MAXWELL’S DEMON KIND MACHINES
Perpetual motion machines of the second kind

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Abstract

In this paper, we propose several Maxwell's demon-like machines. Most of them are made from semipermeable membranes, thermal engines, and ideal gases. The presentation of each machine is followed by few thermodynamic calculations and conclusions. Most of solutions are done by means of classical thermodynamics but references to statistical thermodynamics are also done. Our demons are non-sentient, they act by natural processes [2]. Our hypothetical semipermeable membranes do all the work, without the need of external work, information storage or other entropy increasing mechanisms. As Maxwell's demon thought experiment has been widely used in papers regarding information entropy, computing etc we must clarify that our demons have nothing to do with the above, but only with a "thermodynamic" world.

1. Introduction

The second law of thermodynamics is awe-full in its breadth and depth of applicability - from quarks to cosmos from chemical reactions to perpetual motion machines. Its supremacy has never been expressed more eloquently than by Sir Arthur Eddington [1] many years ago, with the firm conclusion: "**…if your theory is found to be against the Second Law of Thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.**

On the other hand when Pascal Blaise was asked for the probability that God exists he said: "it is probably non possible but if you will have a place in heaven without cost why not say he exists..."

The de Fineti game is a good way for someone to tell the truth about how possible he believes it is, to observe in the next 50 years an EVENT that opposes to the second law of thermodynamics. One bag has $10^{1000000}$-1 white balls and only one red. You will win one billion euro if you pull out randomly the red ball or you will win one billion euro if in the next fifty years the EVENT happens. What do you choose?

Let us suppose that the EVENT A would be: heat will be transferred from a body with lower temperature T_2 to a body with higher temperature T_1 means $T_2<T_1$.

Let us suppose that the EVENT B would be: Maxwell's demon will be invented and high energy molecules will be separated from low energy.

Let us suppose that the EVENT C would be: Any event that opposes to the second law of thermodynamics.

Probably you will agree that:
Possibility of EVENT A < possibility of EVENT B < possibility of EVENT C
if this is the case, please read this paper

but, if you believe that :
Possibility of EVENT A = possibility of EVENT B = possibility of EVENT C = zero
it is better not to spend time in this paper.

2. Maxwell's angel

Maxwell thought experiment is well known, but just to refresh our memory here it is [3]. Maxwell imagines one container divided into two parts, A and B. Both parts are filled with the same gas at equal temperatures and placed next to each other. Observing the molecules on both sides, an imaginary demon guards a trapdoor between the two parts. When a faster-than-average molecule from A flies towards the trapdoor, the demon opens it, and the molecule will fly from A to B. Likewise, when a slower-than-average molecule from B flies towards the trapdoor, the demon will let it pass from B to A. The average speed of the molecules in B will have increased while in A they will have slowed down on average. Since average molecular speed corresponds to temperature, the temperature decreases in A and increases in B, contrary to the second law of thermodynamics.

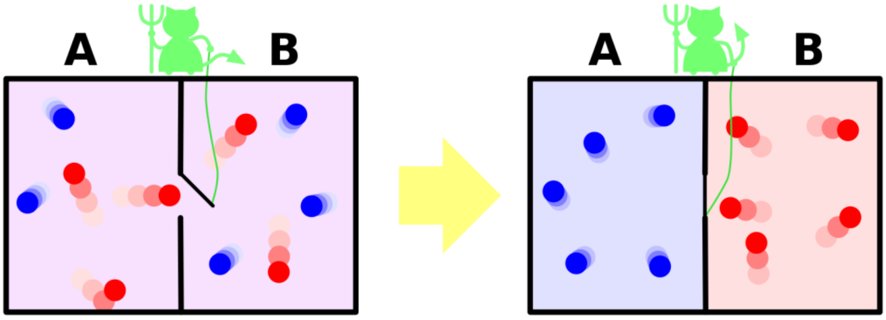


Fig 2.1

Thompson in 1874 christened this being a "demon". The question that arrives is why this creature was named "demon"? Maybe because this creature does not obey to divine law?! If we were to baptise this creature today we would give the name "angel". Only an angel can save us from the energy sources global war!

3. Hypothesis problem

When a hypothesis is made while solving problems, the hypothesis itself could be the problem. At Maxwell's demon the problem is the demon! It is the creature we do not have to build this machine.

If we said "Suppose a creature would raise stones from a valley to a mountain without using external work. We do not care how. Maybe by "teletransporting!" We could use these stones to produce useful mechanical work, do the math for that case and as conclusion free energy for all.

Below we make some hypotheses about semi permeable membranes and these are our demonic (angelic) creatures. As science moves deeper into the nanoworld, further towards statistical thermodynamics, more and more into molecular pistons, it is more possible to observe a violation of the second law. And this does not mean that the second law is not valid, but is the same as Newtonian mechanics vs. Einstein mechanics.

4. Approximations

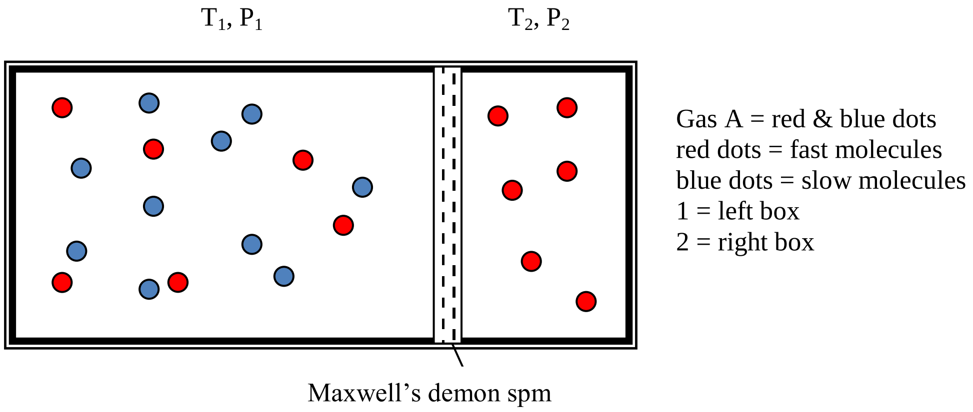
We are working with ideal gases. Entropy of mixing ideal gases $\Delta S=0$.
Quasi static irreversible process.
Frictionless, adiabatic walls, etc....

5. Semipermeable membrane

A semipermeable membrane, 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. We use different semipermeable membranes in this paper. These membranes are different by definition, by what we need them to do. We do not explain how this semipermeable membranes do what we ask, most of them do not exist in real word, but semipermeable membranes are running on the back of nanomaterials and in huge development now days. Because the words semipermeable membranes will be used abundantly, the abbreviation “spm” will be used. The common factor in all our spm is that they do not use any form of external energy to perform their work. Do not imagine them only as biological thin walls or nanomaterials thin walls but as walls that do what we define them to.

5.1 Maxwell’s semipermeable membrane

Replace the door and demon in Maxwell experiment with a semipermeable thermally insulated membrane. This spm does not need to know the speed of molecules or atoms, does not use other energy sources, but allows only fast molecules to pass from the left box to the right one. One could also say that this is a one direction energy barrier. Only molecules carrying enough energy shall pass from left to right.
Obviously we have a violation of the second law of thermodynamics. By adding a heat engine between box 1 and 2, we can extract work from a single thermal pool of initial temperature T_0.
This spm does not exist and nothing that we know is near it.



5.2 Concentration semipermeable membrane

Imagine a spm that lets only one gas to pass and not others. The simplest spm of all would only let small molecules to pass. Hydrogen, oxygen, nitrogen spms are already widely used. This spm allows only one gas to pass in **both** directions. All chemical elements have different properties so every element can have his selective membrane.

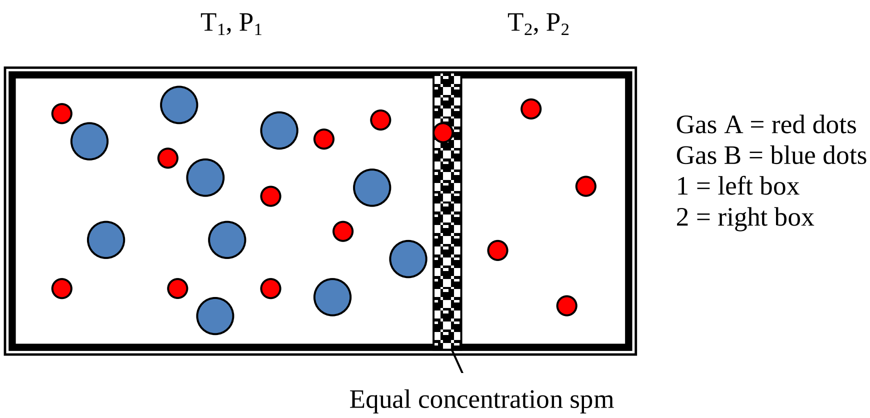


Fig. 5.2.1

For our selective gas the concentration spm is an invisible wall, while for the rest is a wall! Red dots are gas A and blue dots are gas B. The concentration of gas A in both boxes is the same. The boxes are connected with thermal conductors. The equations that describe this thermodynamic state are:

$P_1=P_{1A}+P_{1B}$ eq 5.2.1
$P_2=P_{2A}$ eq 5.2.2
$P_{1A}=P_{2A}$ eq 5.2.3
$T_1=T_2$ eq 5.2.4
$P_1 > P_2$ eq 5.2.5
$c_i=\frac{n_i}{V}$ eq 5.2.6
$c_{1A}=c_{2A}$ eq 5.2.7

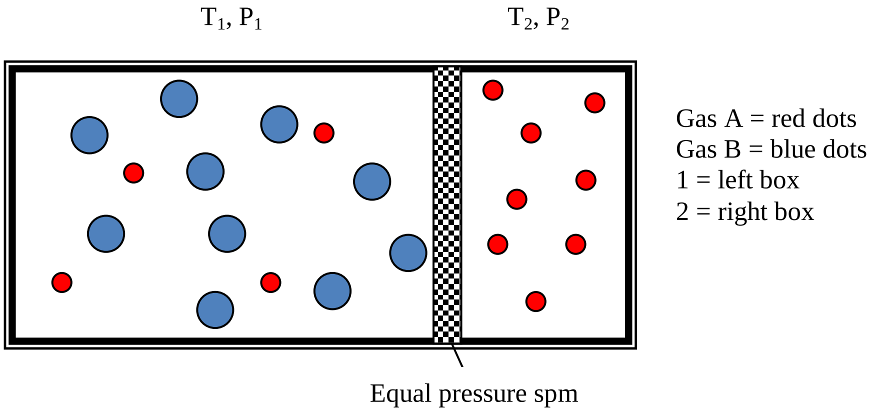
Where P_{1A}, P_{1B}, P_{2A}, P_{2B} are partial pressures.
c_i = concentration
n_i = moles

From statistical thermodynamics point of view the equal concentration semipermeable membrane would allow a gas to pass in both directions. Equilibrium would have been reached when the rate of the particles (molecules) passing from right to left would be equal to the rate of particles passing from left to right. If we suppose that after equilibrium gas A has a partial pressure in mixture of e.g. 0,1 of total pressure, that means that our concentration spm would receive nine (9) collisions with gas B for every one (1) particles A passing through the wall.

5.3 Pressure semipermeable membrane

Imagine a spm than allows only one gas to pass until the pressure in both sizes is equal.

Red dots are gas A and blue dots are gas B. Concentration of gas A in box 2 is bigger than concentration in box 1. We will also define that amount of gas A is big enough to fill box 2, otherwise the pressure in both sides would never be equal.



The equations that describe this thermodynamic state are:

$P_1=P_{1A}+P_{1B}$ eq 5.3.1
$P_2=P_{2A}$ eq 5.3.2
$P_{1A} < P_{2A}$ eq 5.3.3
$T_1 = T_2$ eq 5.3.4
$P_1 = P_2$ eq 5.3.5
$c_{1A} < c_{2A}$ eq 5.2.7

Where P_{1A}, P_{1B}, P_{2A} , P_{2B} are partial pressures.
c_i = concentration
n_i = moles

From statistical point of view an equal pressure semipermeable membrane would allow gas A to pass but mainly in one direction. In equilibrium particles A will flow in both directions. For every particle A passing from left to right another one will pass from right to left. If again we assume that gas A has partial pressure in mixture 0,1 of total pressure, then our equal pressure membrane would receive at least ten (10) collisions of gas A from one side and nine (9) collisions of gas B plus one (1) of gas A on the other side. Before equilibrium is reached, when pressure $P_1>P_2$, our spm would receive e.g. nine (9) collisions of gas B and two (2) of gas A total eleven (11) collisions from left size and nine collisions of gas A from right size – and still would let one particles of gas A to pas from left to right. How can this happen???
Well, that is why it is a demonic one!

6. Alpha perpetual machine

Boxes 1, 2 are separated by a pressure spm. Boxes 1, 3 are separated by a concentration spm. Only gas A can go to all three boxes. Between box 2 and 3 there is a open/close valve and a turbine operating between pressure P_2 and P_3 and producing work $W_{2\text{-}3}$. The turbine is connected with a battery inside the system which stores energy. Gas A and B do not chemically react. The entire system is separated from the universe by adiabatic walls. The system including the valve, battery and turbine is in thermal equilibrium temperature T_0.

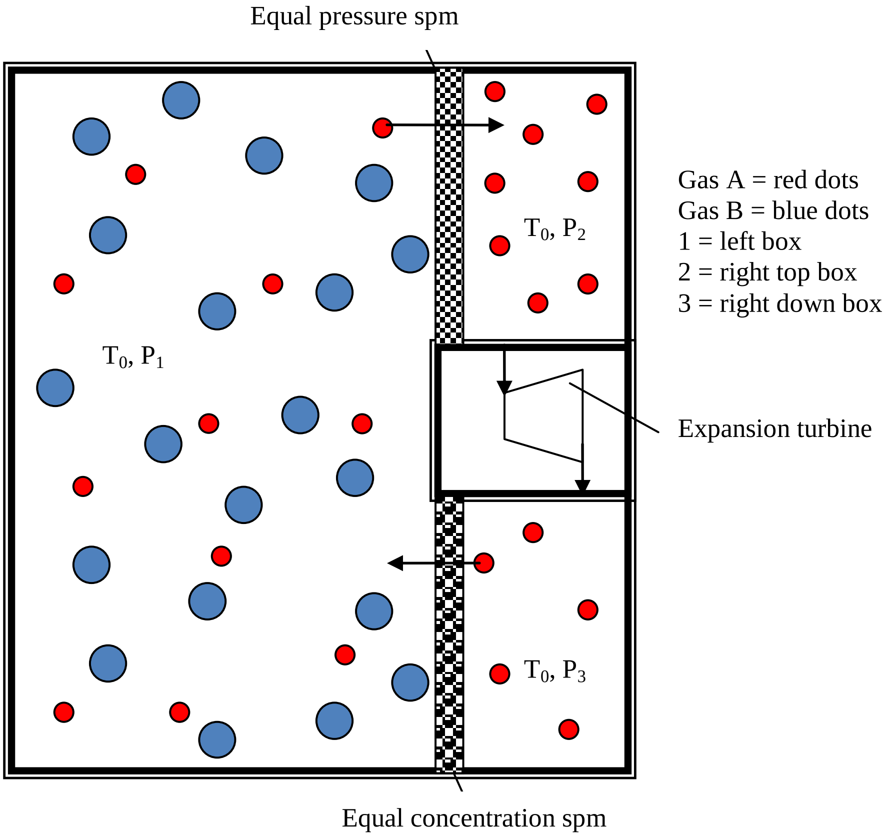


Fig. 6.1

The equations that describe this thermodynamic state are:

$P_1=P_{1A}+P_{1B}$ eq 6.1
$P_1=P_2=P_{2A}$ eq 6.2
$P_{1A}=P_{3A}$ eq 6.3
$P_1>P_{1A}$ eq 6.4
$P_{3A}=P_3=P_{1A}$ eq 6.5
and $P_{2A}>P_{3A}$ or $P_2>P_3$ eq 6.6

The valve is closed. The whole system is in thermodynamic equilibrium. Pressure in box 2 is equal to pressure in box 1 from the definition of pressure spm. Pressure in box 3 is equal to partial pressure of gas A in box 1 from the definition of concentration spm.

We open the valve. As pressure in box 2 is higher than pressure in box 3 gas A will move from box 2 to 3. During the expansion from 2 to 3 work $w_{2,3}$ will be done at the expansion turbine. Assume that boxes are quite big comparing to flow from 2 to 3 in dt time.

$dw_{2-3} = mRTln\frac{P_2}{P_3}$ eq 6.7

$du = dq + dw = 0$ eq 6.8

$dq=dw$ eq 6.9

$dw=dw_{2-3}$ eq 6.10

$dq= dw_{2-3}$ eq 6.11

$U_{system,init} = c_{pA}*(T_{init})*m_A+ c_{pB}*(T_{init})*m_B$ eq 6.12

$U_{system,end} = c_{pA}*(T_{end})*m_A + c_{pB}*(T_{end})*m_B + (w_{2-3})*dt$ eq 6.14

$U_{system,init} = U_{system,end}$ eq 6.13

$cp_A*(T_{init})*m_A+ cp_B*(T_{init})*m_B = cp_A*(T_{end})*m_A + cp_B*(T_{end})*m_B + (w_{2-3})*dt$

$(T_{init})*(cp_A*m_A+cp_B*m_B) - (w_{2-3})*dt = (T_{end})* (cp_A*m_A+cp_B*m_B)$

$T_{end} = T_{init} - \frac{w_{2-3}}{cp_A m_A + cp_B m_B} dt$ eq 6.15

Init = Initial

End = End after dt time

c_P=constant pressure heat constant

m=mass

As mass and specific heat are constant the only properties that changes in time dt is temperature which is lowered by dT

$T_{end} = T_{init} – d(T)$ eq 6.16

$dT<<T_{init}$ eq 6.17

For the system entropy as $dT<<T_{init}$:

$dS = \frac{dQ_R}{T} = \frac{dw_{2-3}}{T}$ eq 6.18

As work is done by the system dw_{2-3} is negative for the system so dS is negative which opposites to the second law of thermodynamics.

In words, we produced and stored mechanical energy dw from a thermal lake in temperature T_0 by lowering it thermal energy by dQ.

If we had installed a fun at box number 1 powered by turbine 2-3 we would have a **perpetual machine of second kind**.

7. Chemical kinetics & perpetual machines

Below we will imagine a lot of perpetual machines, but there is something common in all them. As known, in chemical reactions, chemical equilibrium is not reached when the reactants stop reacting, but when the rate of reactants transforming into products is equal to the rate of products transforming into reactants.

Suppose that we have a box with three gases A, B and AB. The reaction is exothermic from left to right and endothermic for vice versa.

$$A_2+B_2 \Leftrightarrow 2AB \quad \text{eq 7.1}$$

If we separate the three dimensional space in the box, there is a $dV_{A2+B2=>2AB}$ volume where an exothermic collision happens and a $dV_{A2+B2<=2AB}$ volume where an endothermic collision happens. So, while in a thermal pool of temperature T_0, we have two dV spaces, the one with temperature $T_{exothermic}>T_0$ and the other with temperature $T_{endothermic}<T_0$.

If we put a thermal machine or a fuel cell type machine between these spaces we could produce mechanical energy, with other words a perpetual machine of second kind. The reason we cannot do that in practice is the same with the reason we cannot extract energy from the movement of molecules in a gas.

What we can do in an easier way is to continuously remove reactants from the main box in two different boxes for each gas, make them react in a Carnot or fuel cell machine and return the products in the main box.

8. Catalysts

If we could use a catalyst to speed a reaction in one direction only, we could make a perpetual machine of second kind. But catalysts do no not work like this. They work in both directions and do not affect the chemical equilibrium. This cannot stop us from using them in multiple steps reactions and use of our semipermeable membranes. Instead of:

$A_2+B_2 \Leftrightarrow 2AB$

We could have:

$2AB+C_2+D_2 \Leftrightarrow 2AC+2BD$

$2AC+2BD \Leftrightarrow A_2+B_2+C_2+D_2$

Catalysts are useless in affecting chemical equilibrium but can be very helpful in affecting the needed thermal pool temperature or make most of reactions happen in a selected area e.g. near the spm walls.

9. Beta machine – chemical photovoltaic panels

This one is not a perpetual one because an external source of energy will be used. The reason we included it in this paper is because it could became a highly efficient machine to transform sun or chemical energy into mechanical work.

This machine will work with the help of a concentration semipermeable membrane for atomic gas A, meaning that atomic gas A will pass the membrane from high concentration to low.

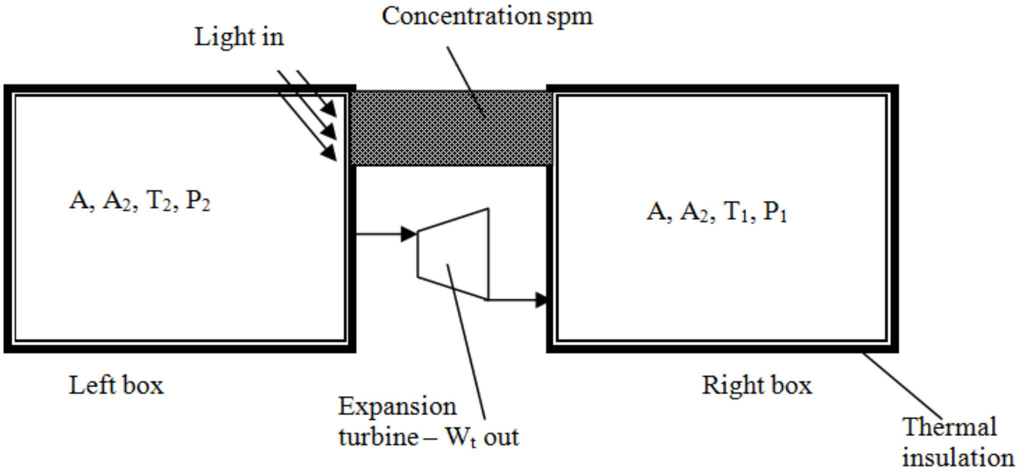


Fig. 9.1

Suppose that reaction of atomic gas A to molecule A_2 is altered by light. The left size of our concentration spm is lighted so atomic gas A reacts exothermally and produces A_2 molecules. The exothermal reaction increases temperature and pressure in left box. As temperature increases, due to chemical equilibrium more A_2 reacts endothermally to produce atomic A. As pressure rises more A reacts exothermally to produce A_2.

As there is less atomic gas A in the left part of spm gas A passes from right to left. As atomic A leaves the right container, A_2 reacts endothermally to produce atomic A – so temperature and pressure decrease at the right container.

As temperature and pressure are higher in the left box than the right box we can put an expansion turbine to extract mechanical work W_t.

Our system is thermally isolated, has light energy coming in and technical work coming out – 100% of light energy becoming mechanical work! If we produced light with our mechanical energy and send it in, then we will have a perpetual machine of a second kind and violation of the second law.

If our system is not perfectly thermally isolated or we need to extract some thermal energy in order to e.g. cool a shaft, then our efficiency of turning light to mechanical power would be lower than 100% and in this case a violation of the second law is not observed in the system.

Why does this machine have such an increased efficiency? Because it does not only use the energy of light but also creates two thermal pools of different temperatures from one single pool temperature T_0 as described in chapter seven.

$$T_2>T_0>T_1$$

Analysis is similar if light would increase the rate of A_2 reacting endothermally to produce atomic A.

Analysis is similar if diatomic gases or complex molecules would have been used.

Analysis is similar if chemical energy would have been used instead of light energy.

But these go further than the purpose of this paper – a thought experiment.

10. Gama machine

Gama machine will work by simple use of a pressure semipermeable membrane. The left container has a wall from spm allowing only gas A to pass. The right container has walls from spm allowing only gas B to pass.

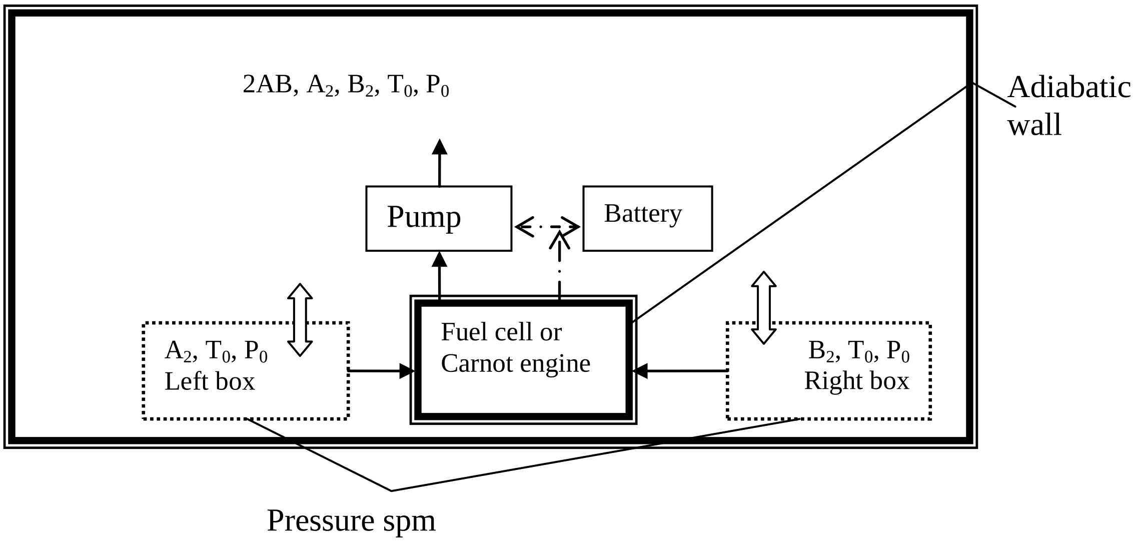


Fig 10.1 Gama machine

- Our system is adiabatically separated from the universe
- At the fuel cell or Carnot engine part of the chemical energy is transformed into mechanical work and stored into battery or generally mechanical work reservoir. Below we will not refer any more to fuel cell for simplicity reasons but is the same and only better from the thermal engine as efficiency is not limited.
- Thermal or Carnot engines will work between temperature $T_{productts}$ and T_0.
- From definition pressure semipermeable membranes allow A_2, B_2 to pass until the pressure $P_{system}=P_{A2left}=P_{B2right}$
- Frictionless etc….

10.1 Process

Initial state:

- Our adiabatic container has 2AB, A_2, B_2 in chemical equilibrium, temperature T and pressure P. (e.g. H_2O, H_2, O_2 or HBr, H_2, Br_2)
- Our adiabatic container is very large compared to left and right containers.
- Left container has gas A_2 only.
- Right container has gas B_2 only.
- Fuel cell or Carnot engine ready to operate but without flow yet.
- Battery is empty
- Pump is off

We start the pump. By assuming frictionless operation, steady state etc the work needed at the pump is zero

$$W_{tpump} = 0 \quad \text{eq 10.1.1}$$

or tends to zero

$$W_{tpump} \rightarrow 0 \quad \text{eq 10.1.2}$$

as pressure at the exit of thermal engine (Carnot engine) or fuel cell is equal at the start of operation with the container pressure.
We need the pump (compressor) in order to start the operation. Otherwise, as the system is in equilibrium it would not have any reason to start.
After the start, as pressure at the exit of thermal engine is higher that the system pressure, the pump is no longer needed.

So again, we start the pump.
A_2, B_2, will react at the thermal engine. The reaction is exothermic. As our thermal engine is adiabatically separated from the total container the temperature and pressure will rise. So until now we had a thermal pool in temperature T_0 only, and after start we have a second thermal pool with temperature $T_{products}>T_0$ and we can produce useful mechanical work.
As our thermal engine starts to operate gases A_2 and B_2 are consumed from left and right container. Their pressure is reduced. In order for the pressure equilibrium to resettle A_2 will pass from total container to left container and B_2 will pass to right container.
In order to restore chemical equilibrium at the total container gas 2AB will react endothermally to produce gas A_2 and B_2. This will reduce the initial temperature T_0.
If we assume that all these will happen in time dt, work dWt will be stored at the battery. We could write all the equations and at the end we would have:

$$ds = \frac{dq}{T_0} = -\frac{dw_t}{T_0} \qquad \text{eq 10.1.3}$$

In other words, the entropy of the system (the entropy of the universe) will be decreased by the fraction of work stored at the battery and temperature. **This is a violation of the second law of thermodynamics**.

If we let the machine work, it would work until the temperature drops to a point where endothermic reactions cannot happen. The machine would stop and mechanical work would have been stored to the battery.

By replacing the battery with a fan we would have a **second kind perpetual machine.**

By removing the adiabatic walls and putting the machine into an infinite thermal pool of temperature T_0, mechanical work could be produced infinitely.

11. Delta machine

Delta machine works by using a semipermeable membrane which will give us a final concentration of gases A_2 and B_2 lower than the pressure spm but higher than the concentration spm. Let’s suppose that an imperfect equal pressure semipermeable membrane has been built and at equilibrium the pressure of our selective gas A or B is not equal to the total pressure but lower. We assume the same machine as the Gamma but in order to return the combustion product in the total container we must first compress reactants from their partial pressure to the thermal pool pressure.

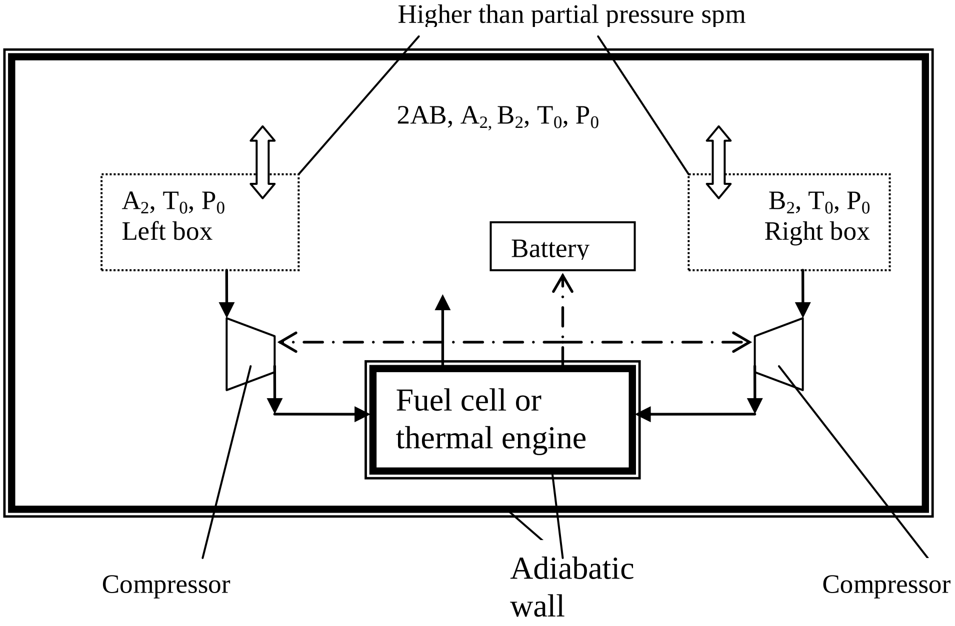


Fig. 11.1

Working principle etc… are as Gamma machine. We start the compressors. In order for this machine to work perpetually or to store energy the work required for the compression must be less than the work produced by the thermal engine.

If this is the case, we have a perpetual machine of the second kind…

The reason we introduced the Delta machine is that the equal pressure semipermeable membrane is not the only one leading to a violation of the second law. As seen above at ALPHA perpetual machine **any** selective membrane or wall or magic than can separate a gas with higher concentration than the one in the mixture (or higher pressure than the partial in mixture) can lead toa violation of the second law of thermodynamics.

12. Epsilon machine

Epsilon machine will work by use of concentration semipermeable membranes which will give us an equilibrium concentration of gases A_i and B_j ... I_k equal to their concentration in the mixture.

Assuming that the reactions of A_i and B_j ... I_k react exothermally and their product(s) at working temperature is(are) liquid or solid, then the compression work needed to return products into initial mixture is very small compared to gas compression.

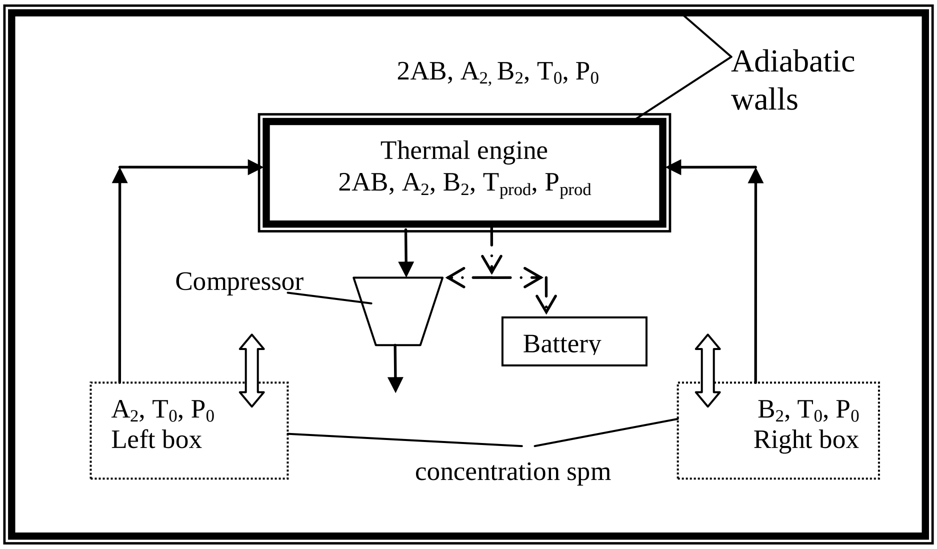


Fig. 11.1

- Our system is adiabatically separated from the universe.
- At the thermal engine part of the chemical energy is transformed into mechanical work and stored into the battery or generally mechanical work reservoir. Thermal engine will work between temperature $T_{productts}$ and T_0.
- From definition concentration semipermeable membranes allow A_2, B_2 to pass until the pressure $P_{A2center}=P_{A2left}$ and $P_{B2cente}=P_{B2right}$
- Frictionless etc….

12.1 Process

Initial state:

- Our adiabatic container has 2AB, A_2, B_2 in chemical equilibrium, temperature T and pressure P. (e.g. H_2O, HCl, H_2, O_2, Cl_2)
- Our center (total) container is very large compared to left and right containers.
- Left container has gas A_2 only.
- Right container has gas B_2 only.
- Thermal engine ready to operate but without flow yet.
- Battery is empty
- Compressor is off

We start the compressor. By assuming frictionless operation, steady state etc the work needed at the compressor is small.

A_2, B_2, will react at the thermal engine. The reaction is exothermic. As our thermal engine is adiabatically separated from the total container the temperature and pressure will rise. So until now we had a thermal pool in temperature T_0 only, and after start we have a second thermal pool with temperature $T_{products}>T_0$ and we can produce useful mechanical work.

As our thermal engine starts to operate gases A_2 and B_2 are consumed from left and right container. Their pressure is reduced. In order for the concentration equilibrium to resettle A_2 will pass from total container to left container and B_2 will pass to right container.

In order to restore chemical equilibrium at the total container gas 2AB will react endothermally to produce gas A_2 and B_2. This will reduce the initial temperature T_0.

If we assume that all these will happen in time dt, work dWt will be stored at the battery. We could write all the equations and at the end we will have :

$$ds = \frac{dq}{T_0} = \frac{dw_t}{T_0} \qquad 12.1.3$$

In other words, the entropy of the system (the entropy of the universe) will be decreased by the fraction of work stored at the battery and temperature. **This is a violation of the second law of thermodynamics**.

13. Conclusions

Several demon-like machines were theoretically presented. One kind relies on pressure semipermeable membranes and the other on making exothermal reactions happen in different spaces than endothermal reactions and producing work between these thermal pools.

Further work can be done with more realistic semipermeable membranes and working gases, fluids.

14. Contact

If you find errors in this paper, please contact me at oikili[at]hotmail[dot]com

If you have any questions or want to discuss this papers please email at oikili[at]hotmail[dot]com

If you have not received reply within a week (spam, mistyping etc) feel free to call at 0030 6973 38 32 eight nine - from 10.00 to 20.00 GMT +2 local time.

REFERENCES

1. Eddington, A. S. *The Nature of the Physical World*; Macmillan: New York, 1928; p 74.
2. Vladislav Chapek - Daniel P. Sheehan Challenges to the Second Law of Thermodynamics ISBN 1-4020-3015-0
A great book!
3. wikipedia.org – Maxwell demon
http://en.wikipedia.org/wiki/Maxwell%27s_demon
Wikipedia - A great idea!
4. Thermodynamics – Hans Dieter Baehr
Greek version ISBN 0-387-06029-4
5. Thermodynamics of Materials – John Hudson ISBN 0-471-31143-X