

## Reflections on Caloric Theory and Thermal Energy

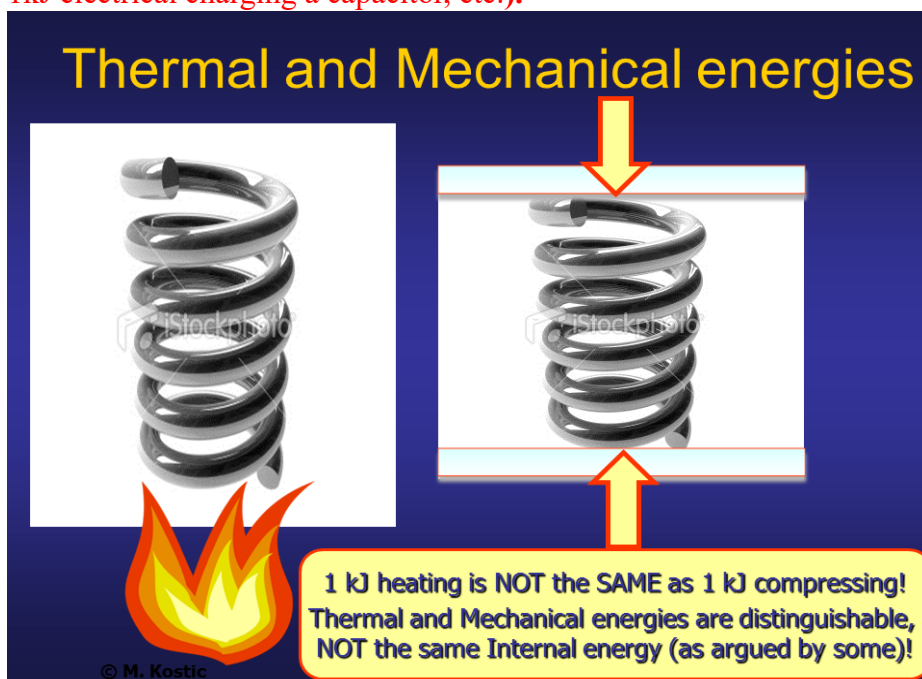
Excerpts from [2013 Presentations](#) ... [More Reflections](#) also [The Fundamental Laws of Thermodynamics and Nature](#)\* [The Second Law](#) (Abstract)\* [Clausius Theory of Heat](#) \* [Nature of Thermal and Mechanical Energy Transfer](#)\*

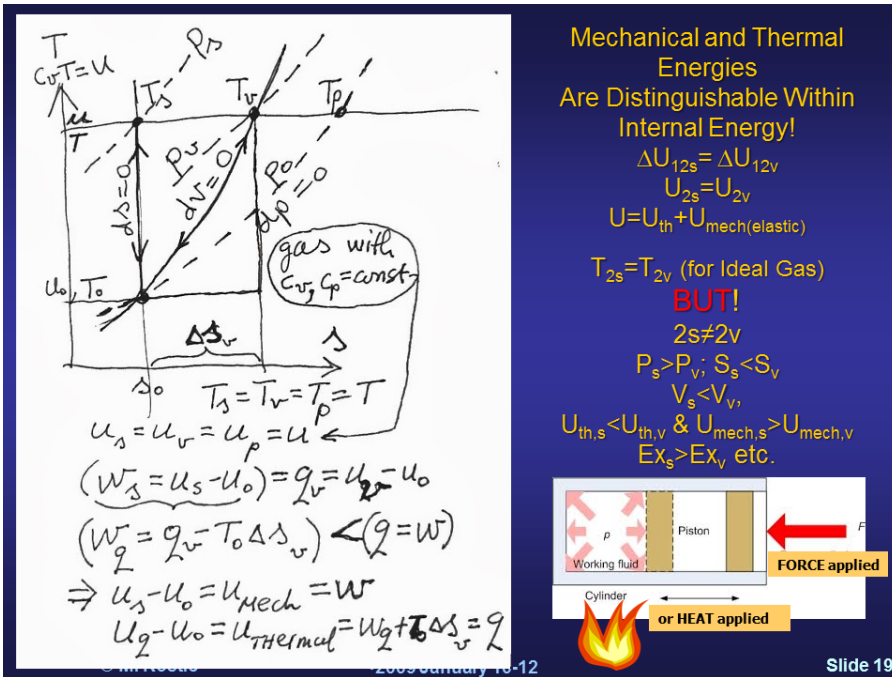
**Internal-Thermal and Internal-Mechanical (elastic) energies are DISTINGUISHABLE/DISTINCT and not the same type** (in "*simple compressible substances*") !

There are different types of clearly distinguishable/distinct internal-energies (particularly in more complex systems), including mechanical-elastic (compressible or sheared), electrical, magnetic, chemical, nuclear ..., i.e., many different system-states with the same total internal-energy, but different other relevant state-properties)! These different types of internal energies are stored (and coupled) within a material substance-structure, but may be converted from one to another type during a process. The thermodynamic state is defined by minimum number of independent properties equal to the number of energy types being able to be stored by such material substance structure. For example, two independent properties for "*simple compressible substance*," able to store heat and compression-work only, like properties of ideal-gasses and many substances listed in common Thermodynamic Tables.

For example,

**1 kJ of heating is NOT the same as 1 kJ of mechanical compressing** (or 1kJ electrical charging a capacitor, etc.).





<<< Click on the Images [above](#) to enlarge

## Denying existence of *thermal energy* is the same as denying existence of its transfer (*heat transfer*)!

Some deny existence of 'Thermal energy'. Thermal and mechanical (and other types of) energies are distinguishable, NOT the same 'Internal energy' (as argued by some)! [For example](#), 1 kJ heating is NOT the SAME as 1 kJ compressing! Philosophically, we cannot transfer something that does not exist. That is, we cannot transfer water unless we have water - we cannot transfer heat (transfer of thermal energy) unless we have thermal energy (stored as property or generated in a process). We cannot transfer energy (of any type) without having it somewhere (stored or generated) to transfer it, and then store it somewhere else (as property). In the process (while transferring) we may convert/reprocess, i.e., generate/produce (modify the "original structure") into another form, while conserving the underlying substructure (true elementary particles): existential (mass-energy) conservationism.

Nothing is wrong with the [Caloric theory](#) if there is no heat generation and work interactions - then, the thermal energy is conserved, i.e., when "[Carnot thermal work potential](#)" is dissipated then the thermal energy/caloric is conserved, i.e. [calorimetry](#) and classical heat transfer theory are as valid as always!

[Lavoisier](#) and his contemporaries reasoned ingeniously, long before the conservation of energy was established, that heat must be a conserved substance ([caloric](#)) contained in material systems which can be "poured" (transferred) within and between the systems. If conversion of all other energy types to heat is included (thermal energy "generation" from all types of "phlogistons"), i.e. conservation of energy in general, then caloric theory will be valid in general as stated by [Clausius](#). How ironic, Lavoisier may be right, since [this treatise](#) reaffirms that 'caloric,' although not conserved in general, is a "transferred substance" after all.

“There is an important peculiarity about heat transfer processes without any work interactions (like within heat exchangers): no heat conversion to work like in heat engine, and no other than 'thermal work potential' dissipation and heat generation, therefore the thermal energy (like original *caloric*) is conserved on its own. We like to name such processes, without work interactions, as "*caloric processes*" or caloric heat transfer. We also could define "reversible heat transfer" at infinitesimally small temperature difference, as an ideal limiting case, achieved by an ideal Carnot cycle, when the heat source and sink are at a finite temperature difference, so that work potential is extracted, instead of being dissipated as heat, like in the above caloric processes, while heat transfer takes place at infinitesimally small temperature difference at each temperature level ( $dT \rightarrow 0$ ) [7]. Therefore, during the reversible heat transfer from higher to lower temperature reservoirs, see [Figure 2](#) (left), the work potential is extracted and less heat is reversibly transferred ( $Q_{Rev2} = Q_1 T_2 / T_1$ ) to the reservoir at lower temperature (consider it to be a system,  $T = T_{Sys} = T_2$ ), for the amount of the extracted work (as per the Carnot

ratio or Carnot efficiency, and energy conservation), so the entropy is conserved since no entropy was generated in the reversible cycle (note  $Q_{Rev}/T = \text{constant}$ ) [[Kostic 2014](#) & [2004](#)].”

## Reflections on the Caloric Theory and Thermal Energy as a Distinguished Part of the Internal Energy

Nature of heat was a mystery for a long time. Lavoisier proposed that "heat is a subtle, weightless substance called caloric." Being a substance, the conservation of caloric was a central assumption, long before the energy conservation was established. Furthermore, the kinetic theory existed in the late eighteenth century that could explain the heat and other thermal phenomena. Regardless of ingenious developments, the Caloric Theory has been discredited since the caloric was not obviously conserved during heat generation processes, like drilling, and similar. In modern times, there is a tendency by some scientists to unduly discredit the thermal energy as being indistinguishable from other internal energy types. Denying existence of thermal energy is the same as denying existence of its transfer (heat transfer). Some others consider the Thermodynamic internal energy to be the thermal energy, although the former represents all energy types stored as the kinetic and potential energies of the constituent microstructure, namely, the thermal and mechanical elastic energies in simple compressible substances, in addition to the chemical and nuclear internal energies. In more complex system structure there may be more energy types. The stored system heat increases the system thermal energy that is distinguished from the system internal, mechanical (elastic) energy. For example, the heating or compressing an ideal gas with the same amount of energy will result in the same temperatures and internal energies, but different states, with different volumes and entropies, and similar for other material substances. Reversible heat transfer and caloric heat transfer, without work interactions, are introduced as limiting processes of heat-work interactions. It is reasoned and deduced here, that the thermal energy is distinguishable, regardless of its coupling with the other internal energy forms, and thus pave the way to further illuminate other critical concepts, including Thermodynamic entropy and the Second Law of energy degradation and entropy generation.

\* [Clausius Theory of Heat](#)

## Furthermore ... (Under development) !

The complexity and confusions are due to rather complex mass-energy structures in nature and even more complex process-interactions with conversions of one form of energy to other(s) and therefore couplings, transfers and storage within a material substance mass-energy structures. The apparent duality (in "simple compressible substances") or multiplicity (in general) of "internal energy" is evident and quantified by measurement in reference data tables, and "thermal energy" is only qualitatively defined as part of internal energy, but the two are not the same; see also [Reflections on the Caloric Theory and Thermal Energy](#) by M. Kostic

Some use interchangeably the "internal" and "thermal" energy terms and thus imply as if the two are the same concepts, but they are not! This may add to the confusion instead of clarifying it. Because of the coupling/duality of internal energy in the "simple compressible systems" (like ideal gasses, but also many others) which structures allow storage of thermal heat and mechanical compression (without any chemical and nuclear reactions, thus neglecting the changes (and ignoring) the chemical and nuclear energies), the stored energy is NOT named "thermal," but more generally "internal." The thermal energy is defined in many references, but descriptively only, as related to the thermal random motion of molecules, as are the other thermal properties, like temperature, entropy and others. However, in all reputable references (known to me), the quantitative stored energy in thermodynamic tables is named "internal energy" and not as "thermal energy" since the two are not the same. In more complex than the "simple compressible substances" the internal energy is stored in many different forms like electrical (in capacitors), electro-magnetic (magnets), mechanical-torsion (torsion elastic springs), etc., not to mention chemical and nuclear (relevant if chemical and nuclear processes are involved). I am not aware of any specific reference/s that precisely/accurately define and quantify the "thermal" energy as being different or the same as "internal" energy.

Actually the fundamental concepts are equally valid in general for all substances, but the constitutive property correlations are complex, since the thermodynamic state is defined by minimum number of independent properties equal to the number of energy types being able to be stored by such material substance structure. For example, two independent properties for "simple compressible substance", able to store heat and compression-work only, like properties of many substances listed in common Thermodynamic Tables.

For example, the  $P \cdot v$ , the mechanical properties' product, is equal to  $RT$  for ideal gases, and thus function of temperature only, as is, for example, the specific enthalpy,  $h = u + Pv = u + RT = \text{function}(T)$  only! The mechanical and thermal properties, although distinct, are coupled and related through the constitutive equation of any substance, being simply  $Pv = RT$  for ideal gasses.

The temperature is proportional (i.e., related) to the AVERAGE **kinetic energy of molecules**, or the kinetic energy of a (single) molecule representing the average kinetic energy of ALL molecules: temperature is an intensive macro-property of large number of molecules), while the "*random kinetic energy of [all] molecules*" is the internal energy of a mono-atomic ideal gas!

Thermal Energy is part of (Thermo-Mechanical) Internal Energy ([Cumulative narrative](#)):

<https://docs.google.com/document/d/1F...TtcY/edit>

Thermal\_energy-Howard.pdf (How to distinguish thermal energy emails?):

<https://docs.google.com/file/d/0B...MdkE/edit>

Thermal and Mechanical Energy-MK.pdf (DeVoe-work availability emails?):

<https://docs.google.com/file/d/0B...KMW8/edit>

[Duality-Multiplicity of Internal Energy of Ideal gas](#) \* <http://physics.muni.cz/~adamt/blundell.pdf> \*

<http://physics.weber.edu/thermal/>

From an initial to a final state one may get with a polytrophic process (exchanging heat and work), or isochoric (thermal) and isentropic (mechanical) processes, or along any two iso-property processes!

**PPS: We are aware that the thermal phenomena are very elusive and coupled with other energy forms.**

I am working to de-couple thermal, from other internal forms of energies, where the "caloric processes" (only heating/cooling with full dissipation of work potential) and "reversible heat transfer" (with extraction of full Carnot work potential) are two extreme cases. A reasonable physical intuition have an advantage over "drry" analytics. For example, intuitively the change of Exergy should not depend on value of reference dead state ( $P_o, T_o$ ), event though the Exergy does, and analytics may misguide the physicality:

Exergy of heat  $Q_1$  at temperature  $T_1$  is  $Ex_1 = Q_1(1 - T_o/T_1)$  and for state 2 would be  $Ex_2 = Q_2(1 - T_o/T_2)$ , so:

$$Ex_1 - Ex_2 = Q_1(1 - T_o/T_1) - Q_2(1 - T_o/T_2), \text{ as if it is a function of } T_o.$$

However, for Exergy, i.e., the reversible work potential, the  $Q_2/T_2 = Q_1/T_1$ , the relevant quantities are correlated, so the above is reduced to:

$$Ex_1 - Ex_2 = Q_1(1 - T_o/T_1) - (Q_1 T_2/T_1)(1 - T_o/T_2) = (Q_1/T_1)(T_1 - T_2), \text{ thus } \underline{\text{NOT function of } T_o!}$$

The similar applies in general where internal energy  $U$  is used, since relevant  $U_2$  is correlated to  $U_1$  etc...