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► To cite this version:

Qiong Ye, Jeremy Cocks, François-Xavier Machu, Qiuping A. Wang. You certainly know the second law of thermodynamics, Do you know its connection to other laws of physics and chemistry?. The European Physical Journal Plus, 2022, 137 (11), pp.1228. 10.1140/epjp/s13360-022-03446-4 . hal-03469396v3

HAL Id: hal-03469396

<https://hal.science/hal-03469396v3>

Submitted on 8 Nov 2022

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You certainly know the second law of thermodynamics,
Do you know its connection to other laws of physics and chemistry?

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Abstract

Since the discovery of the second law of thermodynamics, skeptics have never ceased to challenge the absolute validity of the law, leading to a situation where the claim of violation of the second law has almost become routine today. This situation is also a serious threat to the fundamental status of thermodynamics. In this work, we bring to light evidences to prove the absolute validity of the second law as a fundamental law of physics. For this purpose, we propose a short revisit of the history of the discovery of the second law in order to highlight the connection between the second law and the first law of energy conservation. We then demonstrate that the perpetual motion machine of the second kind also violate the first law of thermodynamics, albeit indirectly, contrary to the common belief. This result confirms the second law is an inviolable fundamental law of physics, just like the law of energy conservation. Denying one of these conjoined twin laws is to deny the other. Any presumed violation of the second law, even a probabilistic one, inevitably violates the laws of energy and mass conservation, and undermines all fundamental laws of physics and chemistry. We conclude by summarizing a perspective of the interpretation of the second law taking into account the multiplicity of paths of random motion.

Keywords: Entropy, second law of thermodynamics, random dynamics, energy, energy conservation, Carnot engine, perpetual motion machine.

1) Introduction

It is beyond any doubt that thermodynamics is among the most important theories of physics, with very wide applications in almost all domains of natural science and engineering [1] as well as in social sciences [2]. However, despite the great confidence the scientists and engineers have in their applications [1][2], serious doubts persist, from the beginning of the theory until today, about whether thermodynamics is a fundamental physics theory (like for example classical and quantum mechanics), and whether the thermodynamic laws are exact rules and universal truth [3][4]. One of the origins of this skepticism is the statistical interpretation of the behaviors (temperature, pressure etc.) of thermodynamic systems [3][4][5], especially the statistical interpretation of one of its basic laws : the second law of thermodynamics (second law for short) [5][6][7]. According to this interpretation, the second law is only a probabilistic emergence from other more basic laws of mechanics, hence a non-fundamental rule in the sense that the law is reducible to other laws and, in addition, it does not always hold [3][4][5][6].

The second law of thermodynamics stipulates that entropy S always increases in the evolution of an isolated system and remains constant when the system reaches thermodynamic equilibrium. Entropy S of a system is defined by its small variation $dS = \delta Q/T$ [1] when a small quantity of heat δQ is absorbed by the system from its surroundings, where T is the absolute temperature of the system. This system which is in an ideal and quasi-equilibrium undergoes a reversible process [9][10]. For any real (non-ideal) irreversible process, $dS > \delta Q/T$ [1]. This inequality is the mathematical expression of the second law. When the system is isolated with $\delta Q = 0$, the second law becomes $dS > 0$ as stipulated above¹. According to a widely accepted interpretation, entropy represents a measure of the uncertainty or disorder in the movement of the molecules composing any thermodynamic system. This idea is reflected in Boltzmann's definition of entropy $S = \ln w$ [1][11] where w is the total number of microstates (arrangements of the position and momentum of the molecules) in the system. The greater is w , the more the molecules are moving in disorder. The second law means that the

¹ It is worth mentioning that the entropy is only defined for equilibrium states. It has been extended to non-equilibrium systems changing sufficiently slowly so as to keep local equilibrium and to apply equilibrium thermodynamics to each of the sufficiently small partitions [13].

system always evolves towards macrostates having a greater number of microstates, i.e., towards more and more disorder. A familiar example is the expansion of gas in an isolated recipient from a part of the container to the whole container, because the number of microstates in the whole volume is larger than in a part of it. The entropy reaches its maximum when the gas uniformly fills the volume in an equilibrium state [1].

The statistical interpretation of the second law by Boltzmann [11], a point of view shared by Maxwell [12], was formulated within classical (Newtonian) mechanics with the help of an H function depending on the states of the particles in a thermodynamic system, H function decreases as the system evolves [11][14], contrary to entropy which increases instead. This formulation encountered serious criticisms, supported by mathematical proofs and irrefutable arguments based on the time reversibility and recurrent behavior of mechanical motion [14][15][16]. A reconciliation between the irreversible behavior of entropy in the second law and the time reversible laws of classical mechanics seems necessary, leading to a statistical argument stating that the entropy increase is only the consequence of an overwhelmingly large probability, but the probability of entropy decrease is nevertheless not zero, albeit very small [11][14]. A thought experiment proposed by Maxwell [17] uses a demonic intelligence able to follow precisely the movement of all the individual particles in a system, and to sort them according to their velocities², showing that entropy of the isolated system could indeed decrease. The pros and cons about this demon continue today from different considerations based on information [18], quantum property [19], or classical random motion [20]. The Maxwell demon is still there haunting the second law.

As a matter of fact, the signification of the Maxwell demon goes farther than decreasing entropy. According to Laplace [21], such a demon would be able to know every detail of the motion of the particles of a system of any size (even the whole universe) if the particles obey

² ...if we conceive a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are still as essentially finite as our own, would be able to do what is at present impossible to us. For we have seen that the molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform ... Now let us suppose that such a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower ones to pass from B to A. He will thus, without expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics.

classical mechanics, making it possible to put in a complete equation of motion the data of the trajectories of all particles from the past to the future³. He then does not need to observe and to measure the positions and the velocities of the particles and to open (or not) the door of the hole to sort the particles. As he knows when and how each particle with given velocity moves to the hole, he can build an automatic door controlled by a program in which he puts the data of the motion of each particle. He then just take a coffee waiting for the entropy decrease produced by the door alone. With this demon, the information consideration [18] can no more avoid the violation of the second law. Worse, for this demon, there is no disorder at all in the system. No disorder means no entropy. Actually, he does not see the entropy we are describing with the second law. This gives to the concept of entropy a subjective character depending on the perception or mental state of the observer. This demon cannot but deepen the doubt about the fundamentality of entropy, of the second law, and of the theory of thermodynamics.

In this uncertain context of the second law, the statistical interpretation seems the only refuge of the second law [5]. It has actually become the mainstream interpretation of entropy increase, despite the firm belief in its fundamental nature claimed by many (see for example the citation of Edington⁴ [22]) and the great confidence in the application of thermodynamics laws in technology (see for example [23][24] and the references there-in). There was even a statistical theory formulated around a fluctuation theorem [25], allowing systematic violation of the second law. In this formulation, the second law violation, despite its small probability, becomes a ubiquitous phenomenon in every non-equilibrium process [25]. Today it is quite common to see violation of the second law in the literature, supported either by experimental evidence [26][27] or by theoretical arguments [6][28][29][30], many reports being based on

³ We may regard the present state of the universe as the effect of its past and the cause of its future. An intellect which at a certain moment would know all forces that set nature in motion, and all positions of all items of which nature is composed, if this intellect were also vast enough to submit these data to analysis, it would embrace in a single formula the movements of the greatest bodies of the universe and those of the tiniest atom; for such an intellect nothing would be uncertain and the future just like the past would be present before its eyes [21].

⁴ The law that entropy always increases holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations - then so much the worse for Maxwell's equations. If it is found to be contradicted by observation - well, these experimentalists do bungle things sometimes. But if your theory is found to be against the Second Law of Thermodynamics I can give you no hope; there is nothing for it to collapse in deepest humiliation.

quantum mechanical consideration [27][28]. We also noticed the publication of some very radical criticisms such as the second law is fallacious based on flawed reasoning from Carnot's theorem [31], the entropy of the second law is not a meaningful physical quantity [32], and entropy is just a mathematical contrivance without solid physics background [33]. There are also efforts to construct engines challenging Carnot's efficiency but keeping the validity of the second law [34][35][36]. Many authors seem to ignore both the unbreakable connection between the Carnot's theorems and the second law, and the dangerous consequence of the breakdown of Carnot's theorems.

There are many efforts, from both philosophers [4][6] and physicists [7][14][37], defending the fundamental status of the second law against the statistical interpretation of the second law, but their defense is often based on conceptual belief and plausible arguments without convincing (mathematical) proof. The aim of this work is just to contribute to this effort by proposing a convincing proof of the fundamental nature of the second law as an inviolable iron rule. This proof is simply the fact that the second law is tightly connected to the laws of conservation of energy and mass. This work did not invent this proof which is in fact visible in some episodes of the discovery of the second law [1][7][38] over almost 40 years through the work of Carnot [9] and Kelvin [17][39] all the way to Clausius [10]. This is why we propose in what follows a summary of this history in a short form of trilogy, in order to highlight this unbreakable mathematical link between the second law and the first law of energy conservation. This link implies that if the second law is violated, the first law is violated as well, which would be a disaster of natural science and must be avoided. This conclusion is very important from the conceptual point of view in order to give back to thermodynamics its unquestionable fundamentality. It is also crucial from the practical point of view for applying thermodynamics to the study of the world around us and to the development of energy technology with more confidence and correct vision.

Nomenclature

S – entropy	E – energy
dS – entropy change	w – number of microstates
Q – heat transferred to a system	W – mechanical work
ΔQ or δQ – small heat transfer	U – internal energy
R – heat reservoir	θ – temperature of arbitrary scale
η – efficiency of heat engine	T – absolute temperature
PMM – perpetual motion machine	PMM1 – perpetual motion machine of first kind
PMM2 – perpetual motion machine of second kind	

2) Discovery of entropy

It is sometimes said that the second law is an empirical finding⁵. This is not exactly true. The discovery of the second law, in its most profound form in terms of entropy, is actually a result of pure thought experiments and mathematical calculations.

Historically, the discovery of entropy has something to do with a decree of the Academy of Science of Paris in 1775 declaring they would not examine any proposition concerning perpetual motion machines [40]. The decree concerned what we call today perpetual motion machines of the first kind (PMM1)⁶. Since then, the impossibility of PMM1 began to be taken for granted on the basis of a common belief that energy and motion cannot be created from

⁵ https://en.wikipedia.org/wiki/Second_law_of_thermodynamics

⁶ A dream of many engineers of that time was to construct what is called today the perpetual motion machine of the first kind, a machine that can produce an unlimited amount of work without consuming heat or other energy. This machine violates the law of energy conservation. There is another type of perpetual motion machine called the second kind capable of transforming heat from a single reservoir completely into work. It is straightforward to show that this engine makes heat flow from a cold to a hot body, hence violate the second law. We will show later in this paper that this machine turns out to violate the first law of energy conservation as well because we can use it to fabricate a perpetual motion engine of the first kind.

nothing [9]; the law of energy conservation was not yet known at that time. Today we have the mathematical proof that this machine cannot exist because it violates the first law of thermodynamics, the law of conservation of energy. This decree is the starting point of the remarkable work of Carnot in the study of the efficiency of thermal engine [9], leading to the second law many years later. We can at once guess that there must have some vital connection between the second law and its starting hypothesis. In order to highlight this connection and the mathematical rigor in it, we will retrace the impressive trilogy from the impossibility of perpetual motion all the way to the discovery of the second law. The reader will see a summary of the key elements of the story below. The details of the mathematics are described in Appendix.

a) From perpetual motion machines to Carnot theorem

Carnot was concerned with heat engines and their efficiency. In 1824, he published the extraordinary idea of a reversible heat engine⁷, now called a Carnot engine [1]. This ideal engine can work in a reversible cycle between two heat reservoirs (R1 and R2), one (R1) at higher temperature θ_1 and the other (R2) at lower temperature θ_2 . The engine can work in a forward cycle, extracting heat Q_1 from θ_1 , emitting heat Q_2 ($<Q_1$) to θ_2 and producing a mechanical work $W = Q_1 - Q_2$; it can also reverse the cycle, extracting heat Q_2 from R2, absorbing work W , and emitting heat Q_1 to R1. The Carnot engine works in both directions with the same efficiency defined by $\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$ [1]. This is a purely ideal machine which cannot exist in reality. It is impossible for a real machine to perform such a reversible operation due to friction or other form of energy loss. For this reason all real engines are irreversible machines. By examining this ideal machine, Carnot discovered the efficiency limit for all possible engines; which he described this in the first part of his theorem, asserting that⁸:

All irreversible heat engines between the two reservoirs are less efficient than the reversible engine working between the same reservoirs.

⁷ Ref [9], pp17-20

⁸ The maximum motive power achieved by the use of vapor is also the maximum motive power achievable by any other means. Ref [9], p22

Carnot proved this theorem by *reductio ad absurdum* based on the impossibility of PMM1⁹. The details of his proof are illustrated in Appendix I. To summarize, this theorem is true if and only if the PMM1 does not exist. In other words, if an irreversible engine working between the same reservoirs is more efficient than the Carnot engine, we can then use this irreversible engine to construct a PMM1 (Figure A1 of Appendix I) to produce energy with no need of energy source. This engine would solve our big worry about renewable energy source and environment¹⁰.

We will see below that the meaning of the existence of this PMM1 goes much deeper than simply giving a solution to our energy concerns. This first part of Carnot's theorem was crucial for the discovery of the second law. However, the second law would be impossible without the second part of Carnot's theorem.

The second part of Carnot's theorem is in some way implicit in the first part. Since the Carnot engine is the most efficient of all possible engines, all Carnot engines, each working with a different substance (air, steam, etc.), must be equally efficient. If two Carnot engines were not equally efficient, we would be able to replace the first irreversible engine in Carnot's proof (Appendix I) by this more efficient Carnot engine, in order to make a PMM1. All Carnot engines, therefore, have the same efficiency regardless of their working substances. This efficiency, which we call η , can only depend on the temperatures θ_1 and θ_2 of the reservoirs R1 and R2, respectively. The second part of the theorem states [9]:

All Carnot engines have the same efficiency regardless of their working substances; this efficiency only depends on the temperatures of the reservoirs: $\eta(\theta_1, \theta_2)$.

For Carnot, the only interest of his magic engine is to specify the limit of the efficiency of all possible heat engines. A practical question is how to calculate this limit $\eta(\theta_1, \theta_2)$ when the temperatures of the reservoirs are given? Physicists had to wait about thirty years to find the answer, which was given by Kelvin [39].

⁹ Ref [9]. pp21-22

¹⁰ Ref [9], p22

b) Kelvin's efficiency of Carnot's engine

In 1854, Kelvin found the expression of $\eta(\theta_1, \theta_2)$ by considering the second part of the Carnot theorem and using a new scale of temperature called absolute temperature denoted by T [39]. The expression is [1]

$$\eta = 1 - \frac{T_2}{T_1} \quad (1)$$

for a Carnot engine working between two reservoirs of absolute temperature T_1 and T_2 ($T_1 > T_2$). This expression can be found in a general way using a combination of two Carnot engines in series, the first one working between the reservoir R1 at T_1 and the reservoir R2 at T_2 ($T_1 > T_2$), the second one working between the reservoir R2 and the reservoir R3 at T_3 ($T_2 > T_3$). The mathematics is straightforward as shown in Appendix II. Kelvin's equation (1) is an unavoidable consequence of the second part of the Carnot theorem that the efficiency only depends on the temperatures of the two reservoirs.

Now let ΔQ_1 be the heat absorbed by the Carnot engine from R1, and ΔQ_2 the heat it "absorbs" from R2 (it actually emits $-\Delta Q_2$ to R2). After a complete cycle, the engine returns to R1. The work done during the cycle is given by $W = \Delta Q_1 - (-\Delta Q_2)$. It is obvious that the efficiency $\eta = \frac{W}{\Delta Q_1} = 1 - \frac{(-\Delta Q_2)}{\Delta Q_1} = 1 - \frac{T_2}{T_1}$, which gives us $\frac{\Delta Q_1}{T_1} + \frac{\Delta Q_2}{T_2} = 0$. Suppose now we increase the number of reservoirs to N , where the i^{th} reservoir ($i = 1, 2 \dots N$) at temperature T_i gives δQ_i to the engine. Kelvin obtained the following equation [1]

$$\sum_{i=1}^N \frac{\delta Q_i}{T_i} = 0 \quad (2)$$

But he stopped here in his quest for the second law without reaching the concept of entropy [7][39].

c) Clausius' perception

The discovery of what is called the second law of increasing entropy finally came to Clausius who, like Kelvin, also derived Eq.(2) [10]. But he saw something deeper in it. If the number of reservoirs is very large, Eq.(2) takes the form of a closed line integral : $\oint \frac{\delta Q}{T} = 0$. This integral over a reversible cycle implies that the quantity $\frac{\delta Q}{T}$ represents the variation of a variable S which is a state variable. During contact with a reservoir at temperature T , the engine

receives heat δQ as well as undergoing a variation of S : $dS = \frac{\delta Q}{T}$. After a complete cycle, the engine comes back to its initial state, and the total variation of S is zero: $\oint dS = \oint \frac{\delta Q}{T} = 0$ [1].

Clausius didn't stop here with $dS = \frac{\delta Q}{T}$ for a reversible process. He had the brilliant idea of using the same analysis as above for a real but irreversible engine, of efficiency η' , cycling between the same reservoirs R1 and R2, absorbing ΔQ_1 and ΔQ_2 , and doing work W' during a cycle. We have $\eta' = \frac{W'}{\Delta Q_1} = 1 - \frac{(-\Delta Q_2)}{\Delta Q_1}$. Then he used the first part of Carnot's theorem which states that the efficiency of an irreversible engine is less than that of a reversible engine i.e. $\eta' < \eta$, and using Kelvin's limit $\eta = 1 - \frac{T_2}{T_1}$, he wrote

$$1 + \frac{\Delta Q_2}{\Delta Q_1} < 1 - \frac{T_2}{T_1} \quad (3)$$

which means $\frac{\Delta Q_1}{T_1} + \frac{\Delta Q_2}{T_2} < 0$. For a large number of reservoirs on the cycle, he wrote $\oint \frac{\delta Q}{T} < 0$, which yields (see Appendix III) [1][10]:

$$dS \geq \frac{\delta Q}{T} \quad (4)$$

for both irreversible ($>$) and reversible ($=$) processes. Clausius coined the term *entropy* for this variable S because he wanted to find a Greek word that is parallel and analogous to the Greek word *energy*¹¹ [41]. He certainly felt some intrinsic link between energy and entropy, himself having just at that time proposed the first law of thermodynamics about energy conservation [42].

3) If we backtrack the trilogy

By summarizing the trilogy of discovery of the second law, we wanted also highlight the infallible mathematics going from the impossibility of perpetual motion machine all the way to the second law. These rather straightforward mathematical deductions show that, if perpetual

¹¹ I prefer going to the ancient languages for the names of important scientific quantities, so that they may mean the same thing in all living tongues. I propose, accordingly, to call the entropy of a body, after the Greek word 'transformation.' I have designedly coined the word entropy to be similar to 'energy,' for these two quantities are so analogous in their physical significance, that an analogy of denomination seemed to me helpful [41].

machine is impossible, then there must be the Carnot theorem, and then the second law follows; you cannot get other thing different. And inversely, if the second law is broken, i.e., Eq.(4) breaks down, you can backtrack all the mathematical calculations of Clausius from Eq.(2) to Eq.(4), to prove Eq.(3) untrue. Eq.(3) stems from Eq.(1) and the first part of Carnot theorem. Its falseness implies either the falseness of Eq.(1) or that of the first part of Carnot theorem.

Now suppose Eq.(1) is false, in view of the infallible mathematics of Kelvin using Figure A2 (Appendix II), the second part of Carnot theorem must be untrue. In other words, different Carnot engines using different working substances may have different efficiencies. According to the discussion in the section 3a), we will be able to construct a PMM1 using two Carnot engines of different efficiencies.

If we suppose Eq.(1) and the second part of the Carnot theorem are true but the first part of the theorem is false, so there may be engines more efficient than Carnot engine. Then we can use these more efficient engines, as shown in Figure A1 of Appendix I, to fabricate PMM1, which will give us infinite quantity of clean energy we need to preserve our pet planet.

Up until now, we have only talked about PMM1. The reader may wonder what would happen if the perpetual motion machine of the second kind (PMM2) is involved. PMM2 is a machine transforming heat from a single heat reservoir into mechanical work with no other effects. Unlike PMM1, PMM2 does not violate the first law [1], because it transforms a heat Q into mechanical work W of same quantity of energy ($W=Q$). It only violates the Kelvin-Planck expression of the second law [17][39] stipulating, simply, that the perpetual machine PMM2 is impossible. This machine is widely regarded as an example of the violation of the second law without violating the first law of energy conservation [1]. In what follows, we will prove that PMM2, despite its conservation of energy in a cycle, indirectly violates the first law of energy conservation through its violation of the second law. For this purpose, we will show first how it violates the second law in allowing heat flow from colder body to hotter body.

As shown in Figure A4 of Appendix IV, we can combine a PMM2 pumping heat Q_3 from a colder reservoir R2 at T_2 and does a work $W_3 = Q_3$, with a Carnot engine which uses W_3 in order to pump a heat Q_2 from the reservoir R2 and to give the $Q_1 = Q_2 + Q_3$ to a hotter reservoir R1 at T_1 ($T_1 > T_2$). In this cycle, the hotter reservoir R1 gets the heat Q_1 from the colder reservoir R2 without leaving any side effect, leading to the total entropy variation $\Delta S = \frac{Q_1}{T_1} - \frac{Q_1}{T_2} < 0$, a violation of the Clausius's expression of the second law $\Delta S \geq 0$ for the isolated

system composed of the two engines and the two reservoirs. In this case, we can construct an engine with an efficiency η' larger than the efficiency of the Carnot engine η , i.e., $\eta' > \eta = 1 - \frac{T_2}{T_1}$. This engine, violating the first part of the Carnot theorem, can be of course used in Figure A1 of Appendix I to construct PMM1 (see Appendix IV, Figure A5) which violates the first law of energy conservation. To summarize, the violation of the second law by PMM2 necessarily entails the existence of PMM1 providing free energy. Well, PMM1 and free source of energy come into being! So much the better, granted! So what!

4) So what if the second law is violated?

The most important implication of the violation of second law is not the existence of perpetual motion machine (PMM) as a source of infinite energy. There is another much deeper meaning behind the PMM : energy becomes something you can create or annihilate as much as you please. It loses at once the attribute of a conservative fundamental quantity of motion, regardless of its form, thermal, mechanical, electromagnetic, gravitational, and so on. The first mathematical consequence is the collapse of the first law of thermodynamics $dU = \delta Q + dW$. Why? Because after a cycle of the PMM in the Figure A1 of appendix I for instance, $dU = \delta Q = 0$, but $dW \neq 0$; this is the work done by the perpetual engine without consuming heat. Needless to say, the whole theoretical edifice of the thermodynamics will collapse.

This is not all. As well known, energy conservation is not only one of the cornerstone of thermodynamics, it is also a key pillar of the whole edifice of physical and chemical science, as well as a fundamental rule guaranteeing the stability of all natural systems. For example, our pet planet is in stable revolution around the sun because its total mechanical energy remains constant (conserved) when the pair earth-sun is a good isolated system, at least for a period sufficiently long for our intelligence to develop, fortunately. Now if the energy of the isolated earth-sun was no longer a constant and can arbitrarily change (maybe due to a PMM in the system modifying arbitrarily the energy of the earth without changing anything else), the earth would have fallen in the sun or flight to the border of Milky Way since long. Please make the same reasoning for nuclei, atoms, molecules and any energy conservative system in Nature; do you think that they can be there as stable components of our universe? Imagine also that you want to make a solid state synthesis; you put the prepared sample in the oven and increase the temperature to 1000 K. But one day you realize that the sample is freezing! Why? Because the heat is flowing from the colder sample into the hotter oven, a direct consequence of the violation

of the second law and of the energy conservation! Moreover, from a fundamental point of view taking into account the Einstein's formula for energy-mass equivalence¹², if energy loses its attribute of a conservative quantity, the mass can no longer be a conserved quantity, so that the mass conservation is no longer a fundamental law of nature, at least conceptually. It is well known that most, if not all, fundamental equations in physics and chemistry are based on the energy and mass conservation. If energy and mass were no more conserved quantities, we would see the disappearance of Newtonian equation, Maxwell's equations, chemical reaction equations, stoichiometry formula, the laws of diffusion of matters and heat, Einstein's equation of general relativity, and, finally, Schrödinger equation! After these losses, what does remain in physics and chemistry?

Indeed, when the violation of the second law, together with the time reversibility, is regarded as isolated phenomenon, it looks like something plausible and interesting even exciting to investigate. However, when this violation is coupled to the violation of the laws of energy and mass conservation, we quickly understand to what extent the second law of thermodynamics is an inviolable iron rule. Can we imagine a violation of energy and mass conservation, even probabilistic with infinitesimal likelihood, as the fluctuation theorem stated for second law violation [25][26]? Can we imagine that energy and mass are no more conservative quantities? Simply we cannot! That would be a fatal menace for the whole edifice of physics and chemistry; the whole nature would collapse into nil even if the violation of the second law and of energy-mass conservation took place during only a fraction of a second.

If one suggests the violation of the second law, he should first explain how and why both energy and mass become non-conservative quantities, in both classical and quantum systems! He must also provide an explanation why and how the universe and the world around us can continue to exist while all the physics and chemistry laws have disappeared.

Now we understand better the comment of Edington about the absolute validity of the second law (footnote p.2) [22].

¹² In special relativity theory, we have the famous formula $E = mc^2$, where E is the energy of a matter, m its mass, and c the velocity of light in vacuum.

5) Concluding remarks and perspectives

The objective of this work is to provide a proof of the fundamental nature of the second law as an inviolable iron rule. We have first reviewed the uncertain situation concerning the fundamentality of the second law and thermodynamics in general, in order to highlight that the statistical interpretation of the second law based on classical mechanics is the main origin of the impressive confusion in the understanding of the second law and the concept of entropy. In order to reach our objective, we have first summarize the history of the discovery of the second law by Carnot, Kelvin and Clausius in three episodes, to highlight an unbreakable connection between the second law and the first law of energy conservation. We have then proved that, the perpetual motion machine of the second kind, regarded most textbooks [1] as a process violating the second law but not the first law, also necessarily violate the first law of energy conservation, albeit indirectly. This result confirms the unbreakable link between the two laws.

Now we see that entropy increase is not an isolated phenomenon on its own in nature. It is an unavoidable consequence of the conservation of energy. The violation of the second law, even a statistical one, necessarily leads to the fatal failure of the laws of energy and mass conservation, and to the conceptual breakdown of the whole physics and chemistry science. In view of the incontestable universal validity of energy and mass conservation, it can be concluded that any claim of violation of the second law, be it classical or quantum, is necessarily questionable. If a theory, well confirmed both theoretically and empirically in its domain, leads to the violation of the second law, the only plausible explanation is either the theory is incorrectly applied to thermodynamics, or the "entropy" violated is simply not the entropy of the second law of thermodynamics.

To our eyes, this conclusion is important from the conceptual viewpoint for thermodynamics to be regarded as one of the most fundamental theory of physics. It is also important from practical viewpoint for scientists and engineers to be more confident in the application of thermodynamics to the understanding of the world at different scales up to the universe, to the prediction of its future evolution, and to the development of technology especially for the production of sustainable energy [23][24][34][35][36].

It is worth noticing that this conclusion emphasizes once more the discordance between the second law of thermodynamics and its statistical interpretation based on classical mechanics [1][11][12]. Although the statistical interpretation is widely accepted by both the philosophy

and physics community [4][5], it is always challenged by the irrefutable criticisms [5][14] based on the Liouville theorem [43], the Poincare recurrence theorem [15] and the time symmetry of classical mechanical motion [43][44]. The first law – second law connection revealed in this work with mathematical proof constitutes another hard obstacle on the pathway from classical mechanics to the second law.

One of the possible interpretation of the second law is to consider the quantum mechanical behavior of the particles of thermodynamic systems [19][45]. But this approach has its own uncertainty because, as mentioned above, there are more and more propositions of violation of the second law in quantum regime [27][28][29]. The last word needs further investigation. Anyway, quantum interpretation is not all because a great number of systems around us obeying the second law are not quantum. In our opinion, it is of first necessity to interpret the second law within classical mechanics before addressing its quantum origin. We would like to mention here a candidate formalism in this direction. This formulism considers an essential difference between the classical mechanics motion, which is regular, deterministic, and characterized by the uniqueness of path of each particle [43], and the thermodynamic motion, which is random, indeterministic, and characterized by the multiplicity of paths of each particle between an initial state and a final one. For this kind of motions, the fundamental principle of least action and the equations of motion, working only for single path motion [43], must be extended in such a way to include many paths and their probability to occur. Although many results have been achieved within this multiple path approach through either informational consideration [46][47] or generalization of the basic principle of classical mechanics [48], further effort is necessary to be able to finally formulate complete interpretation of the second law [49][50].

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Appendix

This is a summary of the history of the discovery of the second law of thermodynamics over thirty years starting from 1824.

I) Carnot theorem from a thought experiment

Figure A1 illustrates a combination of an irreversible real engine and a reversible Carnot engine, both working between a hot reservoir R1 at temperature θ_1 and a cold reservoir R2 at temperature θ_2 . The irreversible engine produces a work $W' = Q_1 - Q_2$ in absorbing a heat Q_1 from the hot R1 and emitting a heat Q_2 to R2. Its efficiency is given by $\eta' = \frac{W'}{Q_1}$ [1]. The reversible engine is working in the inverse direction using a work W to absorb the heat Q_2 from R2 and give a heat Q_1 to R1. Its efficiency is given by $\eta = \frac{W}{Q_1}$. After a cycle, the two reservoirs recover their initial states respectively because they didn't obtain nor lose heat.

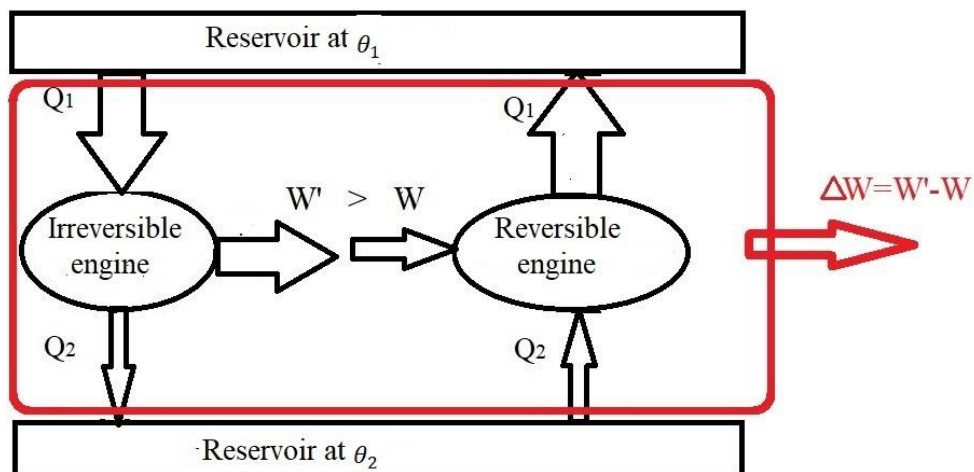


Figure A1: Illustration of a PMM1 (red line) composed of a real irreversible engine having efficiency $\eta' = \frac{W'}{Q_1}$ and a Carnot engine having the efficiency $\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$. If $\eta' > \eta$, the PMM1 is able to produce the work $\Delta W = W' - W$ after each cycle without consuming heat, so that the energy ΔW is created from nothing.

Now Carnot supposed that the irreversible engine has a larger efficiency than the reversible engine, $\eta' > \eta$, or $\frac{W'}{Q_1} > \frac{W}{Q_1}$, leading to $W' > W$. In this case, the reversible engine can use a part of W' to produce the work W , so that after a cycle, the only thing changed is the extra work $\Delta W = W' - W > 0$ produced by the ensemble of two engines (red line in Figure A1). This means that the ensemble of two engines is a perpetual motion machine of the first kind (PMM1) producing the work ΔW from nothing, which Carnot thought impossible according to a common belief that mechanical work and motion cannot be created from nothing (a rudimental idea of energy conservation). Conclusion: η' can never be larger than η ; which is the first part of Carnot theorem $\eta' \leq \eta$ [9].

From the same reasoning, we can prove that all reversible engines must have the same efficiency regardless of their different working substances. This is because if a reversible engine was more efficient than another one, we could combine them in the same way as in Figure A1 with the more efficient Carnot engine replacing the irreversible one; this would make a PMM1 (absurd). Conclusion: *all Carnot engines must have the same efficiency depending only on the temperatures of the reservoirs θ_1 and θ_2* , which is the second part of Carnot theorem [9].

II) Kelvin's efficiency

It is quite logical that the efficiency η of Carnot engine depends only on the temperature of the reservoirs. But what is the form of the function $\eta(\theta_1, \theta_2)$? Kelvin is concerned with this question, and made a calculation [39] which can be illustrated by the connection of two Carnot engines as shown in Figure A2. The first engine works between two reservoirs R1 at θ_1 and R2 at θ_2 ($\theta_1 > \theta_2$), absorbing Q_1 from R1, emitting Q_2 to R2 and doing a work $W_1 = Q_1 - Q_2$; the efficiency is $\eta_1 = 1 - \frac{Q_2}{Q_1}$. The second engine works between the above reservoir R2 and a third reservoir R3 at θ_3 ($\theta_2 > \theta_3$), absorbing Q_2 from R2, emitting Q_3 to R3, and doing a work $W_2 = Q_2 - Q_3$; its efficiency is $\eta_2 = 1 - \frac{Q_3}{Q_2}$. On the other hand, these two engines connected in series can be considered as a third engine, working between the hot reservoir R1 at θ_1 and the cold reservoir R3 at θ_3 , absorbing Q_1 from R1, emitting Q_3 to R3, and doing a work $W_3 = W_1 + W_2 = Q_1 - Q_3$; its efficiency is $\eta_3 = \frac{W_3}{Q_1} = 1 - \frac{Q_3}{Q_1}$.

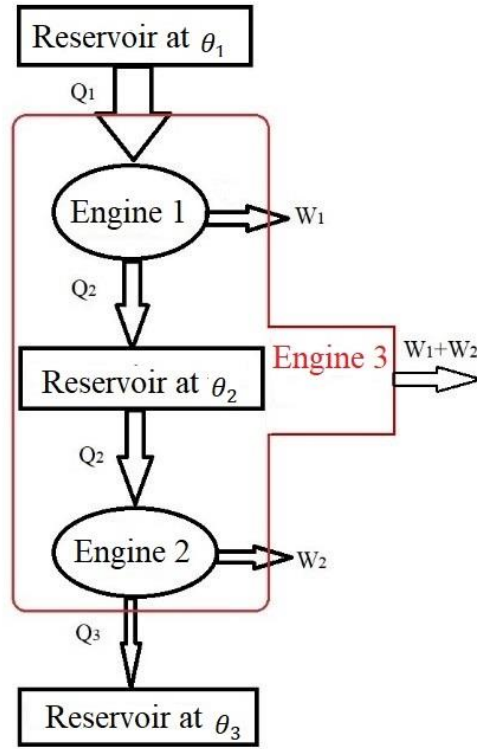


Figure A2: Illustration of Kelvin's idea to connect two Carnot engines in series to compose a third Carnot engine (red line) working between θ_1 and θ_3 .

The mathematics is the following: from the three efficiencies $1 - \eta_1 = \frac{Q_2}{Q_1}$, $1 - \eta_2 = \frac{Q_3}{Q_2}$ and $1 - \eta_3 = \frac{Q_3}{Q_1}$, it is straightforward to write $(1 - \eta_1)(1 - \eta_2) = 1 - \eta_3$. As all Carnot engines have the same efficiency depending only on the temperature of the reservoirs, we can write $1 - \eta_1 = g(\theta_1, \theta_2)$, $1 - \eta_2 = g(\theta_2, \theta_3)$ and $1 - \eta_3 = g(\theta_1, \theta_3)$, leading to $g(\theta_1, \theta_2)g(\theta_2, \theta_3) = g(\theta_1, \theta_3)$, where $g(\cdot)$ is any continuous function. The only way to reach this last equation is to let $g(\theta_1, \theta_2) = \frac{f(\theta_2)}{f(\theta_1)}$, $g(\theta_2, \theta_3) = \frac{f(\theta_3)}{f(\theta_2)}$ and $g(\theta_1, \theta_3) = \frac{f(\theta_3)}{f(\theta_1)}$ with certain function $f(\theta)$. Now let us simply take $f(\theta)$ as a temperature scale, say, $(\theta) = T$, which turns out to be the absolute temperature. Kelvin finally got $1 - \eta_1 = \frac{T_2}{T_1}$, $1 - \eta_2 = \frac{T_3}{T_2}$ et $1 - \eta_3 = \frac{T_3}{T_1}$, or in general, for a Carnot engine working between T_1 and T_2 ($T_1 > T_2$): $\eta = 1 - \frac{T_2}{T_1}$ [39].

III) Clausius' discovery

Clausius' work [10] starts with a Carnot engine working between T_1 and T_2 . He writes $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$, or $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$, and $0 = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$. With a change of notation $\delta Q_1 = Q_1$, and $\delta Q_2 = -Q_2$, he obtained $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$. Notice that δQ is a heat absorbed by the engine from a reservoir (see Figure A3). Obviously, if the engine is in contact with N reservoirs during a cycle, and absorbs δQ_i from a reservoir at T_i , we necessarily have $\sum_{i=1}^N \frac{\delta Q_i}{T_i} = 0$ (Figure A3).

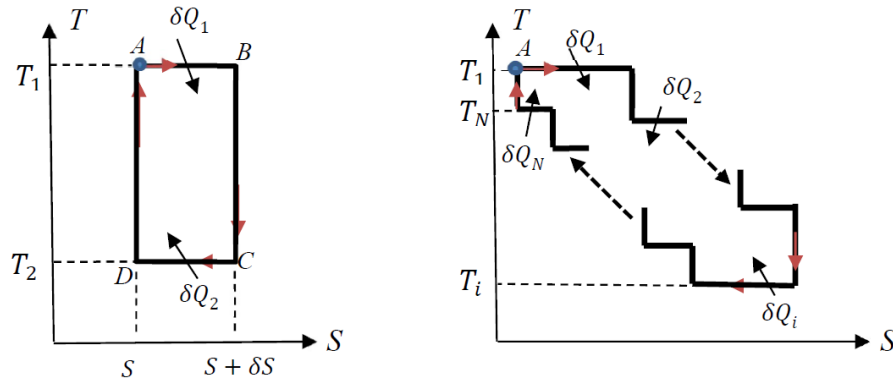


Figure A3: Examples of the cycle of Carnot engine in the $T - S$ diagram. The horizontal segments represent the contact of the engine with the reservoirs to absorb heat. The vertical segments represent adiabatic compression (left sides) and expansion (right sides). **Left** : a cycle starting from and ending at an initial state A after two contacts with T_1 and T_2 , leading to $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$. **Right** : a cycle starting from and ending at the initial state A after the contacts with N reservoirs at different temperature T_i , each giving δQ_i to the engine, leading to $\sum_{i=1}^N \frac{\delta Q_i}{T_i} = 0$.

Clausius understood at once that $\frac{\delta Q}{T}$ is the variation of a variable of state, he denoted by S ($\delta S = \frac{\delta Q}{T}$) and coined the name *entropy*, because when the engine comes back to its initial state after a cycle and a series of variations $\frac{\delta Q_i}{T_i}$, this variable also comes back to its initial value with zero variation $\sum_{i=1}^N \frac{\delta Q_i}{T_i} = \sum_{i=1}^N \delta S_i = 0$. If N is vary large, we can write a closed line integral $\oint dS = 0$ over a cycle.

Clausius made the above analysis with Carnot engine. What does happen with a real irreversible engine working between the same reservoirs with $\eta' = 1 - \frac{Q_2}{Q_1}$? Considering $\eta' < \eta$ and $\eta = 1 - \frac{T_2}{T_1}$, we get $1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}$ or $\frac{Q_1}{T_1} - \frac{Q_2}{T_2} < 0$. The same formal change as above yields $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} < 0$. With N reservoirs during a cycle, we have $\sum_{i=1}^N \frac{\delta Q_i}{T_i} < 0$ or $\oint \frac{\delta Q}{T} < 0$. Suppose that the variation of entropy of the engine at each equilibrium contact with a reservoir is δS_i , we have, after a cycle, $\sum_{i=1}^N \delta S_i = 0$, or $\oint dS = 0$ for large N . Compare $\oint dS = 0$ to $\oint \frac{\delta Q}{T} < 0$, it is straightforward to write $dS > \frac{\delta Q}{T}$ for irreversible engine, or $dS \geq \frac{\delta Q}{T}$ for any engine, reversible or irreversible. This inequality is the mathematical expression of the second law of thermodynamics. For an isolated system without exchange of heat with the exterior, $\delta Q = 0$, and $dS \geq 0$. This is why the second law is often referred to as the law of increasing entropy. Notice that the entropy of an open system exchanging heat with environment has $dS \geq \frac{\delta Q}{T}$ and can decrease ($dS < 0$) if the system loses heat $\delta Q < 0$ (like our body); this decrease does not violate the second law. Again, *the violation of the second law implies the decreases of entropy in an isolated system.*

IV) Perpetual motion machine of the second kind

As shown in Figure A4, a perpetual motion machine of the second kind (PMM2) is capable of extracting a heat Q_3 from a cold reservoir R2 at T_2 and transform it entirely into a mechanical work $W_3 = Q_3$. This cycle of PMM2 does not violate the first law of energy conservation.

However, the work W_3 can be used by a Carnot engine in an inverse cycle, as shown in Figure A4, to extract a heat Q_2 from the colder reservoir R2 and to transfer a heat Q_1 to a hotter reservoir R1 at T_1 , with $Q_1 = Q_2 + W_3 = Q_2 + Q_3$. During this cycle, the reservoir R2 loses an entropy $\Delta S_2 = -\frac{Q_2+Q_3}{T_2}$, and the reservoir R1 receives an entropy $\Delta S_1 = \frac{Q_1}{T_1} = \frac{Q_2+Q_3}{T_1}$, giving a total entropy change $\Delta S = \Delta S_1 + \Delta S_2 = Q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) < 0$, which violates the Clausius expression of the second law Eq.(4) $\Delta S \geq 0$ for the isolated system composed of the two reservoirs and the engines in Figure A4.

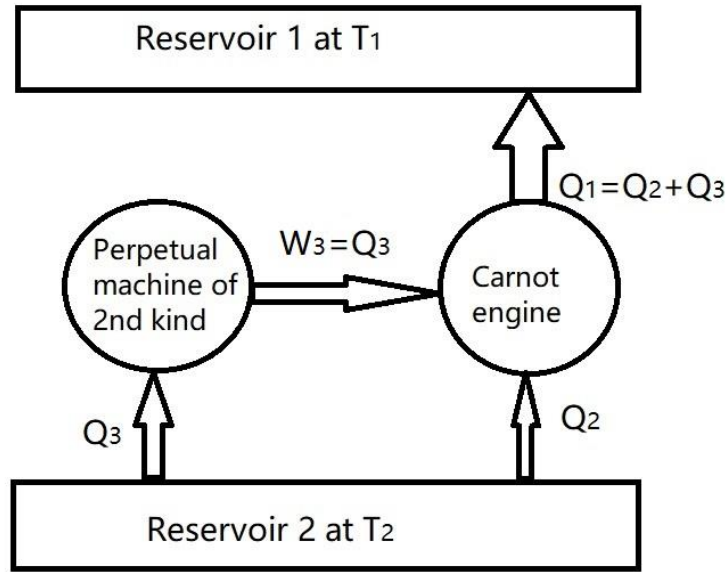


Figure A4: Illustration of how a perpetual machine of the second kind (PMM2) allows a flow of heat $Q_1 = Q_2 + Q_3$ from a colder body to a hotter body without any other effects upon the environment.

In order to show how this violation of the second law by PMM2 enables PMM1, we introduce a second Carnot engine in Figure A4 (see Figure A5), which absorbs Q'_1 during a cycle from the reservoir R1, does a work W to the environment, and emits a heat Q'_2 to the reservoir R2. Its efficiency is $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{Q'_2}{Q'_1}$, leading to $\frac{Q'_1}{T_1} = \frac{Q'_2}{T_2}$. During the same cycle, the system composed of the two engines in Figure A4 transfers a heat Q_1 from R2 to R1. The ensemble of the three engines in Figure A5 (surrounded by red line) is equivalent to an global engine which in one cycle absorbs a heat $Q'_1 - Q_1$ from R1, does a work W , and emits a heat $Q'_2 - Q_1$ to R2, leading to an efficiency $\eta' = 1 - \frac{Q'_2 - Q_1}{Q'_1 - Q_1}$. It is easy to prove that $\frac{Q'_2 - Q_1}{Q'_1 - Q_1} < \frac{Q'_2}{Q'_1}$, making $\eta' > \eta$ for any $Q_1 > 0$. It turns out that the global engine in Figure A5 is more efficient than the Carnot engine (violating the first part of Carnot theorem). We can of course use it to construct a PMM1 with the same tricks of Figure A1.

In similar way, we can also create a PMM1 using a PPM2 associated with an irreversible engine replacing the second Carnot engine in Figure A5. In this case, the entropy increase

created with the system of two engines of Figure A4, $\Delta S = Q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$, must be larger than

$$\frac{Q'_2}{T_2} - \frac{Q'_1}{T_1}, \text{ i.e., } Q_1 > \frac{\left(\frac{Q'_2}{T_2} - \frac{Q'_1}{T_1} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)}.$$

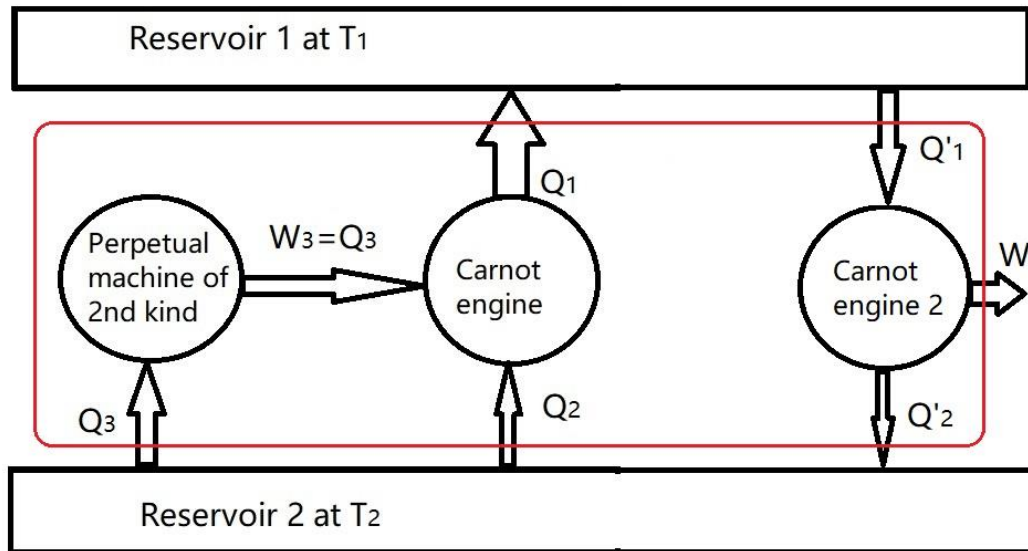


Figure A5: Illustration of an engine (red line) having an efficiency $\eta' = 1 - \frac{Q'_2 - Q_1}{Q'_1 - Q_1}$ larger than the efficiency of the Carnot engine $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{Q'_2}{Q'_1}$.