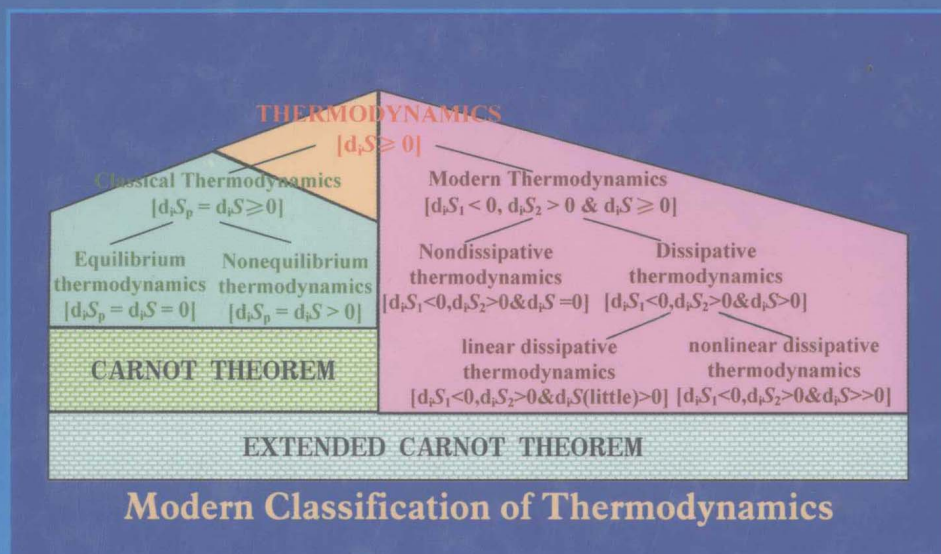


MODERN THERMODYNAMICS

BASED ON THE EXTENDED CARNOT THEOREM

Ji-Tao WANG



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Modern Thermodynamics

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Ji-Tao WANG



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Preface

A senior American Professor, C. Truesdell (1919—2000), said:

Every physicist knows exactly what the first and second laws mean, but it is my experience that no two physicists agree on them.

Based on my own experience in the last 20 years, Truesdall's experience or feeling was correct. It meant that nobody really understood "What is the second law of thermodynamics?" in the whole 20th century.

It is well known that **Carnot theorem** is the foundation stone of thermodynamics (especially of classical thermodynamics) and the starting point of the second law of thermodynamics. Carnot summarized daily macroscopic experiences of human beings in 1824. Carnot theorem could not be deduced from any basic law of other disciplines of science. Carnot theorem is that the efficiency of a reversible heat engine is the highest. Carnot theorem emphasized "reversibility" of Carnot cycle, and resulted in the establishment of thermodynamics for reversible processes (i.e. equilibrium thermodynamics) together with thermodynamics for irreversible processes (i.e. nonequilibrium thermodynamics) in classical thermodynamics. However, now it has been found that the general necessary and sufficient condition for the highest conversion efficiency of energy is "nondissipation" of process or system but not "reversibility" of process or system. This is an **extended Carnot theorem**. A nondissipative cyclical process (such as a nondissipative Carnot cycle) must be reversible, so the extended Carnot theorem has already included the Carnot theorem, but not vice versa. The extended Carnot theorem is an extended foundation stone of thermodynamics (especially of modern thermodynamics) and a new starting point of the second law in the current 21st century. The extended Carnot theorem results in the establishment of a new field of nondissipative thermodynamics (i.e. thermodynamics for nondissipative processes) together with dissipative thermodynamics (i.e. thermodynamics for dissipative processes) in modern thermodynamics.

Thermodynamics is a part of science doing research on energy and energy transformation, and its research objects are the change, development and evolution of macroscopic systems consisting of a large number of particles. It is well-known that the nature of the second law of thermodynamics is the irreversibility of time for the development of macroscopic systems, i.e. "arrow of time". However, Carnot theorem emphasized "reversibility". Such a paradox existed and lasted more than 180 years in the past. This was just the root of puzzlement in thermodynamics. Such a situation of advocating classicism and excluding modernization is rarely found in other disciplines of science, or we may even say that up to now this is unique.

In 1865, to introduce the cyclical process assumption on the basis of Carnot theorem, Clausius said:

In order to express analytically the second fundamental theorem in the simplest manner, let us assume that the changes which the body suffers constitute a **cyclical process**, whereby the body returns finally to its initial condition. . . .

Thus, the Clausius inequality or the entropy increase principle for isolated (or adiabatic) systems was obtained. That was the mathematical expression of the second law of classical thermodynamics. However, the “cyclical process” assumption was not included in Clausius inequality or the entropy increase principle at that time. Now the general mathematical expression of the second law of thermodynamics could be written in its entropy production form for any system, i.e. entropy production of any system is never negative [$d_i S \geq 0$]. Adding the “cyclical process” assumption into his mathematical expression, the mathematical expression of the second law in classical thermodynamics should clearly be written as [$d_i S_p = d_i S \geq 0$].

In the same famous paper, Clausius also said:

The second fundamental theorem, in the form which I have given to it, asserts that all transformations occurring in nature may take place in a certain direction, which I have assumed as positive, by themselves, that is, without compensation; but that in the opposite, and consequently negative direction, they can only take place in such a manner as to be compensated by simultaneous occurring positive transformations.

Clausius’ “compensation” is now called thermodynamic coupling. The system including only “positive” spontaneous process(es) “without compensation” is called uncoupling system, and the system including “negative” nonspontaneous process(es) “compensated by simultaneous occurring positive” spontaneous process(es) is called coupling system.

The first half of this citation confirmed the expression of [$d_i S_p = d_i S \geq 0$] for classical thermodynamics. That is, only simple uncoupling systems are considered in classical thermodynamics. Meanwhile, the second half of this citation meant that the mathematical expression of the second law in modern thermodynamics for complex coupling systems should be clearly written as [$d_i S_1 < 0, d_i S_2 > 0$ & $d_i S \geq 0$]. Thermodynamic coupling is the watershed between classical thermodynamics and modern thermodynamics. Here, $d_i S_1$ and $d_i S_2$ (or $d_i S_p$) are the entropy production of nonspontaneous process(es) and the entropy production of spontaneous process(es), respectively. $d_i S$ is the entropy production of the system, $d_i S = (d_i S_1 + d_i S_2)$. Of course, during Clausius’ time there were no terms of “classical thermodynamics” and “modern thermodynamics”, but there were still differences between uncoupling systems “without compensation” and coupling systems with compensation.

Based only on the extended Carnot theorem, on the local equilibrium approximation for description of nonequilibrium states and on mathematical expressions of the second law of thermodynamics mentioned above, a basic complete classification of the thermodynamics discipline can be presented by a building-image, as shown in Fig. 0.1. The whole of the thermodynamics building-image based on the extended Carnot theorem is more general than the classical one based on the Carnot theorem.

More progress in modern thermodynamics can be found in this book and in future work. The whole thermodynamics discipline, including classical thermodynamics and modern thermodynamics, seems to be so simple as said in 1881 by Gibbs:

One of the principle objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity.

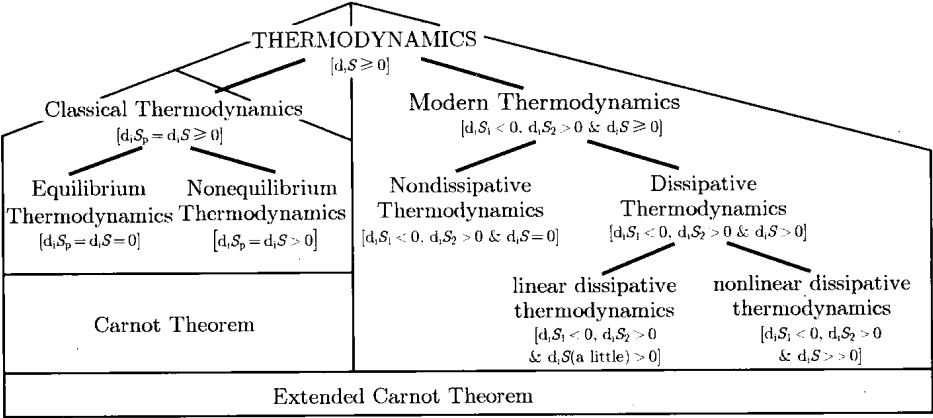


Fig. 0.1 A building-image of the complete thermodynamics discipline

This book can be used as a textbook in universities and colleges for the modernization of the thermodynamics discipline. There are not too much mathematical deductions in this book, so it is also suitable for readers to read and learn by themselves.

Based on the author’s experiences, the modernization of the thermodynamics discipline is not easy, so the book is written in three levels. The first level is about 800 words in **Preface**; the second level is an outline of about 8, 000 words in **Chapter 1**, which was originally a reply in 2006 to a reviewer, a person described in his own words as being “through my personal journey through the realm of equilibrium thermodynamics and nonequilibrium thermodynamics and through my own work therein over decades”; and the third level is the detailed discussions in other parts of the whole book. Thanks to a native British English speaking Ph.D., Dr. David Scott, for his English language corrections, which were made during his stay in Shanghai.

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Fudan University, Shanghai

Prof. Ji-Tao WANG
May 2009

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Chapter 1

An Outline of Modern Thermodynamics

Abstract Thermodynamics is a core part of science. Nearly all scientists should have a basic knowledge of thermodynamics. Thermodynamics is a science of development, and is a viewpoint on scientific development in natural sciences. The achievement of thermodynamics has influence not only on natural sciences, but also on social sciences and philosophy. Fundamental concepts and definitions are very important for any discipline of science, so what thermodynamics is and what the second law of thermodynamics is have become the key points of puzzlement in the thermodynamics discipline. It has been found that the root of puzzlement is the Carnot theorem. The Carnot theorem emphasized “reversibility”, but the nature of the second law of thermodynamics is “irreversibility”, i.e. “arrow of time”. The extended Carnot theorem emphasizes “nondissipation” and results in a new field of nondissipative thermodynamics, which belongs to the equality part of the second law of thermodynamics as well. Some fundamental concepts of thermodynamics are drastically changed.^[1]

1.1 Challenges to the Second Law of Thermodynamics Coming from Two Sides

At present, challenges to thermodynamics are coming from two sides. What is “thermodynamics” and what is “the second law of thermodynamics” may become the key points of puzzlement in thermodynamics.

Truesdell (1919–2000)^[2] was an American senior professor who wrote two books related to thermodynamics, “*The Tragicomical History of Thermodynamics, 1822—1854* (Springer, 1980)” and “*Rational Thermodynamics* (Springer, 1984)”.¹ He said that

Every physicist knows exactly what the first and second laws mean, but it is my experience that no two physicists agree on them.

At first glance, his words seemed to be inconsistent, but his experience might give him such a strong feeling. If such an experience or feeling was correct, it meant that the recognition of the second law of thermodynamics in the 20th century was puzzled and has continued to be so. At the beginning of the 21st century, challenges to the second law of thermodynamics are coming from two sides.

The book, “*Challenges to the Second Law of Thermodynamics: Theory and Experi-*

¹ http://en.wikipedia.org/wiki/Clifford_Truesdell. Cited 12 Oct 2008

ment",^[2] written by V. Capek and D.P. Sheehan in 2005 is a representation of challenges from one side. That book emphasizes that the second law

Once established, it settled in and multiplied wantonly; ... Not all formulations are equivalent, such that to satisfy one is not necessary to satisfy another. Some versions overlap, while others appear to be entirely distinct laws.

Thus, Capek and Sheehan listed 21 kinds of the so-called "second law of thermodynamics" and the "expressions of entropy". Alongside the statements and expressions proposed by Sadi Carnot, Lord Kelvin, Rudolf Clausius, Josiah Willard Gibbs, et al., they also confusedly listed Boltzmann "probability entropy", Shannon "information entropy", "entropy" defined by density functions of quantum mechanics and so on. Their list also included Clausius' "fundamental laws of the universe". Based on these, Capek and Sheehan proposed their "quantum challenges" and "gravitational challenges". Of course, these so-called "the second law of thermodynamics" and "entropy" extended by them are different from those accepted by most thermodynamicists. At least their "challenges" do not belong to the academic discipline of thermodynamics, but belong to "other kind of disciplines" out of thermodynamics.

On the other hand, challenges are coming from a few classical (traditional) thermodynamicists. They mainly aggrandize the role and applicability of classical thermodynamics, and want to limit applicability of thermodynamics to the same as that of classical thermodynamics, i.e. they regard classical (or traditional) thermodynamics as the whole of thermodynamics. For instance, *"Non-equilibrium Thermodynamics and the Production of Entropy — Life, Earth, and Beyond"*,^[3] edited by A. Kleidon and R.D. Lorenz in 2005, is a book in which all kinds of complex systems are intended to be treated by the "maximum entropy principle" on the basis of classical thermodynamics. In their preface they cited Einstein's famous words in 1949,

A theory is more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It 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.

In fact, Einstein only said that "within the framework of the applicability of its basic concepts, it (classical thermodynamics) will never be overthrown", but out of "the framework of the applicability of its basic concepts", classical thermodynamics may not be suitable anymore.

A new Chinese book on thermodynamics written by Z.-H. Lin in 2007^[4] may be taken as another example, in which the English name of thermodynamics, including "dynamics", was regarded as "morbidity (or unsuitable)". His reason was that there is "no time variable included in the theory of traditional thermodynamics", and he limited thermodynamics into the category of classical thermodynamics. Lin denied the objective existence of "classical thermodynamics" and "nonclassical thermodynamics" (i.e. "modern thermodynamics") by the quillet that thermodynamics is a macroscopic theory without partition of "classical" and "quantum". In Lin's book the usual classical thermodynamics was called "traditional thermodynamics". That may be OK. However, in that book once the name of "traditional thermodynamics" had been changed into "(traditional) thermodynamics" with a pair of

brackets, and once the brackets together with the word of “traditional” had further been deleted, “traditional thermodynamics” was immediately changed into the full discipline of “thermodynamics”. That is a distortion and may leave harmful impressions for young students. The macroscopic theory of thermodynamics may also be divided into a “classical (or traditional)” part and a “modern” part. This is the development of the thermodynamics discipline.

To sum up, what is “thermodynamics” and what is “the second law of thermodynamics” become the key points of puzzlement.

1.2 Root of Puzzlement: Carnot Theorem

Carnot theorem was the foundation stone of thermodynamics and classical thermodynamics. It was also the starting point of the second law of thermodynamics. The extended Carnot theorem is an extended foundation stone of thermodynamics and a new starting point of the second law in the current 21st century. The “reversibility” is not a general necessary condition for the highest conversion efficiency of energy, but “nondissipation” is really the necessary and sufficient condition for the highest conversion efficiency of energy.

It is well known that Carnot theorem and the basic laws of thermodynamics were established on the basis of a large number of human daily macroscopic experiences, but not deduced from any basic law of other disciplines of science. Carnot theorem was the foundation stone of thermodynamics and the starting point of the second law of thermodynamics. Carnot theorem told us: **the reversible heat engine is of the highest conversion efficiency of energy among all other heat engines working between the same hotter heat reservoir and the same colder heat reservoir.** That was an important human experience at that time (1824) summarized by Carnot. Now that more than 180 years has passed, the human experience has developed, and the framework and the deepness of applicability of thermodynamics are also in development. The research objects of thermodynamics have been extended from heat-work conversion into any kind of energy-conversion under thermodynamic consideration.^[5] For instance, the chemical energy of the reaction between methane (CH_4) and oxygen (O_2) in fuel-battery can be converted into electric energy. It can be imagined that if the chemical energy can completely convert into the electric energy without dissipation (i.e. 100 %), then its conversion efficiency must be the highest. Therefore, **the efficiency of any nondissipative process or system for macroscopic conversion of energy must be the highest.**^[6, 7] That is the **extended Carnot theorem**. Should we pursue a reversible fuel-battery for getting the highest conversion efficiency of energy? No, it is not necessary. Obviously, from the produced carbon dioxide (CO_2) and water (H_2O), and the electric energy released by the fuel-battery, it is impossible to obtain the equal amount of methane and oxygen consumed, because during the synthesis of methane a series of organic hydrocarbon like methane will inevitably be obtained. The “reversibility” in Carnot theorem is not a general necessary condition, but “nondissipation” is just the necessary and sufficient condition for the highest macroscopic conversion efficiency of energy.

Any nondissipative cyclical process must go back to its initial state, so nondissipa-

tive Carnot cycle must be reversible. Therefore, the extended Carnot theorem includes the Carnot theorem, but not vice versa. The extended Carnot theorem is the extended foundation stone of thermodynamics and a new starting point of the second law in the current 21st century.

The nature of the second law of thermodynamics is the irreversibility of time in the development of macroscopic systems, i.e. the characteristics of “arrow of time”. However, Carnot theorem did just emphasize “reversibility”. Such a paradox existed always in classical thermodynamics, and that is what is just the root of puzzlement in thermodynamics and the limitation of classical thermodynamics. Such a status lasted more than 180 years and has rarely been found during the modernization of other disciplines of science, or we may even say that up to now this is unique.

1.3 Uncertainty or Incompleteness of Clausius Inequality

If we first talk about the written statement of what “thermodynamics” is and what “the second law of thermodynamics” is, then the argument will be long lasting because the detailed written statements are at least a little different from each other in different textbooks on thermodynamics. In textbooks of physical disciplines, discussions on mathematical expressions are usually preferred. Therefore, we will first discuss the mathematical expression of the second law of thermodynamics, which is the core of thermodynamics.

Based on the development of thermodynamics in the 19th century and at the beginning of the 20th century, the following three kinds of mathematical expressions of the second law of thermodynamics for different systems are widely accepted.

1. Entropy increase principle for isolated (or adiabatic) macroscopic systems.

$$(dS)_{iso} \geq 0. \quad (1.1)$$

Here, $(dS)_{iso}$ is the entropy change of an isolated (or adiabatic) system.

2. Gibbs free energy decrease principle for isothermal isobaric macroscopic systems.

$$(dG)_{T,p} \leq 0. \quad (1.2)$$

Here, $(dG)_{T,p}$ is the Gibbs free energy change of an isothermal isobaric system.

3. Positive entropy production principle for any macroscopic systems.

$$d_i S \geq 0. \quad (1.3)$$

Here, the entropy change of system dS has been divided into two parts: The part of entropy production of the system $d_i S$ (the part of entropy change due to the irreversible processes inside the system), and the other part of entropy flow of the system denoted by $d_e S$ (the part of entropy change due to exchanges of energy and/or matter with the surroundings), i.e. $dS = d_i S + d_e S$. Under isothermal isobaric conditions, there is a relation between the entropy production and the Gibbs free energy change, i.e.

$$(dG)_{T,p} = -T d_i S. \quad (1.4)$$

Because the positive entropy production principle is suitable not only for isolated systems, closed systems and open systems, but also for isothermal isobaric systems and nonisothermal nonisobaric systems, it is called the general mathematical expression of the second law of thermodynamics. Another advantage of the positive entropy production principle is that the entropy production of a system is directly connected with the internal irreversible processes of the system, so the entropy production of a system is the sum of entropy productions of internal irreversible processes. Therefore, hereafter in this book our discussions are mainly based on the form of entropy production. If someone is not familiar with or is doubtful of the form of entropy production, please convert it into the form of Gibbs free energy under isothermal isobaric conditions by using Eq. (1.4), and it will be more easy to understand.

Note that temperature was defined and measured under heat equilibrium conditions, and the local equilibrium approximation had already been introduced since Carnot and Clausius discussed body with different temperatures. Here, “any macroscopic systems” should also satisfy the requirement of the local equilibrium approximation. If discussions are concerned with nonequilibrium systems, the local equilibrium approximation has already been included. Of course, the mathematical expression of the second law of thermodynamics could also be written in the form of the free energy decrease form: $(dF)_{T,V} \leq 0$ and so on (but do not include Boltzmann “probability entropy”, Shannon “information entropy”, “entropy” defined by density functions of quantum mechanics, and others). We will not discuss them any more here.

It is well-known that the first mathematical expression of the second law of thermodynamics was proposed by Clausius in his famous paper published in 1865. He said: (p. 328-329)^[8]

In order to express analytically the second fundamental theorem in the simplest manner, let us assume that the changes which the body suffers constitute a **cyclical process**, whereby the body returns finally to its initial condition. ...

In this way he obtained Clausius inequality

$$dS \geq \frac{\delta Q}{T} \quad (1.5)$$

and the entropy increase principle for isolated (or adiabatic) systems, as shown in Eq. (1.1). However, the assumption of “cyclical process” was not included in the Clausius inequality and the entropy increase principle. Based on such a cyclical-process assumption, the entropy change for an arbitrary irreversible process would be calculated on the basis of the entropy change for a reversible process with the same initial equilibrium state and the same final equilibrium state. That is a severe limitation of classical thermodynamics. Both the same initial state and the same final state must be in equilibrium, because in a reversible process the system must be always in equilibrium state. The entropy change of process must be always equal to the entropy change of the system in classical thermodynamics. Therefore, Eq. (1.1), Eq. (1.2) and Eq. (1.3) should be changed a little, as shown in Eq. (1.6), Eq. (1.7) and Eq. (1.8) for classical thermodynamics.

$$(dS_p)_{\text{iso}} = (dS)_{\text{iso}} \geq 0. \quad (1.6)$$

Here, $(dS_p)_{iso}$ is the entropy change of a process in an isolated (or adiabatic) system.

$$(dG_p)_{T,p} = (dG)_{T,p} \leq 0. \quad (1.7)$$

Here, $(dG_p)_{T,p}$ is the Gibbs free energy change of a process in an isothermal isobaric system.

$$d_i S_p = d_i S \geq 0. \quad (1.8)$$

Here, $d_i S_p$ is the entropy production of a process.

In the same paper, Clausius also said: (p. 364) [8]

The second fundamental theorem, in the form which I have given to it, asserts that all transformations occurring in nature may take place in a certain direction, which I have assumed as positive, by themselves, that is, without compensation; but that in the opposite, and consequently negative direction, they can only take place in such a manner as to be compensated by simultaneous occurring positive transformations.

In the first half of this citation, it is clearly confirmed that only the spontaneous process(es) in “positive” direction and “without compensation” is(are) under consideration in classical thermodynamics, so the Eq. (1.8) is correct for classical thermodynamics. Now the “compensation” is called thermodynamic coupling, so systems including only spontaneous process(es) in “positive” direction and “without compensation” are called simple uncoupling systems or uncoupling systems for short. That is, **Eq. (1.8) is the mathematical expression of the second law of thermodynamics for simple systems (or better to say, for uncoupling systems) in classical thermodynamics**, and the cyclical-process assumption in classical thermodynamics has already been included in Eq. (1.8). Once it is found that the entropy production of an internal process does not agree with the entropy production of the system, classical thermodynamicists like to call the corresponding process “abnormal”, “mystery”, or maybe “violating the second law of thermodynamics” and so on.

In the second half of this citation, it is clearly confirmed that both the spontaneous process(es) in “positive” direction and the nonspontaneous process(es) in “negative” direction with compensation are under consideration in modern thermodynamics. Therefore, **the mathematical expression of the second law of thermodynamics for complex systems (or better to say, for coupling systems) in modern thermodynamics** should be more clearly written as

$$d_i S_1 < 0, d_i S_2 > 0 \text{ \& } d_i S \geq 0. \quad (1.9)$$

The entropy production of nonspontaneous process(es) in the system is negative, i.e. $d_i S_1 < 0$; the entropy production of the spontaneous process(es) is positive, i.e. $d_i S_2 > 0$; and after compensation the entropy production of the system is never negative, i.e. $d_i S = (d_i S_1 + d_i S_2) \geq 0$.

Clausius did not write out the mathematical expression of the second law of thermodynamics for complex systems with compensation for modern thermodynamics. Of course, the terms, “classical thermodynamics” and “modern thermodynamics” did not exist at that time, but Clausius had already divided systems into two kinds of systems: systems “without compensation” and “compensated” systems, i.e. uncoupling systems and coupling systems. That is clear enough to know that thermodynamic coupling, or called “compensa-

tion”, is the watershed between classical thermodynamics and modern thermodynamics, and that thermodynamic coupling is the core of modern thermodynamics.

To sum up, the uncertainty or incompleteness of Clausius mathematical expressions at that time was: (i) Clausius inequality did not include his cyclical-process assumption; (ii) Clausius did not write out his “compensation” in mathematical expression. Now mathematical expressions of the second law of thermodynamics should be written as $[d_i S_p = d_i S \geq 0]$ for simple uncoupling systems in classical thermodynamics; and for complex coupling systems in modern thermodynamics it should be written as $[d_i S_1 < 0, d_i S_2 > 0 \ \& \ d_i S \geq 0]$.

1.4 Classification of Thermodynamics in the Current 21st Century

From the extended Carnot theorem and the correct understanding of the second law of thermodynamics in the current 21st century, a basic and complete classification of thermodynamics can be directly and exactly constructed, as shown in Fig. 1.1. [9~12] The corresponding mathematical expressions of the second law of thermodynamics for each field (or subfield) and their individual frameworks of applicability can be more exactly listed in Table 1.1.

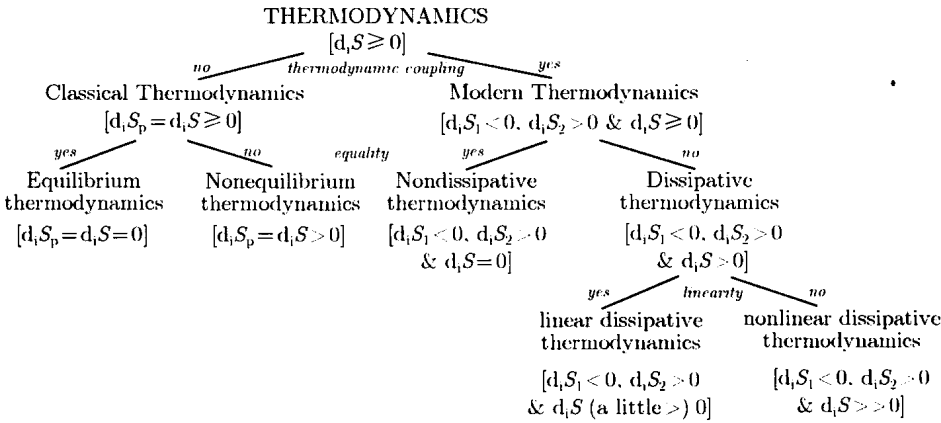


Fig. 1.1 A basic and complete classification of thermodynamics in the current 21st century. $d_i S_p$, $d_i S_1$ and $d_i S_2$ are entropy productions of process(es). $d_i S$ is entropy production of the system, $d_i S = (d_i S_1 + d_i S_2)$.

It should be pointed out that there were at least two books published in 1933 [13] and in 1998 [14], respectively, with the same book title of “Modern Thermodynamics”. The subtitle of the former was “by the methods of Willard Gibbs”, and the subtitle of the latter was “from heat engines to dissipative structures”. Of course, in both these books “modern thermodynamics” meant the current status of thermodynamics at that time. In this book the current status of thermodynamics is still named “thermodynamics”, while the meaning of “modern thermodynamics” here is mainly defined and used as an antonym of “classical thermodynamics”. The title of this book, “Modern thermodynamics”, is an exception as it has a little extension to mean the whole modernized thermodynamics discipline.