

The Second Law of Energy Degradation From Sadi Carnot to Holistic Generalization

Carnot
1824
Heat Engine
Reversibility



Clausius
1850 NO Heat
from cold to hot
1865 Entropy



Kelvin-Planck
1848 Abs. Temperature
1865 NO Work
from single reservoir



Gibbs
1870's Entropy,
Chem. Potential
Phys. Chemistry



AAAS-The 2nd Law Thermo Symposium
Univ. of San Diego, June 14-15, 2011



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Slide 1

THANKS for Invitation ...

- First time at AAAS conference
- First time on a 2nd Law Symposium
- The 2nd Law is my obsession from my college years
😊😊😊
- ... very glad to participate and listen to people who thinks outside the conventional wisdom
- ... this is a mind bugling and stretching meeting

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Humanity's Top Ten Problems for next 50 years

1. ENERGY (critical for the rest nine)

- Water
- Food
- Environment
- Poverty
- Terrorism & War
- Disease
- Education
- Democracy
- Population

2006: 6.5 Billion People
2050: 8-10 Billion (10¹⁰) People



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Thermodynamics ...

The classical, phenomenological Thermodynamics today, almost a forgotten science, has unjustifiably a dubious status. Many modern physicists regard classical Thermodynamics as an obsolete relic. Often, mostly due to lack of subtle comprehension, the Thermodynamics is considered as an engineering subject and thus not as the most fundamental science of energy and nature.

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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 Thermodynamic principles.

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Thermodynamics ...

Apart from the view that Thermodynamics is obsolete, there is a widespread belief among scientists in Thermodynamics' absolute authority. Namely, the phenomenological Laws of Thermodynamics have much wider, including philosophical significance and implication, than their simple expressions based on the experimental observations..

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Thermodynamics ...The 2nd Law

"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" (by M. Kostic)

- ... NO work from Single THERMAL reservoir ALONE (Thermo-Mechanical only)
- ...or NO spontaneous heat from LOWER to HIGHER temperature
- ...but
- Daniel made fire (at HIGER temp) from isothermal LOWER charcoal and wood ☺

- ENTROPY is generated because HEAT/thermal energy is generated by conversion of other energy form
- The BACKWARD is possible BUT according to the 2nd Law ... as will be reasoned next

What is Energy ?



If one could expel all energy out of a physical system ... then empty, nothing will be left ...
... so **ENERGY is EVERYTHING ... $E=mc^2$**

Definition of Energy

"Energy is a fundamental property of a physical system and refers to its potential to maintain a material system identity or structure (forced field in space) and to influence changes (via forced-displacement interactions, i.e. systems' re-structuring) with other systems by imparting work (forced directional displacement) or heat (forced chaotic displacement/motion of a system molecular or related structures). Energy exists in many forms: electromagnetic (including light), electrical, magnetic, nuclear, chemical, thermal, and mechanical (including kinetic, elastic, gravitational, and sound).

"... Energy is the "building block" and fundamental property of matter and space and, thus, the fundamental property of existence. Energy exchanges or transfers are associated with all processes (or changes) and, thus, are indivisible from time." (by M. Kostic)

Definition of Entropy

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

The Grand Law of Nature

The **universe consists of local material (mass-energy) structures** in forced equilibrium and their interactions via forced fields. The **forces are balanced at any time** (including inertial - process rate forces) thus **conserving momentum**, while **charges/mass and energy are transferred and conserved** during forced displacement in space all the times, **but energy is degraded** as it is redistributed (transferred) from higher to lower non-equilibrium potential towards equilibrium (equi-partition of energy). (by **M. Kostic**)

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The screenshot shows a web browser displaying the 'ENCYCLOPEDIA OF ENERGY' website. The main article is titled 'Work, Power, and Energy' by M. Kostic, Northern Illinois University, DeKalb, Illinois, United States. The article's abstract is visible, starting with 'Energy A fundamental property of a system referring to its potential to influence changes to other systems by imparting work (forced directional displacement) or heat (chaotic displacement/motion of system microstructure); energy exists in many forms—electromagnetic, electrical, nuclear, chemical, thermal, and mechanical, where electromechanical energy may be kinetic or potential—and thermal energy represents overall chaotic motion energy of molecules and related microstructure.' A table of contents is also visible, listing: 1. Basic Concepts, 2. Forms, Classifications, and Classification, and 3. Work of Conservative and Non-Conservative Forces and the Work-Energy Principle. The website URL is www.kostic.niu.edu.

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Energy: Global and Historical Background

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Physics of Energy

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Abstract

The concept and definition of energy are elaborated, as well as different forms and classification of energy are presented. Energy is a fundamental concept indivisible from matter and space, and energy exchanges or transfers are associated with all processes (or changes), thus indivisible from time. Actually, energy is "the building block" and fundamental property of matter and space, thus fundamental property of existence. Any and every material system in nature possesses energy. The structure of any matter and field is "energetic," meaning active, i.e., photon waves are traveling in space, electrons are orbiting around an atom nucleus or flowing through a conductor, atoms and molecules are in constant rotation, vibration or random thermal motion, etc. When energy is exchanged or transferred from one system to another it is manifested as work or heat. In addition, the First Law of energy conservation and the Second Law of energy degradation and entropy generation are presented along with relevant concluding remarks. In summary, energy is providing existence, and if exchanged, it has ability to perform change.

- 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* (conservation transformationalism),
- *The Second* (directional transformationalism), and
- *The Third* (unattainability of emptiness).

They are defining and unifying our comprehension of all existence and transformations in the *universe*.

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- 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.

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- 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).

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- 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

Sadi Carnot's Ingenious Reasoning of Ideal Heat Engine Reversible Cycles

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Abstract: - Sadi Carnot, at age 28, published in 1824, new famous "Réflexions sur la puissance motrice du feu (Reflections on the Motive Power of Fire)" which is much more important than what it appears at first. It may be among the most important treatises in natural sciences. At that time, when heat was considered as indestructible caloric and the energy conservation law was not known, when heat engines were in initial stage of development with efficiency of less than 5%, the confusion and speculations flourished. Carnot's reasoning of reversible cycles is in many ways equal if not more significant than the Einstein's relativity theory in modern times. It led to discovery of Thermodynamic absolute temperature and entropy, and the far-reaching Second Law of Thermodynamics. No wonder that Carnot's work 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, ever now. Additional reasoning and conclusions are also presented here.



Sadi Carnot's far-reaching treatise of heat engines was not noticed at his time and even not fully recognized nowadays

In 1824 Carnot gave a full and accurate reasoning of heat engine limitations almost two decades before equivalency between work and heat was experimentally established by Joules in 1843

Sadi Carnot laid ingenious foundations for the Second Law of Thermodynamics before the First Law of energy conservation was known and long before Thermodynamic concepts were established.

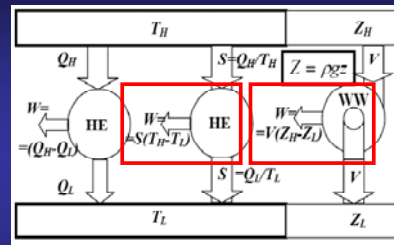


Fig. 1: Similarity between an ideal heat engine (HE) and a water wheel (WW).

$$W = W_{netOUT} = Q_{IN} \cdot f_c(T_H, T_L)$$

$$\eta_{Ct} = \frac{W_{netOUT}}{Q_{IN}} \Bigg|_{Max} = \underbrace{f_c(T_H, T_L)}_{Qualitative\ function} \Bigg|_{Rev.} \quad (1)$$

"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."

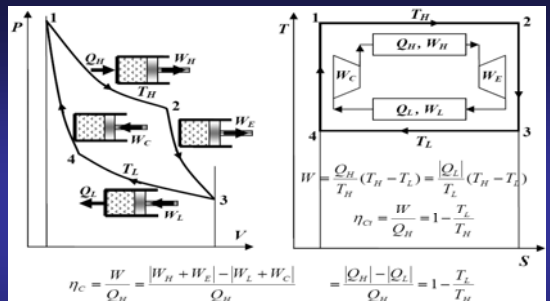


Fig. 2: Heat-engine ideal Carnot cycle: note thermal and mechanical expansions and compressions (the former is needed for net-work out, while the latter is needed to provide reversible heat transfer).

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

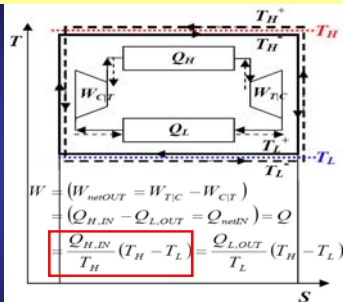


Fig. 3: **Reversible Heat-engine** (solid lines) and **Refrigeration Carnot cycle** (dashed lines, reversed directions).
Note, $W_H = W_L = 0$ if heat transfer with phase change (compare Fig.2).

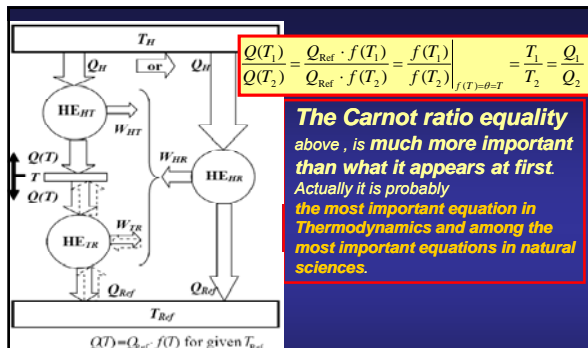


Fig. 5: For a fixed $T_H, T_{Ref}, Q_H,$ and Q_{Ref} , the $Q(T)$ is proportional to Q_{Ref} (efficiency is intensive property) and an increasing function of T for a given T_{Ref} .

The Carnot ratio equality above, 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**.

Clausius (In)Equality

$$\left(W_{Irr} = \oint \delta Q_{Irr} \right) \leq \left(\oint \delta Q_{Rev} = W_{Rev} \right)$$

$$\oint \frac{dQ}{T} \Big|_{Irr} \leq \left(\oint \frac{dQ}{T} \Big|_{Rev} = 0 \right) \text{ or } \oint \frac{dQ}{T} = -S_{Gen} \leq 0 \quad (13)$$

Eq.(10) Any Cycle Clausius Inequality

$$-\oint \frac{dQ}{T} = S_{Gen} \geq 0$$

Any Cycle
Clausius Inequality

Note, $S_{Gen} = S_{out} - S_{in}$, and $\Delta S_{cycle} = (S_{in} + S_{Gen}) - S_{out} = 0$ (any cycle)

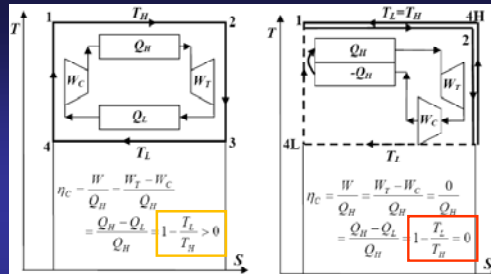


Fig. 7: Heat engine ideal **Carnot cycle** between two different temperature heat-reservoirs ($T_H > T_L$, and $W > 0$) (left), and with a **single temperature** heat-reservoirs ($T_H = T_L$, and $W = 0$, ideal reversible cycle) (right). Low-temperature thermal compression is needed (critical), not the mechanical (isentropic) compression, to realize work potential between the two different temperature heat-reservoirs, due to internal thermal energy transfer via heat ($W < 0, Q > 0$). 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.

Therefore, ...

... the so called **"waste cooling-heat"** in power cycles (like in thermal power plants) **is not waste but very useful heat**, necessary for thermal compression of cycling medium (steam-into-condensate, for example), without which it **will not be possible to produce mechanical work from heat** (i.e., from thermal energy).

$$\{Q_H, Q_L, W_C\} \stackrel{\Leftrightarrow}{\text{IF REVERSED}} \{-Q_H, -Q_L, -W_C\}$$

$$\eta_c = \frac{W}{Q_{IN}} = \frac{f_2(T_H, T_L)}{Q_{IN}} \Big|_{Rev}$$

$$\frac{Q(T)}{Q(T_0)} = \frac{f(T)}{f(T_0)} \Big|_{f(T)=T} = \frac{T}{T_0} = \frac{Q}{Q_0}$$

Carnot Ratio Equality
(by Carnot's followers)

versus $\{E = mc^2\}$

Fig. 8: **Significance of the Carnot's reasoning** of reversible cycles is in many ways **comparable with the Einstein's** relativity theory in modern times. The **Carnot Ratio Equality** is much more important than what it appears at first. It is probably **the most important equation in Thermodynamics and among the most important equations in natural sciences**.

- Reasoning Open Issues And Challenges

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- 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

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- 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

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- Unless otherwise stated all terms used here refer to Thermodynamic (mass-energy) concepts:
Thermodynamic non-equilibrium,
Thermodynamic entropy,
Thermodynamic structure or system,
etc

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- 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.

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- 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

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- At equilibrium, the forces-fluxes will be balanced without net mass-energy transfer.

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- 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

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- Therefore, the force concept is the coupled force-flux cause-and-effect phenomena

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- 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

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- 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

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- 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

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- 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 directional transformationalism towards equilibrium accompanied with entropy generation

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- The Third Thermo Law could be generalized as the Natural law of unattainability of emptiness

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- Actually, the Newton Laws are special cases of each others' and the more general Laws of Thermodynamics.

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- The theory of classical Thermodynamics was originally based on thermal and mechanical energy transformations, but it has been expanded 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."

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- Reasoning the Second Law

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- 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

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- 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

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- Thus in reversible processes the entropy is conserved too, since there is no entropy generation

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- 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 (IMPOSSIBLE)

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- Such processes would be self destructive and unsustainable

Slide 52

- 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.

Slide 53

- 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)

Slide 54

- 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!

Slide 55

- Quantification of the Thermodynamic non-equilibrium of all involved interacting systems is expressed as 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)

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- If work stored within the isolated system, the original non-equilibrium will be rearranged and conserved.

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- Reversibility is "conservation of non-equilibrium" or available energy, i.e., conservation of work potential (or exergy), and also conservation of entropy

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- 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)

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- 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

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- 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

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- 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

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- A boundary/shell structure separates systems in non-equilibrium with large potential gradients, like a mechanical, thermal, electrical or chemical boundary container/shell

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- The boundary structures prevent spontaneous interactions (or more accurately slow down interactions, since there are no perfect boundaries)

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- 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.

Slide 65

- 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)

Slide 66

- Additivity or integrality and conservationism require that phenomena should be the same at all time and space scales without exceptions

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- Due to limitations of our observation tools, including illusion (aliasing phenomena) and comprehension, we may be misled to believe otherwise

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- All interactions in nature are physical and based on simple cause-and-effect conservation laws, thus deterministic and should be without any exception

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- 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.

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- There are many statements of the Second Law which in essence describe the same natural phenomena about the spontaneous direction of all natural processes towards a stable equilibrium with randomized redistribution and equi-partition of mass-energy within the elementary structure of all interacting systems (thus the universe)

Slide 71

- 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).

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- Issues, Confusions, and Challenges

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- The Second Law of Thermodynamics is among the most fundamental principles of engineering, science and nature

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- 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

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- 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.

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- 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 the surroundings at higher potential and the process will take place until new equilibrium is achieved

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- It cannot be done from within that equilibrium (wishful Maxwell Demon could not be utilized since 1867, or Brownian/Feynman-Smoluchowski ratchet, etc.)

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- 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

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- After all, the properties are result of mass-energy structure and interactions, not the other way around.

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- 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).

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- 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

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- We cannot walk forward without moving the Earth backward, the latter not possible to observe or measure easily

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- Similarly we cannot produce cold or hot or life (or any non-equilibrium) from within an equilibrium, without having energy flow from the surroundings or from within, the latter sometimes may be hard or impossible to observe and measure

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- 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!

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

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- The Second Law is often challenged in biology, life and social sciences, including evolution and information sciences, all with history rich in confusion

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- 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

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- 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

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- Namely, statistical disorder is not the same as mass-energy dissipative disordering, regardless that both could be described with similar statistical methodology

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- Therefore, the Thermodynamic entropy [J/K] is not the same as information entropy or other entropy-like but different logical concepts.

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- 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

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- 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

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- 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 thought us many times)

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- Entropy can decrease (locally) but cannot be destroyed (anywhere) !!!

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- The miracles are until we comprehend and explain them!

Slide 96

- 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.

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In conclusion ...

... it is **only possible to produce work** during energy exchange **between systems in non-equilibrium**, not within a single thermal reservoir in equilibrium, for example. 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 – cycle work has to be stored eventually), and such ideal processes could be reversed, and thus named **reversible processes**.

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In conclusion (2)...

... When systems come to the **equilibrium** **there is no potential** for any process to produce (extract) work. Therefore, it is **impossible to produce work from a single thermal reservoir** in equilibrium: **otherwise, non-equilibrium will be spontaneously created**

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In conclusion (3) ...

... It is only possible to produce work from thermal energy in a process between two thermal reservoirs in non-equilibrium (with different temperatures). Consequently, **if heat transfer takes place spontaneously at finite temperature difference**, without possible reversible Carnot work extraction, the latter **work potential will be permanently "lost," thus irreversibly dissipated** into thermal energy.

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Slide

In conclusion (4) ...

... All real natural processes between systems in non-equilibrium have **tendency towards common equilibrium** and thus **loss of the original work potential, by converting ("dissipating") other energy forms into the thermal energy accompanied with entropy generation** (randomized equi-partition of energy per absolute temperature level). **Due to loss of work potential in a real process, the resulting reduced work cannot reverse back the process to the original non-equilibrium**, as is possible with ideal reversible processes.

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Slide

In conclusion (5) ...

... Since non-equilibrium cannot be created or increased spontaneously (by itself and without interaction with the rest of the surroundings) then **all reversible processes must be the most and equally efficient** (will equally conserve work potential, i.e. conserve non-equilibrium, otherwise will create non-equilibrium by coupling with differently efficient reversible processes). The **irreversible processes will loose work potential to thermal energy with increase of entropy, thus will be less efficient** than corresponding reversible processes.

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Slide

Heat transfer is Unique and Universal:

❖ Heat transfer is a spontaneous irreversible process where all organized (structural) energies are disorganized or dissipated as thermal energy with irreversible loss of energy potential (from high to low temperature) and overall entropy increase.

❖ Thus, heat transfer and thermal energy are **unique and universal manifestation of all natural and artificial (man-made) processes,**

... and thus ... are vital for more efficient cooling and heating in new and critical applications, including energy production and utilization, environmental control and cleanup, and bio-medical applications.

For mono-atomic molecule (no rotation and vibration modes):

$$P = \frac{F_x}{A_x} = \frac{1}{A_x} \left[\frac{2Nm\overline{v_x^2}}{L_x} \right] = \frac{2N}{3V} \left[\frac{mv^2}{2} \right]$$

$$T = \frac{2}{3} \frac{1}{k} \left[\frac{mv^2}{2} \right]$$

$$P \cdot V = \frac{N}{n_{\text{atoms}}} \cdot k \cdot T$$

NOTE that molecular motion give rise to both P & T

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REVERSIBILITY AND IRREVERSIBILITY:

ENERGY TRANSFER AND DISORGANIZATION, RATE AND TIME, AND ENTROPY GENERATION

Net-energy transfer is in one direction only, from higher to lower energy-potential, and the process cannot be reversed.

Thus **all real processes are irreversible** in the direction of decreasing energy-potential (like pressure and temperature)

Quasi-equilibrium Process :

in limit, energy transfer process with infinitesimal potential difference (still from higher to infinitesimally lower potential, P).

Then, if infinitesimal change of potential difference direction is reversed

$$P+dP \rightarrow P-dP$$

with infinitesimally small external energy, since $dP \rightarrow 0$, the **process will be reversed too**, which is characterized with infinitesimal entropy generation, and in limit, without energy degradation (no further energy disorganization) and no entropy generation thus achieving a limiting reversible process.

Instant Quasi-Equilibrium:

At instant (frozen) time a locality around a point in space may be considered as instant-equilibrium with instantaneous properties well-defined, regardless of local gradients.

Quasi-equilibrium is due to very small energy fluxes due to very small gradients and/or very high impedances so that changes are infinitely slow, for all practical purposes appearing as equilibrium with net-zero energy exchange.

REVERSIBILITY –Relativity of Time:

Therefore, the changes are ‘fully reversible,’ and along with their rate of change and time, totally irrelevant, as if nothing is effectively changing (no permanent-effect to the surroundings or universe)

The **time is irrelevant** as if it does not exist, since it could be reversed or forwarded at will and at no ‘cost’ (no permanent change and, thus, relativity of time).

REVERSIBILITY –Relativity of Time (2):

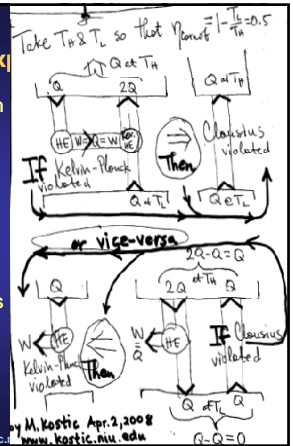
Real time cannot be reversed,

it is a measure of permanent changes, like irreversibility, which is in turn measured by entropy generation.

In this regard the time and entropy generation of the universe have to be related.

The 2nd Law ex

- **Clausius:** HEAT generally cannot flow spontaneously from a material at lower temperature to a material at higher temperature.
- **Kelvin-Planck:** It is impossible to convert heat completely into WORK in a cyclic process
- In a system process that occurs will tend to increase the total ENTROPY of the universe - The entropy of the universe tends to a maximum
- Etc ...



The 2nd Law Definition ...

- **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).

Entropy ...

... 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.

$$dS = \frac{\delta Q}{T} = \frac{\delta Q_{rev}}{T} + \delta Q_{gen} \text{ or } S = \int \frac{\delta Q}{T} + S_{ref}$$

However, the source entropy will decrease to a smaller extent over higher potential, thus resulting in overall entropy generation for the two interacting systems.

Entropy ...

We could consider a system internal thermal energy and entropy, as being accumulated from absolute zero level, by disorganization of organized or higher level energy potential with the corresponding entropy generation.

Thus entropy as system property is associated with its thermal energy (but also space).

Entropy Primer:

entropy could be transferred in reversible processes along with heat transfer, and additionally generated if work or thermal energy are disorganized at the lower thermal potential during irreversible processes.

Once a process completes, any generated entropy due to irreversibility becomes (permanent) system property and cannot be reversed by itself (thus, a permanent change).

Entropy Primer (2):

Thus, entropy transfer is due to reversible heat transfer and could be either **positive or negative**, while **entropy generation is always positive** and always **due to irreversibility**.

Entropy Primer (3):

If heat or work at higher potential (temperature or pressure) than necessary, is transferred to a system, the energy at excess potential will dissipate spontaneously to a lower potential (if left alone) before new equilibrium state is reached, with entropy generation, i.e. increase of entropy displacement over a lower potential. A system will 'accept' energy at minimum necessary (infinitesimally higher) or higher potential. Furthermore, the higher potential energy will dissipate and entropy increase will be the same as with minimum necessary potential, like in reversible heating process, i.e.:

$$dS = \frac{\delta Q}{T} = \frac{\delta Q_{rev} + \delta Q_{gen}}{T} \text{ or } S = \int \frac{\delta Q}{T} + S_{ref}$$

However, the source entropy will decrease to a smaller extent over higher potential, thus resulting in overall entropy generation for the two interacting systems,

Challenges to the Second Law of Thermodynamics

Theory and Experiment

by
Vladislav Čápek and
Daniel P. Sheehan

Springer

Fundamental Theories of Physics

“The Second Law of Thermodynamics

is considered **one of the central laws of science, engineering and technology**. For over a century it has been **assumed to be inviolable by the scientific community**.

Over the last 10-20 years, however, **more than two dozen challenges** to it have appeared in the physical literature - **more than during any other period in its 150-year history.**”

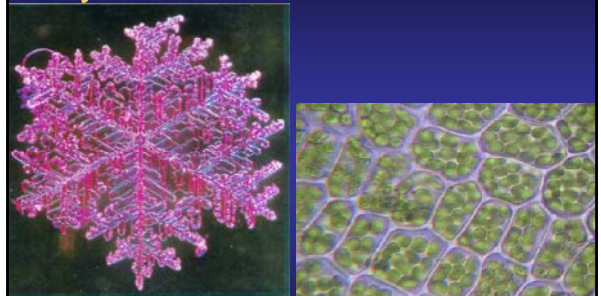
Nature often defy our intuition

- Without friction, clock will not work, you could not walk, birds could not fly, and fish could not swim.
- Friction can make the flow go faster
- Roughening the surface can decrease drag
- Adding heat to a flow may lower its temperature, and removing heat from a flow may raise its temperature
- Infinitesimally small causes can have large effects (tipping point)
- Symmetric problems may have non-symmetric solutions

Living and Complex Systems

- Many **creationists** make claims that **evolution violates the Second Law**. Although biological and some other systems may create local non-equilibrium and order, the net change in entropy for all involved systems is positive and conforms to the Laws of Nature and the Second Law for **non-equilibrium open systems**.

Crystal “self-formation” ...



... and Plant Cells growth

YES! Miracles are possible !

It may look 'perpetuum mobile' but miracles are real too ...

Things and Events are both, MORE but also LESS complex than how they appear and we 'see' them-- it is **natural simplicity in real complexity**

- ... we could not comprehend energy conservation until 1850s: (mechanical energy was escaping without being noticed)
- ... we may not comprehend now new energy conversions and wrongly believe they are not possible: ("cold fusion" seems impossible for now ... ?)
-Let us keep our eyes and our minds 'open'

YES! Miracles are possible !

... but there is **NO** ideal 'Things and Events' ...

'Things and Events' are both, MORE but also LESS complex than how they appear and we 'see' them-- it is **natural simplicity in real complexity**

- ... there are **no ideal things**, no ideal rigid body, no ideal gas, no perfect elasticity, no adiabatic boundary, no frictionless/reversible process, no perfect equilibrium, not even steady-state process ...
- ... there are **always processes** - energy in transfer or motion, all things/everything ARE energy in motion with unavoidable **process irreversibilities**, however, in limit, an infinitesimally slow process with negligible irreversibility appears as instant reversible equilibrium -- thus, **everything is relative** with regard to different space and time scales ...
-Let us keep our eyes and our minds 'open'

All processes are transient ...

- All processes are transient (work and heat transfer in time), even Eulerian steady-state processes (space-wise) are transient in Lagrangian form (system, from input to output), but equilibrium processes and even quasi-static (better, quasi-equilibrium) processes are sustainable/reversible.

If we are unable to observe ...

- If we are unable to measure something **it does not mean it does not exist** (it could be sensed or measured with more precise instruments or in a longer time scale, or in similar stronger processes; $mc^2!$).
- So called "self-organizing" or entropy increasing processes appear so, since we may be unable to measure entropy change of affecting boundary environment, for such open processes.

However, ...

- ... the miracles are until they are comprehended and understood !

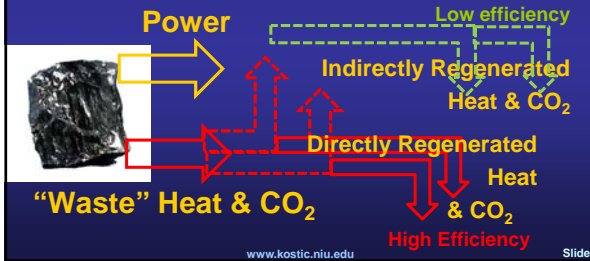
Energy Future Outlook:

...a probable scenario ... in the wake of a short history of fossil fuels' abundance and use (a bleep on a human history radar screen), the following energy future outlook is possible...

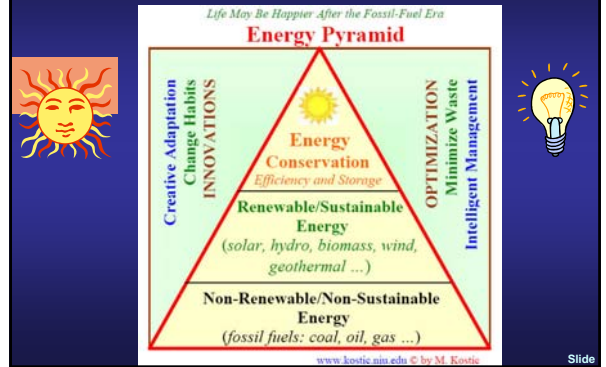
1. Creative adaptation and innovations, with change of societal and human habits and expectations (life could be happier after fossil fuels' era)
2. Intelligent hi-tech, local and global energy management in wide sense (to reduce waste, improve efficiency and quality of environment and life)
3. Energy conservation and regeneration have unforeseen (higher order of magnitude) and large potentials, particularly in industry (also in transportation, commercial and residential sectors)
4. Nuclear energy and re-electrification for most of stationary energy needs
5. Cogeneration and integration of power generation and new industry at global scale (to close the cycles at sources thus protecting environment and increasing efficiency)
6. Renewable biomass and synthetic hydro-carbons for fossil fuel replacement (mobile energy, transportation, and chemicals)
7. Advanced energy storage (synthetic fuels, advanced batteries, hydrogen,...)
8. Redistributed solar-related and other renewable energies (to fill in the gap...)

Efficient: do MORE with LESS

Improve true (2nd Law) efficiency
by conserving energy potentials: REGENERATE
before “diluting” and losing it!



How To “Use” Energy ?



More information at:
www.kostic.niu.edu/energy

Solar 1.37 kW/m², but only 12% over-all average 165 W/m²

Work, Power, and Energy

However, regardless of imminent shortages of fossil fuels, the **outlook for future energy needs is encouraging**. Energy conservation “with **existing technology**” (insulation, regeneration, cogeneration and optimization with energy storage) has real **immediate potential** to substantially **reduce energy dependence on fossil fuels** and **enable use of alternative and renewable energy sources**. There are many diverse and abundant energy sources with promising future potentials, so that mankind should be able to **enhance its activities, standard and quality of living**, by **diversifying energy sources**, and by **improving energy conversion and utilization efficiencies**, while at the same time **increasing safety and reducing environmental pollution**.

After all, in the wake of a short history of fossil fuels’ abundance and use (a blip on a human history radar screen), **the life may be happier after the fossil fuel era!**
More at: www.kostic.niu.edu/energy