Thermal Conversion

1. History

Thermal physics is among the older scientific disciplines, having roots in the speculations of Greek philosophers and other ancient peoples. The first reaction turbine was built as a curiosity by Hero of Alexandria (AD c. 120) and consisted of a pivoted copper sphere with two bent nozzles and partially filled with water. It was heated by a fire and rotated.

The rebirth of scientific activity in Europe in the 16th century and beyond brought new enthusiasm to the study of thermal phenomena and the technology that depended on heat for alchemical, chemical, or motive purposes. The three most important problems before about 1870 were 1) explaining the behavior of ideal gases, 2) understanding the nature of heat (was it a substance or a kind of motion?), and 3) determining how to harness the "motive power of fire" with optimal efficiency.

From a modern perspective, it is most remarkable that the term *energy* does not become widely applied in its modern sense until the 1840s, and it was in that decade that several scientists expressed the notion of the conservation of energy. Below is a very cursory overview of the significant conceptual and technological developments on the path to understanding how to build efficient heat engines and refrigerators.

Phlogiston In the late 17th century, the change of a material upon combustion was explained as the departure of a material substance called phlogiston on burning.

Caloric In 1789, Antoine Lavoisier thermally decomposed mercuric oxide, disproving the phlogiston theory. He replaced it with the caloric theory of heat. Caloric was a fluid surrounding the atoms of substances that could be removed during a reaction. Heat flow from warm to cold occurs because caloric particles repel one another.

Steam Engine Thomas Savery developed a steam-operated pump, which was developed further by Thomas Newcomen into a piston engine in 1712. In 1769 James Watt produced an improved steam-powered piston engine (that operated at higher temperatures and pressures).

Converting Work into Heat One of the first American scientific heroes, Sir Benjamin Thompson, also known as Count Rumford, whilst serving as minister of war in Bavaria (!) in 1798, and thereby overseeing the boring of cannon, noted that an apparently *inexhaustible* supply of heat came out of the cannon. This appeared inconsistent with the caloric hypothesis. He further remarked that on boring underwater, the water always took the same amount of time to boil. Thus, he reasoned, work was being converted into heat. However, the issue was hardly settled by his observations.

Carnot Sadi Carnot's analysis of heat engines in *La puissance motrice du feu* (1824) suggested that the maximum efficiency of a device operating in steady state or cyclically to convert heat into mechanical work was independent of the working substance and depended only on the temperature of the heat reservoirs involved.

Clapeyron In 1834, the French engineer B. P. Émile Clapeyron carried out studies on liquids and gases, which were later refined by Clausius. The relationship between the equilibrium vapor pressures of a liquid, its temperature, and its molar heat of vaporization is called the Clausius-Clapeyron equation.

Clapeyron also "borrowed" a technical development of Watt's, which helped determine the work performed by an engine in one cycle.

Equivalence of Work and Heat Julius L. Mayer suggested in 1842 (as had many before him) that heat is simply a result of molecular motions, but added the insight that combustion (oxidation) was responsible for the generation of heat in animals. He also suggested the mechanical equivalent of heat by noting that as a vat of paper pulp was stirred through an appropriate linkage by a horse, that the temperature of the pulp increased.

James Joule, a brewer and amateur scientist, showed in 1843 that mechanical work done by stirring water was converted into heat energy and obtained in 1849 the conversion between mechanical work and calories. He also demonstrated the equivalence of electrical work and thermal energy using resistors (Joule heating).

Announcing in 1843 (1849?) the result of his studies, he wrote: "The work done by the weight of one pound through 772 feet in Manchester will, if spent in producing heat by friction of water, raise the temperature of one pound of water by one degree Fahrenheit."

Entropy Following Carnot's and Clapeyron's insights, Rudolf Clausius showed that the quotient of the heat transferred and the absolute (ideal gas) temperature was an important quantity (1854), which he named *entropy* after the Greek in a paper of 1865. Ludwig Boltzmann first related entropy to disorder at the molecular level.

Clausius, William Thomson (later Lord Kelvin), and others developed "obscure" expressions of the Second Law of Thermodynamics such as *It is impossible for a self-acting machine, unaided by external agency, to convey heat from a body at one temperature to another body at a higher temperature* and *it is impossible by a cyclic process to take heat from a reservoir and convert it into work without, in the same operation, transferring heat from a hot to a cold reservoir.*

Kinetic Theory The kinetic theory of gases was developed largely by Ludwig Boltzmann and James C. Maxwell in the 1870s. It provided a means to derive the ideal gas law from simple assumptions, accounted for the heat capacities of monatomic gases, lent powerful support to the atomic theory of matter, and suggested a very profound failure of classical physics in the heat capacity of diatomic gases. Maxwell recognized very clearly the problem, pronounced it fundamental, and speculated that the answer would require some great new insight in mechanics. The answer would require more than fifty years.

Gibbs In a series of papers published between 1875 and 1878 in the *Journal of the Connecticut Academy*, Josiah Willard Gibbs invented statistical mechanics by postulating that the "proper" way to count states in phase space is equally with respect to positions and momenta (not energy). Maxwell champions Gibbs's work, which was translated into German in 1892.

Blackbody Radiation Studies of the radiation produced by heated bodies led to the recognition that all bodies that absorbed all the radiation incident on them produced identical spectra, irrespective of composition. In 1879 Josef Stefan found that the radiation emitted by a heated body was proportional to T^4, a result that was derived five years later by Boltzmann. The classical theory of thermal radiation was worked out by Rayleigh and Jeans; it predicted $u(\lambda) = 8\pi k_\mathrm{B} T \lambda^{-4}$, which is indeed observed for large wavelengths. However, it also prediced a divergent energy at short wavelengths (the ultraviolet catastrophe).

Planck Planck derived the correct expression for the spectral density of thermal radiation by focusing on the entropy in the radiation field. He introduced an *ad hoc* assumption into the classical statistical mechanics of Boltzmann: he assumed that energy could only be exchanged between the walls of the blackbody cavity and the electromagnetic (radiation) field in units which were proportional to the frequency. This quantum hypothesis solved the short-wavelength divergence by cutting off the infinity of high-energy modes at energies greater than $k_\mathrm{B} T$.

Boltzmann Having struggled for acceptance of his ideas on the probabilistic nature of entropy for thirty years, and being depressed and in poor health, Boltzmann commited suicide in 1906. Soon thereafter, Jean Perrin verified much of his theoretical work.

1.1 References

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2. How to Think About Thermal Devices

Before turning to an example of a heat engine, I would like to summarize how we analyze the optimal behavior of engines, heat pumps, and refrigerators, all of which are fundamentally similar in their thermodynamics. The rules for physicists are two:

1. **Thou canst not create energy out of nothing.**

2. **Thou canst do no better than to create no entropy.**

Besides this, there is the problem of the definition of the term **efficiency**. I use the following definition:

The efficiency of a device is the ratio of the thing you want to the thing you have to pay for.

So, for example, for an engine that converts heat into work, the thing you want is **work** and the thing you pay for is **heat**. Hence, the efficiency of an engine is

$$\eta = \frac{W}{Q_{\text{in}}}$$

In a refrigerator, things are different. What you want is heat removed from the "cold space" and what you pay for is work (in the form of electrical power). Hence, the efficiency (or coefficient of performance) of a refrigerator is

$$\eta = \frac{Q_{\text{in}}}{W}$$

Now a restatement for engineers. A heat engine is a device for converting "heat energy" into useful work.

1. Entropy cannot pile up in such a device; to work in steady state, the net change in the entropy of the device must vanish.

2. Energy cannot pile up in such a device either.

3. The best you can do is to avoid straying from equilibrium. In equilibrium, flows of heat between bodies are reversible.

Carnot's great insight was to think about the procedure without regard to the details of the substances involved, concentrating on the "motive power of fire."

2.1   Heating Processes

When a warmer object is placed in contact with a cooler object, energy flows from the warmer to the cooler object. In the process of losing energy, the entropy of the warmer object declines by

$$\Delta S_w = \frac{Q}{T_w}$$

where Q is the (heat) energy transferred from the object, and the temperature of the warm object is T_w. Similarly, the entropy that arrives in the cooler object is given by

$$\Delta S_c = \frac{Q}{T_c}$$

The change in the combined entropy of the warmer and cooler object in this process is thus

$$\Delta S = \frac{Q}{T_c} - \frac{Q}{T_w} = Q \frac{T_w - T_c}{T_w T_c} \geq 0$$

In the limit that $T_w \to T_c$, no new entropy is created. When $T_w > T_c$, more entropy arrives in the cold object than left the warm one.

3.   Simple Heat Engine

The simplest heat engine consists of a cylinder of gas fitted with a movable piston that may be heated by contact with a hot brick (a proxy for the hot exhaust gases of a combustion process), and cooled by contact with a cold brick (a proxy for contact with a water bath, typically). The four steps are

1. An adiabatic[1] compression: the cold gas is compressed by the piston, which adds energy to the gas, raising its temperature. In the best of all possible cases, the entropy of the gas remains constant as its energy and temperature increases from T_C to T_H. $\Delta E_{\text{gas}} = W_1$ and $\Delta S = 0$.

2. The cylinder is now placed in contact with the hot brick at temperature T_H. The brick heats the gas, which pushes on the piston and expands. The heat extracted from the brick, Q_2, flows into the gas, carrying with it an entropy $\Delta S_2 = Q_2/T_H$. The energy of the gas remains constant during this phase because as Q_2 flows in, the same energy leaves the gas as (desired) work W_2.

3. The cylinder is removed from the hot brick and the gas is allowed to expand adiabatically until it has cooled to T_C. If this is done carefully, no new disorder is introduced in the gas; its entropy remains constant ($\Delta S = 0$). The internal energy of the gas declines as its temperature falls, and this energy is given off as useful work done by the gas. $\Delta E_{\text{gas}} = -W_3$.

4. The cylinder is placed in contact with the cold brick at temperature T_C and is compressed. This requires an amount of work W_4 to be supplied to the gas. The temperature of the gas remains constant, and so the energy of the gas remains constant as well (at least, if the gas is ideal). $\Delta E = 0$. Entropy leaves the gas as it heats the cold brick: $\Delta S_{\text{gas}} = -Q_4/T_C$.

Now we apply the fundamental laws. The first one says that the net energy change of the gas must vanish:

$$\Delta E = W_1 - W_3 = 0 \tag{1}$$

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[1]*Adiabatic* means that no heat flows into or out of the gas during this process.

Furthermore, during the two isothermal processes, $Q_2 = W_2$ and $Q_4 = W_4$.

The second says that the entropy change in the gas in going through a full cycle must vanish (in steady state). Because in our analysis we neglect any additional entropy production (arising from uneven heating, friction, or other irreversibilities),

$$\Delta S = \frac{Q_2}{T_H} - \frac{Q_4}{T_C} = \frac{W_2}{T_H} - \frac{W_4}{T_C} = 0 \tag{2}$$

The net work done by the gas during a cycle is

$$W_{\text{net}} = W_2 + W_3 - W_4 - W_1 = W_2 - W_4 \tag{3}$$

while the heat supplied to the gas from the hot brick is

$$Q_{\text{in}} = Q_2 = W_2 \tag{4}$$

Therefore, the Carnot efficiency is

$$\eta_{\text{Carnot}} = \frac{W_{\text{net}}}{Q_{\text{in}}} = \frac{W_2 - W_4}{W_2} = 1 - \frac{W_4}{W_2} \tag{5}$$

Solving Eq. (2) for the work ratio and substituting into Eq. (5) gives

$$\boxed{\eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_C}} \tag{6}$$

The reversible (Carnot) limiting efficiency is given by the ratio of the temperature difference between the hot and cold bricks (reservoirs) and the temperature of the cold brick. From a practical point of view, the cold reservoir is apt to be some water reservoir at a temperature near to room temperature, give or take 10°C or so. Therefore, the way to maximize efficiency is to increase T_H, the temperature at which energy is added to the working fluid.

3.1   Practical Power Production

Although the Carnot efficiency describes the limiting that can be obtained, in practice it requires way too much patience to be realized. This is because the two heat transfer steps (when the cylinder is in contact with one brick or the other) occur at constant temperature. **The rate at which heat flows from a hot object to a cold object in contact with it is proportional to the difference in temperature between them.** This is the essence of Fourier's law of thermal conduction. To achieve the Carnot efficiency requires us to allow the heat to flow across a negligible temperature difference. This takes too long.

In practice we must accept a finite temperature difference between the working fluid (in the cylinder) and the hot or cold brick, so that (1) more entropy arrives in the working fluid than leaves the hot brick in step 2, and (2) less entropy leaves the working fluid than arrives in the cold brick in step 4. The efficiency expression has the same form, but we understand that T_H refers to the temperature of the gas in the cylinder, not the temperature of the hot brick; and T_C is the temperature of the gas, not the temperature of the cold brick.

A somewhat more sophisticated computation of the efficiency of the engine when optimized for

the output power, rather than the energy conversion efficiency, yields the **endoreversible** efficiency,[2]

$$\eta_{\mathrm{erp}} = 1 - \sqrt{\frac{T_C}{T_H}} \tag{7}$$

In a typical coal-burning boiler, $T_H \approx 825$ K and the cooling tower would be at $T_C \approx 300$ K, producing a reversible efficiency of 64% and a more realistic endoreversible efficiency of 40%.
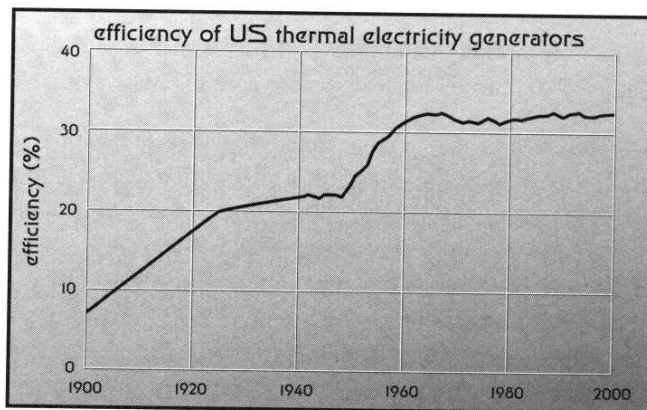

Figure 1.17
By 1960 the average efficiency of the U.S. thermal generation of electricity surpassed 30% and while the best power plants now operate with efficiencies just above 40% the nationwide mean has stagnated for 49 years, clearly an unacceptable waste of resources. Plotted from data in USBC (1975) and EIA (2001a).

Figure from Vaclav Smil, *Energy at the Crossroads* (MIT, Cambridge, 2003) p. 41.

4.   Improvements

There are ways to extract more use from the fuel energy used to produce electricity. One is **co-generation**, in which the waste heat is used for some other purpose. Examples include the heating of homes and other buildings and the heating of chemical reactors. Using cogeneration it is possible to use up to 70% of the chemical energy in the fuel. This approach was much discussed in the 1970s in the U.S., but by the late 1990s only about 6% of the total U.S. electricity generating capacity uses cogeneration. By contrast, "Denmark receives 40% and the Netherlands and Finland about 30% of electricity from combined heat and power, mostly from district energy systems."[3]

Another approach is **combined cycle** generation of electricity. This technique combines a gas turbine with more conventional steam turbine generation. Because of material-property limitations, the high-temperature limit for steam generation is about 655°C = 928 K, whereas the combustion products tend to have temperatures as high as 1200°C or more. Because gas turbines can operate at these higher temperatures, but tend to produce exhaust gases that are still very high (450°C to 650°C), the exhaust gases are used to heat the water/steam for the steam turbine. Hence, by combining two

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[2] This may be computed by defining a warm temperature T_w at which the energy arrives in the working fluid from the hot box, and T_t is the tepid temperature at which it leaves the working fluid to make its way to the cold reservoir. Finding the right combination of T_w and T_t that maximizes the output power gives η_{erp}.

[3] Smil, *Energy at the Crossroads*, p. 235.

generators, it is possible to achieve a much greater temperature difference between the heat source and the cold reservoir, significantly increasing the Carnot efficiency. Taking T_H = 1200°C = 1473 K as the high temperature and keeping T_C = 300 K, we see that

$$\eta_{\text{Carnot}} = 80\% \qquad \text{and} \qquad \eta_{\text{erp}} = 55\% \tag{8}$$

Hence, converting the existing stock of thermal generation systems to one form or the other of these high-efficiency production methods would significantly decrease the U.S. demand for coal and hydrocarbons, and significantly decrease our carbon emissions.

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The Efficiency of a Heat Engine Maximized for Power

The Carnot efficiency is the maximum ratio of work extracted to heat absorbed achieved in a reversible heat engine. Heat flows spontaneously from hot objects to cold ones, but not the other way around. Such a flow of energy increases the entropy of the combination of reservoirs, which is a fancy way of saying that it is *much* more probable than the reverse process.

If a little bit of thermal energy δQ flows from a hot reservoir at temperature T_h to a slightly cooler reservoir at temperature $T_w < T_h$, then the entropy change of the hot reservoir (which is large enough and well mixed so that we may assume its temperature is uniform and constant) is

$$\Delta S_h = -\frac{\delta Q}{T_h} \tag{9}$$

It is negative because the energy flow out of the reservoir carries entropy with it. This energy arrives in the warm reservoir which is also large and maintained at temperature T_w, so its entropy increases by

$$\Delta S_w = \frac{\delta Q}{T_w} \tag{10}$$

In the limit that $T_w \to T_h$, the same amount of entropy enters the warm reservoir as leaves the hot one. But if there is a significant temperature difference, more entropy arrives in the warm reservoir than left the hot one. *Heat flow across a temperature gradient creates entropy.*

5.   The Endoreversible Heat Engine

Problem 1 – The Endoreversible Engine   What is the efficiency of a heat engine that takes heat from a hot reservoir at T_h and rejects waste heat to a cold reservoir at T_c when the engine is optimized to produce maximum power?

Solution: The problem with the Carnot cycle is that it takes a great deal of patience to wait for the heat to flow from the hot reservoir into the working fluid when the difference in their temperatures is negligible. If we want to speed things up, we can allow a temperature drop across the heat exchanger that transfers energy from the "hot box" at T_h into the working fluid, which has temperature T_w. This means that more entropy arrives in the working fluid per unit time than leaves the hot box. For a cyclic engine, this means more entropy per unit time must be removed from the working fluid (after it has done its useful work). To get this entropy out at a reasonable rate, we must accept a temperature drop across the second heat exchanger. So, the fluid arrives at the heat exchanger at T_t and exits into the cold reservoir (river) at T_c. How should we choose T_w and T_t to maximize the generated power?

Suppose that rate at which heat leaves the hot reservoir is $\dot{Q}_h$. This rate will be proportional to the temperature drop across the heat exchanger, so

$$\dot{Q}_h = k_h (T_h - T_w) \tag{11}$$

for some proportionality constant k_h that depends on the design of the heat exchanger and the rate at which the fluid flows through the exchanger.

Similarly, the heat flow out of the working fluid through the second heat exchanger is

$$\dot{Q}_c = k_c (T_t - T_c) \tag{12}$$

where k_c is some other constant that may be the same as k_h or quite different. If the engine operates reversibly between T_w and T_t, then the power out is given by

$$\dot{W} = \dot{Q}_h - \dot{Q}_c = k_h (T_h - T_w) - k_c (T_t - T_c) \tag{13}$$

by conservation of energy and all the entropy that flows into the fluid at T_w must leave at T_t, so

$$\dot{S} = \frac{\dot{Q}_h}{T_w} - \frac{\dot{Q}_c}{T_t} = 0 \qquad \text{or} \qquad \dot{S} = \frac{k_h (T_h - T_w)}{T_w} - \frac{k_c (T_t - T_c)}{T_t} = 0 \tag{14}$$

This is a maximization problem in the two dimensional space of T_w and T_t. At the maximum, $\dot{W}$ must be stationary with respect to variations in both T_w and T_t. But,

$$d\dot{W} = \frac{\partial \dot{W}}{\partial T_w} dT_w + \frac{\partial \dot{W}}{\partial T_t} dT_t = -k_h \, dT_w - k_c \, dT_t \tag{15}$$

from Eq. (13). This is true for arbitrary variations dT_w and dT_t, but we must vary these two parameters consistent with Eq. (14). Differentiating this latter equation gives

$$d\dot{S} = \frac{\partial \dot{S}}{\partial T_w} dT_w + \frac{\partial \dot{S}}{\partial T_t} dT_t = -\frac{k_h T_h}{T_w^2} dT_w - \frac{k_c T_c}{T_t^2} dT_t \tag{16}$$

Setting $d\dot{W}$ to zero gives $k_c \, dT_t = -k_h \, dT_w$, which we can substitute into the condition that $d\dot{S} = 0$ from Eq. (16) to get

$$d\dot{S} = 0 = -\frac{k_h T_h}{T_w^2} dT_w + \frac{k_h T_c}{T_t^2} dT_w = \left(-\frac{T_h}{T_w^2} + \frac{T_c}{T_t^2} \right) k_h \, dT_w \tag{17}$$

Therefore,

$$\frac{T_c}{T_h} = \frac{T_t^2}{T_w^2} \qquad \Longrightarrow \qquad \boxed{\frac{T_t}{T_w} = \sqrt{\frac{T_c}{T_h}}} \tag{18}$$

Since the heat engine is presumed to operate reversibly between T_w and T_t, its efficiency is

$$\boxed{\eta_{\text{erp}} = 1 - \frac{T_t}{T_w} = 1 - \sqrt{\frac{T_c}{T_h}}} \tag{19}$$

which is smaller than the Carnot efficiency. For $T_h = 800\,\text{K}$ and $T_c = 300\,\text{K}$, the Carnot efficiency is 62.5%, while the endoreversible efficiency is 38.8%.