Extension on the Gibbs Paradox

Violation of the second law of thermodynamics?

There are several versions and continuous discussion of the so-called Gibbs paradox. In this paper we are not trying to prove one more time that there is no paradox or that there is one, but to prove that similarity of different gases, or otherwise gases than slightly differ, leads to the violation of the second law of thermodynamics.

1. Mixing entropy

According to Baehr and for the major part of the scientific community, Gibbs paradox is solved quite simple. **For any reversible process the change in entropy is zero. Reversible process means ΔS=0**. We start from a thermodynamic state, perform a cyclic process e.g. mixing and separation, and at the end we have the same thermodynamic state (without adding external work etc). For nonindistinguishable gases this could be done by insertion of a partition only. For different gases, with the help of a semipermeable membrane we can mix and separate different gases and for the total process ΔS=0. Reversible mixing can be done either by the device in figure 1.1

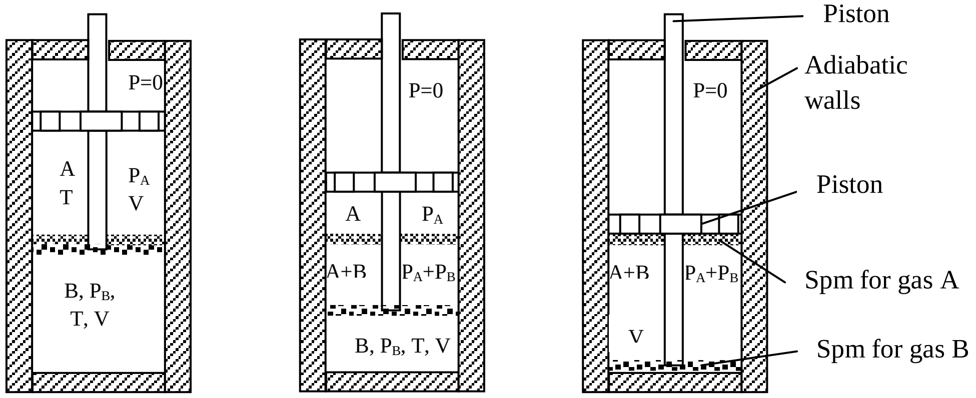

FIG 1.1 Reversible mixing of two ideal gases A and B with two semipermeable membranes

or by reversible isothermal expansion and reversible isothermal compression in figure 1.2. Gases A, B are expanded isothermally from pressure P to partial pressure P_A, P_B. Thermal energy Q_{in} is absorbed from the surroundings and work W_t is produced. They are mixed at the left box with the help of two semipermeable membranes and then separated at the right box. Finally they are compressed from partial pressure P_A, P_B to P. During this entire closed circle the temperature T_0 remains constant. Work done on the left is equal to the needed work on the right and thermal energy given on the left is equal to the thermal energy taken out on the right.

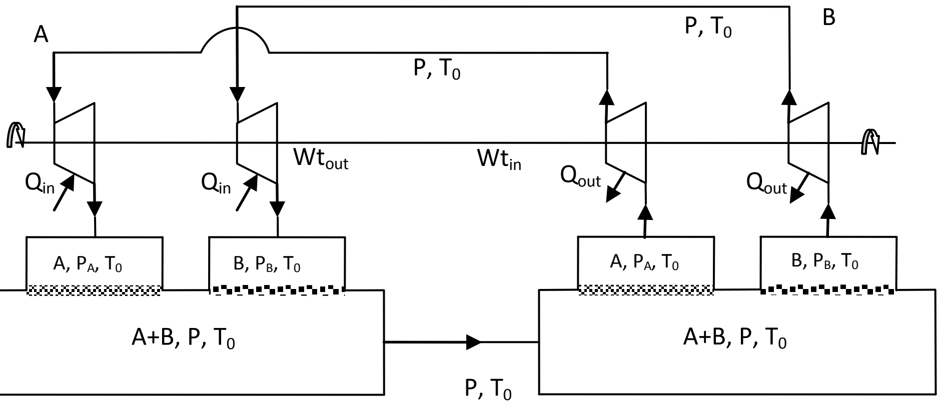

FIG 1.2 Mixing & separation of two ideal gases "reversibly" in a closed loop

If we give to these gases one initial "push", it is obvious that in the real world the two ideal gases would not mix and separate perpetually, but in our imaginary frictionless world they would.

2. Semipermeable membrane

A semipermeable membrane (spm), also termed a selectively permeable membrane, a partially permeable membrane or a differentially permeable membrane, is a type of membrane that will allow certain molecules or ions to pass through it.

Equal concentration semipermeable membrane

Imagine a spm that allows only one gas to pass and not others. The simplest spm of all would only let small molecules to pass. This spm allows only one gas to pass in both directions. Equilibrium is reached when the number of gas A molecules passing from mixture box to the separated gas is equal to them passing from separated gas to mixture box. Or, when the partial pressure of gas A in the mixture will be equal to total pressure of gas A in the separated box.

$$P_r = P_{rA} = P_{lA}$$

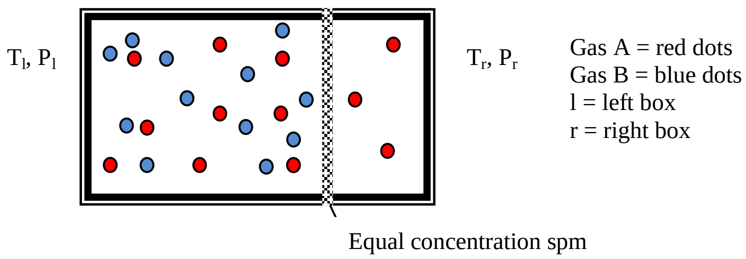

Fig 2.2 Gas A is separated from the mixture at the right box and has pressure equal to it partial pressure at the left box

Hydrogen, oxygen, nitrogen spms are already widely used but not so simply. They need a pressure gradient in order to operate.

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Equal pressure semipermeable membrane

Imagine a spm than allows only one gas to pass until the pressure in both sizes is equal. Equilibrium is reached when the number of gas A molecules passing from mixture box to the separated gas is equal to them passing from separated gas to mixture box.

$$P_r=P_{rA}=P_l=P_{lA}+P_{lB}$$

Equal pressure semipermeable membranes are a thought experiment and not reality.

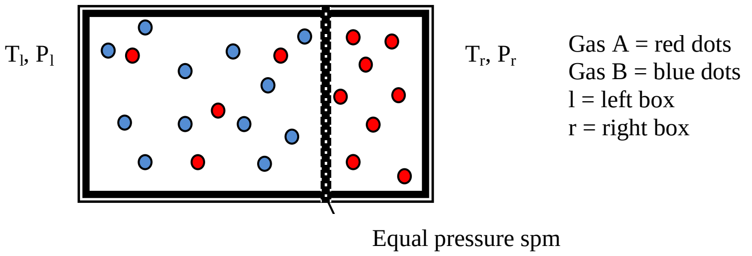

Fig 2.1 Gas A is separated from the mixture at the right box and has pressure equal to the total pressure at the left box

Nothing that we know is near it. If we had this membrane e.g. for oxygen, we would separate oxygen from air and would have pure oxygen in 1atm pressure without the use of any work!!!

3. Similar gases

When can we say that two gases or two billiard balls are similar? Same properties, same color? It can not be done otherwise, only by definition. So for the purpose of this paper only, two gases A and B will be called similar when a molecule (particle) can not tell the difference if near it is a molecule A or B. They will distinguish in one thing though... Only gas A can pass through a semipermeable membrane.

If gases A and B were different, gas A would pass from the left box to the right box until

$$P_r=P_{rA}=P_{lA}$$

as in fig 2.1 Equal concentration.

But, because gas A and B are similar,

$$P_{rA}= P_{rB}=P_r$$

gas A will pass from center box to left box until

$$P_{lA}= P_{rA}=P_r$$

So, for similar gases equal concentration spm is the same as equal pressure spm.

4. Chemical kinetics

As described by Ikonomis [3] (Gamma machine), theoretically, if we had three similar gases A_2, B_2, AB, which react according to the exothermal reaction:

$$A_2+B_2 \Leftrightarrow 2AB + \text{energy}$$

then, at the center box in chemical equilibrium gases A_2 and B_2 react to form 2AB and vice versa. These three gases are similar, so molecules of A_2 move freely to and from left box, molecules of B_2 move freely to and from right box. All three boxes have same temperature and pressure. Left box has only gas A_2, right box only gas B_2. A_2 and B_2 react exothermally in a reactor. As temperature and pressure in the reactor are higher than in the center box, we can extract mechanical work between these. Conservation of energy gives us:

$$dW_t = dQ$$

$$dS = \frac{dQ}{T} < 0$$

a violation of the second law of thermodynamics!

In words, at dt time, for an adiabatic system as A_2 and B_2 leave center box, 2AB separates endothermaly to restore chemical equilibrium, and temperature T drops slightly dT. From the thermal machine A_2, B_2, 2AB return to the center box but they have left some energy dW_t. Internal energy is transformed into chemical energy and part of it produces work. If we return work dW_t in the system e.g. with a fun, we will have a perpetual machine of the second kind. If all system is in an infinite thermal pool with temperature T, than it can produce work infinitely!

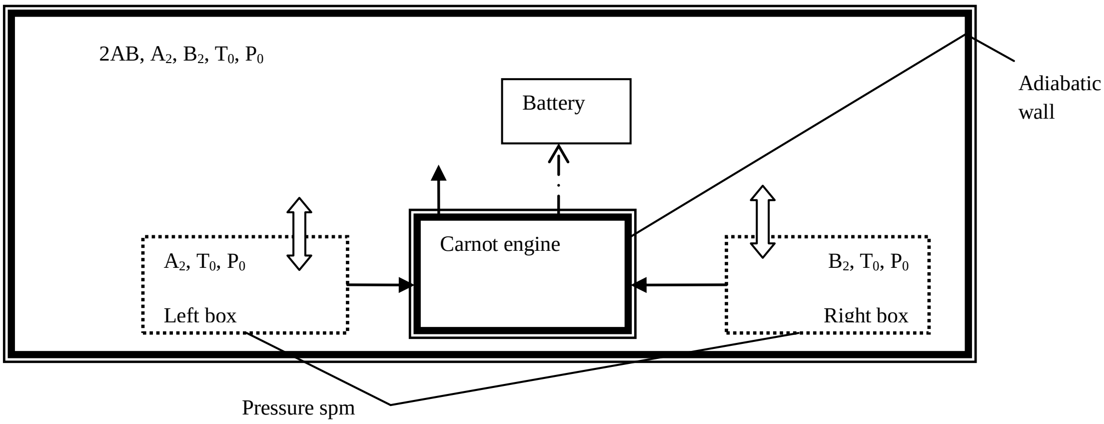

Fig 4.1 Gama machine

This machine produces mechanical work so the frictionless assumption it is not needed any more. Part of the produced energy would be used to overcome friction.

5. Conclusions

There are a lot of “ifs” for this machine to work. One could say that this is a proof that these semipermeable membranes and similar gases can not exist. But for the moment the question is: If we had the spms and the gases would we have a violation of the second law of thermodynamics?

6. References

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2. On the So-Called Gibbs Paradox, and on the Real Paradox - Arieh Ben-Naim, *entropy* ISSN 1099-4300
3. Maxwell’s demon kind machines – Ikonomis, archive.org
4. A list of papers mainly published in journals on the Gibbs paradox could be found at mdpi.org.
5. The Gibbs Paradox Revisited, Dennis Dieks, arxiv.org

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