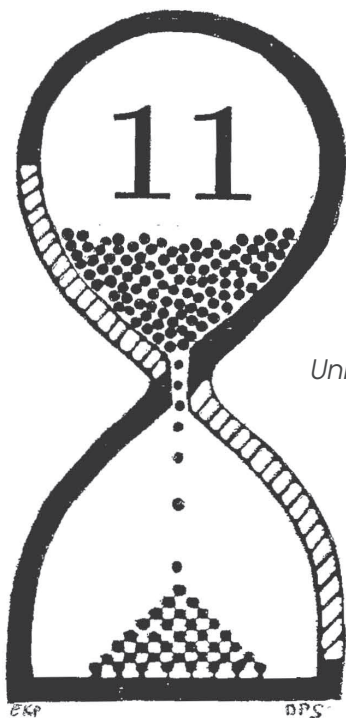


# SECOND LAW OF THERMODYNAMICS: STATUS AND CHALLENGES

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# Revisiting The Second Law of Energy Degradation and Entropy Generation: *From Sadi Carnot's Ingenious Reasoning to Holistic Generalization*

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**Abstract.** Sadi Carnot's ingenious reasoning of reversible cycles (1824) laid foundations for *The Second Law* before *The First Law* of energy conservation was even known (Joule 1843) and long before Thermodynamic concepts were established in 1850s. A century later, Bridgman (1941) 'complained' that "there are almost as many formulations of *The Second Law* as there have been discussions of it." Even today, *The Second Law* remains so obscure, due to the lack of its comprehension, that it continues to attract new efforts at clarification, including this one.

The *Laws of Thermodynamics* have much wider, including philosophical significance and implication, than their simple expressions based on the experimental observations – they are *The Fundamental Laws of Nature: The Zeroth* (equilibrium existentialism), *The First* (conservational transformationalism), *The Second* (irreversible directional transformationalism), and *The Third* (unattainability of emptiness). They are defining and unifying our comprehension of all existence and transformations in the *universe*. The *forces*, due to *non-equilibrium* of *mass-energy* in space (non-uniform 'concentrations'), causing the *mass-energy* displacement, thus defining the process direction, are manifested by tendency of *mass-energy* transfer in time towards common equilibrium -- cause-and-effect forced tendency of equi-partition of mass-energy. It should not be confused with local creation of non-equilibrium and/or 'organized structures' on expense of 'over-all' non-equilibrium, by spontaneous and irreversible conversion (dissipation) of other energy forms into the thermal energy, always and everywhere accompanied with *entropy* generation (randomized *equi-partition* of energy per absolute temperature level).

The fundamental laws of nature are considered to be axiomatic and many believe they could not be explained, proven or questioned. However, everything may and should be questioned, reasoned, explained and possibly proven. The miracles are until they are comprehended and understood.

**Key Words:** Sadi Carnot, Heat engine, Non-equilibrium, Reversibility, Work availability, Exergy, Irreversibility, Thermodynamics, Temperature, Clausius Inequality, Energy, Entropy, Second Law of Thermodynamics.

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## INTRODUCTION AND BACKGROUND: Reasoning Open Issues And Challenges

This treatise has an objective to put certain physical and philosophical concepts in perspective, to revisit the fundamental laws of nature, as well as to initiate discussion and constructive criticism about these fundamental concepts.

The Second Law made its appearance around 1850, but a half century later it was already surrounded by so much confusion that the *British Association for the Advancement of Science* decided to appoint a special committee with the task of providing clarity about the meaning of this law. However, its final report (Bryan, 1891) did not settle the issue. Half a century later, the physicist/philosopher Bridgman (1941) still complained that “*there are almost as many formulations of the Second Law as there have been discussions of it.*”

And even today, the Second Law remains so obscure, due to the lack of its subtle comprehension, that it continues to attract new efforts at clarification, including this one.

The theory of classical Thermodynamics was originally based on thermal and mechanical energy transformations, and is characterized by a so-called “phenomenological” approach, formulated on empirical, but universal principles that deny the possibility of various kinds of perpetual motions, while at the same time avoids speculative assumptions about the microscopic constitution and complex dynamics of the involved material systems. The physical systems are regarded as “black boxes” and all specific Thermodynamic quantities and their general properties are derived by means of these principal laws. This is the approach to the theory taken by the pioneers: Carnot [1], Clausius, Kelvin, and Planck, and with some exceptions by Gibbs.

The classical, phenomenological Thermodynamics today has unjustifiably a dubious status. Some modern physicists regard classical Thermodynamics as an obsolete relic. Often, mostly due to lack of dubious comprehension, the Thermodynamics is considered as an engineering subject and thus not as the most fundamental science of energy and nature. However, a number of prominent modern physicists have acknowledged fundamental importance of Thermodynamics. Einstein, whose early writings were related to the Second Law, remained convinced throughout his life that “*Thermodynamics is the only universal physical theory that will never be refuted.*” Many other renowned physicists have been impressed by the universal and indisputable validity of Thermodynamics principles. Apart from the view that Thermodynamics is obsolete, there is a widespread belief among scientists in Thermodynamics absolute authority.

Maxwell (1877) regarded the Thermodynamics theory as “*a science with secure foundations, clear definitions and distinct boundaries.*” But there are also others who dispute its clarity and rigor. Arnold (1990) stated that “*Every mathematician knows it is impossible to understand an elementary course in Thermodynamics.*” Von Neumann once remarked that “*whoever uses the term “entropy” in a discussion always wins since no one knows what entropy really is, so in a debate one always has the advantage.*”

The historian of science and mathematician Truesdell (1966) explains in his essay of *Method and taste in natural philosophy*: “*Heads have split for a century trying to define entropy in terms of other things. Entropy, like force, is an undefined object, and*

*if you try to define it, you will suffer the same fate as the force-definers of the seventeenth and eighteenth centuries: Either you will get something too special or you will run around in a circle."*

Trying to reason, understand and explain fundamental concepts is a daunting endeavor, and different from understanding other concepts derived from the fundamental ones. However, there is factual reality that we should be always aware of and guided by. The fundamental interactions and their inter-relations along with subtle reasoning may help to resolve ambiguities and close the needed loops. "Going in a circle" does not mean we are not going anywhere as long as we succeed in comprehension of the "circular" subtle interactions, including interrelated causes-and-effects (chicken-and-egg) phenomena. A barrier between our understanding and reasoning explanation is a language ambiguity, which could be partially offset by more objective and more primitive mathematics, and a price paid is the discrepancy between reality and mathematical idealizations and simplicity, but sometimes unnecessary complexity. Another critical tool for resolution of reasoning ambiguities is experimental ingenuity with observation and quantification of reality, and again the price paid is the discrepancy between reality and experimental limitations, including inevitable and unconscious errors and uncertainties. We must bear in mind that new ideas and concepts (a way one perceive reality) are not only difficult for a reader to grasp but equally difficult and excruciating for an author to express, as it is experienced here. *There is a need of using synonyms, redundant and imaginative explanations, quotation marks for words that are not quoted, and similar, since new or creative ideas, concepts and explanations are to be expressed with existing terminology.*

There are many puzzling issues surrounding the Second Law and other concepts in Thermodynamics, including subtle definitions and ambiguous meaning of very fundamental concepts. Further confusions are produced by attempts to generalize some of those concepts with similar but not the same concepts in other disciplines, like *Thermodynamic entropy* versus other types of (quasi)entropies.

Unless otherwise stated all terms used here refer to Thermodynamic (mass-energy) concepts: Thermodynamic non-equilibrium, Thermodynamic entropy, Thermodynamic structure or system, etc. Furthermore, the mass and energy are manifestation of each other and are equivalent; they have a holistic meaning of *mass-energy*, and will often be referred to simply as *energy*.

Structural, Thermodynamic non-equilibrium [in energy units], further-on simply denoted as "*non-equilibrium*," refers to the forced non-uniform distribution of mass-energy in space, which has forced tendency to equalize the mass-energy in space (force-flux cause-and-effect phenomena) ultimately resulting in quasi-uniform and quasi-steady randomized *Thermodynamic equilibrium*, represented by uniform temperature, in Kelvin degree unit, and uniform other intensive macroscopic properties. At equilibrium, the forces-fluxes will be balanced without net mass-energy transfer.

Any process requires mass-energy flux exchange, i.e., it is a forced displacement of mass-energy in space and time, ultimately resulting in forced equilibrium. Therefore, the force concept is the coupled force-flux cause-and-effect phenomena. Furthermore, the directional energy flux could be effectively represented by related linear momentum. In that regard the Newton's Laws of forces are special cases of more general Thermodynamic Laws, which could be further generalized as *Fundamental*

*Laws of Nature.* Namely, the First Newton Law of innate (inertia) of mass-energy to stay stationary or in uniform motion unless forced otherwise, is equivalent to the Zeroth Law of Thermodynamic equilibrium or the *Natural law of equilibrium existentialism*. The Second Newton Law of forced acceleration is a special case of reversible energy transfer from an energy source (acting system) to an energy sink (accelerated system or body), described by both the First and Second Law of Thermodynamics. The First Thermo Law refers to conservation of mass-energy or the *Natural Law of conservational transformationalism*, and the Second (Thermo) Law refers to forced process direction, from non-equilibrium towards equilibrium or the *Natural Law of irreversible directional transformationalism towards equilibrium accompanied with entropy generation*. The Third Thermo Law could be generalized as the *Natural law of unattainability of emptiness*. Actually, the Newton Laws are special cases of each others' and the more general Laws of Thermodynamics.

The theory of classical Thermodynamics was originally based on thermal and mechanical energy transformations, but it has been expended to all other types of work and heat interactions and thus effectively has resulted in Thermo(multi)dynamics, the general energy science, considered by some to be “the *Mather of all sciences*.”

### **Reasoning the Second Law**

During any process (mass-energy transfer), there will be some dispersion or dissipation of directional, available energy (work potential) within the surrounding substructures, whereby the energy will be directionally randomized into thermal energy with the corresponding entropy generation, equal to the dissipated energy per absolute temperature of that system. In limiting, ideal and the most efficient process without energy dissipation, the non-equilibrium of all involved/interacting systems will be conserved and the process could be reversed. Thus in reversible processes the entropy is conserved too, since there is no entropy generation. Therefore, it is impossible to have a hyper-reversibility with ever-increasing efficiency beyond the limiting reversible efficiency since it would produce a black-hole-like singularity with ever increasing mass-energy concentration and self-increasing forces. Such processes would be self destructive and unsustainable. If hyper-reversibility exceptions are possible and multiplied, they would “clean” the existing mass-energy space (and ultimately universe) into unobserved singularity (like black-hole), thus destroying the energy we know about and effectively violating the First Law of energy conservation.

Furthermore, we know that process forcing has to come from somewhere, i.e., from existing interacting systems with higher mass-energy concentration (Third Newton Law of action and reaction), thereby rendering the destructive hyper-reversibility and violation of the Second law impossible (ever increasing self-forcing displacement without surrounding support would be impossible). On the other hand, a frictional traction is needed as a support to enable a purposeful real (irreversible) processes: to walk, drive, swim or fly, even keep a clock running; nothing will be permanently accomplished without irreversible friction, but everything would reversibly oscillate in place within inertial-elastic structures, how ironic!

Quantification of the Thermodynamic non-equilibrium of all involved interacting systems is expressed as available/useful energy or work potential [in energy unit], i.e.,

the maximum possible work to be extracted (and reversibly stored, otherwise it will be irreversibly dissipated via heat to thermal energy), if the systems are reversibly brought to a common equilibrium while extracting work (also known as exergy if brought to the equilibrium within a very large, reference surrounding system). Note, to bring reversibly an isolated non-equilibrium system to the equilibrium, the extracted work would have to be allowed out of the “isolated” system (to be stored and would increase non-equilibrium somewhere else), otherwise it would irreversibly dissipate within the isolated system. If stored within the isolated system, the original non-equilibrium will be rearranged and conserved.

Reversibility is “conservation of non-equilibrium” or available energy, i.e., conservation of work potential (or exergy), and also conservation of entropy. It is “true equivalency” since the “input” and process “output-result” could be reversed and are truly equivalent, as first ingeniously deduced by Sadi Carnot (as detailed below). Reversible processes are the most efficient, thus ultimate ideal processes since they do not degrade (dissipate) energy and could be reversed back to the original state without any loss of original work potential. In real irreversible processes the “outcome” could not be reversed back to “input,” thus, does not have the same “equivalency,” i.e., the same usefulness or quality, since it cannot by itself (spontaneously) produce the original existence, regardless that the mass-energy is conserved.

Irreversibility [in energy unit] is dissipation of “work potential” via heat to thermal energy, i.e., ordered/structural energy (mechanical, electrical, chemical, nuclear, etc.) conversion to random thermal energy. A boundary/shell structure separates systems in non-equilibrium with large potential gradients, like a mechanical, thermal, electrical or chemical boundary container/shell. The boundary structures prevent spontaneous interactions (or more accurately substantially impede interactions, since there are no perfect boundaries). Namely, so-called ridged boundary will prevent volume expansion and pressure equalization (prevent mechanical work transfer), or adiabatic boundary will prevent entropy interchange and temperature equalization (prevent heat transfer), or dielectric boundary will prevent charge interchange and voltage equalization (prevent electrical work transfer), etc.

Furthermore, due to diverse system structures (all structures are energetic, i.e. possess energy) and thus diverse energy forms or types, during energy transfer of one energy type from high to low potential, it is possible, due to “process inertia,” to increase potential (i.e. non-equilibrium) of another energy type; however the over-all net-potential (and non-equilibrium) of all involved systems (thus universe) will be reduced, and only in limit conserved, but never could be increased (by itself between systems within isolated enclosure).

Additivity or integrality and conservationism require that phenomena should be the same at all time and space scales without exceptions. Due to limitations of our observation tools, including illusion (aliasing phenomena) and comprehension, we may be misled to believe otherwise. All interactions in nature are physical and based on simple cause-and-effect conservation laws, thus deterministic and should be without any exceptional phenomenon. Due to diversity and complexity of large systems, we would never be able to observe deterministic phenomena with full details but have to use holistic and probabilistic approach for observation; therefore, our observation

methodology is holistic and probabilistic, but phenomena have to be deterministic, not miraculous nor probabilistic.

There are many statements of the Second Law which in essence describe the same natural phenomena about the spontaneous direction of all natural processes from non-equilibrium towards a stable equilibrium with randomized redistribution and equipartition of mass-energy within the elementary structure of all interacting systems (thus the universe). All the Second Law statements are essentially equivalent since they reflect equality of work potential between all system states reached by any and all reversible processes (reversibility is measure of equivalency) and impossibility of creating or increasing over-all non-equilibrium and aver-all work potential (of all interacting systems).

### **Issues, Confusions, and Challenges**

The second law of Thermodynamics is among the most fundamental principles of engineering, science and nature. Since its discovery about one-and-a-half century ago, no violation has been recognized by the scientific community, and its status is generally considered supreme. However, in addition to long-standing and wishful, so-called “thought-experiments,” the Second law has come under unprecedented scrutiny during the last couple of decades [2], by research groups worldwide, as evidenced by a number of specific challenges documented in more than 50 published papers, including several laboratory challenges.

If we somehow “trick” existing quasi-equilibrium (has to be caused somehow with energy transfer process, not just wishful thinking), it has to be from within or the surroundings at higher potential and the process will take place until new equilibrium is achieved. It cannot be done from within that equilibrium (wishful Maxwell demon could not be utilized since 1867, or Brownian/Feynman-Smoluchowski ratchet, etc.). Inserting a device, with desired differential properties to achieve needed functionality (with non-uniform elasticity, emissivity, rigidity, etc.) into an equilibrium system to “separate” random non-uniformity and then extract useful work, will disturb that equilibrium and initiate a transient process to a new equilibrium, including possible change of the inserted device properties, thus making such a device useless in a new equilibrium. After all, the properties are result of mass-energy structure and interactions, the cause and effect phenomena, a local and/or transient source of non-equilibrium cannot be sustainable.

We also may arrive in a state with perpetually rotating wheel without load (just motion without load, thus without useful work) or elastic (hot-cold, etc.) oscillator (reversible rearrangement of non-equilibrium, fluctuation theorem), and mistakenly believe that the former violates the First Law (Perpetual Motion 1) and the latter the Second Law (Perpetual Motion 2).

It is possible to have water run uphill, heat transferred from colder to hotter body, build functional (organized) structure, and yes, have natural and life processes create amazing organization and species, but all due to external energy flow with dissipation and, yes!, with entropy generation. We cannot walk forward without moving the Earth backward, the latter not possible to observe or measure easily. Similarly we cannot produce cold or hot or life (or any non-equilibrium) from within an equilibrium, without

having energy flow from the surroundings, the latter sometimes may be hard or impossible to observe and measure. Without environmental influence (mass-energy transfer always accompanied with entropy generation) there would be no formation of cyclones, crystals, life! Until couple of hundred years ago we did not know what happens with a falling stone energy after it hits the ground, because we could not easily observe or measure it! The miracles are until they are comprehended and understood!

## **Production of Functional Form-Order Does Not Destroy Entropy**

The Second Law is often challenged in biology, life and social sciences, including evolution and information sciences, all with history rich in confusion. There are other types of “organized structures” than the mass-energy non-equilibrium, like functional-design form-structures or information-algorithm-template structures with deferent functions and purposes. Even though the organizational form-structures and energy-structures are similar in some regards and may be described with the same math-statistical methods, they are not the same and do not have the same physical meaning nor the physical units. Namely, statistical disorder is not the same as mass-energy dissipative disordering, regardless that both could be described with similar statistical methodology. Therefore, the Thermodynamic entropy [J/K] is not the same as information entropy or other entropy-like but different logical concepts.

Organization/creation of technical (man-made) and natural (including life) structures and thus creation of "local non-equilibrium" is possible and is always happening in many technical and natural processes, using another functional structures (tools, hardware/software templates, information-knowledge-"intelligent" templates, DNAs, etc. However, the mass-energy flow/transfer within those structures will always and everywhere dissipate energy and generate entropy (according to the Second Law!), i.e. on the expense of surrounding/boundary systems' non-equilibrium. It may appear that the created non-equilibrium structures are self-organizing from nowhere, from within an equilibrium (thus violating the Second Law), due to the lack of proper observations and "accounting" of all mass-energy flows, the latter maybe in “stealth” form or undetected rate at our state of technology and understanding (as the science history has though us many times). Entropy can decrease (locally) but cannot be destroyed anywhere. The miracles are until we comprehend and explain them!

*It is crystal-clear (to me) that all confusions related to the far-reaching fundamental Laws of Thermodynamics, and especially the Second Law, are due to the lack of their genuine and subtle comprehension.*

## **SADI CARNOT’S INGENIOUS REASONING OF REVERSIBLE PROCESSES AND CYCLES**

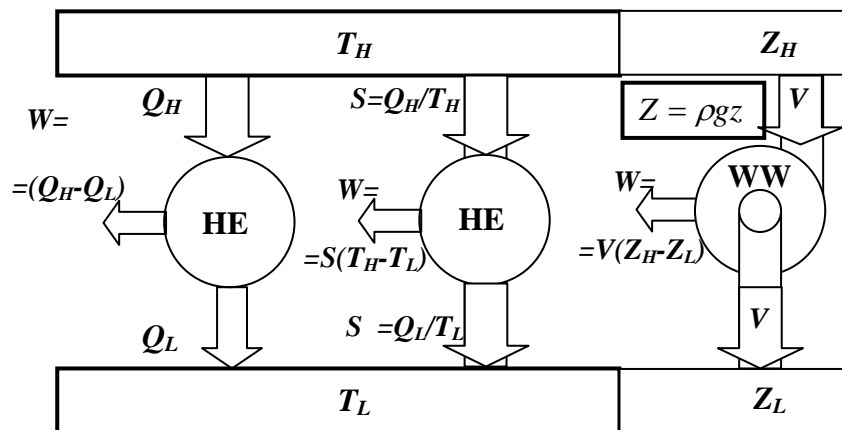
In historical context, it is hard to comprehend now how Carnot, at age 28, ingeniously and fully explained the critical concepts of reversible thermo-mechanical processes and limits of converting heat to work at inception of the heat engines’ era when nature of heat was not fully understood. No wonder that Sadi Carnot’s “*Réflexions sur la puissance motrice du feu (Reflections on the Motive Power of Fire* [1]),” original version published in 1824, was not noticed at his time, when his



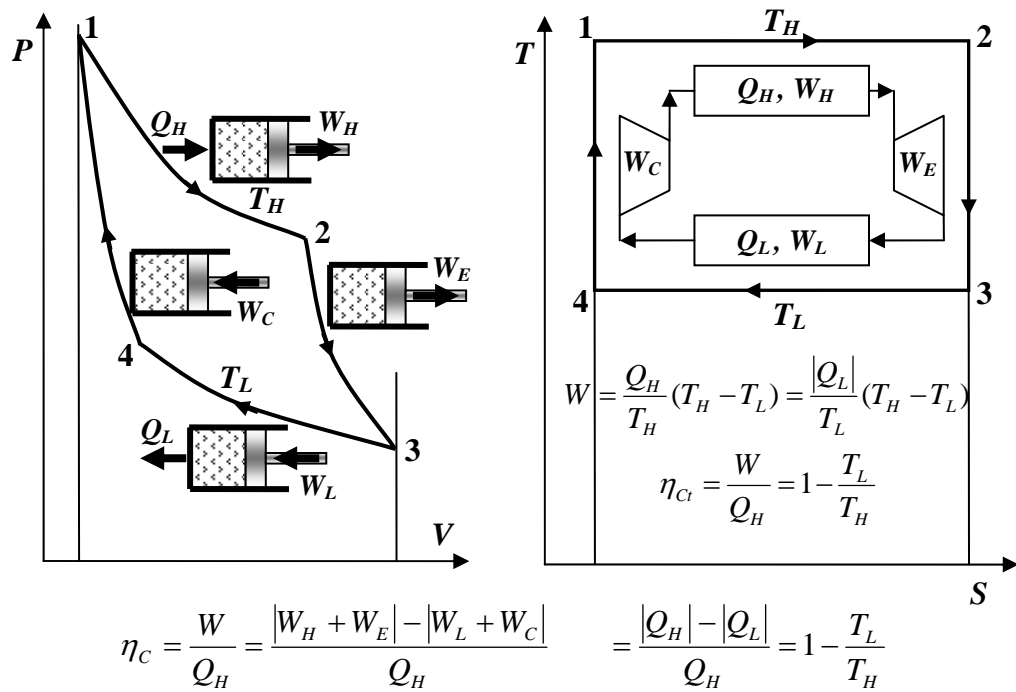
ingenious reasoning of ideal heat engine reversible cycles is not fully recognized, and may be truly comprehended by a few, even nowadays. He gave a full and accurate reasoning of heat engine limitations of “converting heat to work” at the time when caloric theory was flourishing and almost two decades before equivalency between work and heat was experimentally established by Joule in 1843. Sadi Carnot laid ingenious foundations for the Second Law of Thermodynamics before the First Law of energy conservation was even known and long before Thermodynamic concepts were established. Sadi Carnot, who died at age 36 from cholera epidemic, could not have been aware of immense implications of his ingenious reasoning at that time.

At that time, when the energy conservation law was not known and heat was considered as indestructible caloric, when heat engines were in initial stage of development with efficiency of less than 5%, the confusion and speculations flourished. Can the efficiency be improved by different temperatures or pressures, a different working substance than water; or some different mode of operation than pistons and cylinders? With ingenious and far-reaching reasoning, Carnot answered all of those questions and reasoned (thus proved) that maximum, limiting efficiency of heat engine does not depend on medium used in the engine or its design, but only depends on (and increases with) the temperature difference between the heat source and cooling medium or heat sink, similarly to the water wheel efficiency dependence on the waterfall height difference (see Fig. 1, formulas are developed after Carnot followers’ work). The most importantly, Carnot introduced the reversible processes and cycles and, with ingenious reasoning, proved that maximum heat engine efficiency is achieved by any reversible cycle, thus, all must have the same maximum possible efficiency, see Eq (1).

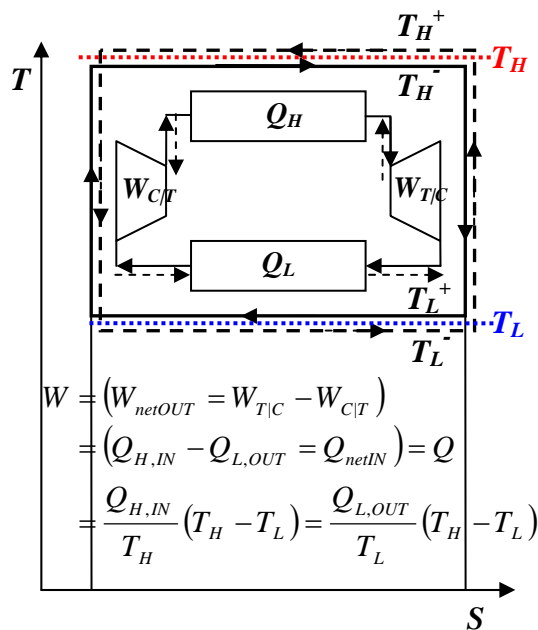
*“The motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of the caloric.” [1].*



**FIGURE 1.** Similarity between a heat engine (HE) and a water wheel (WW).



**FIGURE 2.** Heat-engine ideal *Carnot* cycle: note thermal and mechanical expansions and compressions (the former is needed for net-work out, while the latter is needed to provide reversible heat transfer).

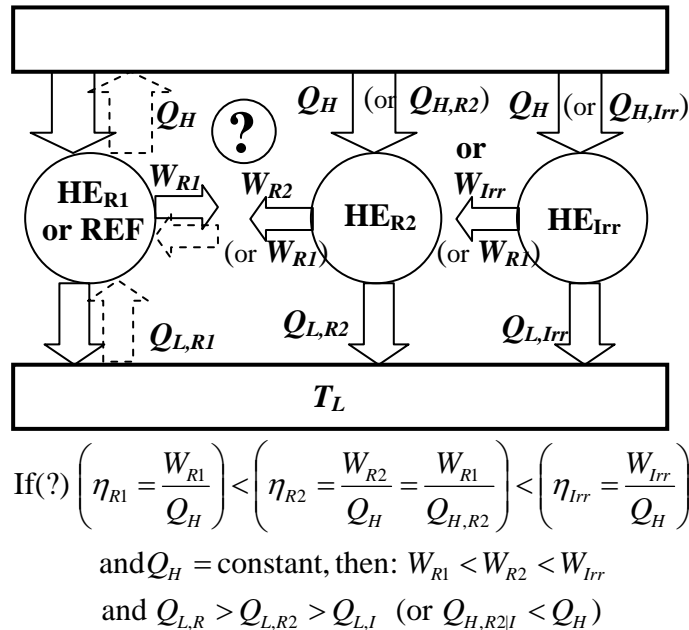


**FIGURE 3.** Reversible Heat-engine (solid lines) and Refrigeration (dashed lines, reversed directions) *Carnot* cycle.

$$W_C = W_{netOUT} = Q_{IN} \cdot f_C(T_H, T_L); \quad \eta_C = \frac{W_{netOUT}}{Q_{IN}} \Big|_{Max} = \underbrace{f_C(T_H, T_L)}_{\text{Qualitative function}} \Big|_{Rev.} \quad (1)$$

Carnot cycle consists of four reversible processes, see Fig. 2: isothermal heating and expansion at constant high-temperature  $T_H$  (process 1-2); adiabatic expansion to achieve low-temperature  $T_L$  (process 2-3); isothermal cooling and contraction at constant low-temperature  $T_L$  (process 3-4); and adiabatic compression to achieve high-temperature  $T_H$  and complete the cycle (process 4-1). All processes are reversible, thus the cycle could be reversed along the same path and with the same quantities of all the heat and work in opposite directions (in-to-out and vice versa), see Fig. 3, i.e.:

$$\{Q_H, Q_L, W_C\} \underset{\text{IF REVERSED}}{\rightleftharpoons} \{-Q_H, -Q_L, -W_C\} \quad (2)$$



**FIGURE 4.** If a reversible heat engine ( $HE_{R1}$ ) has a smaller efficiency than other reversible  $HE_{R2}$  or irreversible  $HE_{Irr}$ , then if  $HE_{R1}$  is reversed (Refrigeration-REF cycle) and combined with other HEs, it will result in impossible net-work from a single reservoir ( $W_{R2/I} - W_{R1}$ ), or heat transfer from low to high temperature ( $Q_H - Q_{H,R2/Irr}$ ).

The consequence of a process and cycle reversibility is the most ingenious and is far-reaching, see Fig. 4 (see also next Section). Carnot's simple and logical reasoning that mechanical work is extracted in heat engine due to the heat passing from high to low temperature, led him to a very logical conclusion that any heat transfer from high to low temperature (like in a heat exchanger) without extracting possible work (like in a limiting heat engine) will be a waste of work potential -- so he deduced that any heat transfer in ideal, limiting heat engine must be at infinitesimally small temperature difference, achieved by mechanical compression or expansion of the working medium (required temperature adjustment without heat transfer), as Carnot ingeniously advised

in full details [1]. Then he expended his logical reasoning to conclude that all limiting (ideal) heat engines must have equal and maximum possible efficiency, otherwise if reversed, the impossible “perpetual motion” will be achieved. What a simple and logical ingenious reasoning!

Let us revisit Carnot’s reasoning and consider three heat-engine (HE) cycles on Fig. 4: two reversible,  $HE_{R1}$  and  $HE_{R2}$ , and third irreversible,  $HE_{Irr}$ . Let us *assume* that the cycles are taking place between the same temperature reservoirs (one at higher temperature  $T_H$  and other at lower  $T_L < T_H$ ) and consuming the same quantity of heat  $Q_H$ , but have different efficiencies ( $\eta_{R1} < \eta_{R2} < \eta_{Irr}$ , where  $\eta = W_{netOUT} / Q_H$ ). If we reverse the reversible  $HE_{R1}$  with the smallest efficiency and couple it with either  $HE_{R2}$  or  $HE_{Irr}$  then the net-effect will be production of net-work ( $W_{Irr} - W_{R1} > W_{R2} - W_{R1} > 0$ ) while consuming heat from one thermal reservoir only (at  $T_L$  since  $Q_H$  will be returned back at  $T_H$ ), thus violating the Second Law of Thermodynamics (*perpetual motion machine of the second kind*), see Fig. 4, established later after Carnot’s death. However, at the time, Carnot thought that the above scenario will be producing work without spending any caloric ( $Q_{L,R2|Irr} = Q_{L,R1} = Q_H$ , see below, thus  $Q_{L,R2|Irr} - Q_{L,R1} = 0$ ) and therefore violating the impossibility of the *perpetual motion machine* (of the first kind; note that for rather very low HE efficiency at that time  $Q_L \approx Q_H$ , and that neither Thermodynamics nor its energy conservation law were established at that time) [3,4,5]. Carnot erroneously assumed that the same caloric (heat) will be passing through the engine and extract (produce) work by lowering its temperature, similarly to the same water flow passing through the water-wheel and producing work by lowering its elevation potential (see Fig.1). This error, considering the knowledge at the time, in no way diminished the Carnot’s ingenious reasoning and conclusions about limiting reversible processes and accurate limitations of heat to work conversion. Alternatively, similar reasoning as above, if the three heat-engines of Fig. 4 produce the same amount of work  $W_{Irr} = W_{R2} = W_{R1}$ , then the assumed higher efficiency engines will require less heat consumption ( $Q_{H,Irr} < Q_{H,R2} < Q_{H,R1}$ ) with the corresponding heat rejection at lower temperature ( $Q_{L,Irr} < Q_{L,R2} < Q_{L,R1}$ ), and then the net-effect will be transferring heat ( $Q_{L,R1} - Q_{L,R2|Irr} = Q_{H,R1} - Q_{H,R2|Irr}$ ) from low-to-high temperature reservoirs only (from  $T_L$  to  $T_H$ ), again violating always observed direction of spontaneous heat transfer from higher to lower temperature, later generalized into the Second Law of Thermodynamics. The above analysis proves that a reversible cycle cannot have smaller efficiency than any other cycle, thus all reversible cycles (we could have reversed either  $HE_{R1}$  or  $HE_{R2}$  but not  $HE_{Irr}$  irreversible one) must have the same maximum possible efficiency (the reversible equivalency) for the given temperature of the two thermal reservoirs, independently from anything else, including the nature of heat-engine design and its agent undergoing the cyclic process. Since the irreversible cycles could not be reversed they may (and do) have lower than maximum reversible efficiency up to zero (no net-work produced, if all work potential is dissipated to heat) or even negative (external work input required to run such a “parasite” engine which will dissipate such work in addition to original work potential into heat), i.e.:

$$\eta_{irr} < \underbrace{\eta_{Rev} = \eta_{max}}_{\text{Reversible}} = f_C(T_H, T_L) \quad (3)$$

Carnot did not provide quantitative, but (above) qualitative relation for the ideal heat engine efficiency, and accurately specified all conditions that must be satisfied to achieve reversibility and the maximum efficiency: the need for “*re-establishing temperature equilibrium for caloric transfer*,” i.e. reversible processes, where the reversible heat transfer has to be achieved at negligibly small (in limit zero) temperature difference at both temperature levels,  $T_H$ , high temperature for heat source (reversible heating), and  $T_L$ , low temperature for heat sink (reversible cooling of heat-engine medium), see Fig. 3; otherwise the work potential from heat transfer due to temperature difference will be irreversibly lost (the main Carnot’s cause-effect reasoning).

Carnot reasoned that mechanical expansion and compression are needed to decrease and increase the temperature of the engine medium to match the temperature of the high- and low-temperature thermal reservoirs, respectively, and thus provide for the reversible heat transfer [6-8]. Carnot then reasoned that in limiting case such an ideal cycle could be reversed using the obtained work and transfer back the caloric (heat) from low- to high-temperature thermal reservoirs, thus laying foundations for the refrigeration cycles as reversed heat engine cycles, see Fig. 3 and Eq. (2).

Actually, Carnot (1824) established the fundamentals for the second Law of Thermodynamics (Clausius 1850, and finalized by Thomson in 1874), before the First Law was even known (Meyer, 1841; Joule, 1843, and finalized by Helmholtz, 1847).

### **Kelvin’s Absolute Thermodynamic Temperature**

Carnot analyzed critical concepts and qualitative relations related to the “*motive-power equivalent of heat*” through his ingenious reasoning of reversible cycles, before the Joule’s “*mechanical equivalent of heat*” was even known. Only after the latter was established it was possible (actually easy) to quantify Carnot engine efficiency, i.e.:

$$\eta_c = \frac{W_{netOUT}}{Q_{IN}} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \quad (4)$$

The above Eq. (4) is valid for both, real-irreversible and ideal-reversible heat engine cycles. However, for *reversible* Carnot cycles the efficiency depends only on the temperature values of the two heat reservoirs, as originally reasoned by Sadi Carnot (Eq. 1). Furthermore, more specific relation for the Carnot efficiency could be inferred by considering the three related Carnot cycles on Fig. 5. For a given  $T_H$ , for arbitrary high-temperature reservoir and given arbitrary low  $T_{Ref}$ , for reference-temperature reservoir, the combined Carnot efficiency of the two heat engines,  $HE_{HT}$  and  $HE_{TR}$ , cascaded at an arbitrary intermediate temperature level  $T$ , must be the same as the corresponding Carnot efficiency of a third heat engine  $HE_{HR}$  (due to reversible equivalency discussed above), running between the two temperature reservoirs with the same heat input  $Q_H$ , and thus releasing the same heat  $Q_{Ref}$ , at a given reference temperature  $T_{Ref}$ , see Fig. 5. Thus, for everything given as fixed quantities, but intermediate temperature  $T$ , the heat  $Q(T)$  transferred from  $HE_{HT}$  to  $HE_{TR}$  engine must

be directly proportional to  $Q_{Ref}$  (efficiency is an intensive HE property) and an increasing function of  $T$  only, i.e.:

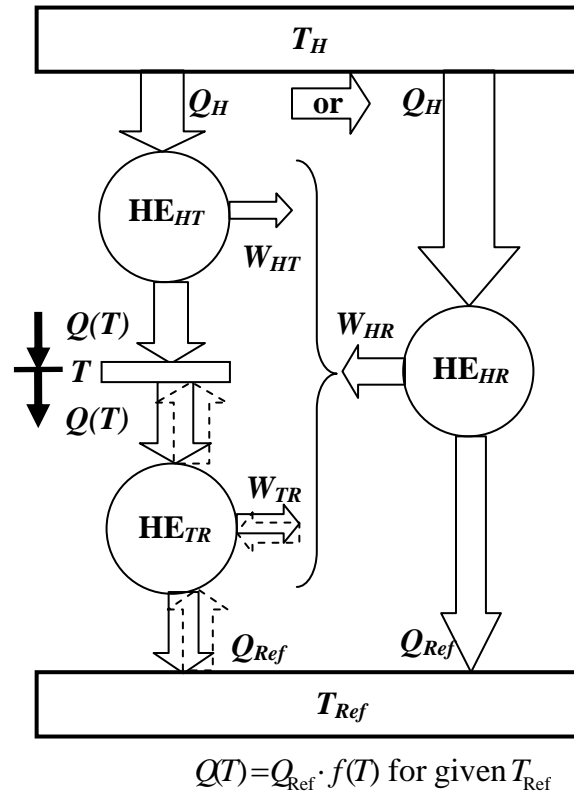
$$Q(T) = Q_{Ref} \cdot f(T, T_{Ref}) \Big|_{T_{Ref}=given} = Q_{Ref} \cdot f(T) \quad (5)$$

Then, the above could be applied for any temperature level, say  $T=T_1$  or  $T=T_2$  or  $T=T_H$ , and very important correlation deduced:

$$\frac{Q(T_1)}{Q(T_2)} = \frac{Q_{Ref} \cdot f(T_1)}{Q_{Ref} \cdot f(T_2)} = \frac{f(T_1)}{f(T_2)} \Big|_{f(T)=\theta=T} = \frac{T_1}{T_2} = \frac{Q_1}{Q_2} \quad (6)$$

The above function  $f(T)$  could be any arbitrary, but non-negative and increasing function of temperature, thus defining a new absolute temperature scale, say  $\theta = T \geq 0$  (for simplicity, but could be another function). It is shown elsewhere that this simple temperature function is the same as temperature function (temperature scale) obtained using ideal gas thermometer with constant specific heat.

*The above function, the Carnot ratio equality (Eq. 6), is much more important than what it appears at first. Actually it is probably the most important equation in Thermodynamics and amongst the most important equations in natural sciences.*



**FIGURE 5.** For a fixed  $T_H$ ,  $T_{Refs}$ ,  $Q_H$ , and  $Q_{Refs}$ , the  $Q(T)$  is proportional to  $Q_{Ref}$  (efficiency is intensive property) and an increasing function of  $T$  for a given  $T_{Ref}$ , see Eq.(6).

Not only that Eq. (6) defines the Thermodynamic absolute temperature scale, which is independent of the substance of a thermometer (HE media and type), but it will define a fundamental property of matter, the entropy  $S$ , the related process-equilibrium functions and correlations, and quantify irreversibility (loss of work potential), and the far-reaching Second Law of Thermodynamics.

In some other references the above Carnot ratio equality of heat and related absolute temperature ratios, is deduced from the following reasoning using Eq.(1), see Fig. 5 again:

$$\left(\frac{Q_{\text{Ref}}}{Q_H}\right) = \underbrace{1 - f_C(T_H, T_{\text{Ref}})}_{\text{Not function of } T} = f_{C1}(T_H, T_{\text{Ref}}) = \left(\frac{Q_T}{Q_H}\right) \cdot \left(\frac{Q_{\text{Ref}}}{Q_T}\right) = \underbrace{f_{C1}(T_H, T_T) \cdot f_{C1}(T_T, T_{\text{Ref}})}_{\text{Dependance of } T \text{ must cancel}} \Bigg|_{\text{must be}} \quad (7)$$

$$= \left(\frac{f(T_T)}{f(T_H)}\right) \cdot \left(\frac{f(T_{\text{Ref}})}{f(T_T)}\right) = \left(\frac{f(T_{\text{Ref}})}{f(T_H)}\right) = \left(\frac{Q_{\text{Ref}}}{Q_H}\right)$$

Now, it is convenient to write a simple correlation,  $f(T)=T$ , to define the absolute temperature scale for a given arbitrary reference temperature and unit increment, say  $T_{\text{Ref}}= 273.15 \text{ K}$  and unit of absolute temperature  $1 \text{ K} = 1^\circ \text{C}$  (Kelvin, 1848), i.e.:

$$\frac{T}{T_{\text{Ref}}} = \frac{Q(T)}{Q(T_{\text{Ref}})} = \frac{Q(T)}{Q_{\text{Ref}}}, \text{ therefore, } T = \frac{Q(T)}{Q(T_{\text{Ref}})} T_{\text{Ref}} = \frac{Q(T)}{Q_{\text{Ref}}} T_{\text{Ref}} \quad (8)$$

Where,  $Q(T)$  and  $Q_{\text{Ref}}$ , are heat transferred in any reversible Carnot cycle working between an arbitrary temperature  $T$  and the reference temperature  $T_{\text{Ref}}$ , which is independent from the (working) medium of the reversible heat-engine, the latter functioning as a thermometer.

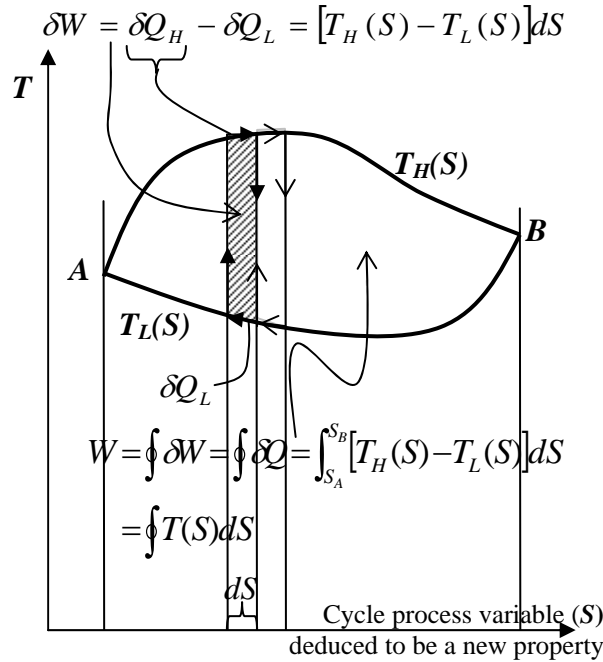
### Clausius Equality (Entropy) and Inequality (Entropy Generation)

Another important consequence of the Carnot ratio correlation, Eq. (6), for a Carnot cycle working between the two different, but constant temperature thermal-reservoirs,  $T=T_H$  and  $T=T_L$ , is:

$$\frac{Q_{H,IN}}{T_H} - \frac{Q_{L,OUT}}{T_L} = \frac{Q(T_H)}{T_H} + \frac{Q(T_L)}{T_L} = 0; \text{ where } Q(T) = Q_{IN} = -Q_{OUT} \quad (9)$$

Or in general, a reversible cycle working between the variable temperature thermal-reservoirs, see Fig. 6, could be accomplished with infinite number of coupled infinitesimally small Carnot cycles each working between two temperature reservoirs at specified temperatures and finite temperature difference. After the cycle-integration of Eq. (9) for infinitely many Carnot cycles of infinitesimally small heat transfer  $\delta Q$ , we have:

$$\int_A^B \left( \frac{\delta Q_{H,IN}}{T_H} - \frac{\delta Q_{L,OUT}}{T_L} \right) = \oint \left( \frac{\delta Q(T_H)}{T_H} + \frac{\delta Q(T_L)}{T_L} \right) = \oint \frac{\delta Q(T)}{T} = 0 \quad (10)$$



**FIGURE 6.** Variable temperature reservoirs require multi-stage Carnot cycles

Eq.(10) is well-known Clausius equality (more about Clausius inequality later), which defines new fundamental property entropy, since its integral is independent on process path  $Q(T)$  between any two points  $A$  and  $B$ , namely (compare with Eq. 10):

$$\oint_{\text{Cycle}} \frac{\delta Q}{T} = \int_A^B \frac{\delta Q(T_H = T_{\text{any}})}{T_H} \Big|_{\text{Rev}} + \int_B^A \frac{\delta Q(T_{L, \text{as given}})}{T_L} \Big|_{\text{Rev}} = \int_A^B \frac{\delta Q(T_H = T_{\text{any}})}{T_{H, \text{Any}}} \Big|_{\text{Rev}} - \int_A^B \frac{\delta Q(T_{L, \text{as given}})}{T_{L, \text{given}}} \Big|_{\text{Rev}} = 0$$

Any Rev. Path
Fixed Pat
Any Rev. Path
Fixed Pat

$$S_B - S_A = \int_A^B \frac{\delta Q(T_H = T_{\text{any}})}{T_{\text{Any}}} \Big|_{\text{Rev}} = \int_A^B \frac{\delta Q(T_{L, \text{as given}})}{T_{\text{as given}}} \Big|_{\text{Rev}} = \text{const} \{ \text{independent of path } Q(T = T_{\text{any}}) \}$$

Any Rev. Path
Fixed Path
Thus System Property

$$S_{B|Any} = S_{A|Ref} + \int_{A|Ref}^{B|Any} \frac{\delta Q(T_{Any})}{T_H} \Big|_{\text{Rev}}$$

Any Path (Reversible)

(11)

Let us reiterate, the reversible process/cycle equivalency deduced by Sadi Carnot has resulted in the Clausius equality (Eq.10): Efficiency of any reversible cycle between any two temperature reservoirs cannot be smaller than any other cycle efficiency, thus all reversible cycle efficiencies between the two reservoirs must be the same and maximum possible. This subtle reasoning allowed definition of the absolute Thermodynamic temperature, Eq.(8), and deduction, and thus proof based on the Carnot's reasoning, of the Clausius equality, Eq.(10), and definition of the new



property, *entropy*, up to an arbitrary reference value, Eq.(11). Additional consequence of Carnot's reasoning is that non-reversible (irreversible) cycles must have smaller efficiency than maximum possible reversible efficiency, thus allowing deduction and thus proof of the Clausius inequality based on the same Carnot subtle reasoning, see next. We have to keep in mind that Carnot's reasoning is based on impossibility of making an autonomous machine (to spontaneously work on its own), which will be equivalent of having higher efficiency of any cycle than any other reversible cycle, or having a heat engine producing work from a single reservoir by transferring heat from colder to hotter reservoir (after accounting for Joule's energy conservation), which is in turn equivalent to the deduced Clausius inequality (see next), the latter in limit being an equality for reversible cycles.

Namely, as reasoned by Carnot and reemphasized above, for real irreversible cycles (*Irr*), the heat engine efficiency is smaller than for reversible cycles (*Rev*, otherwise the *Irr* cycle will be reversible), i.e., for everything else being the same, then  $W_{Irr} < W_{Rev}$ . Thus we can reason the proof of the famous Clausius inequality as follow:

$$\left( W_{Irr} = \oint \delta Q_{Irr} \right) < \left( \oint \delta Q_{Rev} = W_{Rev} \right) \quad (12)$$

Considering the inequality Eq.(12) and expanding on derivation of Clausius equality, Eq.(10),  $(\delta Q/T)_{Irr} < (\delta Q/T)_{Rev}$  ( $T$  is non-negative absolute temperature), we have:

$$\oint \frac{\delta Q}{T} \Big|_{Irr} < \underbrace{\left( \oint \frac{\delta Q}{T} \Big|_{Rev} = 0 \right)}_{Eq.(10)}, \text{ or for both, reversible and irreversible cycles:}$$

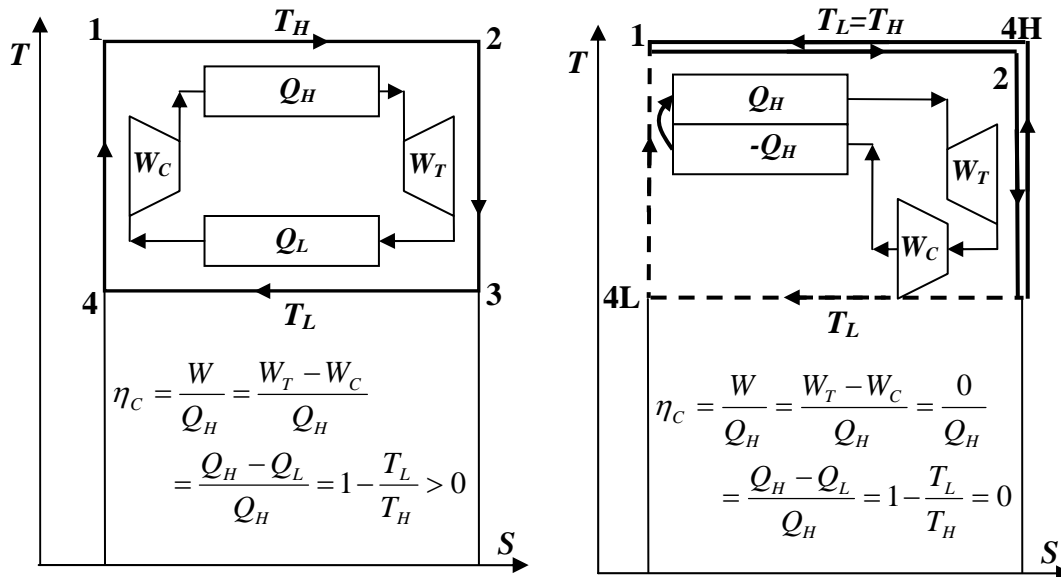
$$\oint \frac{\delta Q}{T} \leq 0 \quad (13)$$

Everything reasoned above is deduced from, and thus equivalent to “*impossibility of heat to be transferred spontaneously (without any external influence) from colder to warmer body/reservoir, nor it is possible to construct any device to achieve it in an autonomous process (a process without any external influences).*” A new material property, *entropy*, was defined using the cyclic Clausius equality, Eqs.(10&11).

The cyclic Clausius inequality, Eq.(13), affirms that cycle net-influx of the new quantity, *entropy*, within a cyclic process must be negative (must be net-outflux), since the working medium comes back to the same state (and thus the same all properties) after completing the cycle. This imply that all real irreversible cyclic processes must produce (generate) the new property *entropy*, which in limit is conserved in reversible processes. Thus, it would be impossible to have a cyclic process to destroy entropy, since it would be equivalent to spontaneous heat transfer from a colder to a hotter body, never observed in nature. Similar reasoning has been further extended to all types of energy processes and thus establishing universality of the Second Law of entropy generation and energy degradation.

## ADDITIONAL REASONING OF THE CARNOT WORK EQUIVALENCY OF HEAT

Joule's experiments have proved the equivalency of fully irreversible conversion of mechanical work to heat or more accurately via generated heat into the internal thermal energy (of a single thermal reservoir). However, the Joule's "*mechanical equivalent of heat*" does not apply for thermal energy (or heat) conversion to mechanical energy (or work), since it is not possible to reverse original, fully-irreversible Joule's process and convert heat (thermal energy) from a single reservoir to work without any other interaction with the surroundings. Here the Carnot principle provides the missing "*heat equivalent of work*" or "*Carnot motive-power equivalent of heat*" via reversible heat-engine conversion of thermal energy into mechanical work. In order to extract work from a heat reservoir, it is necessary to employ a heat engine running a power cycle, while transferring part of the heat from a high-temperature reservoir to a low-temperature reservoir, that is, it is necessary to have, in addition to high-temperature reservoir for heating, also a low-temperature reservoir for cooling a part of the heat-engine cycle. Without the low-temperature reservoir to provide thermal compression by cooling (cycle heat removal), all obtained expansion work (or even more in non-ideal cycle) will be needed to compress the cycle medium to the



**FIGURE 7.** Heat engine ideal *Carnot* cycle between two different temperature heat-reservoirs ( $T_H > T_L$  and  $W > 0$ ) (**left**), and with a single temperature heat-reservoirs ( $T_H = T_L$  and  $W = 0$ , ideal reversible cycle) (**right**). Low-temperature thermal compression is needed (critical), not the mechanical (isentropic) compression, to realize work potential between the two different temperature heat-reservoirs, due to internal thermal energy transfer via heat ( $W = Q_H - Q_L > 0$ ). The isentropic expansion and compression are needed to provide temperature for reversible heat transfer, while net thermal expansion-compression provides for the net-work out of the cycle (see Table

original temperature and pressure, and all absorbed heat (or even more in non-ideal cycle) has to be removed out from the cyclic medium in order to complete the cycle, see Fig. 7.

Therefore, the so called waste cooling-heat in thermal power plants is a useful heat for cycle execution, necessary for thermal compression (volume reduction) of cycling medium (e.g., steam to condensate), without which it will not be possible to produce (cyclic) mechanical work from heat of fuel. In ideal reversible cycles, the exhaust heat will be in equilibrium with the surroundings without any additional value, and thus is not a waste at all.

Thermal and mechanical energy and their energy-potentials, temperature and pressure, are interrelated (coupled). Reversible addition of work (mechanical compression) or heat (heating via thermal energy transfer), or irreversible heating (via loss of work or work potential) will increase simultaneously pressure (mechanical elastic energy potential) and temperature (thermal energy potential), and vice versa.

**TABLE 1.** Carnot cycle with ideal gas as working medium (see Figs. 2 & 7).

| Process   | Condition            | $Q_{netIN} = \Delta U + W_{netOUT}$                     | $W_{netOUT} = Q_{netIN} - \Delta U$                                 |
|---|----------------------|---|---|
| 1-2<br>Isothermal heating   | $T_H = const$        | $0 + R_g T_H \ln \frac{V_2}{V_1} = Q_{H(IN)}$           | $R_g T_H \ln \frac{V_2}{V_1} - 0 = W_{H(OUT)}$                      |
| 2-3<br>Isentropic expansion   | $S_E = const$        | $C_v \ln \frac{T_L}{T_H} + R_g \ln \frac{V_3}{V_2} = 0$ | $0 - C_v (T_L - T_H) = W_{E(OUT)}$                                  |
| 3-4<br>Isothermal cooling   | $T_L = const$        | $0 + R_g T_L \ln \frac{V_4}{V_3} = -Q_{L(OUT)}$         | $R_g T_L \ln \frac{V_4}{V_3} - 0 = -W_{L(IN)}$                      |
| 4-1<br>Isentropic compression   | $S_C = const$        | $C_v \ln \frac{T_H}{T_L} + R_g \ln \frac{V_1}{V_4} = 0$ | $0 - C_v (T_H - T_L) = -W_{C,IN} = -W_{E(OUT)}$                     |
| <b>1-2-3-4-1</b>  | <b>Cycle</b>         | $Q_{netIN} = R_g (T_H - T_L) \ln \frac{V_2}{V_1}$       | $W_{netOUT} = Q_{netIN}$<br>$= R_g (T_H - T_L) \ln \frac{V_2}{V_1}$ |
| <b>(1-2)<br/>+(3-4)</b>   | <b>All Thermal</b>   | $Q_{netIN} = R_g (T_H - T_L) \ln \frac{V_2}{V_1}$       | $W_{netOUT} = Q_{netIN}$<br>$= R_g (T_H - T_L) \ln \frac{V_2}{V_1}$ |
| <b>(2-3)<br/>+(4-1)</b>   | <b>All Adiabatic</b> | $Q_{netIN}^{ad} = 0$                                    | $W_{netOUT}^{ad} = 0$   |
| NOTE: From $Q_{2-3} = Q_{4-1} = 0$ it follows that $\frac{V_3}{V_2} = \frac{V_4}{V_1}$ or $\frac{V_2}{V_1} = \frac{V_3}{V_4}$ . Then, $\frac{Q_L}{Q_H} = \frac{R_g T_L \ln(V_4/V_3)}{R_g T_H \ln(V_2/V_1)} = \frac{T_L}{T_H}$ , confirms equality of ideal gas and Thermodynamic absolute temperature scales. Overall adiabatic processes do not contribute to any net-energy conversion, but only adjust temperature for reversible heat transfer. |                      |   |   |

The reversible Carnot cycle is the “enabling tool” to uncouple the mechanical energy from thermal energy. If we heat a gas in a piston, its internal energy will increase, and mechanical work potential with regard to other reference thermal reservoir (like surroundings) is expressed with Carnot efficiency (only if non-equilibrium between the two reservoirs exist, otherwise no work potential). The cyclic process is ideal method to decouple and measure the mechanical power-equivalent of the thermal energy with regard to a reference reservoir (often the surroundings). It is accomplished by an intermediary system, which after making the whole reversible cycle (or integer number of cycles), it will not make any trace by itself to the environment (i.e., change of volume or any other property), since reversible processes do not generate entropy, and it will come to the same final state as initial (same temperature, pressure, volume, entropy, energy, etc.). There will be thermal and mechanical expansions and compressions. The net work is due to the net-thermal expansion-compression, since the net-mechanical expansion-compression is zero for any reversible adiabatic (isentropic) cycle exposed to thermal reservoirs only (see Table 1 for ideal gas Carnot cycle; note that phase-change may skew some details of the otherwise invariant phenomenon). However the mechanical expansion-and-compression are needed to adjust temperature for reversible heat transfer to virtually zero temperature difference. Such reversible cycle, in limit, will run spontaneously when transferring heat from high to low temperature reservoirs and extract maximum work possible. If the cycle is reversed by using the obtained work, it will transfer the same heat in reverse, from low to high temperature, thus performing a reversible refrigeration (or heat pump) cycle, to be elaborated elsewhere.

During reversible heat-engine cycle operation, there will be no entropy generation (production) within the engine, so the entropy will be “passing through” unchanged from the heat source to the heat sink (over-all conserved in a reversible net-isentropic cycle including the interacting reservoirs), with maximum possible work extracted in the process, similarly to the water-wheel operation, see Fig. 1, and according to the Clausius equality, Eq.(10). Therefore, the reversible processes are isentropic overall (including all interacting systems). However, due to any cycle irreversibility (dissipation/conversion of work potential to thermal energy, known as heat generation), the entropy will be generated (produced) and transferred along with additional “generated” heat to the heat sink ( $S_{gen}T_o$ ), thus reducing the extracted work for that amount and efficiency of the heat engine, i.e., resulting in the cycle production of entropy with net-outflux or negative cycle net-influx, according to the Clausius inequality, Eq.(13).

## **The Far-Reaching Second Law of Thermodynamics**

As already stated, Carnot’s ingenious reasoning (in 1824) about limiting, reversible heat-engine operation, at the time when little was known about heat and work interactions, much before establishment of the “*mechanical equivalent of heat*” (Joule, 1843) and energy conservation, enabled his followers to extend his work and to define absolute Thermodynamic temperature (Kelvin, 1848) and entropy, a new Thermodynamic material property (Clausius, 1850, Boltzman, 1880), as well as the Gibbs free energy (Gibbs 1878), one of the most important Thermodynamic functions for the characterization of electro-chemical systems and their equilibriums. The Carnot

work, almost unnoticed at his time and not fully recognized even now, has have unprecedented and far-reaching consequences, and was crucial for development of new science of Thermodynamics. Carnot answered many questions related to the equivalency of “*motive power*” and “*heat*” through his ingenious reasoning of reversible cycles.

$$\begin{array}{c}
 \{Q_H, Q_L, W_C\} \rightleftharpoons \{-Q_H, -Q_L, -W_C\} \\
 \text{IF REVERESED} \\
 \\
 \left\{ \begin{array}{l}
 \overbrace{\eta_c = \frac{W}{Q_{IN}} = f_c(T_H, T_L)}^{\text{Carnot}} \\
 \underbrace{\frac{Q(T)}{Q(T_0)} = \frac{f(T)}{f(T_0)}}_{f(T)=T} = \frac{T}{T_0} = \frac{Q}{Q_0} \\
 \text{Carnot ratio equality, Eq.(6) (by Carnot followers)}
 \end{array} \right\} \quad \begin{array}{l}
 \text{Important} \\
 \langle ? \rangle
 \end{array} \quad \begin{array}{l}
 \text{Einstein} \\
 \{mc^2\}
 \end{array}
 \end{array}$$

**FIGURE 8.** The Carnot ratio equality (Eq. 6), is much more important than what it appears at first. Actually it is probably the most important equation in Thermodynamics and among the most important equations in natural sciences. *Carnot’s ingenious reasoning opened the way to generalization of Thermodynamic reversibility and energy process equivalency, definition of absolute Thermodynamic temperature and a new Thermodynamic material property ‘entropy’, as well as the Gibbs free energy, one of the most important Thermodynamic functions for the characterization of electro-chemical systems and their equilibriums, thus resulting in formulation of the universal and far-reaching Second Law of Thermodynamics.*

His reasoning opened the way to generalization of Thermodynamic reversibility and energy process equivalency (conserving non-equilibrium during reversible processes), and formulation of the far-reaching Second Law of Thermodynamics: *Carnot’s reasoning of reversible cycles is in many ways equal to if not more significant than the Einstein’s relativity theory in modern times.*

In summary, the reversible process/cycle equivalency deduced by Sadi Carnot: *efficiency of any reversible cycle between any two temperature reservoirs cannot be smaller than any other cycle efficiency, thus all reversible cycle efficiencies between the two reservoirs must be the same and maximum possible*, has resulted in a number of important corollaries and fundamental discoveries. The subtle Carnot’s reasoning paved the way to the definition of the *Carnot ratio equality*, Eq.(6), absolute Thermodynamic temperature, Eq.(8), and deduction, thus proof of the Clausius equality, Eq.(10), including definition of the new property, *entropy* (up to an arbitrary reference value), Eq.(11). Additional consequence of Carnot’s reasoning is that non-reversible (irreversible) cycles must have smaller efficiency than maximum possible reversible efficiency, thus allowing deduction and thus proof of the Clausius inequality, Eq.(13), in limit being an equality for reversible cycles. The cyclic Clausius inequality, Eq.(13), affirms that cycle net-influx of the new quantity, entropy, within a cyclic process must be negative (must be net-outflux). This implies that all real irreversible cyclic processes must produce (generate) the new property *entropy*, which in limit is conserved in

reversible processes. Thus, it would be impossible to have a cyclic process to destroy entropy, since it would be equivalent to spontaneous heat transfer from a colder to a hotter body, never observed in nature. Similar reasoning has been further extended to all types of energy processes and thus establishing universality of the Second Law of entropy generation and energy degradation.

There are many forms of the Second Law but they are all interrelated and could be deduced, i.e., derived from the impossibility of a process (energy transfer) to spontaneously generate non-equilibrium, thus impossibility to “destroy entropy,” but otherwise – thus all different forms of the Second Law are equivalent.

Not only it is impossible to produce work from a single thermal reservoir, but it is impossible to produce more work between any two thermal reservoirs than by using an ideal Carnot cycle. The latter is more general statement of the former, since the former is a special case of the latter (zero, no work) when the two reservoirs’ temperatures approach each others, thus resulting in a single thermal reservoir.

Heat and work are process quantities (while energy is crossing a real or imaginary boundary) and they cannot be stored within a system as such (for a time being or forever), thus they are not system property. However, there is a fundamental distinction between the two energy-in-transfer types: system boundary is forcibly displaced in specific direction (energy exchange as work during system volume displacement at given pressure, for example), or randomized thermal energy is transferred over stationary boundary via collision of elementary system structure (energy exchange as heat during system entropy displacement at given absolute temperature).

## Entropy and Entropy Generation

*Entropy* is an integral measure of (random) thermal energy redistribution (due to heat transfer or irreversible heat generation due to energy degradation-lost of work potential) within a system mass and/or space (during system expansion), per absolute temperature level. Entropy is increasing from perfectly-ordered (singular and unique) crystalline structure at zero absolute temperature (zero reference) during reversible heating (entropy transfer) and entropy generation during irreversible energy conversion (lost of work-potential to thermal energy), i.e. energy degradation or random equi-partition within system material structure and space per absolute temperature level.

Furthermore, entropy of a system for a given state is the same, regardless whether it is reached by reversible heat transfer or irreversible heat or irreversible work transfer.

Entropy is generated when work potential is lost (randomly equi-partitioned) via heat transfer into the thermal energy at given absolute temperature within the space occupied by the system, including when expansion (elastic) work potential is lost (i.e. energy randomly redistributed within enlarged volume instead of being transferred as work (volume displacement against the surrounding equilibrium pressure), as demonstrated by the entropy dependence on temperature and volume for ideal gas:.

$$dS = C_v \frac{dT}{T} + R \frac{dV}{V} = C_p \frac{dT}{T} - R \frac{dP}{P} \quad (14)$$

$$S(T, V) - S_{\text{Ref}} = C_v \ln(T/T_{\text{Ref}}) + R \ln(V/V_{\text{Ref}}) = C_p \ln(T/T_{\text{Ref}}) - R \ln(P/P_{\text{Ref}})$$

Entropy unit is not exactly the same as for specific heat, since entropy increase at constant volume is equal to the thermal energy increase per absolute temperature level (important) as opposed to per temperature difference for specific heat at constant volume. Entropy also increases with volume increase and/or pressure decrease at constant temperature and during adiabatic expansion (throttling), unless the process is reversible (isentropic; entropy increase due to volume expansion is balanced with equal decrease due to work extraction and the corresponding thermal energy decrease). Therefore during reversible change of volume there is no change of entropy due to change of volume, but only due to boundary heat transfer if any, i.e.:

$$S = \int_{Boundary} \frac{\delta Q}{T} + \int_{System} \frac{\delta W_{Loss}}{T} = \overbrace{\int_{Boundary} \frac{\delta Q}{T}}^{S_{Transferred}} + \overbrace{\int_{System} \frac{\delta Q_{Gen}}{T}}^{S_{Generated}} \quad (15)$$

$$S = \int_{Boundary} \frac{\delta Q}{T} \Big|_{Rev}, \text{ since } \delta W_{Loss} \Big|_{Rev} = 0$$

Where,  $\delta Q_{Gen} = \delta W_{Loss} \Big|_{Irr}$ , is heat generation due and equal to loss of reversible work potential as measure of non-equilibrium of respected systems.

## CONCLUSION AND HOLISTIC GENERALIZATION OF THE SECOND LAW

In conclusion, as stated before, it is only possible to produce work during energy exchange between systems in non-equilibrium (e.g., between two thermal reservoirs at different temperatures), not within a single thermal reservoir in equilibrium. Actually, the work potential is measure of the systems' non-equilibrium, thus the work potential could be conserved only in processes if the non-equilibrium is preserved (conserved, i.e. rearranged; the produced work has to be reversibly stored somewhere!), and such ideal processes could be reversed, and thus named reversible processes. When the systems come to the equilibrium there is no potential for any process to take place and produce (extract) work. Therefore, it is impossible to produce work from a single thermal reservoir in equilibrium, otherwise a non-equilibrium will be spontaneously created and in limit resulting in an infinite potential (infinite mass-energy concentration) within infinitesimally small extent (volume), a "black-hole-like energy singularity," instead of resulting into a lasting equilibrium redistribution with randomized equi-partition of mass-energy at the corresponding equilibrium level (energy potential). Consequently, if heat transfer takes place spontaneously at finite temperature difference (as in heat exchangers), without possible reversible Carnot work extraction, the latter work potential will be permanently "lost," thus irreversibly dissipated into thermal energy, with increase (production) of entropy. All real natural processes between systems in non-equilibrium have tendency towards common equilibrium and thus loss of the original work potential, by converting other energy forms into the thermal energy accompanied with increase of entropy (randomized equi-partition of energy per absolute temperature level). Due to the loss of work potential in a real irreversible process, the resulting reduced work cannot reverse back the process to the original non-equilibrium,

as would be possible with ideal reversible processes. Since non-equilibrium cannot be created or increased spontaneously (by itself and without interaction with the rest of the surroundings, i.e., on the expense of non-equilibrium within the surroundings), then all reversible processes must be the most and equally efficient (will equally conserve the work potential), otherwise will create non-equilibrium by reversing and coupling differently efficient reversible processes. The irreversible processes and cycles will lose work potential to thermal energy with increase of entropy, thus will be less efficient than the corresponding reversible processes as discussed above.

Therefore, the Second Law could be expressed in many forms reflecting impossibility of creating or increasing non-equilibrium and thus work potential between the systems within an isolated enclosure or the universe:

- No heat transfer from low to high temperature of no-work process (like isochoric thermo-mechanical process).
- No work transfer from low to high pressure of no-heat process (adiabatic thermo-mechanical process).
- No work-producing from a single heat reservoir, i.e., no more efficient work-producing heat engine cycle than the Carnot cycle.
- Etc, etc ... for other work forms associated with different energy forms.

All the Second Law statements are equivalent since they reflect the reversible equality of work potential between all system states reached by any and all reversible processes (reversibility is measure of equivalency) and impossibility of creating or increasing over-all non-equilibrium and aver-all work potential (of all interacting systems).

Spontaneous creation or increase of overall non-equilibrium and thus work potential is impossible, but only decrease of work potential and non-equilibrium towards a common equilibrium (equalization of all energy-potentials) accompanied with entropy generation due to loss of work potential to thermal energy at system absolute temperature, resulting in maximum equilibrium entropy.

A process direction (mass-energy transfer) is forced from higher potential (higher mass-energy concentration source) towards lower one (mass-energy sink) thus increasing the lower potential (concentration) on the expense of the higher until a lasting equilibrium with balanced forced potential is achieved.

Reversibility enables evaluation of equivalency, so one violation is equivalent to others: heat engine more efficient than ideal Carnot engine is equivalent to a heat engine working from a single reservoir, or it is equivalent to heat flow from low to high temperature or pumping heat from a single reservoir and generating hotter system. So if one violation would be possible then all other violation would be possible too, thus rendering the Second Law to be invalid.

Ideal reversible processes are the most efficient since they conserve non-equilibrium (available energy or work potential or exergy) and thus conserve entropy; They may be considered as reversible elastic oscillators (rearranging non-equilibrium) at different time scales.

However, real, irreversible processes dissipate (“waste”) work potential to thermal energy and generate entropy. It is impossible to have hyper-reversible processes to generate non-equilibrium (or produce it from equilibrium) and destroy entropy, at any time and space scale, because the process forcing has to come from somewhere, i.e.,



from existing higher potential (existential conservationism) and cannot be created from nowhere (mysterious creationism). During a real process from non-equilibrium towards equilibrium at lower common potential than the forcing subsystem at higher potential, the mass-energy will dissipate (disperse randomly) to finer substructures of involved, interacting (sub)systems, except for interactions among elementary particles without substructure or in ideal elastic, reversible interactions.

**Definition of The Second Law of Energy Degradation and Entropy Generation:**

Non-equilibrium, i.e., non-uniform distribution of mass-energy in space, tends in time to spontaneously and irreversibly redistribute over space towards common equilibrium, thus non-equilibrium cannot be spontaneously created. *All natural spontaneous, or over-all processes (proceeding by itself and without interaction with the rest of the surroundings) between systems in non-equilibrium have irreversible tendency towards common equilibrium - and thus irreversible loss of the original work-potential (measure of non-equilibrium), by converting other energy forms into the thermal energy accompanied with increase of entropy (randomized equi-partition of energy per absolute temperature level)"*

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Therefore, entropy is transferred and can be reduced (locally) but cannot be destroyed (anywhere): entropy is always and everywhere (locally and integrally) generated or produced.

*The miracles are until we comprehend and explain them!*

**REFERENCES**

1. Sadi Carnot, *Reflections on the Motive Power of Heat*, English translation by R.H. Thurston (1824) <http://www.thermohistory.com/carnot.pdf> or <http://www.history.rochester.edu/steam/carnot/1943/>
2. V. Capek and D.P. Sheehan, *Challenges to The Second Law of Thermodynamics: Theory and Experiment (Fundamental Theories of Physics)*, Springer, Dordrecht, Netherlands, 2010. 366 pp.
3. J. Uffink, *Bluff your way in the second law of Thermodynamics*, Studies in History and Philosophy of Modern Physics, 32(3), 305-394 (2001) <http://philsci-archive.pitt.edu/archive/00000313/>
4. E.T. Jaynes, *The evolution of Carnot's principle*, in G. J. Erickson and C. R. Smith (eds.) *Maximum-Entropy and Bayesian Methods in Science and Engineering* vol. 1, p. 267 (1988). <http://bayes.wustl.edu/etj/articles/ccarnot.pdf>
5. H. Erlichson, *Sadi Carnot, 'Founder of the Second Law of Thermodynamics'*, Eur. J. Phys. **20** p. 183-192, 1999.
6. M. Kostic, *Irreversibility and Reversible Heat Transfer: The Quest and Nature of Energy and Entropy*, IMECE2004, ASME Proceedings, ASME, New York, 2004. <http://www.kostic.niu.edu/Kostic-Energy-Entropy-Irreversibility.pdf>
7. M. Kostic, *Treatise with Reasoning Proof of the First Law of Energy Conservation*, Manuscript, Northern Illinois University, 2006 (updated 2007 and later). Last accessed in December 2010. <http://www.kostic.niu.edu/1st-law-proof1-ALL.pdf>
8. M. Kostic, *Treatise with Reasoning Proof of the Second Law of Energy Degradation*, Manuscript, Northern Illinois University, 2006 (updated 2007 and later). Last accessed in December 2010. <http://www.kostic.niu.edu/Kostic-2nd-Law-Proof.pdf>