THE EFFICIENCY OF THERMAL MACHINES
an introduction to second law of Thermodynamics

Contents:

We define as **thermal machine** any device which realizes a transformation of heat into mechanical energy through a process (or, more exactly, a series of cyclical processes) whose duration is undefined. This means that **a thermal machine must be able to produce potentially unlimited amounts of work for undefined time**. From a physical point of view, mechanic structure and technical details of a given thermal machine (t.m.) are not very significant; it's enough to say that the work of a thermal machine is performed by a fluid which by absorbing heat expands doing work; this process can be realized in more than one way, for instance by moving a piston or rotating a turbine. From a thermodynamic point of view, a t.m. is identified by the physical processes operating inside the motor fluid which does it to function.
It's clear that mechanical processes taking place in a t.m. **must be cyclic**, both because generally thermal engines put into action some rotisms (motor tree, gear etc.) and because anyway a fluid will not can produce work by expanding indefinitely; hence we have to think that, if a fluid works by expanding, it should be taken back to the initial volume. Therefore we have to admit that **a thermal machine must operate through a series of thermodynamic cycles** to provide arbitrarily great amounts of work for an undefined long time.
According to Energy Conservation Principle, work must be produced from heat; there must be a **heat source** (at least one) which provides the heat needed. Since work of a t.m. is potentially unlimited, the heat source will be able to supply arbitrarily great amounts of heat without cooling. This means, ideally, that **heat capacity of a heat source must be infinite**, so that, while continuing to provide heat, its temperature doesn't vary; therefore an ideal heat source must be a thermostat. Really, actual machines such as vehicle motors are alimented by combustion processes which transform irreversibly the chemical composition of the motor fluid, which must be replaced at each working cycle. Hence, a real heat source is a chemical transformation continuously repeated, not a persistent physical system.

From an economic point of view, the *optimum* should be a thermal machine which produces work by converting an equivalent amount of heat extracted from the surrounding environment, i.e. by exploiting only the enormous thermal energy contained in the atmosphere, water of oceans, etc… This machine would integrally convert into work the thermal energy absorbed in thermal equilibrium with the environment without need of more heat sources, i.e. exchanging heat with a sole source. Such a device isn't feasible, *but its realization is not prohibited by the principle of equivalence of work and heat or energy conservation law*, which on the contrary establish the possibility of converting mechanical energy into thermal and vice-versa without any limitation, according to the conversion factor 1 cal = 4,186 J ca. But while it's easy to transform mechanical energy in heat transferred to ambient air, it's clear that the inverse process is much more difficult and it can't be realized by exploiting the environment as the sole heat source. Hence we have to consider a **second principle** of Thermodynamics, which limit the possibility of transforming into work the heat absorbed from a sole source.

In fact, any thermal machine, during a single working cycle, absorbs a certain amount of heat Q_1 from a "hot" source (i.e. at a temperature higher than the ambient) and transforms in work W only a part of the thermal energy equivalent to Q_1 ; the remainder is dissipated, directly or indirectly, in the form of unusable and irrecoverable heat, into external environment, defined as "cold" source.

Let's indicate with Q_2 the amount of heat transferred to the cold source. According to the principle of energy conservation (first law of Thermodynamics), if both heat and work are expressed in the same units of measurement, the work produced during a single operating cycle will be given by the equation (1)

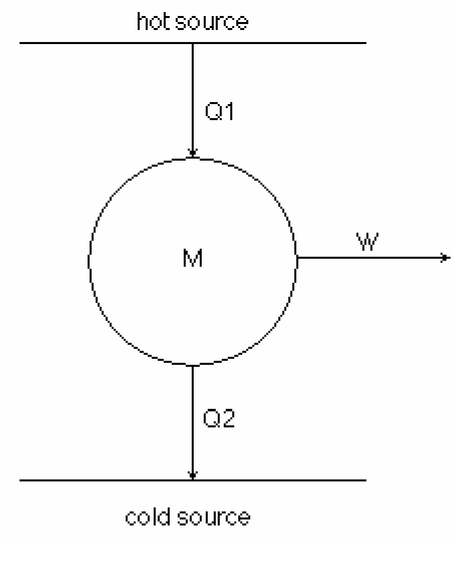
$$\boxed{W = Q_1 - Q_2}$$

The heat transferred Q_2 can never be zero, hence the ratio between W and Q_1 is always less than 1. This ratio is, by definition, the **efficiency** (symbol η) of a thermal machine and it is dimensionless. One can also express it as a percentage: 1 equals to 100%.
Hence we have by definition:

$$\boxed{\eta = \frac{W}{Q_1}}$$

The second principle derives from the discovery that this limitation to efficiency of any thermal machine isn't due to unavoidable technical difficulties or to practical impossibility of thermally isolating engines. Indeed, it's true that an engine will overheat if it doesn't transfer heat into ambient air: therefore thermal dispersions are practically unavoidable, but absolute impossibility to realize 100% efficiency arises from matters of principle independent of practical considerations. In this regard, we have to introduce the **Kelvin's postulate**, which states: a transformation whose only result is the conversion into work of heat extracted from a source at uniform temperature is impossible, therefore **it is impossible in principle to realize a cyclically operating thermal machine to transform integrally into work the whole heat extracted from a thermostat or heat source** (in theory, the temperature of a heat source is constant over time).

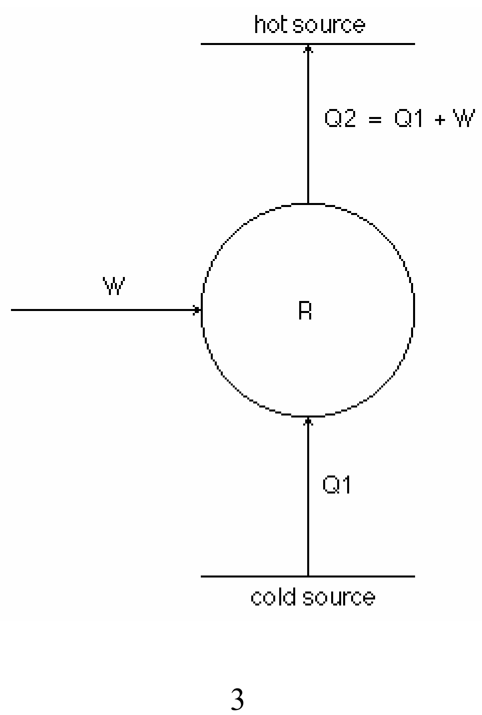
The outline of energy exchanges of a thermal machine – prescinding from effective functioning – is as follows:



where $W = Q_1 - Q_2$ (energy conservation).

To verify that's matter of principle, implying not only technical difficulties, we prove that Kelvin's postulate (KP) is logically equivalent to some even more evident physical principle. In particular, we can verify its connection with **heat exchanges irreversibility**. A phenomenon is said *irreversible* when it evolves according to a certain direction in time and can't be inverted with respect to time, or to put it better, in a irreversible process a physical system evolves from a initial state to a final state through a ordered continuous series of instantaneous configurations, but it's impossible to swap initial and final state simply by inverting the order of all the phases of the process. Many natural processes are irreversible (really, all physical processes are – reversibility is a limit-case), and heat exchanges are among them. In fact, if two bodies in contact are at different temperatures, heat will flow "spontaneously" from the warmer body to the colder one, but the contrary can't happen "spontaneously". In absence of external interventions such as heat transfers, contact between bodies tends to reduce temperature differences to reach an equilibrium state, in which temperature is uniform. However, it's not absolutely impossible to transfer heat from a cold body to a hot body while maintaining or increasing the difference of temperature between them: in fact this is just the process realized by **refrigerant machines**, which therefore generate heat flows in the opposite direction than the natural. However this is an artificial process, which can occur only thanks to the work transferred into refrigerator from an engine (generally an electric one), forcing heat to flow from the cold source to the hot (the external environment). From a thermodynamic point of view, energy flows in refrigerant machines are opposite than thermal exchanges of heat engines: these ones convert into work some of the heat absorbed from a hot source and transfer the remainder to the cold source (external environment), while those ones absorb both heat from a cold source and work from an engine and transfer their sum to the hot source (external environment). The energy balance is the same, as described in the equation (1) $Q_1 - Q_2 = W$, where Q_1 is heat absorbed from a source (hot or cold) and Q_2 is heat transferred into the other source. All the quantities are positive.
The principle, according to which heat flows "spontaneously" from hot bodies to cold bodies, is known as **Clausius' postulate** (CP) , which says: a transformation whose only result is heat transfer from a cold source to a hot source is impossible**,** therefore **it is impossible in principle to realize a cyclically operating refrigerator without exploiting external work**. The principle would be absolutely obvious if not for the phrase "without external work" which clarifies the physical meaning of "spontaneously".

The outline of a refrigerant machine is as follows:



There is a reciprocal implication between Kelvin's Postulate (KP) and Clausius' Postulate (CP), in the sense that if one of them were false also the other should be false. For instance we can demonstrate that **to deny KP implies to deny CP** , i.e., **if to build a machine whose efficiency be equal to 1 were possible (KP false), then also the transfer of heat from a cold source to a hot source without external work should be possible** (CP false). Therefore though apparently quite independent each other, the two statements are physically equivalent and both can be considered as particular formulations of second principle of Thermodynamics (there are many ways to express the second law, depending of particular aspects considered).
Let's deny KP; it implies that a thermal machine "M" is able to convert into work the whole heat Q_1 extracted from a sole heat source at temperature T_1 .

Therefore we get the equation $W = Q_1$

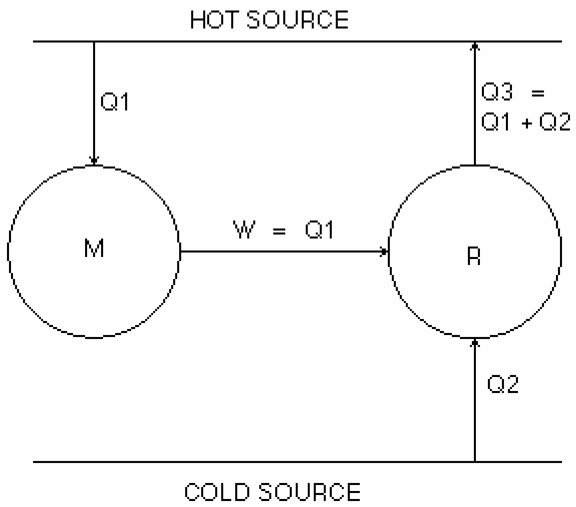
We can employ this work to run a "normal" refrigerator, which extract heat Q_2 from a cold source at temperature T_2 and transfers heat into the same hot source. Denoting by Q_3 the amount of heat transferred from the refrigerator to the hot source, we get according to conservation energy:

$$Q_3 = W + Q_2$$

which implies

$$Q_3 = Q_1 + Q_2$$

$$Q_3 - Q_1 = Q_2$$



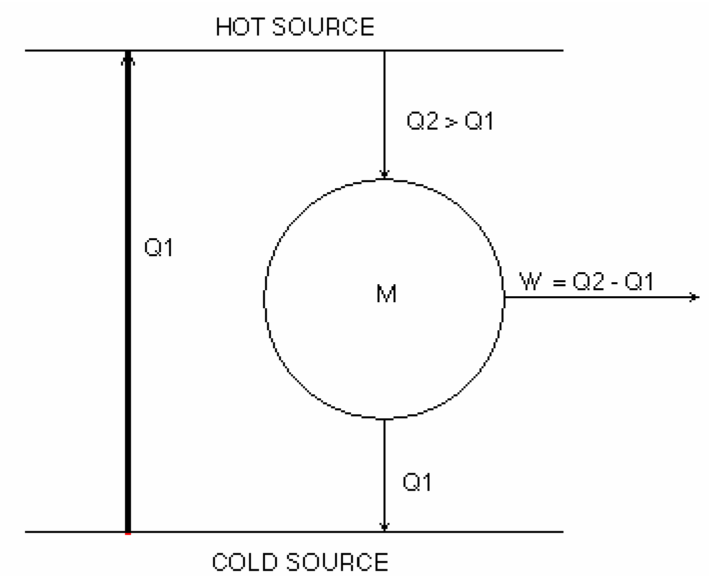
The last equation says that the total heat exchanged between the hot source and the whole system composed of thermal machine and refrigerator, i.e. $Q_3 - Q_1$, is just equal to the heat Q_2 removed from the cold source. Now let's consider the whole device operating between the two sources; **the result of this hypothetical process should be a transfer of heat (Q_2) from the cold source to the hot source without external work** (the system converts work to heat by an internal process). Therefore by denying KP we get a refrigerator operating against CP, i.e. **KP false $\Rightarrow$ CP false** . Since we admit Clausius' statement is true then also Kelvin's statement must be true, *ex absurdo*.

It is possible to invert the logic ordering of this demonstration by verifying that to deny CP implies to deny KP. This means that if "spontaneous" heat transfer from a cold source to a hot source were possible, then it should be possible operate a thermal machine to convert into work the whole heat absorbed from the hot source. Briefly, we can demonstrate that

CP false $\Rightarrow$ KP false

This means that the two statements are *logically equivalent*, in the sense that they must be both true or both false, but not one true and the other false. Hence they both can be considered equally valid formulations of the same principle.

Indeed let's suppose *ex absurdo,* by denying Clausius' postulate, that an amount Q_1 of heat flow "spontaneously" from a cold source to a hot source. Now imagine that during a single operating cycle a "normal" thermal machine extract from the same hot source a greater amount Q_2 of heat , convert into work the difference $Q_2 - Q_1$ and transfer Q_1 into the cold source, according to Kelvin. The overall heat exchanged with the cold source is zero, therefore the whole process has transformed into work the whole heat extracted from a sole heat source, against Kelvin. Hence to deny the Clausius' postulate implies to deny the Kelvin's postulate.



A variant is to suppose that the machine absorb Q_1 from the hot source and transfer Q_2 to the cold one with $W = Q_1 - Q_2$. It is even more paradoxical, since the heat $Q_1 - Q_2$ would be extract from the cold source.

Theorically, a thermal machine can be *reversible* or *irreversible.* An ideal motor cycle working between two sources would be reversible, since irreversibility implies thermal dispersions and work dissipation into heat transferred to environment (the "cold" source). Hence **a real machine is less efficient than an ideal one**, according with the inequalities

$$\eta_{IRR} < \eta_{REV} < 1$$

which apply to machines operating between the same sources.

Concluding remarks: irreversibility and second law of Thermodynamics

The considerations made so far about nature of thermal sources and operation of thermal machines are actually very schematic. For the beginning, not necessarily a heat source is really a thermostat nor it is physically external to the machine; e.g. in common internal combustion engines (such as car or automotive motors in general) and also in gas turbines the hot source in reality is replaced by air-fuel mixture combustion. Hence heat sources are realized by combustion processes indefinitely repeated, i.e. by irreversible chemical transformations. Finally, engine operation implies friction between mechanical parts in contact, which also implies irreversible dissipation of work into heat.

We can also ascertain that real machines are irreversible as follows. The inversion of a reversible motor cycle is an *ideal* refrigerator. It's actually impossible to realize a refrigerator by inverting all mechanical movements and thermal flows of an engine, just because real engines are irreversible. Irreversibility implies that real machines are *repetitive* rather than *cyclical*, since the final state of a real cycle differs from the initial one.

Prescinding from being the theoretical foundation of heat engines operation, thermal machines theory has evidenced the role of the **irreversible processes** in Thermodynamics. While it's possible to convert a certain amount of mechanical energy in heat transferred into the environment or in general into a thermostat, it's not possible convert totally into mechanical energy all the heat extracted from a thermostat. As we have seen, the irreversibility of mechanical energy conversion into heat is physically equivalent to the irreversibility of heat exchanges. Analyzing friction we can see that conversion between work and heat is observed at the "macroscopic" scale, while at the microscopic or molecular scale ordered and disordered forms of energy are transformed into each other. For instance, the kinetic energy of a piston in motion is "ordered" since all the parts of a piston – at the limit, all its atoms – move together (ignoring local microscopic movements like atomic vibrations, etc.). Friction transforms amounts of ordered energy in thermal energy, which is the macroscopic manifestation of molecular energy. Movements of atoms and molecules are chaotic, hence thermal energy is a disordered form of energy. Disordered states of a physical system are generally more probable than the ordered ones, therefore it's easier realize thermal transformations from an initial state into a less ordered final state than into a more ordered one, i.e. at macroscopic scale, to transform work into heat than vice-versa. Irreversibility can be understood as due to transitions from "more ordered" and less probable states to "less ordered" or "more disordered" and more probable states.

Transfer of heat to a body (excluding thermostats) increases both temperature and molecular chaos, therefore higher temperature means greater molecular disorder, lower temperature the contrary. Absolute Zero [1] will be the temperature of a totally ordered system; since molecular energy is disordered, a perfect order is possible only if all the atoms or molecules are motionless. Hence, in Classical Physics, Absolute Zero is the state of total immobility of matter (in Quantum Mechanics, it is only the minimum energy state). See also the endnote.

Therefore we are led to admit that "**spontaneous" processes generate disorder,** i.e**.** in absence of external work a thermally isolated system will evolve into more disordered states, and the final state of equilibrium of an isolate system can't be more ordered than the initial one. Briefly, **the disorder of the whole Universe increases with time**. It may seem that such a rule do not apply to artificial processes such as those above analyzed, but *in nature there not exist "artificial" processes*, since *physical laws are universal and not distinguish between "natural" and "artificial" processes.* Also production of work by *real* machines [2] follows the law of irreversible increase of disorder *applied to the whole universe*, that actually means the union of a physical system (the fluid motor or the whole machine, in this case) with the environment. This is the conceptual root of the **second Law of Thermodynamics**, of which Kelvin's and Clausius' postulates are particular statements.

However, the previous exposition of the second law is largely incomplete, mostly because of the imprecision of the concept of *disorder*, since we have not defined how to measure it .

The measure of disorder is defined by a physical quantity known as **entropy**. Entropy of a physical system thermally and mechanically isolated can't decrease, it increases in irreversible transformations and doesn't vary in the reversible ones. **The entropy rise distinguishes between paste and future**, since – for an isolated system - future entropy amount will be greater than the present one. The Second Principle states that Universe's entropy must increase over time, and its partial formulations as Kelvin's and Clausius' postulates – although apparently limited to circumscribed phenomena and technical problems – express previously its physical meaning.

While the First Principle of Thermodynamics (total energy conservation law) is formulated by an equation, and therefore doesn't define the direction according which a physical process develops and doesn't introduce temporal asymmetries, at the opposite the Second one implies a **temporal asymmetry** according which the whole Universe can't return to any past state (although there exist cyclic transformations, but only on a local scale), i.e. the series of the instants, in which we think to divide time, can't be inverted. Thus it seems that Second Principle defines the direction of time ("*arrow of time"*). The great interest for the second law, from a physical point of view, rises from the statistical nature of irreversibility. This concept can be applied only to many particles systems, because of its statistical character, that we can recognize by its connection with order and disorder – these terms make sense only if referred to large numbers of identical particles. Second law transfers into Physics the mathematical law of the large numbers, therefore it's deeply different from the other physical laws that we find in Dynamics and from first law itself, and can't be reduced to some mechanical principle. [3]

[1] Absolute Zero is the *limit inferior* of any temperature scale rather than the *minimum*, since no series of refrigerant cycles can achieve this point, while it's theoretically possible to reach any temperature higher.

The temperature scales currently in use are: the kelvin (or absolute scale), the Celsius and the Fahreneith. The first and the second ones are universal, but according to the International System of Units (S.I.) the base unit for thermodynamic temperature is the kelvin (K), not the degree Celsius (°C), more used in practice. The thermodynamic temperature expressed in K is the "absolute temperature", which generally physicists refer to, since it expresses average kinetic energy of atoms and molecules. Obviously 0 K corresponds to Absolute Zero. The triple point of water is, by convention, 273.16 K or 0.01 °C (neglecting some details). Differences between two temperatures are the same in kelvin and Celsius scales, that differ by the values assigned to the fixed points. If "T" denotes the temperature in K and "t" in °C, we have $t = T - 273.15$, thus Zero Absolute corresponds to - 273.15 °C.

Fahrenheit scale is commonly used in the U.S.; its unit is the *degree Fahrenheit* (°F) . If "F" denotes the temperature in degrees Fahrenheit, we have $F = 1.8\,T - 459.67$, thus Zero Absolute is at - 459.67 °F.

[2] "Real" machines work through irreversible transformations, which produce rise in entropy. "Ideal" machines are reversible systems, whose entropy doesn't vary. The two postulates are valid for both, so they do not imply necessarily rise of entropy: but this occurs since real machines are irreversible without exception. Vice-versa, irreversibility of engines implies $\eta < 1$.

[3] Newton's mechanics laws imply all motions are reversible. Classical Dynamics and Special and General Relativity are time-symmetric. Such theories imply that whole Universe evolves from initial conditions far from equilibrium. It's not so clear in Quantum Mechanics: the *collapse* of wave function ψ is irreversible, but the formal system (equations and their solutions) is invariant under time inversion. Thus *all commonly accepted fundamental theories are intrinsically time-symmetric*.

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