

THE NONEXISTENCE HYPOTHESIS OF
EQUATION-OF-MOTION FOR ENERGY CONVERSION
PROCESSES:
A Quantitative-Descriptive Theory of Thermodynamics

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Abstract

In the second half of the nineteenth century, thermodynamics, which was the product of the synthesis of the caloric theory of heat and the scientific study of heat engines, was "captured" by Newtonianism. Caloric theory of heat became dynamical theory of heat, which, in turn, was transformed into kinetic theory and statistical mechanics or statistical thermodynamics. Thermodynamics became *thermostatics* and *thermostatistics*.

Of course, unidirectional time remains the standing-out feature, which distinguishes thermodynamics from the rest of physics. The verbal or descriptive origin of thermodynamics, as evidenced in its treatment by Carnot, Kelvin, and even Clausius, survives as the implicit and imprecise treatments of thermodynamics by engineers. None the less, the "capturing" of thermodynamics by Newtonianism results in disastrous misunderstanding concerning the true nature of energy conversion processes, especially the meaning of reversible energy conversion processes.

It is pointed out that the satisfactory formulation of the thermodynamic theory requires the replacement of Newtonianism in favor of a new paradigm. Its distinctive feature, in addition to the unidirectional time, is the nonexistence of equation-of-motion for energy conversion processes. In other words: While a physical theory must be a quantitative theory, a quantitative theory does not always imply a mathematical theory that is based on causal law(s) in the form of equation(s) of motion. Thermodynamics, as a different type of quantitative theory, is made up of both the quantitative acausal first law and second law, and the *operational means*, which can not be described in terms of mathematical formula only. Instead, its complete description requires both quantitative and verbal means. For energy conversion processes, it is not only indispensable to subject fundamental concepts to operational analyses (as it is in mathematical theories of "dynamics"), but also necessary to give *each individual process* its operational description.

It is the operational description (means) of individual process that gives, the process its defining characteristics. It is a special kind of operational means that bring about reversible processes. The paper first addresses to the immediate objective of the new theory: the integration of the mathematical theory of *thermostatics* and the "engineering thermodynamics," the implicit practices and the equivocal meanings of which are made into explicit and specific methodology. Comments on *Theory of Dissipative Structures* of the Brussels school and on the epistemological nature of the theory, such as causality, are also made.

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INTRODUCTION

In 1824, the French engineer Sadi Carnot published his seminal treatise, *On the Motive Power of Fire*, inspiring a new scientific field: thermodynamics, the study of energy conversions. Every *energy conversion* process is *intrinsically irreversible*¹ Before the nineteenth century, physics had concerned itself principally with dynamical processes, such as the motion of planets, which are independent of time's arrow. Natural thermodynamic process, however, proceeds in a particular direction only; the opposite direction is "forbidden." Heat flows from hot to cold, not in the opposite direction. Sugar dissolves in a cup of coffee; it does not of its own accord crystallize back into a lump. A spinning top winds down; it does not spontaneously speed up.

By mid-nineteenth century, there was a crisis in theory of heat: Carnot's principle seemingly contradicted with Joule's doctrine. The conflict between Carnot's principle and the energy conservation principle was resolved by Clausius, who first recognized that there were two principles involved in explaining the conversion of heat to work. Clausius and Kelvin formulated the first law (the energy conservation principle) and the second law (from Carnot's principle), introduced the concepts of energy, absolute temperature, and entropy, and thereby founded the science of thermodynamics. The first part of the second law defines the state variable entropy; the second part of the second law prescribes the innate direction for energy conversion processes. The two parts of the second law may be based on a number of alternative hypotheses – all of which are palpably verbal. While everyone agrees on the two-part, *quantitative* content of the second law, each person seems to have his/her own favorite *verbal* hypothesis. One choice, which was used by Carnot² is the "impossibility of constructing a perpetual-motion machine of the second kind." Like Newton who recognized the connection between a falling apple and planetary motion, Carnot saw the connection between heat always flowing from hot to cold and the possibility or impossibility of constructing a certain kind of machines.

The science of heat, originated by Lavoisier, Black, and Fourier, thus, became the new cosmology of heat and energy conversion. In the words of Cardwell (1971):

...thermodynamics, originated substantially (but of course not wholly) in the power technologies of the eighteenth and early nineteenth centuries – and these had virtually nothing to do with Newtonianism.

Thermodynamics might have begun with reflections on irreversible processes and heat engine technologies, which had nothing to do with Newtonianism. It turned out, however, over the course of the second half of the nineteenth century thermodynamics – instead of challenging the hegemony of Newtonianism – became integrated into Newtonianism. Since the advent of statistical mechanics, physicists and chemists often view thermodynamics as a natural outgrowth of the former. This leads, as argued in this paper, to disastrous misunderstanding concerning the

¹We use *energy conversion* in the narrow sense: the conversion (transport) process involves energy that is a function of temperature (and entropy). Conversion between dynamical energies without dissipation is thus not *energy conversion*, according to our definition; it is a pure dynamical process. With the single exception of the reversible, quasistatic processes (See GLOSSARY), thermodynamic processes and energy conversion processes are synonymous in this paper. All energy conversion processes, including reversible energy conversion processes, are *intrinsically irreversible* in the following sense: Dynamical processes, even irreversible ones, may be made reversible "progressively ... by a suitable selection of circumstances [means to reduce friction]" (Lindsay and Margenau 1957:198). Energy conversion processes, on the other hand, can be made reversible only through the use of some artifice, rather than the simple disappearance of the friction term in the equation of motion.

²Carnot of course did not make the distinction between the perpetual-motion machine of the first kind and the perpetual-motion machine of the second kind, as he developed his principle based on the caloric theory of heat.

true nature of energy conversion processes, especially reversible energy conversion processes.

The trajectories of planets are specified by Newton's law or Newton's *equation of motion (EOM)*. The law and the equation of motion are one and the same. This model – the central role of the equation of motion and the use of trajectory (solution to the equation of motion) to describe the change in a physical system – has been followed repeatedly: Euler's equations of motion for ideal fluid, Maxwell's equations of electromagnetic field, the Schroedinger wave equation, etc.. In each case, a new law (new equation of motion) is formulated. It remains only to explicate the consequences of the law. Even when reversibility does not strictly apply anymore – for example, due to the consideration of friction energy conversion which modifies Euler's motions into Navier-Stokes equations of motion, or due to the act of observation in applying (statistical interpretation to) the Schroedinger wave equation – formulating *EOM* and then seeking solution to the equation remain the standard method of scientific investigations. Physical theories in the Newtonian tradition, including quantum mechanics and the two relativity theories, are *mathematical theories*.

This tradition, this model, this worldview may be referred to as the Newtonian paradigm (Newtonianism) or the mechanistic paradigm. From the time of Enlightenment on, the mechanistic paradigm – its principal 17th century architects were: Bacon, Descartes, Newton, and Locke – has been wholeheartedly embraced by the scientists and most modern thinkers in the Age of the Machine. Some of the central scientific ideas (as opposed to the social or humanistic implications) of the mechanistic paradigm are:

.....

Paradigm Chart

<i>Mechanistic Paradigm:</i>	<i>Nature of Thermodynamic Theory:</i>
(a) Reversible time	(a) Unidirectional time
(b) Mathematical theory — laws and <i>EOM</i> are one and the same	(b) Is the thermodynamic theory a mathematical theory?
(c) Epistemological nature of the theory	(c) Epistemological nature of the theory?

.....

The last point, (c), will be commented on at the end of this paper. Also shown in the right column in the above chart are the irreversible characteristics of energy conversion processes and the question marks in (b) and (c), concerning, respectively, the methodological nature of a thermodynamic theory and the epistemological nature of the theory.

Today, however, the Age of the Machine, the Industrial Age, is screeching to a halt. The mechanistic paradigm is ill-suited as the world organization principle for the post-Industrial Age. The innate irreversible (temporal) nature of energy conversion processes, as opposed to the atemporal and deterministic nature of dynamical processes, certainly suggests that thermodynamics may become a candidate for developing into a new, alternative, world model which, due to its unidirectional-time characteristics, is better suited to describing the temporal and complex Nature.

Already, Ilya Prigogine and his colleagues (Glansdorff and Prigogine 1971; Nicolis and Prigogine 1977; Prigogine and Stengers 1984) have put forward the *theory of dissipative structures* as the new scientific paradigm for precisely such a objective.

The work reported in the present paper was initiated without any of the larger implications and applications described in the above paragraph in mind. For many years, I have been intrigued by the wide-spread misunderstanding in the thermodynamic theory and the apparent unawareness of the existence of such disastrous misunderstanding. The scientific and engineering community is "schizophrenic" towards the meaning of a thermodynamic theory – vacillating between thermodynamics as *thermostatics*, which is of only limited usefulness,

Thermodynamics does provide two methods that permit us to infer some limited information about processes, but each of these methods is indirect and each yields only the most meager return. First, by studying the initial and terminal equilibrium states, it is sometimes possible to bracket a process and thence to determine the effect of the process in its totality. Second, if some process occurs extremely slowly, we may compare it with an idealized, nonphysical, quasistatic process (Callen 1960:283).

and thermodynamics as the *science of complexity and becoming* (Prigogine and Stengers 1984:208), upon its broad foundation a possible reunification of the sciences and the humanities may be built toward a new view world. In between these two views engineers have been *applying*³ thermodynamic laws to an extraordinary range of problems with the most productive return. I have now come to the view that the root of this confusion is due to the misguided instinct to fit thermodynamics, despite its distinctive irreversible-characteristics, into Newtonianism; thermodynamics must first be free of the thrall of the Newtonian model. *The satisfactory development of thermodynamics, as a branch of physics, requires a new scientific paradigm.* A new scientific paradigm must be formulated, not only for serving the general need of scientists and philosophers as a new world model of the post-Industrial Age (Prigogine and Stengers 1984; Rifkin 1980), but for a more compelling specific reason – a consistent thermodynamic theory depends on it.

A key question here concerns the *existence of equation-of-motion* in thermodynamic theory, which is essentially the methodological question (b) in the paradigm chart, "*Is thermodynamic theory a mathematical theory?*" Most of this paper is devoted to this issue. Toward the end of the paper, however, the epistemological matter (c) is discussed as, only by considering the epistemological subject, can we contemplate: the relationship between the Newtonian scientific paradigm and the new scientific paradigm, and the question, "Is a nonmathematical theory 'inferior' to a mathematical theory?"

BASIC CONSIDERATION

1. THE MATHEMATICAL THEORY OF THERMOSTATICS

Gibbs found the thermodynamics of Kelvin and Clausius a science which is – though quantitative – implicit and unfinished.

It is an inference naturally suggested by the general increase of entropy which accompanies the changes occurring in an isolated material system that when the entropy of the system has reached a maximum, the system will be in a state of equilibrium. Although this principle has by

³ Explicit meaning of "applying thermodynamic law" is the very topic of this paper.

no means escaped the attention of physicists, its importance does not appear to have been duly appreciated. Little has been done to develop the principle as a foundation for the general theory of thermodynamic equilibrium" (Gibbs 1878).

The mathematics of thermostatics was made explicit and precise in 1875 by Gibbs ...” (Truesdell 1966:102).

Gibbs transformed the implicit and imprecise science of thermodynamics into a mathematical theory of *thermostatics*.⁴ His achievement is monumental. Thermodynamics that we study today owes as much to him as to Carnot, to Joule and Mayer, and to Kelvin and Clausius.

But it is imperative that we understand *thermostatics* in the proper perspective. *Thermostatics* is that part of thermodynamics that is amendable to – perhaps, more accurately, that physicists have succeeded to subject to – mathematical treatment. It is not even the core part of thermodynamics, i.e., the study of energy conversion processes. We are not to be deceived by the words “(reversible) quasistatic process,” for these are mere names to cover the absence of real energy conversion processes. Yet, this important, but none the less non-core, part of thermodynamics is sometimes considered to be the only part worthy of study. Consider the following comment (on why the book was written) in the preface of an excellent *thermostatics* book:

... if we reject the ones [books] which G. N. Lewis so aptly described as containing “cyclical processes limping about eccentric and not quite completed cycles” and consider only those which present thermodynamics as an exact science (Guggenheim 1967:v).

The “exact science” means, of course, the mathematical science of thermostatics. This mathematization was carried to the logical conclusion by Tisza (1966) and Callen (1960; 1985), which is an especially elegant work, in a postulational formulation, which replaces the more verbal statements of the first law and the second law with the less verbal four-part postulates.

That most scientists hold the above view can only be understood in the realization that the scientific and engineering community mostly still operates, at least subconsciously, under the thrall of the Newtonian paradigm – thermodynamics should be a mathematical science. A physical theory certainly must be a quantitative theory. But, is a quantitative theory synonymous with a mathematical theory? Must the thermodynamic theory be a mathematical theory? After all, the original statements of the first law and the second law are palpably verbal.

Beyond Thermostatics

Carnot was an amateur devotee of science. His approach to problems was less inhibited by the “establishment science” of his day. In fact, Carnot’s idea was so original that he was far before his time; the 19th century science establishment and the 19th century Machine Age society were too dominant to be challenged. His innovative ideas and methods were dissected: part of them were incorporated into the prevailing scientific body, which then grew and developed into a satisfactory system *thermostatics*; the rest, the more innovative part, survived and evolved into the fragmented, implicit practices – though very useful – of engineers. The haphazard combination of the implicit engineering practices and the systematic *thermostatics* is the standard form of “engineering thermodynamics” today.

⁴ *Thermostatics* is defined in this paper in the narrow sense that it deals with “reversible quasistatic processes” and “virtual processes” (Tisza 1966:43) only.

Another 19th century challenge to the mechanistic paradigm by the even more comprehensive *Darwin's theory of biological evolution* originally met with the same fate. "Instead Darwin's theories became an appendage to the Newtonian world machine. The full implications of Darwin's discoveries were never [sic] really explored. Instead, some of the more superficial trappings of his theory were immediately taken hold of and exploited in a way that further legitimized the mechanical world view" (Rifkin 1980:28). Darwin's rejection of Cartesian-Newtonian determinism (and *finalism*) did prevail completely, of course, since the *evolutionary synthesis* of 1936 to 1950 (Mayr 1991). This has led to the abandonment of *physicalism* in evolutionary biology.

What is interesting in the present work is that in looking back at Carnot's work more than one century and a half later one finds seeds of ideas challenging physicalism (mechanistic paradigm) in physics itself.

2. IS THE FIRST LAW EQUATION AN EQUATION-OF-MOTION? THE JOULE EXPERIMENT

Universal law of gravitation is an integral part of Newton's *EOM*. In *EOM*s of other physical theories, the corresponding laws of forces are also integral parts of the *EOM*s. There is a one-to-one correspondence between the trajectory and the precisely (if possible) prescribed *initial condition*.⁵ Once the *initial condition* of a system is known⁶, the trajectory of the system can be completely determined – though the *trajectory* of a nonlinear, unstable system can be highly sensitive to its *initial conditions*. And once the *trajectory* is known, everything about the process or the change in the system is specified.

Every known *EOM* in standard physical theories is consistent with the energy conservation principle. There is no need for an *independent* energy conservation equation in the physical theories based on *EOM*. It is interesting to note that *thermostatics* is like the standard physical theories in this respect. The Gibbs equation for a closed system,

$$dU = TdS - PdV, \quad (1)$$

and the Gibbs equation for an open system,

$$dU = TdS - PdV + \sum \mu_i dN_i, \quad (2)$$

serve as a kind of *EOM* for reversible quasistatic processes. (The Gibbs equations are the differential of the respective fundamental functions: $U = U(S, V)$ and $U = U(S, V, N_i)$.) These reversible quasistatic processes are described as, for example, isothermal process, or isobar process, etc.. The isothermal condition or isobar condition may be considered as a kind of boundary condition (which is a part of the *initial condition*). The first law equation for the reversible quasistatic processes becomes identical with (see section 6) the Gibbs equation for the closed system; in *thermostatics* the first law equation is not an independent equation.⁷

⁵ the term *initial conditions* is used here both in the customarily specific sense, and in the general sense of any condition, including the boundary conditions, that limits or restricts the general solutions to the equation of motion.

⁶ In classical mechanics, any arbitrary initial state is a physically possible initial state. In other words, dynamics does not rule out any arbitrary initial state. In recent years Prigogine and collaborators have advanced the *microscopic theory of irreversible processes* with the assertion that time's arrow excludes initial conditions of "infinite information content." While this new theory is consistent with dynamics, it cannot be derived from dynamics. More comment on this work will be given at the end of the paper.

⁷ Note that there is no energy conservation hypothesis in the four-part hypotheses of Callen (1960).

First Law as an Independent Principle

The similarity of *thermostatistics* with the standard physical theories is superficial, as it is only applicable to artificial “reversible quasistatic processes” and “virtual processes.” The nature of real thermodynamic processes is very different. The Gibbs equations are not *applicable*⁸ to irreversible thermodynamic processes – though they can be used for studying the artificially constructed paths linking the two end states for determining property changes between the end states. The first law equation, which is now independent from the Gibbs equation, *is* applicable to any real thermodynamic process. That an independent energy conservation principle is an indispensable tool is a unique feature of thermodynamics; it is tempting to associate this feature immediately with the idea that there is no *EOM* in thermodynamic theory.

Before we firmly come to adopt that hypothesis, let us consider the validity of the proposition that the first law serves the same purposes as an *EOM*.

Instead of forces in an *EOM* of the standard physical theories, one finds heat and work in the first law equation. While there are only a handful of fundamental forces and apparent forces, whose natures can be described by mathematical laws, it is not possible to incorporate the many varieties – almost myriad possibilities – of heat interactions and work interactions into *laws*. The many and varied natures of heat and work are such that they can not be exclusively represented by mathematical laws (see comment on *governing equations of transport processes* in a later section); the “global” descriptions required for heat and work can only be represented in terms of quantitative *and* verbal means. Specifically, they can not be incorporated into pure mathematical expressions either as a part of the first law equation or as a part of the *initial condition*. The causal relationship that the *trajectory* is a specific solution (to the *EOM*) which is completely defined (restricted) by the *initial condition* (including the boundary condition) is lost. Clearly, the first law equation does not serve the same purpose as *EOM* serves in a standard physical theory in this respect.

This is confirmed by the observation in the following paragraphs that a *trajectory* does not define a process either. (Examples of the global, nonmathematical (verbal) description of heat and work are also given.)

The Joule Experiment

The classical *Joule experiment* and its variations provide particularly instructional insight into the nature of energy conversion processes: heat and work can not always be represented by mathematical expressions in the first law equation or in an *initial condition* (pointed out in the above subsection), and *trajectory* alone does not define process.

The original *Joule experiment* is the free expansion of an ideal gas, which initially occupies one part of an container, into a vacuum (the other, evacuated part of the container) with the whole container submerged in an insulated heat bath. Joule found that at the final end state the temperature of the heat bath remains the same. This of course means that the temperature of ideal gas at the end of free expansion also remains the same, and that there is no net heat exchange between

⁸ It is clear that the Gibbs equation does not apply to irreversible processes with no defined paths between end states far apart. However, for irreversible processes that the “paths” are defined, such as the “micro” free-expansion process described later in this section, the Gibbs equation can be used for relating property change between the two (very close) states, thus applies to the *path*. The *applicability* of the Gibbs equation in thermostatistics means, on the other hand, that *both heat is equal to TdS and work is equal to PdV* during the reversible quasistatic process. Furthermore, it is widely misunderstood that heat and work are path functions (see rest of the paper on this very important point), thus it is likely, by saying “the Gibbs equation is applicable to a process,” to imply exactly the same situation existing in thermostatistics. In order to avoid the possibility of any such misunderstanding, we agree *not* to regard the Gibbs equation *applicable* to irreversible processes, but hold the Gibbs equation applicable to *irreversible paths*, whenever they are defined.

the ideal gas and the heat bath for the whole duration. (From this result, Joule deduced Joule's law, $U(T, V) = U(T)$, which is applicable to ideal gases.)

We may modify the experiment slightly without altering any thing of physical essence by permitting the ideal gas to expand from V to $V + dV$, instead of from V to, say, $2V$. It is necessary to replace the original partition with a reusable piston, with a succession of stops (constraints). Depending on how close the stops are placed, dV can be made as small as necessary. The ideal gas container itself may be kept adiabatic, deleting the insulated heat bath. Repetition of the adiabatic, "micro" free-expansions, $V \rightarrow V + dV$, leads to an isothermal process for the ideal gas until the final volume becomes again $2V$. At that point the system is at exactly the same final end state of the original Joule experiment. This *quasistatic process* of repeated "micro" free-expansions reproduces exactly everything of physical significance in the original process – with the added feature that it now has a *trajectory (path)*, a dense succession of equilibrium states. Both heat and work are zero throughout the quasistatic process. (Work is zero simply because no mechanism exists to take work away, or to transmit and store work.) Most significantly, the quasistatic process is every bit as irreversible as the original free expansion process⁹; the existence of a *quasistatic path* does not necessarily make a process any more reversible, despite the often stated association between the *quasistatic process* and the *reversible process*. Comment by Landsberg (1961:94) is telling:

Many authors take reversible processes and quasistatic processes to be synonymous terms. ... Others use both terms with slightly different shades of meaning, and there does not seem to be unanimity on the precise difference between them.

Also note that despite the well defined path in this case, work, δW , is not equal to PdV . Work is not always a path function, with its value represented by the mathematical "law,"

$$\delta W = PdV. \tag{3}$$

(Equation (3) is applicable only to systems which are internally-reversible mechanically during a process.) With or without a path, the specification of work also requires a verbal, nonmathematical description, including the means of transmission and storage.

Let us continue with a variation of the example. We now change the quasistatic process of "micro" free-expansion into a fundamentally different "quasistatic process." The ideal gas container is again submerged in a very large heat bath – so large that it may be considered to be a heat reservoir of infinite heat capacity. Work transmission means and work storage means are added to the system in the form of piston rod, cam, and weight as shown in Fig. 1. With a properly designed cam, the forces on both sides of the piston can be maintained to be nearly balanced. With the deliberate, slight imbalance, the ideal gas will expand against the piston undergoing an isothermal expansion process. The process remains isothermal, because the force imbalance is slight and the piston motion is sufficiently slow that heat absorbed by the expanding ideal gas from the heat reservoir keeps the ideal gas at constant temperature. The internal energy of the ideal gas remains constant (recall the Joule law). This "quasistatic process" then shares exactly the same path (trajectory) as the above irreversible quasistatic process. Yet, this process is a *reversible process*¹⁰ – a process fundamentally different from the above irreversible quasistatic process. As a result of the transmission means and the storage means,

⁹ See a especially revealing discussion by Callen (1985:99).

¹⁰ **Reversible process and reversible quasistatic process are two distinctive processes** in this paper. See GLOSSARY and later discussion in the paper.

equation (3) is applicable. Useful work¹¹ done by the ideal gas expansion against the piston is

$${}_1(W_{use})_2 = {}_1W_2 = \int_1^2 PdV = mRT \ln 2. \quad (4)$$

Heat absorbed by the ideal gas from the heat reservoir is

$${}_1Q_2 = T(S_2 - S_1) = TmR \ln 2 \quad (5)$$

which is of course exactly equal to the work (useful work) because the internal energy of the ideal gas remains constant. Note that heat is converted completely (100%) into work! This work is stored away as potential energy of the weight.

We learn in these two examples: First, work and useful work values are dependent on path *and* verbal means, such as the transmission means and the storage means, which is an essential part of defining a process. It is not surprising then that path alone does not completely specify a thermodynamic process, including whether a process is reversible or irreversible.

3. NONEXISTENCE HYPOTHESIS OF EOM

The first law equation is not an *equation of motion*. There is either an *EOM* in the classical sense of Newtonianism awaiting to be discovered, or *EOM* does not exist. The fact that *path* – defined by the existing thermodynamic variables – does not completely specify a thermodynamic process does not support the first option (existence of *EOM*). Certainly, no *EOM* is possible in term of the present known set of thermodynamic variables. It is possible, as a third option, that *path* based on an expanded set of “more complete” thermodynamic variables would make a complete description of a process. While such “*EOM*” can not be ruled out absolutely, even if discovered in the future, may turn out to be a very different sort of “*EOM*,” not the *EOM* in the Newtonian paradigm. We simply have no idea with regard to the nature of such “*EOM*.” What does it do? What role does it play in a theory?

I consider the first option to be extremely unlikely, and the third option to be premature, perhaps futile at the present time. This leaves only the second option as a fruitful one at the present time. The following is thus put forth as a hypothesis,

It is impossible to discover the equation-of-motion which provides the complete, causal descriptions of all possible changes in an energy conversion system.

The *nonexistence hypothesis* stresses the impossibility of *mathematical and causal*, description, which was put in this way by Bridgman,

... why is thermodynamics restricted to the formulation of necessary conditions, and why is it so impotent in its endeavor to frame sufficient conditions? Other branches of physics are not thus restricted (Bridgman 1941:5).

My answer to Bridgman’s question is: yes, the quantitative first law and second law are impotent to frame sufficient conditions (mathematical and causal description); no, thermodynamics is not restricted to the formulation of necessary conditions only. It requires nonmathematical means in addition to the quantitative laws to frame sufficient conditions. Note also the *nonexistence hypothesis* asserts only that it is

¹¹In this case, useful work and work done by the system are the same since the expansion is against the vacuum.

impossible to have mathematical and causal description of *all possible* changes between two end states; certain change such as pure dissipative heat transfer processes is described mathematically and causally by *governing equation*.¹²

Since the means to frame sufficient conditions involves non-mathematical means, it is doubtful that a complete list of such means can ever be compiled. The *nonexistence hypothesis*, therefore, implies that it is no longer possible to achieve all-inclusiveness. Wishes such as:

All cases are foreseen, all imaginable movements are referred to ...
(Carnot 1824).

The discovery of the complete equation of motion – the equation of motion that describes all physical phenomena contemplated by thermodynamics – remains a subject of research at the frontier of science ...
(Gyftopoulos and Beretta 1991:210).

are denied by the *nonexistence hypothesis*.

In acknowledging the *impossibility* of mathematical description and its implied all-inclusiveness, one is directed to the essential question, "What brings about the change?" No more idle philosophical reflection or wishful thinking. This is then the main usefulness in adopting the hypothesis. It compels us to consider carefully, every time we study an individual process using the first law and the second law, all things pertinent with what bring about a process. This is what we mean by *applying thermodynamic laws*. It should not be an afterthought.

4. THE OPERATIONAL MEANS

Operational Character of Concepts

In the standard physical theories the fundamental concepts must have meaning in terms of instrumental or verbal operations according to Bridgman (1927;1959). These rigorously defined concepts then become mathematical terms in the *EOM* of a physical theory. There is no further need to ask the operational meaning of an individual process – which is merely the consequences of the *EOM*. And indeed, physicists are wont to be uninterested with such questions. They remain uninterested, even when they study energy conversion processes. It is telling to consider the following.

The maximum useful work of an air-fuel mixture at the initial atmospheric pressure is first shown by Gibbs to be,

$$W_{max\ use} = (H - H_{P0}) - T_0(S - S_{P0}) \quad (6a)$$

where H is the enthalpy, T the temperature, and S the entropy; subscript 0 denotes the atmospheric conditions (temperature and pressure) and subscript P0 denotes the product mixture at the atmospheric conditions. Gibbs is content with what might possibly happen, without attempting to construct the operational steps for the actual realization of the reversible process that produces the maximum useful work – a perfectly normal practice for a scientist schooled in the Newtonian paradigm.

Gibbs's handling of the question of the maximum useful work is in sharp contrast with Carnot's. Carnot asked the same nominal question of the maximum useful work to be derived from an air-fuel mixture. He wrote, "Nature, in providing us with *combustibles* [air-fuel mixture] on all sides, has given us power to produce, at all times and in all places, heat and the impelling power which is the result of it.

¹²Note that a *governing equation* is not an *equation of motion*. See more discussion on this distinction in the next section.

To develop this power, to appropriate it to our uses, is the object of heat-engines." Heat from the combustible is

$$H - H_{P0}$$

and *impelling power* from the same combustible undergoing a reversible transformation to (burned) product in an ideal combustion heat engine is, according to equation (6a),

$$(H - H_{P0}) - T_0(S - S_{P0})$$

Instead of equation (6a), Carnot and Kelvin (with the introduction of the absolute temperature by Kelvin) gave the celebrated, but incorrect,¹³ - incorrect for ideal combustion heat engines - Carnot-Kelvin formula,

$$W_{use} = Q_H [1 - (T_0/T_H)] \quad (7)$$

$$\approx (H - H_{P0})[1 - (T_0/T_H)] \quad (7a)$$

where Q_H is often, though it is really an approximation, taken to be the heat of combustion, $(H - H_{P0})$. Eqn. (7a) is clearly not in agreement with eqn. (6a). T_H is supposedly the temperature of the heat reservoir. For combustion heat engines, however, there is no heat reservoir. T_H is often taken, then, to be the peak cycle temperature of a heat engine; the peak cycle temperature is of course not unique value, dependent instead on the (arbitrary) heat engine design. This is contradictory with the maximum useful work theorem, according to which $W_{max\ use}$ is a function of the property of the fuel-air mixture and the surroundings condition only, independent of the (reversible) heat engine design. The whole situation is very vague.

The Operational Description of Individual Processes

None the less, the strength of Carnot's treatment, as against Gibbs's treatment, is that Carnot provided the actual operational steps that a reversible heat engine¹⁴ operates. The operational description is so important to "engineers" - though never explicitly acknowledged - that this incorrect formula, rather than the correct Gibbs's formula, had been until recent years and is still for large number of "engineers" the ideal - the ultimate possibility - for combustion heat engines.

It is an astonishing observation! Such a situation can only exist, I think, because, though the importance of operational description is appreciated implicitly, there is no clear, explicit acknowledgement that the totality of operations bringing about a process - the operational means - is an integral part of thermodynamic theory. The *nonexistence hypothesis* forces the explicit acknowledgement upon us. For energy conversion processes, it is not only indispensable to subject fundamental concepts to operational analyses,¹⁵ but also necessary to give an individual process its operational description.¹⁶ Without the operational means, thermodynamics can only formulate necessary conditions; with the operational means, thermodynamics can endeavor to frame sufficient conditions for a process, including its rate of change.

The *operational means* is the *totality* of operations - instrumental operations, verbal operations, quantitative (mathematical) operations - that bring about a process. This includes the operational means of the first kind, the second kind, the third kind, and the fourth kind (excluding the reversible quasistatic artifice):

¹³ A brief discussion will be given in section 10. A more complete consideration is given in another paper (Wang *et al.* 1992), which is solely devoted to this problem.

¹⁴ Again, his reversible heat engine is not a reversible combustion heat engine.

¹⁵ The most successful example is the analysis of Caratheodory.

¹⁶ The best example is of course the Carnot heat engine cycle.

1. Initiation actions. Including initiation of the whole process or initiations of small quasistatic-steps. This operation is sometimes called relaxation-of-constraint operation.
2. External heat-and-work coupling. These descriptions are not entirely in terms of mathematical variables of the system. Verbal means (or instrumental means) are required to describe the relational (global) picture of the system and the *external* elements that the system directly interact with or indirectly interact with. This is the operational means that gives *defining characteristics of the work producing processes*, including the special class which brings about the reversible energy conversion processes.
3. Internal transport processes. It will become clear in section 7 that the distribution of heat or work within a thermodynamic composite system can not be fully answered (even for a quasistatic process) unless the operational means also include descriptions – by using the governing equations of transport processes – of internal transport processes. Note that the “governing equations” transport processes, such as Fourier’s equation of heat conduction and the Navier-Stokes equation, are not *EOM* for energy conversion processes (see explanation below); rather, the whole set of the governing equations constitutes the quantitative *operational means* of the third kind.
4. Internal work coupling. An entirely new kind of thermodynamic composite systems can be investigated using the concept of *internal work coupling*. This concept and the new kind of thermodynamic systems will be discussed elsewhere (Wang 1992).

An *equation of motion* should give causal descriptions of *all possible* changes, including reversible changes, between some end states of a thermodynamic system. It is obvious that the governing equations of transport processes gives descriptions of only pure dissipative changes, rather than all possible changes, for a thermodynamic system. Governing equations of transport processes, thus, are not *equation of motion*. It should also be pointed out that, although the governing equations are integral parts of the operational means, explicit solutions to the governing equations are not always insisted. It is sometimes sufficient to merely frame the problem of an energy conversion process by affecting an arbitrary solution, as we shall see in an example in section 7.

The second law points out only the direction (arrow) of time, without giving it a quantitative measure. The *operational means* defined above gives the thermodynamic time *quantitative measure* as well as *directionality*. Thermodynamic time thus acquires its full meaning; the unidirectional time and the dissipative/evolutionary view of nature stand as a *complete* paradigm, as an alternative to the Newtonian paradigm of reversible time and the static (conservative) view of dynamics.

5. NECESSARY CONDITIONS FOR SPONTANEOUS TENDENCY

We shall consider examples of various operational means and how they impart the processes their defining characteristics. The difference in various operational means can be perceived in terms of how they utilize the *spontaneous tendency* in a thermodynamic system. A discussion of conditions for spontaneous tendency is in order.

A natural thermodynamic process proceeds in particular direction; its reversed direction is forbidden. There are two broad types of natural thermodynamic processes:

Pure dissipative processes, where work or dynamical energy (mechanical, electrical, coherent electromagnetic wave, etc.) is converted into heat or thermal energy.

Spontaneous processes towards internal thermodynamic equilibrium or towards internal and external thermodynamic equilibrium.

How does one determine which direction is spontaneous? What is spontaneity?

We do not *make* spontaneous processes happen. On the other hand, a process in the "forbidden" direction has to be made to take place. The key characteristics of spontaneous processes, therefore, is the absence of work and *active* heat source/sink. Spontaneous processes are thus defined to be possible changes in a system (a simple system or a composite system) which is either isolated or in interaction only with *passive* heat/pressure bath(s). To keep the discussion as simple as possible, the passive bath is taken to be an infinite heat/pressure reservoir.¹⁷

The maximum useful work theorem states that, for all possible changes of a system from state 1 to state 2 in interaction with a single (passive) heat/pressure reservoir at T_0 and P_0 and with work reservoir(s), the maximum (possible) useful work is

$${}_1(W_{max\ use})_2 = (E + P_0V - T_0S)_1 - (E + P_0V - T_0S)_2 \quad (6)$$

where E is the total energy, $E = \text{internal energy} + \text{dynamical energy}$. (A process which actually yields the maximum useful work is necessarily a reversible process. One can construct different reversible processes between the same end states; they will produce the same useful work.) Note that the useful work does not include work done by a system on the pressure reservoir. The useful work is the work done by the system that is transmitted to and stored in a work reservoir. (Or, it is the work supplied by a work reservoir and transmitted to the system, in the case that $W_{max\ use}$ is negative.)

Suppose ${}_1(W_{max\ use})_2$ is positive for a certain pair of end states 1 and 2. That is, ${}_2(W_{max\ use})_1$ is negative. According to the maximum useful work theorem, then, any possible process from state 2 to state 1, whether reversible or irreversible, must involve a work reservoir which supplies useful work to *make* the process 2→1 happen. That is, 2→1 can never happen spontaneously or naturally; natural 2→1 process is forbidden.

On the other hand the condition,

$$(E + P_0V - T_0S)_1 - (E + P_0V - T_0S)_2 > 0, \quad (8)$$

does not ensure the possibility of a spontaneous 1→2 process.¹⁸ Equation (8) is, therefore, the necessary condition for the spontaneous processes in the sense that when it is not satisfied the natural 1→2 process is forbidden, and when it is satisfied process 1→2 may occur spontaneously.

One may consider the following special cases of the necessary condition for spontaneous changes.

For pure mechanical systems, V is constant and S is constant (or S is zero). It follows, therefore,

$$E_1 > E_2 \quad (8a)$$

is the criterion for spontaneous change 1→2. Or,

¹⁷The discussion can be generalized to the case of finite heat/pressure bath.

¹⁸One may be able to argue that eq. (8) together with the conditions - state 2 is internally equilibrium and $E_1 > U_2 > U_0$ or $E_1 < U_2 < U_0$ - will guarantee the possibility of spontaneous 1→2 changes.

$$(\text{Potential energy})_1 > (\text{Potential energy})_2$$

in the case of a stationary mechanical object. "Newton's apple could not, by itself, jump back to the branch from which it fell."

For isolated thermodynamic systems interacting with neither a heat/pressure reservoir nor a work reservoir, V is constant and E is constant. The criterion for spontaneous change becomes,

$$(-T_0S)_1 > (-T_0S)_2$$

or

$$S_1 < S_2 \quad (8b)$$

The spontaneous change in an isolated system can only proceed in the direction of increasing entropy. This is, of course, the second part of the second law, which applies to an isolated system and to an "all-inclusive" (thus, isolated) aggregate of interacting systems.

Chemical reactions often proceed under the condition of constant pressure as a result of interacting with its heat/pressure reservoir. Denote the initial (reactant) state and the final (product) state as R and P respectively. $P_R = P_P = P_0$. The criterion for the direction of (spontaneous) reaction is then,

$$(H - T_0S)_R > (H - T_0S)_P$$

or

$$H_R - H_P > T_0(S_R - S_P) \quad (8c)$$

The reaction will proceed in the direction of decreasing enthalpy if the entropy change is small. (This is the empirical rule of Thomsen and Berthelot.) If the enthalpy change is small and the entropy difference is substantial, however, the reaction will advance in the direction of increasing entropy. If both enthalpy change and entropy change are substantial, then the direction of reaction will depend on the combined effects according to inequality (8c).

In the case that T_R and T_P are also equal to T_0 , the reaction is in the direction of decreasing Gibbs function,

$$G_R > G_P \quad (8d)$$

ANALYSIS OF QUASISTATIC PROCESSES

In the Joule experiment examples, we learn that, in transforming a real process without a path into a corresponding quasistatic process with a path, it is possible to preserve the essential nature, including its irreversibility, of the original process. (In turning a real process into one with a path, we are not in danger of making it more reversible. Although existence of a path is a necessary condition of reversibility, the mere creation of a path has no other bearing on whether a process is reversible or irreversible. It is the special *operational means* of the second kind, which endows reversibility on a process.) Since the Gibbs equation(s) can be applied to any quasistatic path, the device of representing a real process in term of its corresponding *quasistatic path* is a very useful one in analyzing thermodynamic processes.

6. REVERSIBLE QUASISTATIC ARTIFICE - REVERSIBLE QUASISTATIC PROCESSES

In THERMOSTATICS, we consider an idealized, nonphysical, quasistatic process, for which

$$\delta Q = TdS \quad (9)$$

$$\delta W_{ther} = PdV$$

$$\delta W_{dyna} = dW_{conservative} = d(\text{dynamical energy}) \quad (10)$$

The first law equation,

$$dE = dU + d(\text{dynamical energy}) = \delta Q - (\delta W_{ther} + \delta W_{dyna}) \quad (11)$$

can be simplified for such idealized processes. Subtraction of equation (10) from equation (11) yields,

$$dU = \delta Q - \delta W_{ther}$$

Substitution of equations (9),(3) into the above equation results in the Gibbs (fundamental) equation for the closed system,

$$dU = TdS - PdV$$

Equation (9),(3) the Gibbs (fundamental) equation and its corresponding fundamental function, $U = U(S,V)$, and the *entropy maximum principle* form the theoretical basis of *thermostatics*.

The requirement for the idealized reversible quasistatic process is, according to Zemansky(1957:43):

During a quasistatic process [reversible quasistatic process, according to our definition], the system is at all times infinitesimally near a state of thermodynamic equilibrium, ...

It is the condition of being *infinitesimally near* thermodynamic equilibrium at all times that leads to the validity of equations (9),(3).

Processes within a composite system driven by infinitesimally small potential gradients are examples of reversible quasistatic processes. (Idealized) condensation of saturated water vapor into saturated liquid water as a result of water coolant of very large (thermal) mass flow – thus its temperature remains nearly constant – at a temperature infinitesimally lower than steam temperature is one example. The maximum useful work of the composite systems remain unchanged during such processes; there is only an infinitesimally weak spontaneous tendency associated with the process. (The process is of course not practical, as it requires a condenser of infinitely large heat transfer area.)

General processes are driven by finite potential gradients within the (composite) system or/and by potential difference between the systems and their surroundings. There are two means¹⁹ to ensure, everywhere, forces (pressures) always nearly balanced, temperatures nearly equal, chemical potentials (concentrations) nearly uniform, ..., that the condition of *infinitesimally near* can be met: an artificial means

¹⁹In this paper only the classical problems of the processes toward (or away from) *internal thermodynamic equilibrium* as a result of internal potential gradients and the processes toward (or away from) *external thermodynamic equilibrium* as a result of potential differences between the systems and their surroundings are considered. There exist, however, another operational means – the *internal work coupling* operational means (to be introduced elsewhere (Wang 1992)) – which brings about *reversible change* within a system that *does not* proceed toward equilibrium states.

adopted in *thermostatics*, and an operational means of the second kind using “reversible coupling.”

The artificial means adopted in thermostatics relies on having the systems in interaction with a sequence of reservoirs to ensure the near “balancing” of forces, or temperatures, or chemical potentials, throughout the reversible quasistatic process.

Mechanical Reversible Quasistatic Processes

We consider again the problem of turning the Joule “micro” free-expansion process into a reversible (quasistatic) process. Instead of having the piston rod/transmission means connected to a mechanical energy storage means, we shall modify the piston rod into a piston-rod-piston set (see Fig. 2), which is connected to a sequence of pressure reservoirs. The ideal gas is still in thermal interaction with a very large heat bath, thus remains isothermal. Let the initial state of the ideal gas be denoted by subscript N and the final state be by subscript 0 and let V_0/V_N be still equal to 2. Let the ratio of piston area in contact with the ideal gas subsystem to piston area in contact with pressure reservoirs be c .

The $N+1$ pressure reservoirs are then at $cP_N, cP_{N-1}, cP_{N-2}, \dots, cP_1, cP_0$, where P_N is the initial pressure and P_0 is the final pressure of the ideal gas. During the $N \rightarrow 0$ reversible quasistatic process, the series of N pressure reservoirs – cP_{N-1}, \dots, cP_0 – is used. The maximum useful work associated with $N \rightarrow 0$ process,

$$\begin{aligned} & [(U + P_0V - T_0S)_{gas} + (P_0V)_{vac}]_N - [(U + P_0V - T_0S)_{gas} + 0]_0 \\ & = T_0(S_0 - S_N) \end{aligned}$$

is not realized in the isothermal reversible quasistatic process; it is “stored” in the series of N pressure reservoirs in the form:

$$P_{N-1}(V_{N-1} - V_N) + P_{N-2}(V_{N-2} - V_{N-1}) + \dots + P_0(V_0 - V_1) \quad (12)$$

$$\left[\approx \int_N^0 P dV = T_0(S_0 - S_N) = mRT_0 \ln 2 \right]$$

(Recall equation (4).) Since the composite system remains isothermal and its internal energy remains constant, the energy in the “stored work” in the series of N pressure reservoirs is derived from heat absorption from the very large heat bath,

$${}_N W_0 = {}_N Q_0 = T_0(S_0 - S_N)$$

where ${}_N Q_0$ is, of course, equal to $T_0(S_0 - S_N)$, because process is reversible.

The reverse process, $0 \rightarrow N$, can be effected by using the series of pressure reservoir: cP_1, cP_2, \dots, cP_N .

Thermal Reversible Quasistatic Processes

A problem parallel to the mechanical reversible quasistatic process is the cooling of a finite thermal mass under constant pressure, $P = P_0$. This is a classical problem described in many thermodynamics texts as an example of “quasistatic increase [or, decrease] of temperature” (Lee and Sears 1963:7).

Let thermal mass system be initially at T_N . It is then brought into thermal contact, in sequence, with a series of large heat baths having temperatures: $T_{N-1}, T_{N-2}, \dots, T_1, T_0$ (see Fig. 3). The thermal mass system thus is transformed to the final state at T_0 . The maximum useful work associated with process $N \rightarrow 0$

$$(H_N - H_0) - T_0(S_N - S_0)$$

is again "stored" in the N heat baths. The increase in the total entropy of the heat baths is,

$$\frac{-{}_N Q_{N-1}}{T_{N-1}} + \frac{-{}_{N-1} Q_{N-2}}{T_{N-2}} + \dots + \frac{-{}_1 Q_0}{T_0} \quad (13)$$

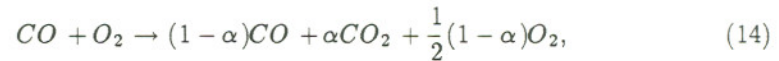
This is approximately equal to the entropy decrease of the thermal mass system,

$$\int_N^0 \frac{\delta Q}{T} = \int_N^0 \frac{dH}{T} = \int_N^0 dS = S_0 - S_N$$

The (approximate) equality applies, again, because process is reversible.

Chemical Reversible Quasistatic Processes

Chemical change can be effected in exactly the same manner. Consider a reactant mixture of gaseous CO and O_2 , which is made to follow a constant-pressure quasistatic path,



where α is the degree of reaction. Let $\alpha_N = 0$, i.e., the initial state of the reactant mixture, and α_0 be the degree of reaction for the product mixture at chemical equilibrium. The partial pressure of the three species are,

$$\begin{aligned} P_{CO} &= [(1 - \alpha)/(1.5 - 0.5\alpha)]P, \\ P_{CO_2} &= [\alpha/(1.5 - 0.5\alpha)]P, \\ P_{O_2} &= [0.5(1 - \alpha)/(1.5 - 0.5\alpha)]P, \end{aligned} \quad (15)$$

Change in the chemical system to its chemical equilibrium state is effected by the reversible quasistatic artifice: bring the chemical system in interaction through appropriate semipermeable membranes, in sequence, with N sets of mass reservoirs - $(P_{CO})_{N-1}, (P_{CO_2})_{N-1}, (P_{O_2})_{N-1}; \dots; (P_{CO})_1, (P_{CO_2})_1, (P_{O_2})_1; (P_{CO})_0, (P_{CO_2})_0, (P_{O_2})_0$. (See Fig. 4.) Subscripts, N-1, N-2, ..., 1, 0, denote partial pressures corresponding to $\alpha_{N-1}, \alpha_{N-2}, \dots, \alpha_1, \alpha_0$ according to equation (15). The system is also in thermal contact with a constant temperature heat reservoir, T_0 .

All diffusion processes take place across infinitesimally small differences in chemical potential, μ . Heat transfer takes place across infinitesimally small temperature difference. The process is therefore reversible. Heat absorbed by system from the heat reservoir is,

$${}_N Q_0 = -T(S_N - S_0)$$

Or, heat rejected by system is $T(S_N - S_0)$. Decrease in Gibbs function, or Gibbs potential, is

$$\int_N^0 dG_{sys} = \int_N^0 \sum_{i=1}^3 \mu_i dn_i = - \int_N^0 \left[\sum_{i=1}^3 \mu_i \nu_i \right] d\alpha \quad (16)$$

This decrease in system Gibbs potential is balanced by gain in Gibbs potentials in the 3N mass reservoirs.

In the above three examples, the spontaneities in the forms of force (pressure) difference, temperature difference, and the affinity of chemical reaction,

$$A = - \left[\sum_{i=1}^3 \mu_i \nu_i \right] d\alpha$$

are *neutralized* by reversible quasistatic artifices, with maximum useful works associated with these spontaneities “stored” in series of reservoirs. (See expressions (12), (13), (16).) These processes are artificial, purely theoretical inventions for the creation of the mathematical theory of thermostatics. These are *not* energy conversion processes. We define *thermodynamic processes* to be consisting of these artificial *reversible quasistatic processes* and *energy conversion processes*. In the rest of the paper, we consider examples of energy conversion processes and their operational means.

7. RELAXATION-OF-CONSTRAINT OPERATIONAL MEANS – IRREVERSIBLE QUASISTATIC PROCESSES

Most processes occurring in nature, once initiated, proceed spontaneously without following paths. The initiation actions – removal of mechanical constraint, opening of a valve, adding catalyst, a spark, ... – are the operational means of first kind, which bring about energy conversion processes. To transform such real processes into ones with paths for theoretical convenience, we introduce the *relaxation-of-constraint* operational means, which is basically repeated initiation actions that permit only small changes in a system between two very close equilibrium states. Repeated removal of thermal insulation and putting it backing after a short time is one example. Repeated introduction of catalyst and then anticycatalyst is another example. What it produces as a result is a dense succession of equilibrium states:

A quasi-static process is thus defined in terms of a dense succession of equilibrium states (Callen 1985:96).

This is the other popular definition of “quasistatic process.” This is, however, a quite different definition of “quasistatic process,” which, without requiring the condition of *infinitesimally near* thermodynamic equilibrium *at all time*, does not ensure reversibility of the “quasistatic process.” Neighboring states may be in thermodynamic equilibrium near each other; when the system disappears from the initial equilibrium state after the removal of constraint, it may not be infinitesimally near either equilibrium state before it settles into the “final” equilibrium state. Only the near elimination of potential gradients or potential differences will ensure that.

Mechanical Irreversible Quasistatic Processes

The irreversible quasistatic processes of Joule’s “micro” free expansion was already considered previously. Let the initial state be denoted now by subscript N , and be final state be 0. The irreversible process is adiabatic,

$${}_N Q_{N-1} = 0.$$

For this particular process (because of piston expansion against vacuum),

$${}_N W_{N-1} = N(W_{use})_{N-1}$$

Without transmission means and work reservoir (without a shaft), the useful work (or, the shaft work) is zero. Therefore,

$${}_N W_{N-1} = 0.$$

The dense succession of equilibrium states brought about by the relaxation-of-constraint operational mean defines an irreversible process, for which

$$\delta W \neq PdV$$

With the generation of turbulent eddies during each "micro" quasistatic step the gas is not internally reversible at all times. Unless the system achieves internal irreversibility, work is not a path function.

It follows then,

$$U_0 = U_1 = \dots = U_{N-1} = U_N$$

The ideal gas subsystem proceeds along the same path as the above reversible quasistatic process. The maximum useful work

$$T_0(S_0 - S_N) (\neq NQ_0)$$

(and the spontaneity) is neither utilized nor "stored." It is "wasted."

Mechanical Irreversible Quasistatic Processes in Composite System - The Operational Means of the Third Kind

The mechanical process problem inspired by Joule's experiment is a special problem selected for the theoretical convenience that the piston expands against a vacuum. In general mechanical processes, a piston expands either against external pressure reservoir, or against gas that fills the chamber on the other side of the piston. Callen(1985:53-54) considered the latter problem of a system made up of adiabatic wall/piston, and pointed out that it is "a unique *indeterminate* problem."

Consider a mechanical composite system made up of two compartments filled with 0.001 kmole of monatomic gas in each compartment, separated by an adiabatic piston. All walls are also adiabatic. Let us make the following specification:

Initial conditions for gas in first compartment	Initial conditions for gas in second compartment
$V_1 = 0.0139m^3$	$V_2 = 0.0499m^3$
$T_1 = 500K$	$T_2 = 300K$
$P_1 = 300,000Pa$	$P_2 = 50,000Pa$

(See Fig. 5) We now let the piston move by small displacement, $dV_1 = V_{1,j+1} - V_{1,j}$. Since, again, there is no transmission means, no shaft, and no work reservoir, the useful work is zero. The net force on the piston is finite. In the above problem, all the gaseous expansion work on the piston is converted back into gaseous turbulent eddies, since the vacuum can not absorb energy. Turbulent eddies are eventually converted into thermal internal energy in the gas. In the present case, gases in *both* compartments can absorb this gaseous expansion work, thus the indeterminate nature of the problem.

Suppose that right after the piston motion, gas 1 experiences isentropic expansion cooling and gas 2 experiences isentropic compression heating:

$$T_{1s,j+1} = T_{1,j} (V_{1,j}/V_{1,j+1})^{k-1}$$

$$T_{2s,j+1} = T_{2,j} [V_{2,j}/(V_{2,j} - dV_1)]^{k-1}$$

The corresponding internal energies right after piston motion are $U_{1s,j+1}$ and $U_{2s,j+1}$. It is obvious that these internal energies are less than the original total internal energy,

$$U_{1s,j+1} + U_{2s,j+1} < U_{1,j} + U_{2,j}$$

Let the difference between them be dU_{mech} , which exists in the form of mechanical (turbulent) eddy kinetic energy, distributed between gas 1 and gas 2:

$$E_{1,j+1} = U_{1s,j+1} + f \cdot dU_{mech}$$

$$E_{2,j+1} = U_{2s,j+1} + (1-f) \cdot dU_{mech}$$

Eventually, all the eddy kinetic energy are converted into thermal internal energy, $U_{1,j+1} = E_{1,j+1}$ and $U_{2,j+1} = E_{2,j+1}$.

The theoretical determination of the mechanical energy distribution, f , can only be made by solving the Navier-Stokes equations, i.e., using the operational means of the third kind. In this example, the construction of a simple "quasistatic" process requires tools consisting of : first law, second law, relaxation-of-constraint operational means, and operational means of the third kind in the form of the governing equations (Navier-Stokes equations).

The actual solution of the governing equation(s) is not always practical. However, even by simply assigning an arbitrary value of f , we are effectively using the operational means of the third kind to remove the indeterminate nature as pointed out by Callen. Three cases corresponding to $f = 0.2, 0.5, 0.8$ are showing in Figures 6a, 6b, and 6c. Mechanical equilibrium states are defined by $P_1 = P_2$, at which entropy (versus V_1) reaches maximum.

Thermal Irreversible Quasistatic Processes

Cooling of the same finite thermal mass considered above between the same initial and final state is now effected by a *thermal conducting bridge* that links the system to a heat reservoir at T_0 . A movable thermal insulation separates the thermal conducting bridge from the system. A quasistatic path is obtained by the repeated pulling out the insulation for short time then putting it back, thus $|{}_j Q_{j-1}|$ amount of heat is removed from the system each time. (See Fig. 7.) This amount of heat, once removed from the system, flows through the thermal conducting bridge and deposits in the heat reservoir, T_0 .

The same amount of heat as the above example in section 6, $H_N - H_0$, is rejected by the thermal mass system. In contrast with the mechanical processes, the closeness of neighboring equilibrium states during irreversible quasistatic process does make the thermal system internally reversible, thus the equality,

$$\delta Q/T = dS$$

is applicable in the quasistatic thermal process. Still, the applicability of equation(9) does not mean, in the present case, that the process is reversible. The present process *is* irreversible, because process in the conducting bridge, outside the system, is irreversible. The maximum useful work,

$$(H_N - H_0) - T_0(S_N - S_0),$$

is neither utilized nor "stored." It is "wasted."

Chemical Irreversible Quasistatic Processes

Repeated introduction of catalyst and anticycatalyst in the CO, O_2, CO_2 mixture can bring about irreversible quasistatic change: $\alpha_N \rightarrow \alpha_{N-1} \rightarrow \dots \rightarrow \alpha_1 \rightarrow \alpha_0$. The idealization of chemical reaction into irreversible quasistatic process was first recognized by W. Schottky. The chemical system experiences the same loss (decrease) in Gibbs potential as the above reversible quasistatic process, given by equation (16), or

$$G_R - G_P = G_N - G_0 = (H - TS)_N - (H - TS)_0$$

The value of heat rejection by the chemical system is, however, completely different from the above case,

$$|{}_N Q_0| = H_R - H_P = H_N - H_0$$

which is typically much greater than $T_0(S_N - S_0)$. We may define a virtual point V and S_V by

$$H_N - H_0 = T_0(S_V - S_0)$$

Process, $N \rightarrow 0$, is shown schematically in Figure 8b. The value of heat rejection is shown as the shaded area in Figure 8b. The value of heat rejection for the reversible quasistatic process is shown as the shaded area in Figure 8a for comparison.

In the four examples in this section the spontaneities in the form of pressure difference, temperature difference, and the affinity of chemical reaction (Gibbs free energy) are *wasted*. No useful work are produced.

8. (PERFECT) COUPLING OPERATIONAL MEANS - REVERSIBLE PROCESSES

The production of motion in steam-engines is always accompanied by a circumstance on which we should fix our attention. This circumstance is the re-establishing of equilibrium in the caloric; ... (Carnot 1824:6).

The "re-establishing of equilibrium," the spontaneity toward equilibrium gives the opportunity for the production of useful work. With a perfect "control" of the spontaneity, one achieves *reversible (energy conversion) processes*. The perfect "control" is a perfect external heat-and-work coupling operational means that overcomes and utilizes every potential gradient and every potential difference by linking the system frictionlessly to a work reservoir, thus yields maximum useful work.

Mechanical Reversible Energy Conversion Processes

A frictionless piston, piston rod, cam, cam shaft, and linkage to the work reservoir (see Fig. 1) are the perfect coupling operational means of the second kind. Details of the example are already discussed in section 2. The spontaneity of the system in its initial state is fully utilized to absorbing heat from the heat bath and transforming it completely into useful work (mechanical energy) in the work reservoir.

Thermal Reversible Energy Conversion Processes

While the coupling operational means for the mechanical process consists of the obvious piston rod, cam shaft, etc., the construction of the coupling operational means for the thermal process requires real intellectual exercise. The answer is of course the Carnot heat engine (see Fig. 9), which "transfers" heat

$$H_N - H_0$$

from the thermal system reversibly and transforms part of it,

$$(H_N - H_0) - T_0(S_N - S_0),$$

into useful work in the work reservoir, and the rest,

$$T_0(S_N - S_0),$$

in the form of heat "transferred" to the T_0 heat reservoir.

The chemical reversible energy conversion process example will be discussed in section 10. It is clear that the existence of a path (a quasistatic path), though a

necessary condition for both reversible quasistatic processes and reversible energy conversion processes, is insufficient by itself to define a reversible process. It is the perfect coupling operational means of the second kind that gives the defining characteristics of reversible energy conversion processes: system frictionlessly coupled to work reservoir, every potential difference kept infinitesimally small, spontaneity fully utilized to produce maximum useful work. The discussion in section 6, 7, 8 may be summarized as follows:

	<i>Reversible quasistatic process</i>	<i>Irreversible quasistatic process</i>	<i>Reversible energy conversion process</i>
<u>Operational means (artifice)</u>	Reversible quasistatic artifice	Relaxation-of-constraint operational means	Perfect coupling operational means
<u>Spontaneity</u>	Neutralized	Wasted	Fully utilized
<u>Irreversibility</u>	Eliminated	In the thermal case, irreversibility occurs outside the system; in the mechanical case, irreversibility may occur inside as well as outside the system	Overcome
<u>Useful work</u>	"Stored"	nil	Maximum useful work produced
<u>Heat & work as path functions</u>	Yes	Heat is path function in the thermal case; work and heat are, however, not path functions in the mechanical case	Yes ²⁰

²⁰ According to maximum useful work theorem, integrals of useful work and work along different paths between the same end states are equal

9. INTERNAL REVERSIBILITY

An interesting point may be noted that in the thermal irreversible quasistatic process example, the first part of the quantitative second law,

$$dS = \delta Q/T$$

remains applicable, even though the process is *irreversible*. The irreversibility is, as noted, entirely outside the system proper. Reversibility is, therefore, not a necessary condition for the applicability of equation (9); though, it is of course a sufficient condition for its applicability. Internal reversibility during a process *is* the necessary and sufficient condition for the first part of the second law,

$$dS = (\delta Q/T)_{\text{internal reversibility}}$$

The existence of a quasistatic path is a necessary, but not a sufficient condition for the applicability of equation (9).

COMMENTS ON SELECTIVE FURTHER EXAMPLES

10. ISOTHERMAL COMBUSTION AND REVERSIBLE COMBUSTION HEAT ENGINE

The simple use of piston rod, cam/cam shaft, etc., transforms a mechanical process into reversible energy conversion process. The Carnot heat engine transforms a thermal process into reversible energy conversion process.

A perfect coupling operational means will also transform chemical change into reversible energy conversion process, involving combustion heat release as a part of the process. Details of such operational means are presented elsewhere (Wang et al. 1992). A brief summary is given in the following.

Reversible chemical energy conversion process can be constructed in two steps: $N \rightarrow V$ and $V \rightarrow 0$ (recall the definition of V in section 7). We shall rename the two steps as $1 \rightarrow 2$ and $2 \rightarrow 3$, where 2 is the previously defined virtual state, V . Again $T_1 = T_3$ and $P_1 = P_3$. In step $1 \rightarrow 2$, each species ($j=1,2$) leaves the reactant box at partial pressure $P_{j,1}$ and undergoes isothermal expansion in an expander to a state at pressure $P_{j,2}$. Expansion is kept isothermal by absorbing heat from an isothermal heat bath. The extent of isothermal expansion $P_{j,1} \rightarrow P_{j,2}$, is chosen that $P_{j,2}$ equals to the partial pressure of the j species in the T_3, P_3 chemical equilibrium mixture in the van't Hoff reaction box. Each species then enters reversibly the van't Hoff reaction box where reversible chemical reaction $2 \rightarrow 3$, takes place.

As shown in Figure 10, which should be compared with Figures 8a and 8b, state 2 is now a real state with S_2 being the sum of entropies of all reactant species after the expanders and before entering the van't Hoff reaction box. State 2 is then the collective state of the reactant species entering the reaction box. State 3 is the state of the product leaving the reaction box. With expansion processes being isothermal, enthalpy of the ideal gaseous reactant species remains unchanged,

$$H_2 = H_1$$

The amount of heat release in the van't Hoff reaction box is, therefore,

$$|Q| = -_2Q_3 = H_2 - H_3 = T_1(S_2 - S_3) = H_1 - H_3$$

which is same value as the heat of reaction, $-_R H_P$, for the isothermal irreversible combustion (the shaded area in Figure 8b). This heat is temporally absorbed in the heat bath, which channels the amount,

$$T_1(S_2 - S_1)$$

of heat to the isothermal expanders, which is in turn converted completely into useful work,

$${}_1(W_{use})_3 = T_1(S_2 - S_1) \quad (17)$$

The rest of the heat - the excess heat - is either stored in the heat bath, or, transmitted outside to keep the whole composite system in steady state; in that case the rejection of excess heat by the whole composite system is

$$\begin{aligned} -{}_1Q_3 &= (H_1 - H_3) - T_1(S_2 - S_1) \\ &= T_1(S_2 - S_3) - T_1(S_2 - S_1) = T_1(S_1 - S_3) \end{aligned} \quad (18)$$

Equation (17) may be rewritten as

$${}_1(W_{use})_3 = (H_1 - H_3) - T_1(S_1 - S_3) = G_1 - G_3 \quad (17a)$$

Equations(17a) and (18) are the "litmus test" that confirms the chemical reaction transformation is reversible.

Reversible Combustion Heat Engine

As shown by Wang et al.(1992), P_3 can be selected that

$$S_3(T_1, P_3) = S_1 \quad (19)$$

This then eliminates the excess heat, ${}_1Q_3 = 0$. The reversible chemical reaction transformation becomes an adiabatic process that converts the heat of reaction completely into useful work!

Let T_0 and P_0 be temperature and pressure of the atmospheric heat/pressure reservoir. Let reactant at T_0, P_0 be denoted by subscript R0 and product at T_0, P_0 be denoted by subscript P0. A *reversible internal combustion cycle* can be constructed, consisting of:

- Isentropic compression of gaseous reactant mixture, R0→1
- Gaseous charge undergoes reversible chemical reaction, 1→2→3, where P_3 is selected according to equation (19)
- Isentropic expansion of gaseous product mixture, 3→4
- Isothermal compression (or expansion), 4→P0

A schematic diagram is shown in Figure 11. The net work output of the four-step cycle is

$$\begin{aligned} W_{use} &= -(H_1 - H_{R0}) + (H_1 - H_3) + (H_3 - H_4) - T_0(S_4 - S_{P0}) \\ &= (H_{R0} - H_{P0}) - T_0(S_{R0} - S_{P0}) = G_{R0} - G_{P0}, \end{aligned}$$

which is a special case of eqn.(6a). We have an operational construction of a heat engine cycle that yields maximum useful work, which *does not* depend on the selection of T_1 .

The celebrated Carnot-Kelvin formula, equation(7a), only applies approximately to irreversible combustion heat engine. The reason for peak temperature dependency of irreversible combustion heat engine is that irreversibility itself depends on combustion temperature. More discussion on this topic can be found in Wang et al. (1992).

11. PROCESSES IN FAR-FROM-EQUILIBRIUM THERMODYNAMIC SYSTEMS

The central concept involved in the discussion of quasistatic processes, spontaneity, useful work, etc., is the concept of equilibrium, including the concept of frozen equilibrium. In the study of physical thermodynamic systems, the end equilibrium states are given. The interesting question is how the change from one end state to the other end state is brought about. How the given end equilibrium state and the given end frozen equilibrium state are maintained is relatively straightforward.

It is clear that a biological system is not a system in thermodynamic equilibrium state. I do not know whether the thermodynamic question will turn out to be as useful when it is applied to biological studies as it is in the investigation of physical sciences. But it is obvious that if thermodynamics is to be useful in biology, a different focus – not equilibrium states, but far-from-equilibrium states – must be directed.

The work of Ilya Prigogine and his colleagues in the Brussels school has been devoted to this question: maintenance of thermodynamic systems far from equilibrium state. Their theory (Glansdorff and Prigogine 1971; Nicolis and Prigogine 1977) is the *theory of dissipative structure*, which maintains that thermodynamic (including biological) systems far-from-equilibrium are maintained by highly *dissipative* processes involving *active* heat, or pressure, or chemical sources/sinks. The theory is significant, as it is the only comprehensive theory-system at present that is potentially capable of providing a scientific basis for the manipulation of “living matters.”

It is interesting to note that the Brussels school uses governing equations of transport processes in their study of dissipative structure. *Thermodynamics practiced in the Brussels school* in effect adopts the reversible quasistatic artifice, relaxation-of-constraint operational means, and the operational means of the third kind as integral parts of thermodynamic theory. It does not find it useful, however, in the operational means of the second kind and the operational means of the fourth kind, both are capable of bringing about reversible energy conversion processes.

Overlooking of the operational means of the second kind is understandable, since even a casual observation indicates no external useful work linkage in the living world. Whether the operational means of the fourth kind – internal work linkage – is relevant to biological systems appears to be an (open) question worthy of further study. Thermodynamic systems at *steady-state* maintained by the operational means of the fourth kind is very different from the *dissipative structure*. It is more akin to a “*reversible structure*.” Further speculative discussion will be given elsewhere (Wang 1992).

EPISTEMOLOGICAL NATURE OF THE THEORY

12. ENERGY CONVERSION PARADIGM

The quantitative-descriptive theory of thermodynamics is not a mathematical theory. Is a nonmathematical theory an imperfect version of — thus, inferior to — a

mathematical theory, yet to be constructed?

Standing in awe of "the unreasonable effectiveness of mathematics in the natural sciences" (Wigner 1960), we often lose sight of one aspect of the use of mathematics, namely,

...behind the equations an enormous descriptive background through which the equations make connection with nature. This background includes a description of all the physical operations by which the data are obtained which enter the equations (Bridgman 1927:64).

The point is then not that a mathematical theory contains no verbal, descriptive, or instrumental operations, but that there is in a mathematical theory a clear *separation* of the descriptive operations in formulating concepts and equations from the mathematical operations in finding solutions, once the equation is formulated.

In a quantitative-descriptive theory, such separation of descriptive operations from quantitative operations is not possible. Instead of merely extracting solutions from the equation of motion, it is necessary to enlist simultaneously the application of the quantitative laws and the construction of the descriptive operation in our study of every individual energy conversion process. The two theories are different. The real question is then whether a mathematical theory or a quantitative-descriptive theory is uniquely appropriate in a scientific area, not which theory is better.

The mathematical theory gives a complete, all-inclusive description in an organized manner. It can be miraculously precise in its prediction, so precise that one has to wonder that it is true. Yet, in our rapture, we should not lose sight of the fact that a mathematical theory is a human invention, though esthetically a most perfect invention. It can be extraordinarily useful. But it is not truth.

In fact, a mathematical theory is rigid, thus fragile. With its predictions fixed, every new test is potentially deadly. A *verified* discrepancy between observation and prediction can force the abandonment of theory, at least the abandonment of the theory outside its useful domain. The rigid mathematical structure of the theory is not amendable to modifications in any fundamental way. Every challenge to the theory is necessarily a crisis.

A quantitative-descriptive theory is not all-inclusive. Nor, does it give a well-organized description. In contrast with the complete and well-organized nature of *mechanics* books, for example, the treatises on various subjects of energy conversion processes are specialized and bear little similarity to each other, although all are based on first law and second law. Think of a book on internal combustion engines, a book on heat transfer, and a book on combustion theory. Even a book on internal combustion piston engines can share little common ground with a book on internal combustion gas turbine engines. Treatment of furnace combustion shares little common ground with that of high explosives. Neither shows much similarity with treatment on rocket propulsion, or with treatment on spark-ignition combustion and compression-ignition combustion. All these energy conversion processes must obey the same first law and the same second law. They are *distinctive* processes within a common framework, because the operational means that bring about these processes are distinctive. More often than not, these distinctive operational means can not be described or represented in an "elegant" manner, to which a scientist used to mathematical theories is accustomed.

It may not be elegant, yet a quantitative-descriptive theory of energy conversion, I hold, is uniquely appropriate. It is obviously useful and enjoys the broadest applicability. That is, the first law and the second law are applicable to all energy conversion processes effected by the broadest possible variety of operational means. This is possible, because the quantitative first and second laws are not burdened by having to give causal, specific description with an inflexible mathematical structure.

The lack of specificity and causality in the two laws not only gives the laws their generality, but also is, I believe, connected with one epistemological aspect of the laws: In comparison with mathematical theories, the two laws came into existence due to less the invention of human, more the dictation of nature. Certainly they smell of their human origin, but their human origin— in the works of Carnot and Kelvin — has more to do with operational means, or the descriptive contents of the original second law, than with the quantitative contents of the two laws.

The quantitative contents of the first law and the second law, therefore, can be expected to be less fragile, more able to stand the supreme test of time than mathematical theories:

It [classical thermodynamics] is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown [Einstein, quoted in Schlipp (1959:33)].

The law that entropy always increases — the second law of thermodynamics — holds, I think, the supreme position among the laws of Nature. If someone points out to you that yourpet theory of the universe is in disagreement with Maxwell's equations — then so much the worse for Maxwell's equations. If it is found to be contradicted by observation — well, these experimentalists do bungle things sometimes. But, if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation (Eddington 1948:74).

The first law and the second law may be only accounting laws (energy accounting and availability accounting) rather than causal laws; they are *supreme accounting laws*. Einstein's and Eddington's conviction can only be boosted by the realization that, without the rigid mathematical structure, the two laws enjoy the flexibility of accommodating new observations.

We may recapitulate the discussion in the completed paradigm chart:

.....

Paradigm Chart

<i>Mechanistic Paradigm:</i>	<i>Energy Conversion Paradigm:</i>
(a) Reversible time	(a) Unidirectional time
(b) Dynamic laws are <i>causal</i> laws	(b) Thermodynamic laws are <i>acausal</i> laws
(c) Mathematical theory — laws and <i>EOM</i> are one and the same	(c) Quantitative-descriptive theory, made up of quantitative first law and second law, and operational means
(d) Predictions are all-inclusive, precise, and fixed; theory has to be accepted or rejected in whole	(d) First law and second law are supreme accounting laws; our knowledge of operational means is not all-inclusive

.....

If we agree with Eddington, we *can not* deduce from dynamics the supreme laws of thermodynamics, as Ludwig Boltzmann attempted in his aborted effort. In an ideal world, we attempt to make dynamics consistent with the supreme laws of thermodynamics. This is the point of view taken by Prigogine and the Brussels school, who have advanced *microscopic theory of irreversible processes* (Prigogine 1980; Prigogine and Stengers 1984), in which classical statistical mechanics and quantum statistical mechanics are to be made consistent with the second law of thermodynamics.

In a unideal world, it is even possible – in disagreement with Eddington — that a theory can be perfectly satisfactory and extremely useful even if it is not consistent with some “supreme laws.” Logical perfection, like elegance, is a luxury we can not afford sometimes.

13. IS THERE CAUSALITY?

The *causality principle* originated from Laplace’s proposition. The modern view of causality — even among those who still believe in it — is considerably modified. It is a controversial subject, which is usually discussed in the context of mechanistic paradigm. In that context, I have nothing to add.

Dynamical systems are not all isolated systems. If their interactions are of passive nature such as heat interaction, it is possible to take the aggregate of the interacting systems to be an isolated whole-system. An entirely different situation arises, however, if the interaction involves useful work interaction, which is brought about by *acausal* operational means, by human actions for example. Unless the acausal operational means can be eventually subjected to mathematical formulation, a possibility that we deny, the causality link is broken and the future of a dynamical system that is subjected to occasional acausal interactions is not “knowable”.

CONCLUSION: The Long Childhood

It is not surprising that the mechanistic paradigm, or physicalism, is abandoned in evolutionary biology, and in social sciences. What is surprising is that physicalism is rejected in thermodynamics, a branch of physics.

Only in this realization that we appreciate the momentous nature of the scientific revolution originated by Carnot. That revolution was temporarily aborted with the “capturing” of thermodynamics by Newtonianism. We now “rediscover” Carnot’s most original idea behind the concept of the reversible process: the operational means, especially the reversible energy conversion operational means. Our knowledge of the operational means is not all-inclusive. What were listed in section 4 is by no means a complete list — only the most important ones as I see it at the present time. The examples of operational means discussed throughout the paper are only small samples of the most tidy type.

The lack of comforting all-inclusiveness is compensated by the realization: On the one hand, the quantitative first law and second law are supreme laws that we can securely rely on for long, long time for the already extraordinarily broad range of problems. On the other hand, the list of operational means will grow as we continue observing nature for inspiration, inventing new processes, new devices, constructing new governing equations, etc., so that first law and second law can be used for increasingly even broader range of problems. The process will go on and the “book” on energy conversion will forever be an open one.

It seems in the nature of scientist/philosopher that he seeks all-embracing scheme, a cosmology, within which everything that exists could be shown to be systemat-

ically - logically and causally - interconnected. There were moments when this ambitious program seemed near completion. Many still believe in the noble goal: a definitive "book" of nature can be written.

Carnot is the quintessential engineer/inventor. I think there is something different in the nature of the engineer/inventor. No one can imagine that the patent office will one day be closed. I may not know the most effective way or the most productive area to construct/seek new operational means. One thing I am absolutely certain of, is that more and more operational means will be constructed and the tree of knowledge will continue growing.

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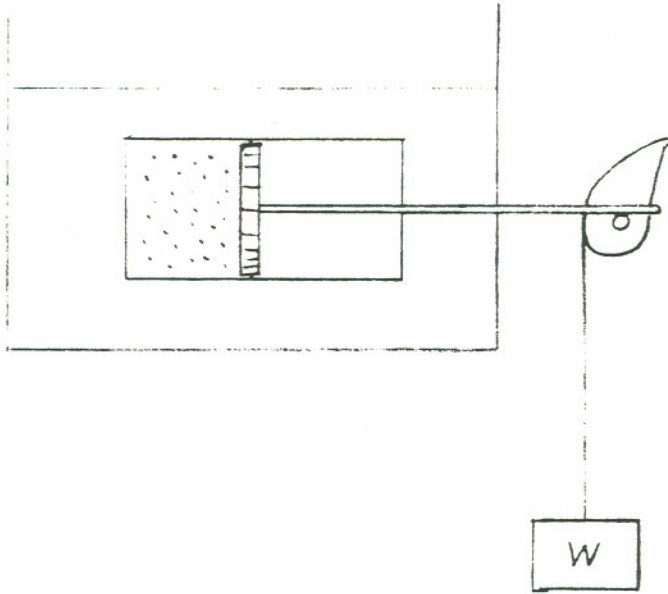


Fig 1

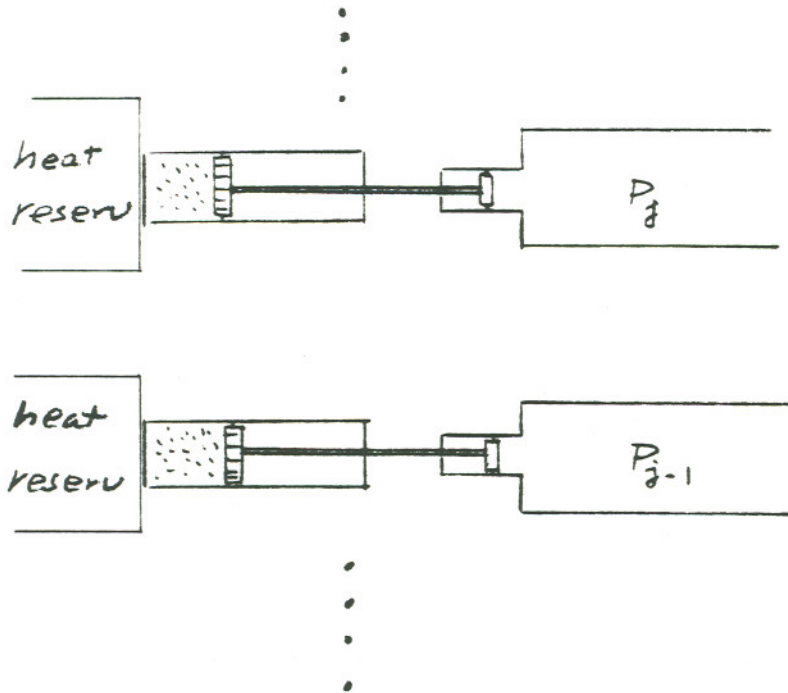


Fig. 2

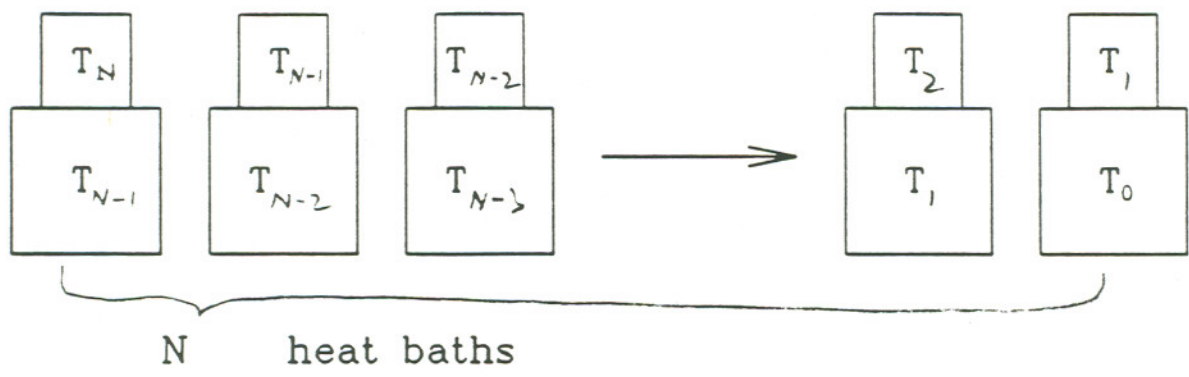


Fig. 3

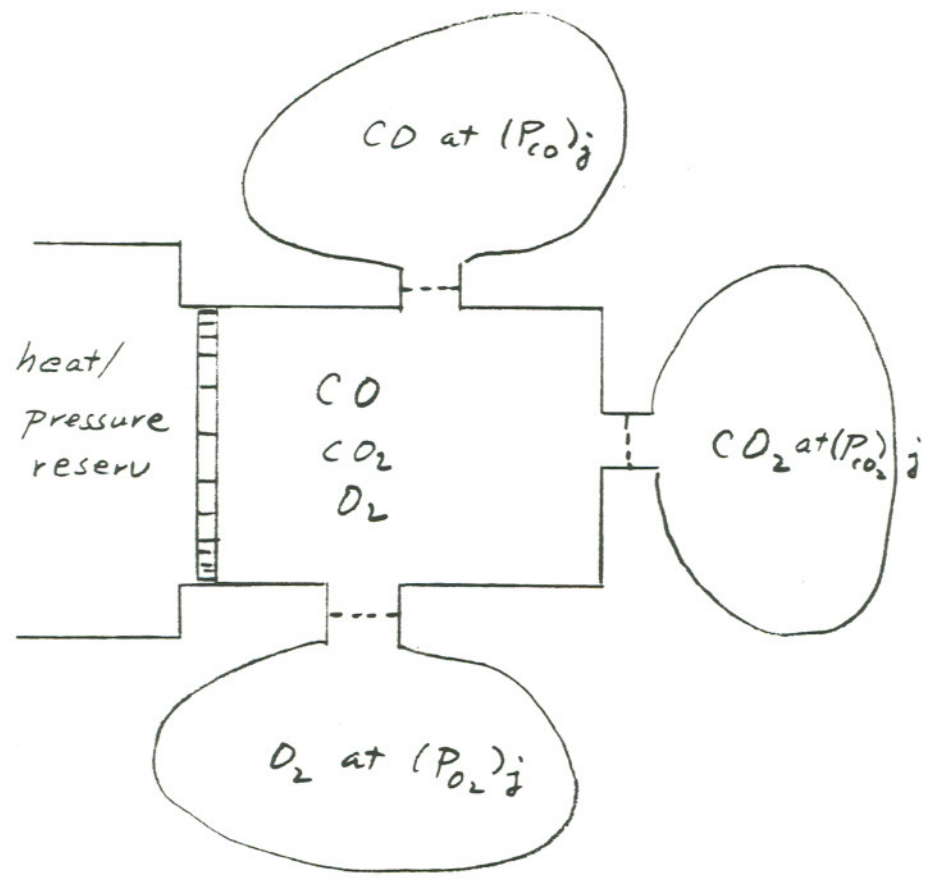
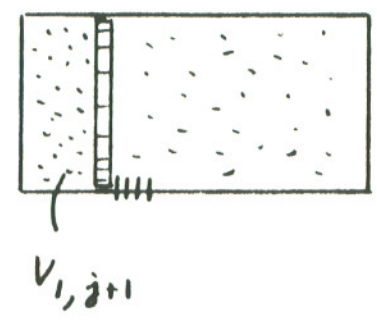
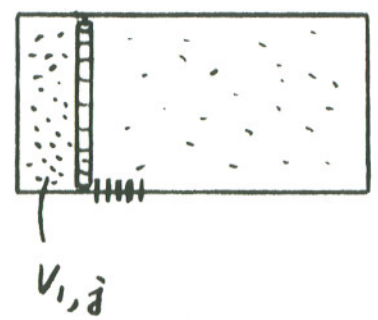


Fig. 4

Fig. 5



DISSIPATIVE FACTOR FU=0.2

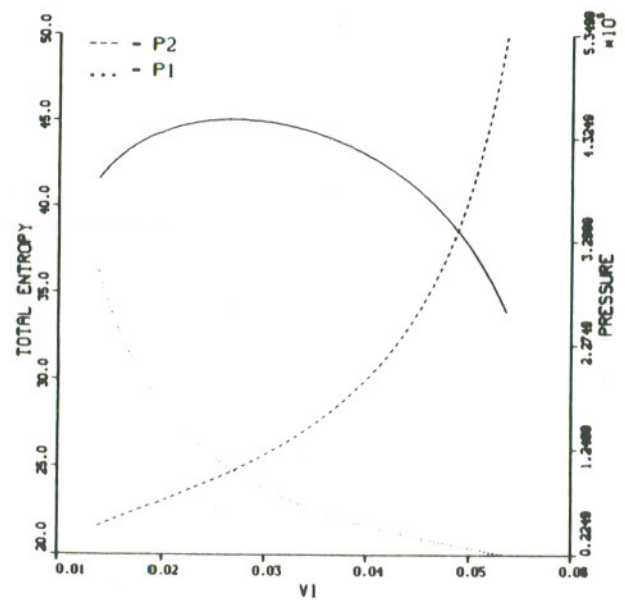


Fig. 6a

DISSIPATIVE FACTOR FU=0.5

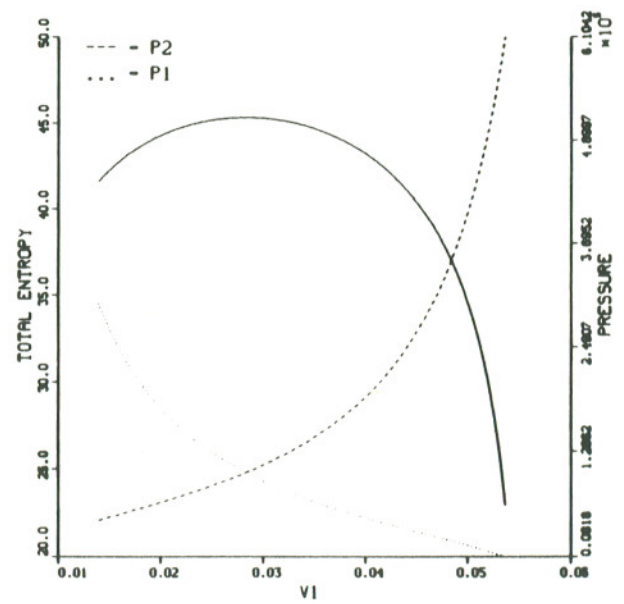


Fig. 6b

DISSIPATIVE FACTOR FU=0.8

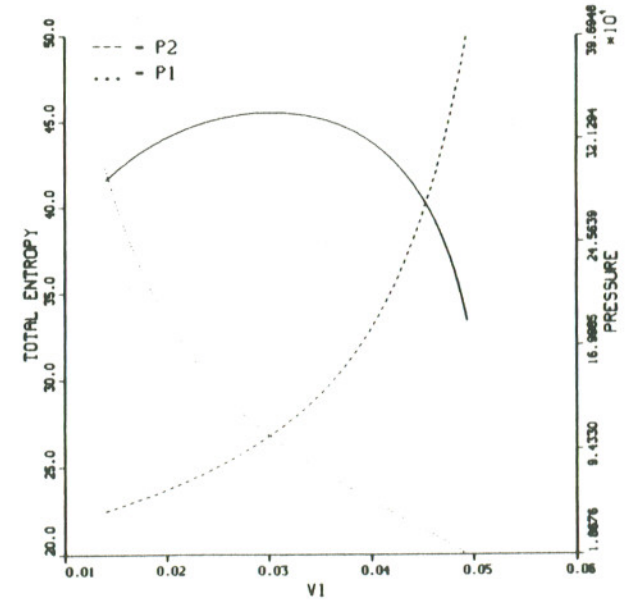


Fig. 6c

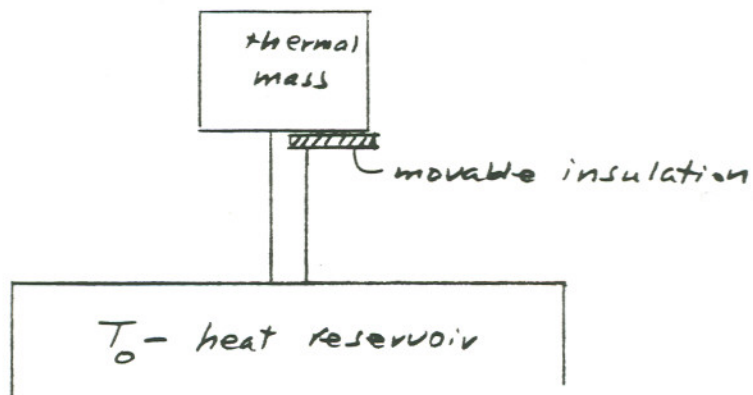


Fig. 7

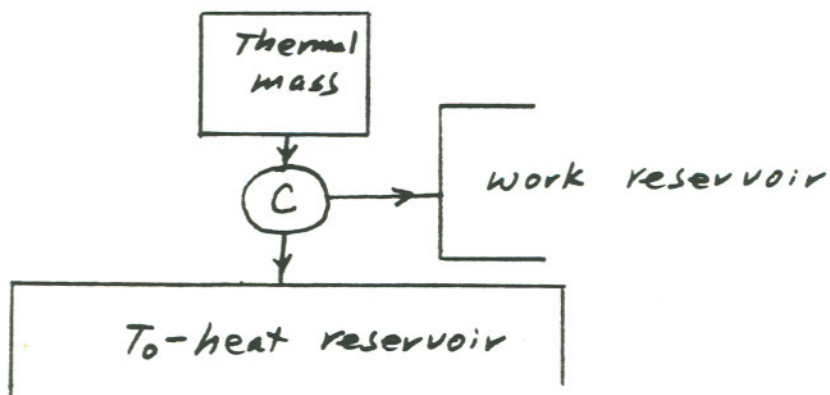
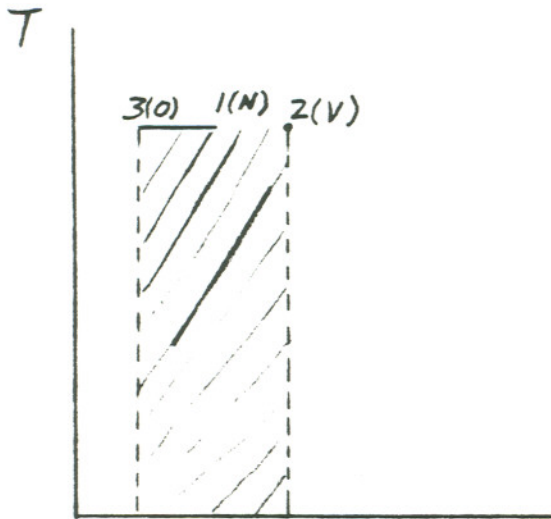
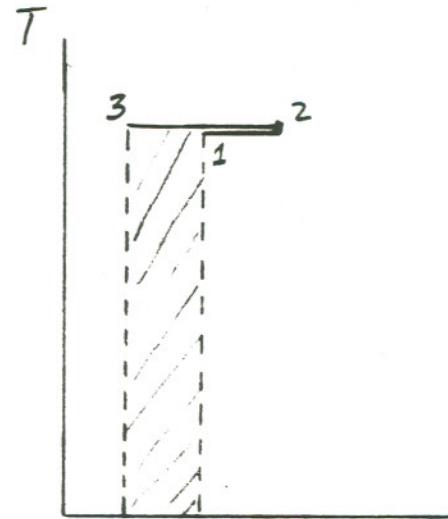


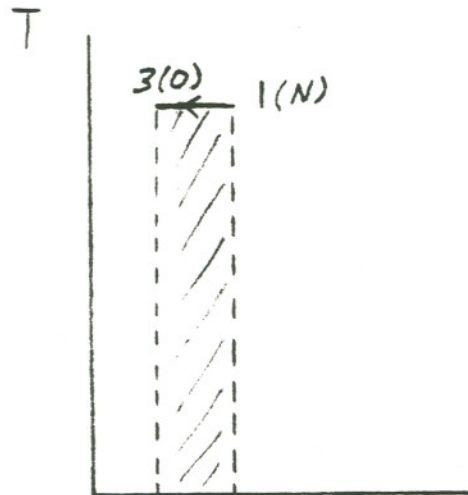
Fig. 9



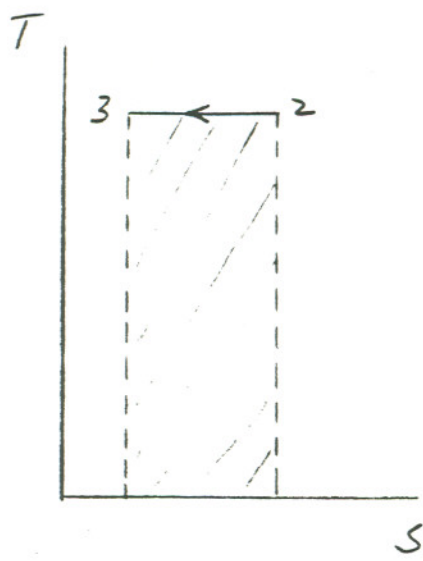
Irreversible Quasistatic Process
Fig. 8 b



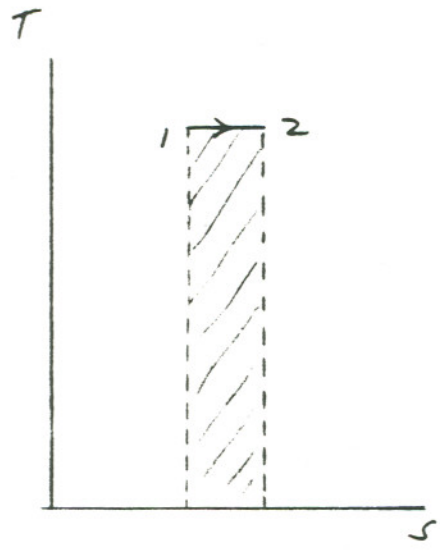
Reversible Energy Conversion Process
Fig. 10(c)



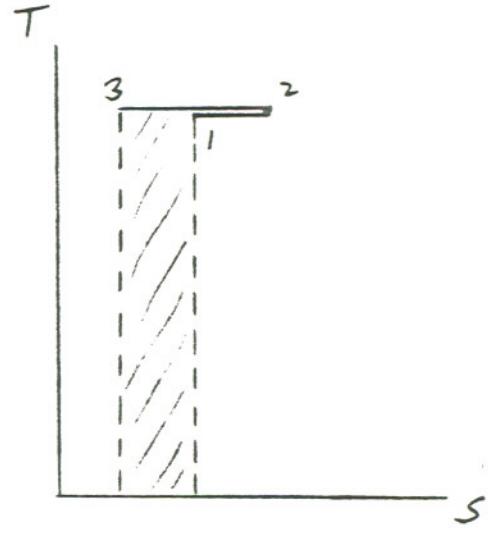
Reversible Quasistatic Process
Fig. 8 a



(a) heat released in reaction box

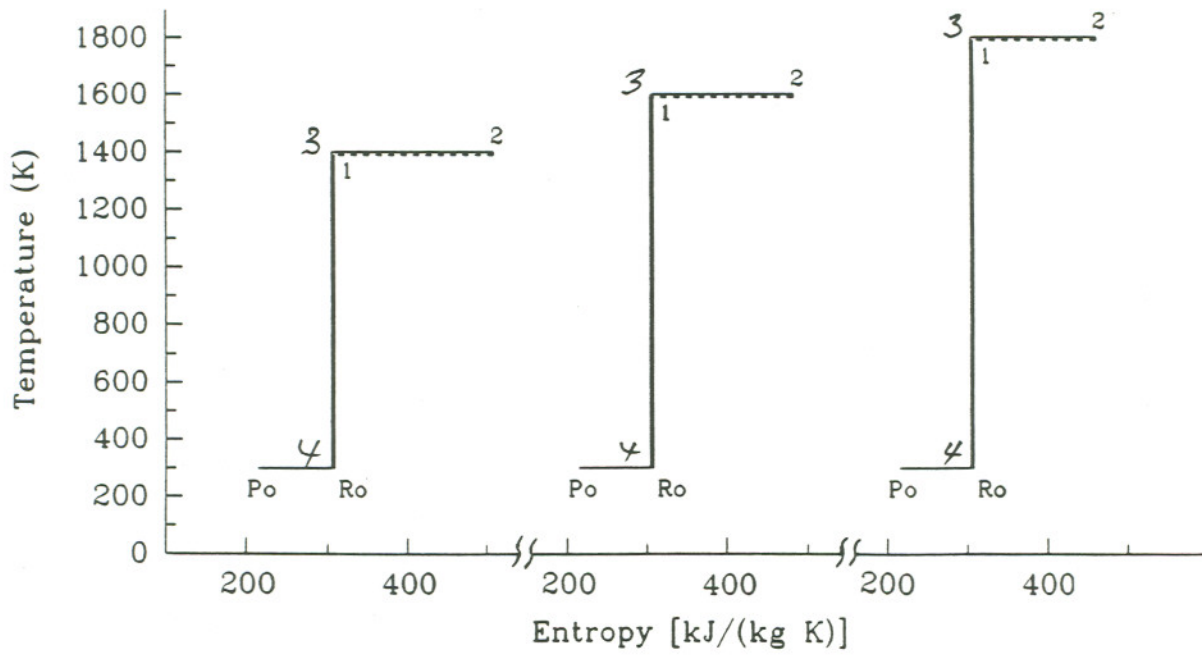


(b) heat absorbed by expanders



(c) net heat output of reversible $1 \rightarrow 2 - r \rightarrow 3$

Fig. 10



Reversible internal combustion heat engine Fig. 11