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Non-Equilibrium and Classical Thermodynamics for Practical Systems: Today Closer Together Than Ever Before

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Abstract

We deal with applications of thermodynamics and availability theory to practical systems where a certain external control is possible in order to achieve improved performance. In particular, results of optimization of endoreversible processes which yield mechanical work are discussed. Equations of dynamics which follow from energy balance and transfer equations are difference constraints for optimizing work. Irreversibilities caused by the energy transport are essential. A model system is developed which incorporates finite heat resistances for an energy conversion process, and may be extended to take into account friction, heat leakage, mixing and other effects decreasing the thermodynamic efficiency. Deviation of efficiencies from their limiting Carnot values are analyzed in terms of the finite heat flux. The variational calculus and optimal control theories are shown to be the basic tools when formulating and solving problems with maximizing work. For a finite-time passage of a resource body between two given temperatures, optimality of an irreversible process manifests itself as a connection between the process duration and an optimal intensity. Extremal performance functions which describe extremal work are found in terms of final states and process duration measured in terms of the number of the heat transfer units. An extended exergy that has an irreversible component and simplifies to the classical thermal exergy in the limit of infinite duration is discussed. With this exergy performance criteria and bounds are defined for real processes occurring in a finite time. Enhanced bounds for the work released from an engine system or added to a heat-pump system are evaluated. A comparison between the optimization in thermodynamics (with exergy) and in economics (with costs) is made. Examples of exergy analysis to seek the best adjustable parameters of solar collectors, separation processes (distillation) and a chemical process with catalyst deactivation are discussed.

Keywords: *Exergy, thermodynamic limits, finite resources, heat transfer.*

1. Introduction

Outlook. Thermodynamics as the science of energy transformations has many faces today. Well-established equilibrium theorems of classical thermodynamics, with solid statistical backgrounds based on partition function and ensemble theory can be contrasted with sometimes nearly heuristic approaches used in some contemporary theories of non-equilibrium thermodynamics. However, an engineer deals usually with nonequilibrium systems in local equilibrium approximation, at which both thermodynamic and transport properties have to be evaluated at various points of the system and possibly for various times. In this case two outlooks, classical and nonequilibrium, have to complement each other. It was not always easy to achieve a consensus between researchers representing these two different outlooks. Recently, however, its seems that the situation has been achieved when the two outlooks converge within the framework of a common thermodynamic theory. This theory uses classical methods and evaluations of thermodynamic and transport properties to describe nonequilibrium passages from one thermodynamic state to another in a finite time. The time here should be understood as a chronological time of an unsteady process or a holdup or contact time in a steady-state process. A description of a finite-time passage is accomplished formally by assuming a finite rate and an irreversible behavior from the very beginning; then the equations describing the system are typically certain evolution equations obtained by combination of evolution equations obtained by combination of balance and transport laws within usually a network-like description. Entropy generation is included as an (finite) irreversibility indicator. The simultaneous analysis of work-production capabilities and losses related to the entropy generation, frequently accompanies an analysis of the evolution equations describing the system. Laws of classical thermodynamics and classical thermodynamic limits are recovered at the quasistatic limit when the rates and entropy generation tend to vanish.

Systems. The systems usually considered within the so-generalized thermodynamics are those with conversion, transfer and accumulation of thermal and chemical energy. They include thermal and combustion engines, solar engines, solar cells, heat exchangers, separation units (e.g. distillation), chemical reactors, fuel cells, energy recovery units, storage systems, chemical reactors, and chemical plants. These are important practical systems most of which can yield mechanical or electrical energy or valuable products.

Models and optimization. Mathematical models are constructed in order to predict the system behavior, find better pathways, reduce possible losses and evaluate the optimal performance of the system in question. For optimization purposes system models contain: i) optimization criterion as a measure of efficiency of our decisions, ii) control (decision) variables, iii) state variables as minimum necessary variables capable of describing the system and iiii) some uncontrolled (fixed) parameters. These models incorporate diverse process characteristics such as finite heat conductances, semiconductor bandgaps, diffusion and beam transfer channels, friction, heat loss, chemical resistances, and other factors which are essential in real energy conversion and transmission processes. The optimization criteria include important physiochemical quantities such as the produced mechanical work, chemical yield, or they are constructed on economic grounds, such as the production costs. It is essential that when the finite time or finite-size constraints are imposed, these criteria take into account a finite investment (even if not explicitly specified). Efficiency is very seldom a performance criterion in an optimization; rather it is one of the system variables which characterize its performance. The second-law based efficiencies are more fundamental than those based on the first law, although an engineer deals usually with the first-law efficiencies.

Efficiency. Consider, for example, the first-law efficiency of a thermal engine. It is defined as $\eta^I = w/q$ i.e. the ratio of the power output to the driving heat input. In other words η^I is the ratio of work produced to the 'valuable' or costly heat. This definition, however, does not attribute any value to the heat; it is obvious that sources releasing the heat q at a higher temperature T will be more valuable (and hence more costly) than those which transfer the same q at lower T's. This flaw in the definition bears the question: Perhaps an efficiency should be defined in terms of values of the quantities involved rather than the quantities themselves? In thermodynamics, the answer is the second-law efficiency in which the thermodynamic work equivalent of heat $q(1-T^e/T)$ is used instead of the heat itself. The second law efficiency $\eta^{II} = w[q(1-T^e/T)]^{-1}$, where T^e is the temperature of the low temperature reservoir or the environment, hence the superscript e. But the superscript also means 'equilibrium' because the temperature T^e is the final temperature of the finite resource in equilibrium with the infinite environment and thus the second law efficiency: $\eta^{II} = \eta^I/\eta_C$ where η_C is the Carnot efficiency. This is a relative efficiency. Sometimes efficiencies of this sort are defined as ratios η^{II}/η, where the subscript max corresponds to an upper limit efficiency which is not necessarily the Carnot efficiency. They are all called the second law efficiencies. In examples which follow we will use for simplicity the bare symbol η for the first-law efficiency. Only in cases when two efficiencies appear simultaneously will their distinguishing be pointed out by indices.

2. Exergy as a Generalized Mechanical Energy

The maximum work a system can deliver upon relaxation to equilibrium with its environment, a reservoir of infinite size with intensities T^e (temperature), P^e (pressure), and μ_i^e (chemical potential of species i), can be described by the availability function $\mathcal{A}$ (Keenan 1941; Gibbs 1993) or the exergy function E_X (Rant 1956; Szargut and Petela 1965; Vogler and Weissman 1988). The techniques of analysis related to $\mathcal{A}$ or E_X are respectively known as availability analysis or exergy analysis; they are both second law analyses. In the availability $\mathcal{A}$ the condition of chemical equilibrium in the reference state is not used. This function deals with the so-called restricted equilibrium and it is not readily applicable to chemical systems (Kotas 1980). Moreover, since chemical potential terms are absent in $\mathcal{A}$, only the exergy E_X can take the diffusion of matter into the system's environment into account. The distinction between $\mathcal{A}$ and E_X in the literature is often ambiguous. The simplest formula for the exergy E_X adds the term $-\mu_i^e(n_i - n_i^e)$ to $\mathcal{A}$.

$$E_x = \frac{1}{2}v^2 + u - u^e - T^e(s - s^e) + P^e(v - v^e) - \sum_i \mu_i^e (n_i - n_{ie}^e) \tag{1}$$

where *u* is the specific internal energy, s is the specific entropy, *v* is the specific volume, and n_i is the number of moles of species i per unit mass. This is valid for the substances which are common constituents of the environment. In the general case the exergy E_X uses a system of environmental reference substances with respect to which, in their environmental states, standard exergies of commonly used chemical elements can be evaluated. Such a reference state is the state of unrestricted thermodynamic equilibrium with the environment. For the principles of computation of the exergy E_X for an arbitrary chemical system based on Szargut´s theory of the reference states (Szargut and Petela 1965) see Kotas's two recent reviews and the book (Kotas 1980, 1985, 1986). The usefulness of the exergy cannot be underestimated. The present work shows merely several examples the common feature of which is that they are dealing with processes of the energy conversion and transport. The energy storage problems are not considered. In this regard it should be realized that the energy storage is, in fact, the storage of the exergy, also energy savings are related to savings of the exergy (Sieniutycz 1991).

Recently an idea was proposed to derive a generalized exergy on kinetic grounds rather than from classical analysis of a limiting quasistatic process (Sieniutycz 1997a, b). Those analyses include a transfer model of heat conduction through boundary layers in which dissipative phenomena occur, thus allowing some inevitable lossy mechanisms. Therein the work produced or the work consumed are described in terms of functionals which depend on the thermodynamic coordinates and their derivatives in time or space. These functionals incorporate the entropy production associated with irreducible irreversibilities as those occurring in the boundary layers. The consequence of the irreversibility is that the finite-time work produced during the relaxation of the system of a body and the bath to the equilibrium (the so-called engine mode) is not equal to the finite-time work consumed during the departure of the system form the equilibrium (the so-called heat-pump mode). This idea is illustrated in *Figure 1*, which in particular contains an explanation why the second work is larger than the first. The related kinetic model of the process is developed in the next section.

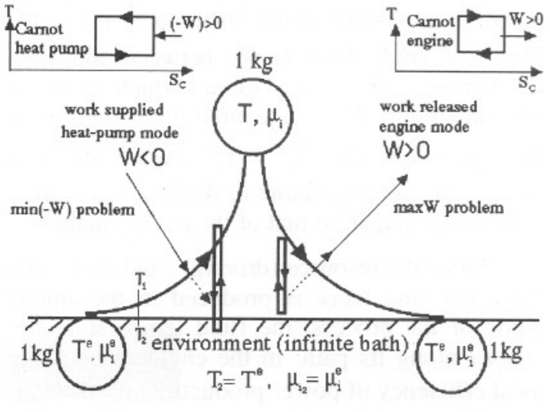

Figure 1. Two works considered in the extended exergy analysis. The work produced (engine mode) characterizes a thermodynamic profit obtained from the process of relaxation of a body to the equilibrium with the bath. The work supplied (heat-pump mode) characterizes a thermodynamic cost necessary to create the nonequilibrium system. In a reversible case the magnitudes of both works are equal. In our example we consider changes of temperatures only.

3. Differential Equations for Endo-reversible Thermal Nachines and Exergy Functionals

Figure 2 depicts the differential part of an engine with dissipative processes, which is, in fact, the differential engine of Novikov, Curzon and Ahlborn (Novikov 1958; Curzon and Ahlborn 1975; de Vos 1992). The differential conductances $d\gamma_1$ and $d\gamma_2$ are present between the working fluid of the Carnot engine and each of two fluids (of finite thermal conductivity). These dissipative elements within the system can be expressed as $d\gamma_1 = \alpha_1 dA_1$ and $d\gamma_2 = \alpha_2 dA_2$, where α_1 and α_2 are the heat transfer coefficients and dA_1 and dA_2 are the corresponding upper and lower exchange surface areas. The corresponding differential increase in the length coordinate x is dx. The conductances link the heat sources with the working fluid of the engine at high and low temperatures. We designate by T_1' and T_2' the upper and lower temperatures of the working fluid which circulates in the differential Carnot engine. A hot fluid (fluid 1) supplies heat to the system at a high temperature T_1; this heat reaches the engine fluid at T_1'. The supplied heat rate, dQ_1, thus depends on the temperatures T_1 and T_1'. In the simplest case considered here, i.e. Newtonian heat exchange, the heat rate dQ_1 is proportional to the temperature difference $T_1 - T_1'$. In the low-temperature part of the Carnot subsystem heat is transferred to an environment (or fluid 2) through another conductance, $d\gamma_2$. The flux of the released heat depends on the temperatures T_2

and T_2' and in the Newtonian case is proportional to the temperature difference $T_2' - T_2$. This low-grade heat flows between the low-temperature part of the engine, which works at the temperature T_2', to the environmental fluid at the low temperature $T_2 = T^e$. Again, this is a case when the temperature of the heat reservoir is constant and equal to that of the environment.

Since the resource (driving) fluid flows at a finite rate and work is produced in the engine mode of the process, the fluid temperature decreases along its path. In the engine mode, any local efficiency of power production, $\eta = dW/dQ_1$, is smaller than the efficiency η_c of a Carnot cycle operating between the temperatures T_1 and T_2. In this mode, which is, in fact, an active (work-producing) heat exchange between two fluids, one may consider the problem of the maximum work delivered in a finite amount of time. For the inverse process in which work is added, the first fluid is heated and the system works as a heat pump. For this case the associated optimization problem is that of finding the minimum work supplied in a finite amount of time.

We will show below that the flux formulae deal with the infinitesimal conductance of the *overall* heat transfer, $d\gamma$. Such quantity is defined through the partial conductances $d\gamma_1$ and $d\gamma_2$ in the standard way. As schematized in Fig. 2 and shown in Eq. (2), this overall conductance can be expressed as the product of an overall transfer coefficient, α', and the differential area dA,

$$d\gamma \equiv \frac{d\gamma_1 d\gamma_2}{d\gamma_1 + d\gamma_2} = \frac{\alpha_1 k dA \alpha_2 (1-k) dA}{\alpha_1 k dA + \alpha_2 (1-k) dA} = \frac{\alpha_1' \alpha_2'}{\alpha_1' + \alpha_2'} dA \equiv \alpha' dA \tag{2}$$

In Eq. (2), $\alpha_{1'} = k\,\alpha_{1'}$, where k is a constant fraction of the upper heat transfer area A_1 in terms of the total area $A = A_1 + A_2$. When-ever A is proportional to the length coordinate x, the above result is pertinent to defining a non-dimensional time for the process. We shall derive some formulae describing the power delivered by this engine. We assume the steady work of the engine. The entropy balance for the reversible part of our differential process

$$\frac{dQ_1}{T_1'} = \frac{dQ_2}{T_2'} \tag{3}$$

and the energy balance in the efficiency form, $dQ_2 = dQ_1(1-\eta)$, yield the stage efficiency given by the Carnot formula

$$\eta = 1 - \frac{T_2'}{T_1'} \tag{4}$$

However η is lower than the Carnot efficiency referred to bulk temperatures of both fluids, T_1 and T_2, as it applies to the intermediate temperatures T_1' and T_2'.

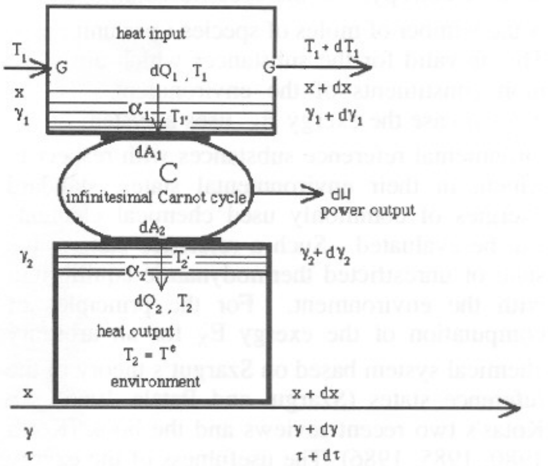

Figure 2 Differential Novikov-Curzon-Ahlborn engine (differential NCA engine).

The temperatures T_1' and T_2' are unknown, hence they should be expressed in terms of the boundary temperatures T_1 and T_2 and a single decision variable, which may be in principle an arbitrary process variable. Here we use the entropy flux entering the Carnot engine or leaving this engine as a suitable decision variable. Its usefulness results from the entropy conservation throughout the Carnot engine, which causes the single entropy flux $d\vartheta = dQ_1/T_1 = dQ_2/T_2$. This quantity is used in the analysis which follows.

One begins by substituting for dQ_1 and dQ_2 their transport expressions. Here we assume the simple Newtonian heat transfer. The reversible entropy balance is then

$$\frac{d\gamma_1 (T_1 - T_1')}{T_1'} = \frac{d\gamma_2 (T_2' - T_2)}{T_2'} \tag{5}$$

The differentials $d\gamma_1$ and $d\gamma_2$ correspond to the infinitesimal length dx, as shown in Fig. 2. In terms of the common differential entropy flux $d\vartheta$, equal to each side of the above equation, the temperatures T_1' and T_2' are

$$T_1' = \frac{T_1}{1 + \dfrac{d\vartheta}{d\gamma_1}} \tag{6}$$

and

$$T_2' = \frac{T_2}{1-\frac{d\vartheta}{d\gamma_2}} \qquad (7)$$

Hence the corresponding heat fluxes are

$$\begin{aligned} dQ_1 &= d\gamma_1 (T_1 - T_1') \\ &= d\gamma_1 \Big(T_1 - \frac{T_1}{1+\frac{d\vartheta}{d\gamma_1}}\Big) = \frac{T_1 d\vartheta}{1+\frac{d\vartheta}{d\gamma_1}} \end{aligned} \qquad (8)$$

and

$$\begin{aligned} dQ_2 &= d\gamma_2 (T_2' - T_2) \\ &= d\gamma_2 \Big(\frac{T_2}{1-\frac{d\vartheta}{d\gamma_2}} - T_2\Big) = \frac{T_2 d\vartheta}{1-\frac{d\vartheta}{d\gamma_2}} \end{aligned} \qquad (9)$$

These fluxes vanish for $d\vartheta = 0$, the situation which corresponds with $\eta = 1-T_2/T_1$, the Carnot efficiency. The work flux (power) at the differential stage equals the difference of the fluxes dQ_1 and dQ_2, that is

$$\begin{aligned} dW &= dQ_1 - dQ_2 \\ &= \Big(\frac{T_1}{1+\frac{d\vartheta}{d\gamma_1}} - \frac{T_2}{1-\frac{d\vartheta}{d\gamma_2}}\Big) d\vartheta \\ &= \frac{T_1}{\frac{1}{d\vartheta}+\frac{1}{d\gamma_1}} - \frac{T_2}{\frac{1}{d\vartheta}+\frac{1}{d\gamma_2}} \end{aligned} \qquad (10)$$

The associated first-law efficiency of the stage is

$$\begin{aligned} \eta &= \frac{dQ_1 - dQ_2}{dQ_1} = 1 - \left(\frac{T_2}{T_1}\right) \frac{\left(1+\frac{d\vartheta}{d\gamma_1}\right)}{\left(1-\frac{d\vartheta}{d\gamma_2}\right)} \qquad (11) \\ &= 1 - \left(\frac{T_2}{T_1}\right) \frac{\frac{1}{d\vartheta}+\frac{1}{d\gamma_1}}{\frac{1}{d\vartheta}-\frac{1}{d\gamma_2}} \end{aligned}$$

For an infinitely slow process the flux $d\vartheta$ vanishes, and efficiency approaches $\eta = 1-T_2/T_1 = \eta_c$, the Carnot efficiency. The flow of the circulating fluid G_C vanishes in this limiting case as well, and the residence time of this fluid in the Carnot loop, $\zeta = G_0/G_C$ (G_0 is the mass of the circulating fluid in the system) tends to infinity. From Eq. (20) the power dW at the stage is then equal to zero. On the other hand whenever $T_2' = T_1'$, the situation corresponding with the equality of expressions given by Eqs. (16) and (17), i.e.,

$$T_1 \Big(1 - \frac{d\vartheta}{d\gamma_2}\Big) = T_2 \Big(1 + \frac{d\vartheta}{d\gamma_1}\Big) \qquad (12)$$

the efficiency η equals zero (no engine) and the associated entropy flux is

$$(d\vartheta)_{\eta=0} = \frac{T_1 - T_2}{\frac{T_1}{d\gamma_2} + \frac{T_2}{d\gamma_1}} \qquad (13)$$

This point, at which $d\vartheta$ is finite, corresponds to the pure heat conduction, without any work production. At this point $\eta = 0$ and again $dW = 0$. Substituting Eq. (13) into Eq. (8) yields the corresponding heat fluxes, dQ_1 and dQ_2 (which are equal in this case)

$$\begin{aligned} (dQ_1)_{\eta=0} &= \frac{T_1 d\vartheta}{1+\frac{d\vartheta}{d\gamma_1}} = \Big(\frac{d\gamma_1 d\gamma_2}{d\gamma_1 + d\gamma_2}\Big)(T_1 - T_2) \\ &\equiv d\gamma (T_1 - T_2) = (dQ_2)_{\eta=0} \end{aligned} \qquad (14)$$

The above expression contains the overall conductance of heat transfer, Eq. (2).

With the entropy flux as the control variable, the maximum power condition at the stage is

$$\begin{aligned} \frac{dW}{d\vartheta} = &\frac{T_1}{(d\vartheta)^2 \left(\frac{1}{d\vartheta} - \frac{1}{d\gamma_1}\right)^2} \\ &- \frac{T_2}{(d\vartheta)^2 \left(\frac{1}{d\vartheta} - \frac{1}{d\gamma_2}\right)^2} \end{aligned} \qquad (15)$$

Thus the common entropy flux which maximizes the power, satisfies the equation

$$\frac{1}{d\vartheta} - \frac{1}{d\gamma_2} = \sqrt{\frac{T_2}{T_1}} \Big(\frac{1}{d\vartheta} + \frac{1}{d\gamma_1}\Big) \qquad (16)$$

or an equivalent formula

$$\frac{1}{d\vartheta}\Big(1 - \sqrt{\frac{T_2}{T_1}}\Big) = \Big(\frac{1}{d\gamma_2} + \frac{1}{d\gamma_1}\sqrt{\frac{T_2}{T_1}}\Big) \qquad (17)$$

Whence, the engine entropy flux at the maximum power condition (superscript 0) equals

$$d\vartheta^0 = \frac{1 - \sqrt{\frac{T_2}{T_1}}}{\frac{1}{d\gamma_2} + \frac{1}{d\gamma_1}\sqrt{\frac{T_2}{T_1}}} \qquad (18)$$

The heat flux at the maximum power point $(dQ_1)^0 \equiv T_1\, d\vartheta^0$ is obtained from Eq. (8) as

$$
\begin{aligned}
(dQ_1)^0 &= \frac{T_1}{(d\gamma_1)^{-1} + (d\vartheta^0)^{-1}} \\
&= \frac{T_1}{\dfrac{1}{d\gamma_1} + \dfrac{\dfrac{1}{d\gamma_2} + \dfrac{1}{d\gamma_1}\sqrt{T_2/T_1}}{1-\sqrt{T_2/T_1}}} \qquad (19)\\
&= \frac{T_1(1-\sqrt{T_2/T_1})}{\dfrac{1}{d\gamma_2} + \dfrac{1}{d\gamma_1}}
\end{aligned}
$$

which yields finally

$$
\begin{aligned}
(dQ_1)^0 &= d\gamma T_1 (1 - \sqrt{\frac{T_2}{T_1}}) \qquad (20)\\
&= d\gamma (T_1 - \sqrt{T_1 T_2})
\end{aligned}
$$

The corresponding extremum power, Eq. (20) for $d\vartheta = d\vartheta^0$, equals after simplifications

$$
\begin{aligned}
dW^0 &= dT_1 \left(1 - \sqrt{\frac{T_2}{T_1}}\right) - d\gamma T_2 \left(\frac{1}{\sqrt{T_2/T_1}} - 1\right) \\
&= d\gamma \sqrt{T_1} (\sqrt{T_1} - \sqrt{T_2}) \qquad (21)\\
&\quad - d\gamma \sqrt{T_2} (\sqrt{T_1} - \sqrt{T_2}) \\
&= d\gamma (\sqrt{T_1} - \sqrt{T_2})^2
\end{aligned}
$$

which is consistent with the single-stage result known from a standard treatment of NCA process (de Vos 1992). The above results, in particular Eqs. (30) and (31), lead one back to the well-known formula for the efficiency at maximum power

$$
\begin{aligned}
\eta^0 &= \frac{dW}{(dQ_1)^0} = \frac{d\gamma(\sqrt{T_1} - \sqrt{T_2})^2}{d\gamma(T_1 - \sqrt{T_1 T_2})} \qquad (22)\\
&= \frac{\sqrt{T_1} - \sqrt{T_2}}{\sqrt{T_1}} = 1 - \sqrt{\frac{T_2}{T_1}}
\end{aligned}
$$

which is called the NCA efficiency. The second derivative of W is negative at the extremal point, hence the extremum is the maximum.

One can also express fluxes of heat and power in terms of the efficiency, η. For this purpose when the function

$$d\vartheta = f(\eta, d\gamma_1, d\gamma_2, T_1, T_2)$$

is evaluated from Eq. (11) and the result substituted into Eqs. (8) and (9). long but straightforward calculations produces

$$
\begin{aligned}
dQ_1 &\equiv d\gamma_1 (T_1 - T_1') \\
&= d\gamma \left[T_1 - \frac{1}{(1-\eta)} T_2 \right] \qquad (23)
\end{aligned}
$$

and

$$
\begin{aligned}
dQ_2 &\equiv d\gamma_2 (T_2' - T_2) \\
&= d\gamma [(1-\eta) T_1 - T_2] \qquad (24)
\end{aligned}
$$

They vanish whenever for $\eta = 1 - T_2/T_1 = \eta_C$ whenever the thermal conductivities are finite. Note that the heat flux formulae deal with the infinitesimal conductance of the *overall* heat transfer, $d\gamma$.

It follows from Eq. (23) that the efficiency in terms of the driving heat flux can be written as

$$
\begin{aligned}
\eta &= 1 - \frac{T_2}{T_1 - dQ_1/d\gamma} \qquad (25)\\
&= 1 - \frac{T_2}{T_1 + dT_1/d\tau}
\end{aligned}
$$

where use was made of the formula $dQ_1 = - G\, c\, dT_1$ and the non-dimensional holdup time τ was introduced defined by the differential expression

$$d\tau \equiv \frac{d\gamma}{Gc} \qquad (26)$$

This is, in fact, a modified definition of the well-known engineering quantity called the number of heat transfer units. Our efficiency formula (25) shows that an effective temperature of the upper source $T' \equiv T_1 + dT_1/d\tau$ plays a role in the efficiency deviations from the Carnot value. In the engine mode T' is lower than T_1 due to the finite heat flux. In effect, the efficiency of the engine mode, where $dT_1 < 0$ because the work is produced, decreases with $dT_1/d\tau$. We can now simplify designations, by using the bare symbol T for the temperature of the first fluid (the resource fluid), and use the symbol T^e for the constant temperature of the second fluid (bath fluid). For example, the efficiency expression (25) in new designations will take the form

$$\eta = 1 - \frac{T^e}{T + \dot{T}} \qquad (27)$$

The corresponding expression for the differential power output per unit flow (the quantity which has the work units) exhibits the deviation from the reversible Carnot theory, caused by the presence of the dissipative elements:

$$dW \equiv \frac{dW}{G} = -c\left(1-\frac{T^e}{T+dT/d\tau}\right)dT$$
$$= -c\left(1-\frac{T^e}{T+\dot{T}}\right)\dot{T}\,d\tau \tag{28}$$

Carnot efficiency is achieved when the effect of the overall resistance $d\gamma^-$ is negligible or the derivative $dT/d\tau$ is very small. The heat-efficiency relationships such as Eq. (23) are called equations of thermal characteristics. Equation (23) states that the efficiency of any NCA process decreases when the intensity of the driving heat flux grows. While the properties of the infinitesimal steps of the process are those known for NCA engines of finite sizes, these properties should be here understood locally, i.e. for each value of the length coordinate x or each value of the conductance coordinate γ. Each infinitesimal step is defined by two basic points: i) the so called *short-circuit point* where $\eta(\gamma) = 0$ and classical heat exchange takes place with $dQ_1 = d\gamma\, \Delta T(\gamma)$, and ii) the so-called *open-circuit point* where $\eta(\gamma) = \eta_c(\gamma)$ and $dQ_1 = 0$ whenever the transport coefficients are finite. At each of these two points the power type derivative $dW(\gamma)/d\gamma = 0$; the power may be produced only in the range of efficiencies between 0 and η_c.

Analogously an unsteady process may be considered between a body which has the temperature T and the bath, T^e. The final formulae are identical but c must in this case, be interpreted as the specific heat under constant volume rather than constant pressure. The differential of the nondimensional time τ is, in this case, defined by equation

$$d\tau \equiv \frac{\alpha' A}{c_v M}dt \tag{29}$$

This definition contains: an overall heat transfer coefficient, α'; an overall area of heat transfer, A; the mass of the resource, $\mathcal{M}$, and the usual chronological time, t. This is related, again, to a modified definition of the number of heat transfer units.

Consider now a finite time transition of a resource between two arbitrary temperatures, T_A and T_B in a process of finite time interaction of this resource with bath. Assume a restricted total duration $\mathcal{T}$; this also means that an average rate of the process must be finite. It follows from Eq. (28) that for processes with pure heat transfer in which cooling of the resource occurs in a sequence of infinitesimal engines (process from A to B; T'< T and $T_B < T_A$; minus subscript at $\mathbf{I}$), the functional of the extremal work $\mathbf{I}$ can be written in the form

$$\mathbf{I}_-(T_A, T_B, T) = \max_{\dot{T}}\left\{-\int_{T_A}^{T_B} c\left(1-\frac{T^e}{T+\dot{T}}\right)\dot{T}d\tau\right\}$$
$$= c(T_A - T_B) - cT^e \ln\frac{T_A}{T_B} \tag{30}$$
$$-T^e \min_{\dot{T}} \int_{\tau_A}^{\tau_B} c\frac{\dot{T}^2}{T(T+\dot{T})}d\tau$$

where the minimized term in the last line describes the entropy production (Sieniutycz 1997a). T is the instantaneous temperature of the resource and $\dot{T}$ is the rate of change of this temperature with respect to the nondimensional time, τ. The minus subscript at symbol $\mathbf{I}$ of the work functional means that the entropy production is subtracted in this case.

For the fluid heating in a heat-pump system (process from B to A; T' > T and $T_B < T_A$; plus subscript at $\mathbf{I}$) an analogous functional holds

$$\mathbf{I}_-(T_A, T_B, T) = \max_{\dot{T}}\left\{\int_{T_B}^{T_A} c\left(1-\frac{T^e}{T+\dot{T}}\right)\dot{T}d\tau\right\}$$
$$= c(T_A - T_B) - cT^e \ln\frac{T_A}{T_B} \tag{31}$$
$$+T^e \min_{\dot{T}} \int_{\tau_B}^{\tau_A} c\frac{\dot{T}^2}{T(T+\dot{T})}d\tau$$

When $T_B = T^e$, both formulae above define a nonclassical finite-time exergy. They show that both work functions are equal, i.e., $\mathbf{I}_- = \mathbf{I}_+$ only in reversible or quasistatic case (T' = T). This equality is the consequence of potential properties of the classical exergy in the thermodynamic state space. Thus, in the reversible case each function represents the same change of the classical exergy.

It is easy to see that classical or 'thermostatic' exergy can be obtained from approaches of this sort directly: by integration of the work integral under the assumption that the process efficiency is that of Carnot

$$E_x = \int_T^{T^e} \eta c dQ$$
$$= -\int_T^{T^e}(1-\frac{T^e}{T})c(T)dT \tag{32}$$

The integration limits used are for the 'engine mode' of the system, i.e. the case when the system produces work. For the heat-pump mode, when the process is from T^e to T, the integration limits are inverted and so is the sign before the integral. One obtains a mode-independent result

$$E_x = c(T - T^e) - cT^e \ln(\frac{T}{T^e}) = A_g \quad (33)$$

which is valid when the specific heat is constant. This is a special case of a more general formula

$$E_x = h - h^e - T^e(s - s^e) \quad (34)$$

which takes into account the temperature dependence of the specific heat. Equation (34) refers to the case of a steady state system, in which case the notion of the exergy of a substance pertains to its exergy at flow, that is, we are looking for a special quantity which is defined as the ratio of the exergy flux (associated with the flow of this substance) to the mass flux of this substance. Equation (34) contains, therefore, the difference of specific enthalpies h instead of the internal energy differences. Correspondingly, Eq. (33) contains then the specific heat at constant pressure instead of at constant volume. However, in the case of the system of the body and bath, where the evolution is in the chronological time, the use of the specific heat at constant volume, c_V, is appropriate. To take into account the two possibilities (a time evolution or a steady-state process) we have used the symbol c without index; this made it possible to assign the index only now to describe the changes of internal energy *or* enthalpy, depending on a concrete situation.

An obvious remark is that in order to generalize exergy to finite durations (finite rates) one has to go to transport properties. In Eq. (2) we have defined the infinitesimal conductance of the *overall* heat transfer, $d\gamma$. Such a quantity is defined through the partial conductances $d\gamma_1$ and $d\gamma_2$ in the standard way. Equations (26) and (29) contain these transport properties explicitly in the definition of the number of the transfer units, τ. One should notice a connection between this quantity and the Stanton number which can be interpreted as the scale for the non-dimensional conductance (Spalding 1963; Bird *et al.* 1966). This should help evaluate all necessary quantities in a concrete situation.

4. Generalization of Carnot formula and exergy to finite time (finite size) processess

When the energy production process evolves, the energy of the resource decreases. The rate of the temperature decrease associated with the Carnot efficiencies in Eq. (32) for the classical exergy is zero, as only then can these efficiencies be assured in systems with finite-resistance characteristics. While remaining Carnot, these efficiencies decrease with decreasing T which ultimately approaches the value T^e at the state of the equilibrium with the environment, the consequence of the finiteness of the resource. At equilibrium, the work production terminates. The Carnot formula can be writtern to describe the quasistatic changes of efficiencies as follows

$$(1 - \eta)T = T^e \quad (35)$$

This is still the Carnot equation which says that when a finite resource interacts with the bath, the product of the resource temperature T and (1 - η) remains constant, this constant being, of course, the temperature of the bath. Now one can ask an important question: How does that simple rule change when the evolution of the resource temperature T in time τ occurs with finite rates which are such that the final cumulative production of work is maximum at a final time instant τ^f ? This question implies, of course, a passage from T to T^e in a finite time, i.e. with a finite mean rate, thus allowing an irreversible process producing the entropy. Below we will show that the simple rule discussed above still holds, although the constant is no longer T^e.

One can derive that for the Fourier model of heat exchange the temperature evolution of the resource in our active (work producing) process is described by the formula

$$\frac{d \ln T}{d\tau} = \frac{\eta - \eta_c(T)}{1 - \eta} = \xi \quad (36)$$

which is a transformed form of an earlier result (Sieniutycz 1997a). The quantity ξ is an intensity parameter which characterizes the change of the logarithm of the resource temperature in time τ. From this we conclude that $\eta > \eta_C$ refers to heating processes of the resource fluid, whereas $\eta < \eta_C$ refers to cooling processes of the resource fluid. When $T > T^e$ the cooling occurs in a sequence of the thermal engines; whereas, the heating occurs in a sequence of the heat pumps. Equation (36) holds for an arbitrary control η. However, if the control is optimal, the logarithmic rate ξ is constant in time (Sieniutycz 1997a), and the corresponding rule for the efficiency change in time is described by an equation

$$\eta = \frac{\xi + \eta_c(T)}{\xi + 1} = 1 - \frac{T^e}{T(\xi + 1)} \quad (37)$$

which follows from Eq. (36). In this (optimal) case the constant numerical value of ξ can be evaluated from the boundary conditions which specify the end temperatures and duration of the process. The integration of the temperature logarithm in Eq. (36) yields immediately,

$$\xi = \frac{\ln\left(T^f / T^i\right)}{\tau^f - \tau^i} \tag{38}$$

With this equation a useful form of the efficiency equation (37) can be obtained in the form of generalized Eq. (35).

$$(1-\eta)T = \frac{T^e}{1+(\tau^f - \tau^i)^{-1}\ln(T^f / T^i)} \tag{39}$$

This again shows the constancy of the product of (1- η) and T, but in reference to a finite-rate process which produces a minimum inevitable amount of the entropy, S_σ. The product $-T^e S_\sigma$ is given in Eq. (40) below. Equation (39) states that the finite-rate efficiencies of the resource cooling processes (associated with work production when $T > T^e$) are lower than η_C at the same T, whereas those of heating processes (associated with work consumption when $T > T^e$) are greater than η_C at the same T. While the qualitative statement can be obtained in classical thermodynamics, the derivation of the quantitative form given by Eq. (39) required the analysis based on combination of the energy balance and kinetics in Section 3. The transport properties are contained in the definition of the number of the heat transfer units, represented by the nondimensional time, τ. For example, Eq. (29) shows that one can accomplish infinite nondimensional durations in the sense of an infinite number of the heat transfer units $(\tau^f - \tau^i)$ even for finite contact times t, whenever the products of transfer areas and the heat transfer coefficients are very large in comparison with the total heat capacity. When these conditions are not satisfied one is dealing with the finite-duration passages in which the process efficiencies are different than those of Carnot. It may be seen that one can identify the right-hand side of Eq. (39) with an effective temperature of the environment. The value of this effective temperature is less than T^e for heating processes (heat-pump modes) and greater than T^e for cooling processes (engine modes). In both cases the effect of the finite rates causes adverse efficiencies.

Equation (36) with a finite constant ξ is, in fact, the relationship which one uses when integrating Eqs. (30) and (31) along an extremal to get Eq. (40). The specific work function follows for every process mode as

$$\begin{aligned} \mathbf{I}(T^i, T^f, \tau^i, \tau^f) \\ &= c(T^i - T^f) - cT^e \ln\frac{T^i}{T^f} + cT^e\left(\frac{\xi}{1+\xi}\right)\ln\frac{T^i}{T^f} \\ &= c(T^i - T^f) - cT^e \ln\frac{T^i}{T^f} - cT^e \frac{\left[\ln(T^i / T^f)\right]^2}{\tau^f - \tau^i - \ln(T^i / T^f)} \end{aligned} \tag{40}$$

The particular extremal work which describes the (generalized) exergy contains the environment temperature as one of the boundary states. The exergy is the maximal work $W_{max} = I(T^i, \tau^i, T^f, \tau^f)$ with $T^i = T$ and $T^f = T^e$ for the engine mode, and the negative minimal work $(-W)_{min} = - I(T^i, \tau^i, T^f, \tau^f)$ with $T^i = T^e$ and $T^f = T$ for the heat-pump mode. For the vanishing intensity ξ the classical thermal exergy is recovered. A general formula for the dissipative thermal exergy is obtained as

$$\begin{aligned} E_x(T, T^e, \tau^f) &= c(T - T^e) - cT^e \ln\frac{T}{T^e} \\ &\pm cT^e \frac{(\tau^f)^{-1}\left[\ln(T / T^e)\right]^2}{1 + \pm(\tau^f)^{-1}\ln(T / T^e)} \\ &= E_x(T, T^e, \infty) \pm T^e S_\sigma \end{aligned} \tag{41}$$

where $E_x(T, T^e, \infty)$ is the classical exergy and we have assumed without any losses in generality that $\tau^i = 0$. Equation (41) simplifies to the classical exergy at the limit of infinite time τ^f. In the above equations the upper sign refers to the heat-pump mode and the lower sign to the engine mode. The general thermodynamic result in the second line of equation (41) is, of course, in complete agreement with the Gouy-Stodola law (Szargut and Petela 1965, Kotas 1985) or with its particular form given by Tollman and Fine (1948). These formulations of the second law link losses of the extremal work, finiteness of the process duration, and the associated minimum entropy generation, S_σ. However, these classical formulations do not provide neither information about analytical forms of the nonclassical contributions to the exergy (and the related quantity S_σ) nor about the time evolution of the system. For that purpose a dynamical model of the evolution and the solution of the related Hamilton-Jacobi equation are necessary, as shown in several recent papers (Sieniutycz 1997a, b). Thus the methods of analytical dynamics and optimal control theory become ingredients of nonequilibrium thermodynamics whenever post-thermostatic (rate penalty) terms are sought for generalized thermodynamic potentials, i.e., when thermodynamic potentials are generalized to finite time durations.

5. Averaged Efficiency for an Energy Production Process With a Finite Resource

The problem of local efficiency changes arises due to the finiteness of amount of the resource. When an averaged first-law efficiency is evaluated from Eq. (40), for the whole engine process between a nonequlibrium state T and the equilibrium state T^e, the reversible result is $\eta_{av} = (1 - T^e/T_{av})$ where T_{av} is the logarithmic mean of the temperatures T and T^e. The quantity η_{av} is smaller than the initial efficiency of the reversible engine mode, $\eta = (1 - T^e/T)$, and it is also smaller than the final efficiency of the heat-pump mode. Therefore, in engine mode, the averaged efficiency deviates adversely from the Carnot efficiency $(1 - T^e/T)$, the effect caused by the finiteness of the resource. The finiteness of the resource is, however, a reversible effect, as it becomes an advantage in the case of the heat-pump mode, where a decreased effort is necessary to achieve the final state. Whenever dissipation occurs, the irreversible duration-related term in the second line of equation (36) enhances the decrease of the averaged efficiency in the engine mode, which decreases below the reversible reference value, described above. Otherwise, the irreversible term increases the averaged efficiency of the heat-pump mode above its reversible value, a detrimental effect again, caused by the dissipation. These conclusions have, of course, a practical value. An example is calculation of an average efficiency and the efficiency formula at the maximum power point for an engine system of a nuclear power plant which has its thermal characteristics similar to those of Novikov-Curzon-Ahlborn system (De Vos 1992; Sieniutycz 1997b). However, we should not expect the coincidence of the maximum-power efficiencies with efficiencies of industrial processes. Economic reasons, associated with trade-off between the investment and fuel costs, determine that the actual efficiency η_{exp} is always smaller than the Carnot efficiency and larger than the maximum-work efficiency. The associated thermoeconomic argument is adduced below.

6. Constraint on Process Duration as a Finite Investment

Any reasonable industrial enterprise has the imposed constraint that investment money be used in finite amounts. A finite investment requires that the system size and/or the residence time of the participating species remain finite. Consequently, finite investments require only finite time to accomplish changes of state in a real process. This characteristic is, however, not taken into account in classical thermostatics in which the reversible changes between any two different states are associated with vanishing rates and hence infinite durations (i.e. infinite investment). However, the finite-time thermodynamics can manage situations in which the investment is finite.

As an example, let us consider work-producing systems, in particular thermal engines. For reasons of economics associated with the tradeoff between investment and fuel costs, actual efficiencies for these engines are smaller than Carnot efficiency. To explain why, let us consider the net profit P as a general criterion of the process. When work units are used for P instead of the conventional economic ones, the net profit takes the form

$$P = c_w W\left\lfloor Q, \dot{Q}, Q^f, \tau^f \right\rfloor - c_\tau \tau^f - c_Q Q^f \qquad (42)$$

where Q is the cumulative or integral heat variable (expensive heat) added to the system during time τ with $Q^0=0$ and $\tau^0 = 0$ and $W\left\lfloor Q, \dot{Q}, Q^f, \tau^f \right\rfloor$ the symbolic notation for the work functional (the gross profit), usually an integral which depends on the current Q, the heat flow rate $\dot{Q} = dQ/d\tau$ and the final values of Q and τ (i.e. Q^f, τ^f). As in the work functionals we use a nondimensional time τ identical to the number of heat transfer units, a quantity proportional to the residence time of the fluid in the system. The symbol Q^f represents the total expensive heat supplied to run the engine system during the total time τ^f. The quantities c_w, c_τ and c_Q are, respectively, the prices of the work, equipment (investment) and of the heat Q. In the engine model used above there is the direct proportionality between the heat Q and the temperature T of the fluid, i.e. $Q = -Gc(T - T^0)$ with T^0 being an initial fluid temperature. [This was, in fact, the reason for which the current temperature variable $T(\tau)$ has been used in place of $Q(\tau)$ as a suitable variable in Eqs. (30) and (31).] We have also to use therein the negative of the derivative $\dot{T} = dT/d\tau$ as a measure of the local intensity of the heat Q.

Thus, Eq. (42) represents an economic extension of Eqs. (30) or (31) that can effectively be used to analyze various realistic cases. The Carnot efficiency corresponds to vanishing rates. This causes infinitely long residence times and infinite equipment sizes necessary for any finite change in the process (at a fixed Q^f). It is inherent in this equation that for any fixed Q^f, work maximization leads to the Carnot point of the engine as an optimal point when the investment is free ($c_\tau = 0$). Otherwise, in a finite investment (fixed τ^f) work maximization leads to an optimal efficiency which is lower than that of the Carnot, even if a heat supply is free ($c_Q = 0$; free fuel). For the special case of infinite resource, the optimal efficiency of the engine is the well-known Novikov efficiency, $[1-(T^e/T)^{1/2}]$. Since in this special case the total heat Q^f (temperature T^f) is unconstrained, the integrand *w* of the integral W is stationary with respect to the rate $dT/d\tau$, and the Novikov efficiency is obtained from the condition $\bullet W_0/\bullet Q = \bullet w/\bullet = \bullet w/\bullet(dT/d\tau) = 0$ at the maximum power point. For example, the condition $\bullet w/\bullet(dT/d\tau) = 0$ applied for the integrand w of functionals (30) or (31) yields $(T + \dot{T}) = (T^eT)^{1/2}$ as the optimal value of the sum $(T + \dot{T})$. When this result is applied in the efficiency expression (27) corresponding with Eqs. (30) and (31) or its modified form Eq. (27') below

$$\eta = 1 - \frac{T^e}{T + \dot{T}} = 1 - \frac{T^e}{T + (\frac{c_v M}{\alpha' A})(\frac{dT}{dt})} \tag{27'}$$

(here we have used the usual contact time t), the already-known result for the maximum power efficiency, Eq. (22) or Eq. (22') below, is obtained

$$\eta = 1 - \frac{T^e}{(T^eT)^{1/2}} = 1 - (\frac{T^e}{T})^{1/2} \tag{22'}$$

Thus the Novikov efficiency is a local optimal efficiency associated with a free fuel cost ($c_Q = 0$) and unlimited heat supply. It applies when the heat capacity of the resource $\mathcal{M}c$ approaches infinity and its temperature T is constant. The efficiencies of real power stations lie between those of the Carnot and maximum power (Curzon and Ahlborn 1975; de Vos 1992). For the general optimization problem which is just the case of a limited resource, the state coordinates of this resource are fixed at the beginning and the end of the process because any finite resource is expensive, and only intermediate states are influenced by our decisions. For this fixed-end case, changes in investment costs are path independent, regardless of the control variations in the process (associated with the path independent properties of the second term in Eq. (1)). Therefore, since the process occurs in a given piece of equipment (fixed investment, fixed exchange area or fixed contact time), the thermoeconomic problem of maximum net profit has a solution which is well described by the solution of the thermodynamic problem of maximal work. This substantiates the important technoeconomic role of the maximum work problem which shows that (due to the tradeoff between the investment and fuel costs) the actual efficiency η_{exp} is always smaller than the Carnot efficiency and larger than the maximum-work efficiency. The consideration in this section has shown that optimizing of the work profit at a fixed finite duration has its equivalent counterpart in optimizing of a reduced work profit (with the investment costs subtracted) at a free or undetermined duration. This proves the sense for thermodynamic optimization in a finite time

7. Reduction of Classical Exergy Consumption in Heat Exchangers and Separation Processes.

Geometrical methods have been used to find optimal paths for thermo-mechanical and separation processes. Two basic results were proven: (i) the entropy production or exergy loss of a given process has a lower bound defined by an expression proportional to the square of the thermodynamic distance between the initial and final states (Salamon and Berry 1983); (ii) the minimum dissipation occurs when the process is carried through at constant thermodynamic speed (Salamon *et al.* 1980; Andresen and Gordon 1994). These results show that constant thermodynamic speed can be used as a design principle. Their application to heat exchangers proved the superiority of countercurrent exchangers over the cocurrent ones (Andresen and Gordon 1992 a, b). Principles of thermodynamic geometry can also be applied to stagewise process with gas separation by diffusion, staged refrigeration, or chemical reactions. They were recently applied by Andresen and Salamon to distillation process (Sieniutycz and de Vos 1999). For a given feed rate and fixed input and output concentrations the distillation column really only has one free control, the heat flow through the column. Energy and mass balance equations from tray to tray then impose the corresponding temperatures and concentrations on each tray. The optimal distillation column has external control of the temperature at each plate. This enables the designer to keep the trays a fixed thermodynamic distance apart, thus minimizing dissipation according to the general result of finite time thermodynamics. The optimal policy is a gradual addition of heat at all trays below the feedpoint and withdrawal of heat at all trays above the feedpoint with a corresponding much smaller heat duties of the reboiler and the condenser. Although the overall amount of heat passed through the column is the same as for the traditional design, most of that heat is degraded over a much smaller temperature difference, thus being equivalent to a sharply reduced expenditure of exergy for separation. A test calculation for the separation of a 1/1 mixture of benzene and toluene into 99% pure products shows a large reduction of the driving exergy by a factor of 4.4.

8. Exergy-Based Optimization of Solar Collectors

Solar collector design is an exemplary problem for demonstrating the importance of second law analysis and the superiority of efficiencies based on the second law over those based on the first law (Bejan 1982, 1988). We follow here an analysis developed by this author.

The simplest solar collector, an isothermal collector characterized by a single temperature T, is a device which absorbs a certain amount Q^S of the solar radiation per unit time, loses a fraction $Q^e = \alpha A(T-T^e)$ of the absorbed radiation to the environment of temperature T^e, and delivers a useful exergy Q to a receiver at the temperature T. Here A is the area of the collector, and α is the heat exchange coefficient. The first law efficiency $\eta^I = Q/Q_S = 1 - Q^e/Q^S$ is described by the formula

$$\eta^I = \frac{Q}{Q^S} = 1 - \frac{\alpha(T-T^e)A}{Q^S} \tag{43}$$

where α is the coefficient of heat losses. The highest possible collector temperature--the stagnation temperature--, $T_m = T^e + Q^S/\alpha A$, is the one at which the efficiency vanishes corresponding to vanishing heat power delivered to the receiver. In terms of the stagnation temperature the first-law efficiency is

$$\eta^I = \frac{Q}{Q^S} = \frac{T_m - T}{T_m - T^e} \tag{44}$$

The above equation indicates that the largest possible first law efficiency ($\eta^I = 1$) occurs when $T = T^e$ corresponding with vanishing heat flux to the environment. However, the exergy of the heat delivered at $T=T^e$ vanishes; in this case the receiver would consume worthless exergy in spite of receiving the largest energy. A second limit, $\eta^I = 0$, occurs when $T = T_m$, i.e. when delivery occurs at the maximum attainable T'. The receiver receives energy of the highest possible quality, but since $\eta^I = 0$, the flow of energy tends toward zero; again no exergy is delivered to the receiver. The maximum (classical) exergy deliverable to the receiver can be determined by maximizing

$$\begin{aligned} B_{out} &= Q(1 - \frac{T^e}{T'}) \\ &= Q_S \frac{T_m - T}{T_m - T^e}(1 - \frac{T^e}{T}) \end{aligned} \tag{45}$$

This maximum also corresponds to the maximum of the exergy efficiency defined as $\eta^{II} = B_{out}/B_{in}$, with constant $B_{in} = Q^S(1 - T^e/T^S)$, where T^S is an effective temperature of the sun. The differentiation of equation (45) with respect to T yields the optimal temperature of the collector $T_{opt} = (T^e T_m)^{1/2}$. This can be generalized to the case where there is a resistance between the collector and the receiver. The analysis can be extended to nonisothermal collectors with a fluid stream, combined convective and radiative heat losses, extraterrestrial systems and to cases where Q_S is periodic (Bejan 1982, 1988).

9. Thermodynamic Aspects of Catalyst Deactivation

Here we present another example showing how thermodynamics can be helpful in engineering analyses. This example, which uses only classical thermodynamic concepts, shows an improvement of model of catalyst decay by taking certain hysteretic properties into account. The basic catalyst deactivation mechanism is that associated with sorption processes in which the irreversible occupation of active sites (blockage) occurs through selective adsorption and subsequent degradation to carbonaceous material (coke) of some of the process components. Mechanistic kinetic models have been derived since 1970s to describe deactivation through coke deposition. These models take into account deactivation as a series of reaction steps together with the main reaction. Extensions have been made of those original models by taking into account aspects such as: various deactivation mechanisms, existence of the limiting residual activity and a maximum coke content, activation of a catalyst, selectivity in deactivation of each individual main reaction, inhomogeneity of active sites, et cetera.

An example deals with the triangular isomerization reaction of n butenes (Gayubo *et al* 1993)

$$(r_{ij})_0 = \frac{k_{ij} K_i P_i}{1 + K_1 P_1 + K_c P_c + K_t P_t} \tag{46}$$

The sorption model implies then the equation of the catalyst deactivation in the form (Gayubo *et al* 1993; Szwast 1994)

$$-\frac{da}{dt} = \frac{k_{d_c} K_c P_c + k_{d_c} K_t P_t + k_{d_1} K_1 P_1}{1 + K_1 P_1 + K_c P_c + K_t P_t} a \tag{47}$$

In a thermodynamic approach to catalyst deactivation, the solid activity a_S is identified with its kinetic activity $a = r/r^0$, where r^0 is the reaction rate on the fresh catalyst. The Gibbs-Duhem equation may be applied to link the decrease of the solid activity a_S in time with the increase of the activity of the adverse component (poison, coke, moisture, ecetera)

$$\begin{aligned} &(RT)^{-1}(d\mu_s + W_c d\mu_c) \\ &= M_s^{-1} d\ln a_s + W_c M_c^{-1} d\ln a_c = 0 \end{aligned} \tag{48}$$

Here μ_s and μ_c are specific chemical potentials of solid and coke, M_S and M_C - corresponding molar masses, W_C -the mass of the coke per unit mass of the fresh solid. We use here the name coke for any adverse component covering the solid and deactivating the catalyst.

Assume that the activity and chemical potential of the coke are measured by its fugacity, which is in principle the vapor pressure of the adverse component at equilibrium with the coke. For a constant T one can operate with the relative vapor pressure β_C. For moist catalysts it is simply the relative humidity of the moisture at equilibrium with solid.

For constant P and T, Eq. (48) yields

$$\begin{aligned} d\ln a_s &= -M_s M_c^{-1} \left(\frac{\partial \ln p_c}{\partial \ln W_c}\right)_{P,T} dW_c \\ &= -M_s M_c^{-1} \left(\frac{\partial \ln \beta_c}{\partial \ln W_c}\right)_{P,T} dW_c \end{aligned} \tag{49}$$

When the coke activity increases, the solid activity a_S decreases. The latter is found as the integral form of Eq. (49)

$$a_s = a_s^0 \exp\left[-\int_{W_c^0=0}^{W_c} \frac{M_s}{M_c} \left[\frac{\partial \ln \beta_c (W_c, P, T)}{\partial \ln W_c} \right] dW_c \right] \tag{50}$$

In the case of approximation of the equilibrium relationship by the straight line $\beta_C = kW_C$, the partial derivative in Eq. (50) is equal to unity. In this case the solid activity decreases exponentially with the coke content W_C,

$$a_s = a_s^0 \exp(-M_s M_c^{-1} W_c) \tag{51}$$

However the curves $a_S(W_C)$ are, in fact, temperature dependent; an experimental fact which proves the superiority of the general equation (50). This equation implies a function $a_S(W_C, T, P)$ rather than the simple function $a_S(W_C)$ described by Eq. (51). Therefore, an improved form of Eq. (51), i.e. Eq. (50) or its differential form Eq. (49), should be used as a more correct form when describing the deactivation and reactivation

$$\frac{da_s}{dt} = -\left(\frac{\partial \ln \beta_c (W_c, T, P)}{\partial \ln W_c}\right)_{P,T} r_s a_s \tag{52}$$

Here $r_s \equiv M_s M_c^{-1} dW_c/dt$ is the molar sorption (desorption) rate of the adverse component, e.g the molar sorption (desorption) rate of a poison or the generation rate (degradation rate) of the coke. Equation (52) comprises the correction coefficient of the hysteretic nature

$$\xi = \partial \ln \beta_c (W_c, T, P) / \partial \ln W_C \tag{53}$$

The coefficient ξ is different for sorption (deactivation) and desorption (activation).

In conclusion, thermodynamics helps to take into account the experimentally observed kinetic hysteresis of the deactivation-reactivation process (Gayubo *et al* 1993) by using data of the sorption-desorption hysteresis. The advantage is that the latter is much better known than the former.

10. Concluding Remarks

Our studies of the application of thermodynamics and availability theory to practical systems have shown that it makes sense to apply thermodynamic ideas to control practical and industrial processes, in order to achieve an improved performance. In particular, the mechanical work generation can be maximized in endoreversible thermal processes, exergy consumption can be reduced in heat exchangers and separation processes, temperature of solar collectors can be optimized for the best exergy delivery, and the chemical and transport systems with decay can be given an improved description. Other examples can be found in the forthcoming book (Berry *et al.* 1999). Extensions of the developed thermodynamic approach to complex chemical networks should be subject of further investigations along the thermodynamic line demonstrated.

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Nomenclature

A	Total transfer area coordinate of the $dA = dA_1 + dA_2$
$\mathcal{A} = E_x^{\infty}$	Classical exergy of mass unit
$\mathcal{A}_g$	Classical specific exergy of fluid phase in heating example
a	Catalyst activity
a_V	Specific area of heat exchange (per unit volume)
c	Specific heat of the driving fluid
E	Energy-like function ('dissipative energy') in terms of the rate $u=dT/d\tau$
E_X	Generalized irreversible exergy of mass unit
$F = dV/dx$	Cross-sectional area of the driving fluid system
F_0	Rate of work production, profit

	rate (-L)
G	mass flux of the driving fluid (fluid 1)
H,	Extremum Hamiltonian function
H_{TU}	Heat of transfer unit
h	Specific enthalpy of the fluid
I	Optimal performance function for the work integral
$N_{TU} \equiv \tau f$	Number of the heat transfer units of the gas heating process in a duct
n_i	Number of moles of i-th component
Q_1, Q_2	Cumulative heat fluxes for upper and lower reservoir, respectively
$Q \equiv Q_1(\gamma)$	Function describing the driving heat flux along the conductance coordinate γ
S_σ-	dissipated entropy per unit mass flux of the driving fluid
S_0	mass of solid in the batch fluidization system
S	specific entropy of the driving fluid
s_I, s_{II}	specific entropies of adiabats for fluid circulating in the Carnot engine
T	contact time of the driving fluid with the exchange surface
$T = (T, \tau)$	vector composed of the temperature and the number of heat transfer units
T_1, T_2	temperatures of upper and lower reservoirs (usually $T_2 = T^e$, and $T_1 \equiv T$)
T^e	constant temperature of environment
T_1', T_2'	upper and lower temperature of the Carnot engine as the part of the HCA engine
U	control vector of the generalized process
$u = dT/d\tau$	rate of the temperature change of the first fluid as the process control
V	volume coordinate of the driving fluid system, satisfying $dV = Fdx$
$v = G/(\rho F)$	linear velocity of the driving fluid
W	cumulative power output
$W \equiv W/G$	total specific work or total power per unit mass flux
X	enlarged vector of state with coordinates W, T and τ.
X	transfer area coordinate
z-	adjoint variable of the work minimization problem, momentum-type variable, $\bullet L/\bullet\dot{T}$
z_σ	adjoint variable of the entropy generation minimization, momentum-type variable, $\bullet L_\sigma/\bullet\dot{T}$
α'	overall heat transfer coefficient
Γ	gauging function
γ_1, γ_2	coordinates of partial conductances
γ-	coordinate of overall cumulative conductance
λ	adjoint variable of work maximization problem, momentumlike variable $\bullet f_0/\bullet\dot{T}$
$\eta = dW/dQ_1$	local efficiency
ρ-	mass density of the driving fluid
τ	dimensionless contact time, number of the heat transfer units (x/H_{TU})
ξ	Logarithmic intensity
σ_s	Entropy production

Subscripts

g-	gas
C	Carnot point
s	entropy related quantity, solid
v	per unit volume
σ	dissipative quantity
1, 2	first and second fluid, respectively

Superscripts

e	environment, equilibrium
f	final state
i	initial state

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