temperature in tank A. Since we know this information, then from above equations we can define without ambiguity the final state reached by each allowed thermodynamic path, and by a trial and error procedure, we may find the mathematical equation of the specific trajectory, as I explained in above paragraphs. I think this is a legitimate scheme to predict the final pressure in tank A, to define completely the final state of each possible path, and to make a thermodynamic model of the process. This was the main objective of my work. No more than that. The important fact, is that, according to thermodynamics laws the final state indicated in my article (1) may be reached by an eventual path.

They also comment about the limits of the final pressure in tank A: " However, we can easily place some limits on the final pressure in tank A . If the compression is assumed to be reversible,  $P_{Af}$  may be calculated from :

$$W_A = - RT \ln ( P_{Af} / P_{Ai} ) \quad (1)$$

The result is 2.92 bar ". Other comment says " He also ignores the fact that, independent of his criteria about entropy creation and destruction there are constraints on the possible final pressure on A – constraints that can not be hand-waved away with appeals of entropy coupling Tykodi (3) and Olivares and Colmenares (3) have given simple mechanical, non thermodynamic arguments that show that JB's values for the final pressure in A (1) to be impossible". In reference to this matter, the limits of pressure of this process can not be obtained using the classical equations of P-V work , as critics did using eq. 1 , because that equation is valid for classical thermodynamics processes that creates internal entropy, only. They should use the following equation that allows the possibility of incorporating the effect of internal entropy destruction:

$$W_A = \int P_A dV - \int T_A d S_{gA} \quad ( 2 )$$

This equation can be obtained by combining eq.38b and eq. 40b. That equation suggests that the compression under internal entropy coupling may reach higher pressure values than 2.92 bar in the connected tanks case. They cannot, reasonably, use the classical equation of work or classical mechanics arguments, when my claim is based on the proposition that such equations and arguments does not apply to the exceptional condition of the system.

Similarly, this process can not be represented by a conventional path on a P-V plot because that graph is unique for classical thermodynamic processes that creates internal entropy, exclusively.

Other consideration about the final pressure in tank A is related to the " separated tanks case". As they express " the scenario is very similar to the "connected tank case" ....However, now tank A and Tank B are separated ". They conclude " If the gas in tank A is compressed isothermally, as specified, then the final pressure in A is the same for

both cases, connected or separated". This is not true, because above cases have a different geometrical arrangement that affect the entropy profile of the process. For example, in the "separated case" there is not possibility for an internal entropy coupling process, because, simply, tanks are separated. Therefore, both systems have a different entropy behavior and achieve different final conditions. In general the behavior of a interconnected system is different to the behavior of its separated parts.

A third objection is related to the concept of isothermal processes. The referees say " He (JB) also states that isothermally means that the temperature is constant or almost constant throughout the process. He does not elaborate on the meaning of "almost" in this context ( e.g 0.1, 1.0, 10.000 ?? + - Kelvin ). Well, what I wanted to say with the word "almost constant" is that in an isothermal process the temperature may vary within the limits of infinitesimal amounts.

They also comment " However, the implication that there is a gradient in the connected tanks case contradicts the stated specifications (1), namely, the compression process in A occurs isothermally . In the connected tanks case, the gases are at different temperatures; there must a gradient somewhere. But if the gas in A is compressed isothermally, as JB specifies , there can be no gradient within the gas, and the surface of the partition M must be at the temperature of the gas. Hence, the gradient must lie totally within the partition M and can have no effect on the final pressure of the gas". In regard to this point, it is clear from the conditions of the process (1) that the temperature gradient is between the gas in tank A , which is at 1500K, and the gas in tank B, where the temperature varies from 373 to 1500K. But inside of tank A there are not finite temperature gradients and it is isothermal as stated in the article(1). The temperature is kept



constant by pushing the piston at such a rate to avoid the evolution of finite temperature gradients within tank A, as it is done in real isothermal compression systems.

They continue "Further in an isothermal compression, the path of the state of the gas as represented on a P-V plot, is -obviously- along an isotherm; as Battino and Wood have noted (2), this is the path followed by the system (gas A) during a reversible (and isothermal) compression; that is, isothermal compressions and expansions are inherently reversible. Therefore, JB's specification that the compression of A occur isothermally in a nonreversible way is self contradictory". In other words, they suggest that irreversible processes can not be isothermal or process in tank A is not isothermal because it is irreversible. This opinion is erroneous because most of the industrial isothermal processes are irreversible, including expansions and compressions, and are treated for engineering design and construction as isothermal. Chemical and mechanical engineering textbooks are full of irreversible isothermal expansion or compression processes. As examples of irreversible expansion and compression isothermal processes, we can visualize problem 5-26 from the book "Introduction to Chemical Engineering Thermodynamics" of J.M Smith and H. C. Van Ness (4), and problems 2.12 and 2.13 from the book "Thermodynamics" of M.M. Abbott and H.C. Van Ness (5).

Then, Freeman et. al express "JB's values for the final pressure in a for the connected case (1, his Dec. 13 letter) is based on at least two contradictions: (i) temperature gradients during an isothermal process; and (ii) an isothermal compression occurring in a nonreversible way". As I have explained in the above last two paragraphs there are not doubts related to the isothermal behavior of tank A or to the

possibility of existence of irreversible isothermal processes. Therefore, there are not contradictions in the proposed process.

Now, I would like to refer to a last point related to the fact that all of the referees of the collective response are experienced thermodynamicists, but, apparently, they do not know about the possibility of existence of internal entropy coupling processes that may take place in non classical thermodynamics events. Some of these ideas appear in Prigogine's books "Thermodynamics of Irreversible Processes" (3) and "The End of Certainty" (6) that talks about the production and destruction of internal entropy.

Finally, with this letter I intend to show that the procedure I used to predict a possible final pressure for tank A is a legitimate thermodynamic scheme for the objective of my article (1). The process maybe difficult to prove and to carry out experimentally, and the trajectory maybe hard and not easy to find, but the process is fundamentally right and not incorrect as Freeman et al. concluded.

#### LITERATURE CITED

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