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EXERGY

Minimum work needed and maximum work obtainable

We said before that energy is preserved for any evolution in an isolated system (what is used to compute input/output energies in non-isolated closed systems), and also that entropy increases for any evolution in an isolated system (used to determine the final state when some restriction is released). Now we are going to analyse a cost/benefit matter: how much work can be extracted from an 'isolated' system not at equilibrium, or how much work must be spent to force an 'isolated' system initially at equilibrium to reach a non-equilibrium state. Quotes on 'isolated' are meant to point out that the system is not strictly isolated because it has to interact with the work-agent (e.g. an ideal electric socket or a hanging weight), that could get or give the wanted work, and that we call Mechanical Reservoir (MR).

The above-mentioned concept of maximum obtainable work (or minimum necessary work), was already analysed by W. Gibbs in 1878, that called it available energy, although today it is known as exergy, a name introduced by Rant in 1956 to mean extractable energy. Notice that when people talk about the energy crisis, they really mean exergy crisis, i.e. the fact that after any evolution (entropy generation), the work obtainable from a given universe decreases (but the energy of the universe remains the same). Notice also that that sometimes one reads that "energy is the capacity to do work", in spite of the fact that it is only the exergy of a system that may be converted to work and not all of its energy (none of its energy for a system at equilibrium).

For a given universe, be it a non-equilibrium system and the MR (or, what is more worldly, a system at equilibrium in an environment at a different state, and the MR), the exergy, Φ , of the system (really of the system and its environment) is defined as:

$$\Delta \Phi \equiv W_u \Big|_{\min} = W_u \Big|_{\Delta S_{\text{univ}}=0} \quad (3.1)$$

where the Δ is used to mean that exergy of a given state is always bound to a reference state (to be detailed below), the subscript 'u' is a reminder that only useful work (that exchanged with the MR) is

valued, and not a possible work exchange with the environment, that, for an infinite non-dissipative atmosphere are related by (1.2):

$$W_u \equiv W + p_0 \Delta V \quad (3.2)$$

Equation (3.2) may be read as follows: the useful work exchanged by a system is the total work exchanged minus the work exchanged with the atmosphere, assumed at constant pressure p_0 . Equation (3.1) then states that exergy, defined as the minimum required work for a process, is the useful work exchanged when the entropy increase for the universe is nil. The proof of this equality in (3.1) is as follows. The energy balance for the evolution of an 'isolated' system (with the MR) is (1.5), $E - E_0 = W_u$, whereas the entropy balance is $S - S_0 \geq 0$ since the MR is assumed ideal (without entropy generation). From these two equations, and the fact that entropy must be a monotonic increasing function of energy for any stable system, one deduces that for minimum W_u (if positive; maximum if negative), E must be minimum since E_0 is constant, but E varies monotonously with S , and S must be greater than S_0 , thus, the minimum of E corresponds to the minimum of S , which is S_0 , demonstrating that for minimum work the process must be without variation of the entropy of the universe.

Notice that exergy refers to limiting exchangeable work, and not heat, as might be understood with a more ambiguous 'available energy'. Notice also that nothing is said about the devices needed to actually get the exergy (the work) out of a universe, except that such devices would remain the same unchanged at the end of the process as they were at the beginning. By the way, the exergy of a universe is not the exergy of its parts (e.g. by separate, a hot body and a cold body have no exergy, but they the ensemble has). Further notice that exergy depends on a given universe as a whole, although one often says 'exergy of a system'; either the system is the whole universe (as in Exercise 1), or we really mean 'the system (and its environment)' with the last part understood (see Exergy in the presence of an infinite atmosphere). Finally notice that the final or dead state of the universe must be specified (to know if we are only considering thermal relaxation, or mechanical relaxation and chemical reactions too).

Irreversibility

The irreversibility of a given process of a system (really of a universe) is defined as the difference between the work actually employed and the minimum work needed:

$$I \equiv W_u - W_u \big|_{\Delta S_{\text{univ}}=0} \geq 0 \quad (3.3)$$

The same equation applies when the W s are negative, since the actual work obtained will be smaller in module than the maximum obtainable work.

The irreversibility is another way to measure entropy generation, or total entropy increase of the universe; in fact, it is easy to demonstrate that $I = T_0 \Delta S_{\text{univ}} = T_0 S_{\text{gen univ}}$ (Guoy-Stodola-1890).

[Exercise 1. Maximum work from a two-body system](#)

Exergy in the presence of an infinite atmosphere

Exergy is always related to a non-equilibrium system, but most of the times it is related to a system at equilibrium in the presence of an environment not in mutual equilibrium, i.e. to a universe not at equilibrium, in any case. The atmosphere is the most common environment on Earth.

A thermodynamic universe is constituted by all participating bodies in a given thermodynamic problem. The idealisation of an infinite atmosphere is very convenient for the analysis of terrestrial problems, since they always occur in the presence of the Earth atmosphere, a huge 10^{18} kg of gaseous environment, and it is also the case for systems surrounded by an ocean of liquid water. For a given reference state of the universe (described below), the energy, entropy, exergy and any other extensive properties of a system are equal to the sum of its parts that can be assumed at equilibrium, thus, it is only necessary to study an equilibrium system in the presence of the infinite atmosphere, since the exergy of two systems relative to the same environment is just the addition of their exergies.

We look for an expression of the exergy of a system (really of the universe composed by the system, the environment and a reversible mechanical reservoir MR) as a function of their state properties: e.g. V , T , p and μ_i for the system, and T_0 , p_0 and μ_{i0} for the environment. If we consider a generic evolution of a generic system, using non-subscripted symbols for system variables and subscript 0 for environmental variables we have (see Fig. 3.1):

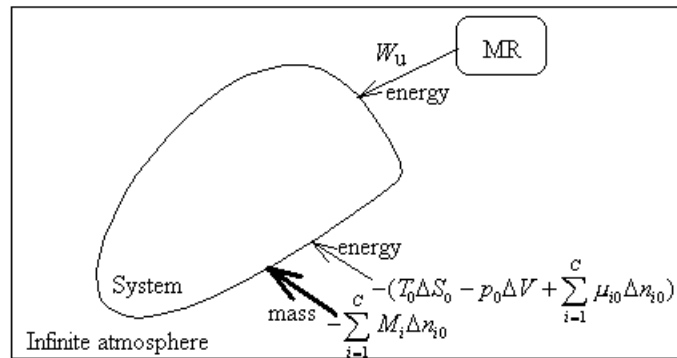


Fig. 3.1. Sketch of general energy and mass transfer between a system, a mechanical reservoir (MR), and the atmosphere.

Energy balance for the universe: $\Delta E_{\text{univ}}=0$, or $\Delta E + \Delta E_0 + \Delta E_{\text{MR}}=0$, and using Eq. 2.8 for the atmosphere:

$$\Delta E + (T_0 \Delta S_0 - p_0 \Delta V_0 + \sum_{i=1}^C \mu_{i0} \Delta n_{i0}) + (-W_u) = 0 \quad (3.4)$$

Mass balance for the universe, for each conservative species. We have in mind mass diffusion flows through the frontier of the system; convective flows are dealt with at [Chapter 5](#) for pure substances and [Chapter 7](#) for mixtures. Leaving out chemical reactions for the moment, we enforce the conservation of every one of the C different chemical species present ($\Delta n_{i \text{ univ}}=0$):

$$\Delta n_i + \Delta n_{i0} = 0, \text{ for } i=1..C \quad (3.5)$$

Entropy balance for the universe: $\Delta S_{\text{univ}} \geq 0$, or $\Delta S + \Delta S_0 \geq 0$, and using Eq. 2.12 and a suitable arrangement:

$$\Delta S + \Delta S_0 = \int \frac{dQ}{T} + S_{gen} + \int \frac{dQ_0}{T_0} = \frac{1}{T_0} \left[T_0 S_{gen} - \int \left(1 - \frac{T_0}{T} \right) dQ \right] \geq 0 \quad (3.6)$$

where $Q_0 = -Q$ has been applied. Finally, applying also volume continuity $\Delta V_0 = -\Delta V$ one may get the following expression for the useful work:

$$W_u = \Delta \left(E + p_0 V - T_0 S - \sum_{i=1}^C \mu_{i0} n_i \right) - \int \left(1 - \frac{T_0}{T} \right) dQ + T_0 S_{gen} \quad (3.7)$$

i.e., the useful work W_u demanded from a MR to change the state of a system, when freely using the atmosphere, has three terms: the increment of a state function, $\Delta(E + p_0 V - T_0 S - \sum \mu_{i0} n_i)$, and two path integrals necessarily positive: an energy dissipation in the frontier due to heat exchange with temperature jump, $-\int (1 - T_0/T) dQ$, and an energy dissipation in the interior, $T_0 S_{gen}$. If one considers the thermodynamic universe to include some thermal reservoirs (a thermal reservoir, TR, is an infinite capacity non-dissipating heat source at a fixed temperature T_i), equation (3.7) becomes:

$$W_u = \Delta \left(E + p_0 V - T_0 S - \sum_{i=1}^C \mu_{i0} n_i \right) - \sum_i \left(1 - \frac{T_0}{T_i} \right) Q_i - \int \left(1 - \frac{T_0}{T} \right) dQ + T_0 S_{gen} \quad (3.8)$$

as can be deduced by redoing the development with the TR inclusion. Notice that now $(1 - T_0/T_i)Q_i > 0$ in all cases, either when the system receives heat from a hot TR ($Q_i > 0$ and $T_i > T_0$), or when it delivers heat from a cold TR ($Q_i < 0$ and $T_i < T_0$), whereas in the case of the environment it is always $\int (1 - T_0/T) dQ < 0$, as seen before. The exergy of thermal reservoirs is further analysed below.

It is concluded that the minimum useful work to change the state of a system, i.e. the exergy required, in the only presence of the atmosphere (i.e. without additional thermal reservoirs), is:

$$\Delta \Phi = \Delta \left(E + p_0 V - T_0 S - \sum_{i=1}^C \mu_{i0} n_i \right) \quad (3.9)$$

Most of the times, the exergy of a state is referred to the dead state of equilibrium between the system and the atmosphere, a kind of absolute exergy for the universe considered, but we still keep the increment symbol to remind that it is a state function, not a path function. It is then usual to separate the energy increment in its thermomechanical part and its chemical part, $\Delta E = E(T, p, \mu_k) - E(T_0, p_0, \mu_{k0}) = E(T, p, \mu_k) - E(T_0, p_0, \mu_k) + E(T_0, p_0, \mu_k) - E(T_0, p_0, \mu_{k0}) = \Delta E|_{n_i} + \sum \mu_k n_i$, where $\sum \mu_k n_i$ is the energy ascribed to the isentropic filling of a volume at atmospheric conditions. Thence, if we write (3.9) for a system relative to the reference atmosphere, we have:

$$\Delta \Phi = \Delta(E + p_0 V - T_0 S)|_{n_i} + \sum_{i=1}^C (\mu_i - \mu_{i0}) n_i \Big|_{T_0, p_0} \quad (3.10)$$

where the first term in the right-hand-side, called the thermo-mechanical exergy of a system is computed at constant chemical concentrations (i.e. for a control mass at the final composition n_i , changing from

state T_0, p_0 to state p, T), whereas the last term, called the chemical exergy is computed on the final composition and corresponds to its chemical-potential change at constant T_0, p_0 from reference-atmosphere concentrations to final-state concentrations in the system. We leave apart nuclear exergy, both of fission and fusion origin, which are due to a change in potential energy of nucleons, associated to the strong and weak nuclear forces (the strong force is responsible for holding nucleons together, whereas the weak force is associated to neutrons-to-protons conversion during beta decay); along the periodic table, in increasing atomic number, nuclides have specific bound energies quickly decreasing to a minimum at ^{62}Ni , and then slowly increasing again.

[Exercise 2. Minimum work to heat a solid](#)

[Exercise 3. Maximum power from a compressed-air tank](#)

Reference atmosphere

The exergy of a system (really of the ‘universe’ it forms with its environment), depends on the conditions of the environment, that must be known, in order to be precise. The reference atmosphere should be the actual local Earth atmosphere at work, but this is not under control (it varies unpredictably with weather) and a given model, a standard, is required for prediction.

To agree on a standard for pressure, p_0 , e.g. $p_0=100$ kPa, is easy since it is rather invariant locally (the mean value is around 101 kPa all year around at all locations at sea-level, with a typical deviation less than $\pm 2\%$), but to agree on a standard for temperature is much more embarrassing since it varies more than 10% around the year and around the globe. Notice, by the way, that a vacuum space has some exergy (relative to the reference environment), even if it has no energy associated to its zero mass.

For a temperature standard, the mean Earth-surface spatial and temporal average seems also a reasonable choice, $T_0=288$ K (15 °C), although the more 'physical' key-point of 0 °C for the freezing point of water, the more 'chemical' key-point of 25 °C of a busy lab, or the more ‘comfortable’ key-point of 20 °C, have also many supporters.

But agreement on atmosphere composition is even harder, although it might seem to pose no problems in principle, since the Earth atmosphere has a rather uniform composition in time and space, with variations less than $\pm 2\%$, mainly due to its water content. The real flaw is that our environment is not only the simple gaseous atmosphere but a complex ecosphere mix (atmosphere, hydrosphere, lithosphere and biosphere).

Thus, the thermodynamic model of an equilibrium system surrounded by an equilibrium environment is too simple in practice: we live in a non-equilibrium environment composed of the Earth atmosphere (from which we take air and some noble gases), the Earth hydrosphere (from which we take water and salts), the Earth lithosphere (from which we take minerals), the Earth biosphere (from which we take plants and animals), all of them integrating our ecosphere, plus our far reaching environment with which we have direct exchanges, mainly the Sun and background space. This abundance of non-equilibrium systems is what we call energy sources and raw materials, and is what makes life possible.

In spite of all these drawbacks, the thermodynamic model of an equilibrium system surrounded by an equilibrium environment is the basis for most current thermodynamic analysis in all fields. For non-chemical thermodynamics (also called thermomechanical problems) the composition of the environment is irrelevant, and the last term in the right-hand-side of (3.10) is skipped. Even in many chemical thermodynamic problems, this chemical exergy is not accounted for, particularly when computing maximum obtainable work, since the technology to profit from concentration gradients to get out energy is in its infancy.

The selection of a reference composition for the atmosphere is based on the following; the simplest composition of interest would be 79% N₂ and 21% O₂ in molar fraction (the rest are traces), since oxygen is far more important than nitrogen, but hydrogen and carbon should be also present due to its outstanding relevance in combustion, so the standard often used is that in Table 3.1:

Table 3.1. Composition (molar fractions) of the reference atmosphere (air with 60% relative humidity at 15 °C).

x_{N_2}	=	0.7720
x_{O_2}	=	0.2080
$x_{\text{H}_2\text{O}}$	=	0.0102
x_{Ar}	=	0.0095
x_{CO_2}	=	0.0003
$\sum x_i$	=	1

We postpone any further analysis of chemical exergy until the dependence of the chemical potential with molar fractions is studied in the [Chapter 7: Mixtures](#).

Exergy of energy and mass sources

Let a universe be a single system in equilibrium; therefore, no further process is possible. Let this system be our reference environment (notice that this is a simplistic model for the Earth atmosphere, which is not at equilibrium). In this situation we wonder how much work can be generated from energy sources (heat or work; e.g. from sunshine) and from mass sources (e.g. from a fuel or a water spring). Figure 3.2 presents the block diagram for these three types of engines: a work source, a heat source, and a mass source.

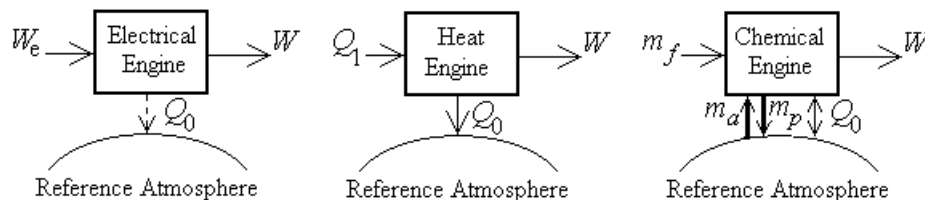


Fig. 3.2. Sketch of the different types of engines from a thermodynamics point-of-view: work engine (here represented by an electrical motor), heat engine, and chemical engine fed by a mass of fuel (and a mass of ambient air).

From a work source, up to 100% work-output may be produced, only limited by friction losses. Electric motors, water wheels, spring-loaded motors, and so on, are practical devices of this type.

From a heat source, the work-output that may be produced depends on the relation between its temperature, T , and the temperature of the reference environment, T_0 . The steam engine is the paradigm of this type of device: a control mass (water in this case) gets some heat from the hot source (a flame or the sunshine) and delivers some work (the rest of the input energy goes to the ambient). This problem is so crucial to Thermodynamics that it is analysed more deeply below, but we advance that the exergy (maximum obtainable work) of heat Q from a heat source at temperature T is $W_{\max}=Q(1-T_0/T)$.

From a mass source, the work-output that may be produced depends on the assumption about the exit of that mass. In the limit one might consider that all the input mass is converted to energy through Einstein relation $E=mc^2$, but we restrict ourselves here to processes with negligible mass loss, so that the same mass exits at steady state. The maximum work obtainable would be when the exit stream is in equilibrium with the ambient (same temperature, pressure and composition). The exergy of a mass source can be deduced from (3.10) when considering a control volume at steady state, and will be developed in Chapter 7 (Mixtures) and Chapter 9 (Chemical reaction). Just to give an example, the exergy (maximum obtainable work) of a source mass m of a pure component present in the reference atmosphere (e.g. a source of pure oxygen) at ambient temperature and pressure is $W_{\max}=-mRT_0\ln x$, where x is the molar fraction of that substance in the environment.

It is appropriate here to remark that, presently, by far the largest share in our primary energy sources corresponds to fossil-fuel mass sources (coal, oil and natural gas). Also, notice that the typical car engine is really a chemical engine as sketched in Fig. 3.2, although it may be modelled in a first approximation as a combination of a chemical reactor and a heat engine; if nowadays car-engines are replaced by fuel-cell engines, the same chemical engine sketch will apply, but the modelling as a heat engine will no longer be valid.

[Exercise 4. Minimum work to produce vacuum](#)

Exergy of infinite-capacity heat sources: heat engines, heat pumps, and refrigerators

Similar to the infinite-environment model, and related to it, is the model of two infinite-capacity heat sources; if the universe were only one system, and in equilibrium as assumed, there will be no further process possible, and if there were more than two, it could be reduced to two because of the additivity of exergy relative to a given environment. In fact, one of the infinite-capacity heat sources is always the environment, and the other is a hotter or colder source, the paradigmatic case being a hot mass permanently kept hot by burning a fuel continuously, as in the steam engine that was the origin of Thermodynamics (Carnot's 1824 treatise "On the motive power of fire").

The work one gets from two infinite sources, or the work one needs to force thermally apart two infinite bodies, is of course infinite; what we look for, is the ratio between the work one gets or puts, and the energy the system loses or gains.

If the environment is the cold source, the question is to find the maximum efficiency to get work from a hot system (heat engine), or the maximum efficiency to use work to keep a system hot in a colder environment (heat pump). If the environment is the hot source, the question is to find the maximum efficiency to get work from a cold system (a thermal engine of little practical use since it is easy to get hot systems by chemical combustion or nuclear fission, but uncommon to have chemical or nuclear reactions that produce cold), or the maximum efficiency to use work to keep a system cold in a hotter environment (refrigerator).

As said before, besides the two infinite-capacity heat sources and the MR, we have to assume that there is another system that may be used without change (an imaginary device running cyclically that acts like a catalyst of the changes in the others). The three types of such devices: heat engine, heat pump and refrigerator, are represented as circles in Fig. 3.2, while the infinite sources by open rectangles, and the definition of their efficiencies, both energetic, η_e , and exergetic, η_x , follows (mind that the chosen system is the device):

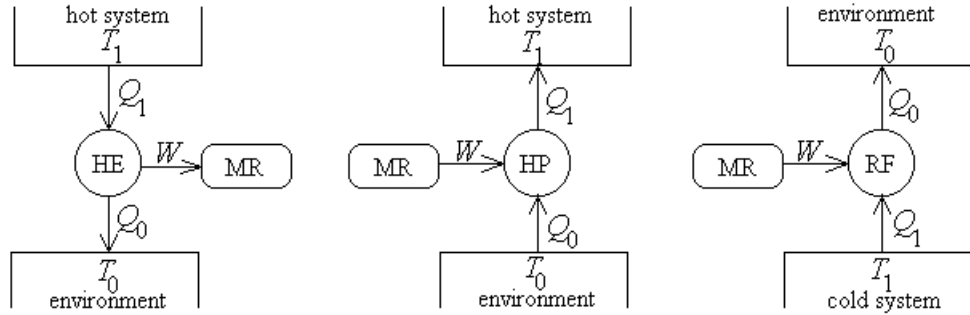


Fig. 3.3. Sketch and nomenclature for a heat engine (HE), a heat pump (HP) and a refrigerator (RF).

$$\text{Heat engine: } \eta_e \equiv \frac{-W}{Q_1}, \quad \eta_x \equiv \frac{\eta_e}{\eta_{e\max}}, \quad \eta_{e\max} = 1 - \frac{T_0}{T_1} \quad (3.11)$$

$$\text{Heat pump: } \eta_e \equiv \frac{-Q_1}{W}, \quad \eta_x \equiv \frac{\eta_e}{\eta_{e\max}}, \quad \eta_{e\max} = \frac{T_1}{T_1 - T_0} \quad (3.12)$$

$$\text{Refrigerator: } \eta_e \equiv \frac{Q_1}{W}, \quad \eta_x \equiv \frac{\eta_e}{\eta_{e\max}}, \quad \eta_{e\max} = \frac{T_1}{T_0 - T_1} \quad (3.13)$$

The maximum values of the efficiencies are found by simply using (3.1), i.e. forcing no entropy generation, e.g. for a heat engine $\Delta S = -Q_1/T_1 + Q_0/T_0 = 0$, that together with the energy balance for the device, $\Delta E = W + Q \rightarrow 0 = -W + Q_1 - Q_0$ yield the result quoted in (3.11), first obtained by N.L.S. Carnot in 1824 and known as Carnot efficiency. The concept of the heat pump was first proposed by Lord Kelvin.

Notice that the above maximum efficiencies (and in particular Carnot efficiency), have been developed for infinite-capacity heat sources. If a finite-capacity heat source is available, its temperature changes with the amount of heat transferred, and the optimisation differs; the case of [a perfect finite body in an infinite environment](#), and that of [two finite bodies](#), have been included as exercises. Practical heat engines, refrigerators and heat pumps, optimised for the temperature glide of finite-capacity sources, have been proposed (e.g. the [Lorenz cycle and Kalina cycle](#)).

Exercise 5. Work needed and work lost

Exergy of radiation. Solar radiation

Exergy, as energy or entropy, can be assigned to the system mass, or to the system volume, what is particularly useful when the system has no mass as in the case of [vacuum](#) or electromagnetic radiation. Energy emission from a blackbody at temperature T is σT^4 , which can be thought as heat transferred to a sink at 0 K. But the exergy of that radiation in a reference environment at T_0 is not given by Carnot's efficiency (3.11) because a radiator at temperature T cannot transfer the amount of heat σT^4 to a heat sink at the same temperature T . In order to avoid any entropy generation, an infinite number of intermediate heat sources at temperature T_i , absorbing radiation at T_i+dT_i and emitting radiation at T_i , can be imagined, with an infinite number of Carnot engines extracting the maximum work from the net heat input at each T_i , $d(\sigma T_i^4)=4\sigma T_i^3 dT_i$, with the result:

$$W_{\max} = \int_{T_i=T_0}^{T_i=T} 4\sigma T_i^3 dT \left(1 - \frac{T_0}{T_i}\right) = \sigma(T^4 - T_0^4) - \frac{4}{3}T_0(T^3 - T_0^3) \quad (3.14)$$

and a corresponding maximum efficiency (relative to the radiation energy):

$$\eta_{\max} \equiv \frac{W_{\max}}{\sigma T^4} = 1 - \frac{4}{3} \frac{T_0}{T} + \frac{1}{3} \left(\frac{T_0}{T}\right)^4 \quad (3.15)$$

always smaller than Carnot's efficiency, $1-T_0/T$, although approaching it as $T \rightarrow \infty$; in the most important case of a radiation source at 5800 K (Sun photosphere) with an environment at 288 K (Earth surface), the maximum conversion efficiency from radiation energy to work is $\eta_{\max}=0.934$ (against a Carnot efficiency of 0.950). Thus, for practical purposes, and taking into account uncertainties in solar insolation data and blackbody deviations, one may assimilate the exergy of solar radiation as the exergy of a normal heat source at $T=5800$ K, and apply Carnot's efficiency (or even taking radiation energy as exergy, i.e. with $\eta=1$, to a first approximation).

The fact that exergy and energy values are nearly the same for several kind of energy sources (solar radiation, fuel, kinetic, potential, and nuclear), explains why the exergy concept has not permeated into common social use, in spite that exergy is the sole tool for comparing energy-resource content with a diverse array of energy forms and quality as those mentioned above an specially chemical-concentration and thermal energy sources.

Dynamic efficiency of heat engines

The maximum energy efficiency of a heat engine, the Carnot efficiency, however important it is to put a limit on what is ultimately achievable from the configuration considered (two infinite thermal reservoirs), is of little interest from the practical point of view where 'time is money' (and individual humans have a life span bounded to 10^9 s). Effectively, to run without entropy generation a heat engine (or any other cyclic process) would have to run infinitely slowly, not only because frictional losses tend to be proportional to the square of the speed, but because the speed of the necessary heat transfer involved is proportional to the temperature gradient, and entropy is generated also proportionally to the square of the

temperature gradient. That is a reason why very slow-running (typically at 1 Hz or 2 Hz) marine engines double the efficiency of fast-running car-engines (typically at 50 Hz). A Carnot engine would produce zero power (energy by time). In conclusion, all practical processes must run at a sizeable speed (usually the faster the better).

It is instructive to consider the model called endoreversible heat engine, consisting of a Carnot engine running between two intermediate temperatures T_1 and T_0 , and heat flows from/to the sources proportional to the temperature difference. If one tries to maximise the power produced, one gets that the efficiency still only depends on the sources temperatures, but now in the way:

$$\eta_e \equiv \frac{-\dot{W}}{\dot{Q}_1} \rightarrow \eta_{e_{\max}} = 1 - \sqrt{\frac{T_0}{T_1}} \quad (3.16)$$

Type of problems

Besides housekeeping problems of how to deduce one particular equation from others, the types of problems in this chapter are two-fold, as all exergy applications:

1. Find the maximum obtainable work from a universe not in equilibrium (e.g. Exercise 1). If two non-equilibrium states of the same system are prescribed, the exergy difference is just the difference between the total exergy of each state. Even though this limit is physically unreachable (there will always be some dissipation) and practically undesirable (the process will run too slow), it is a most valuable indication of the order of magnitude that can be expected.
2. Find the minimum work needed to create a non-equilibrium universe from a universe not in equilibrium (e.g. Exercise 2), or what is equivalent by superposition, finding the minimum work needed for a given change in a universe.

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