Thermodynamics: Extending and Reconstructing of Classical Theoretical Framework

Tang Suyed

(Dated: January 16, 2025)

The deep problems caused from the limitations of theoretical framework itself can only be clarified by extending and reconstructing of the theoretical framework, we extend classical theoretical framework of thermodynamics, break through the limitations of traditional theory, discuss the unsolvable problems in classical theoretical framework. We introduce a new state function to describe the energy of thermal motion, which is the last undefined form of the internal energy, we find that there are three independent forms of the internal energy of thermodynamic system, it implies a broader theoretical framework, we can directly describe the states and the changes of the different forms of the internal energy. We extend the equations of the first law, present the concept of the conversion potential, distinguish the energy transfer and the energy conversion processes by different functions, we confirm the explicit function of the concept of the entropy, and the origin of the configurational entropy, we discuss in detail on the total differential expression of the entropy production and the second law, the three sources of irreversibility, the compensation relationships of the heat conversion, and the causality principle of the second law, an interesting conclusion shows that the second law itself has already contained the internal mechanism of evolution.

INTRODUCTION

The main themes of thermodynamics are to describe the states and changes of a given thermodynamic system, such as the energy transfer and the energy conversion, and in the second law, thermodynamics also involves the description of mass transfer, the states and the changes of the structure of matter, such as the diffusion phenomena described by Fick’s law, in relation to the configurational entropy.

The equation of the first law of thermodynamics indicates that classical thermodynamics is established on such a theoretical framework: which describes different energy exchange processes between thermodynamic system and its surroundings, with the concepts of the heat exchange and the work done, indirectly describes the changes of the internal energy. In classical thermodynamics, the internal energy is defined as the sum of the different forms of the energy within a given system, but these different forms of the internal energy are not clearly defined, in the equation of the first law, the classification of the different forms of energy are only limited to the energy exchange processes between a system and its surroundings, it is only the classification of the process quantities, but not the classification of the state quantities in the usual sense, the introduction of Gibbs free energy partially changed this theoretical framework, but still not establish a complete narrative.

In classical theoretical framework, an obvious problem is that the energy transfer and the energy conversion within a given system can hardly be directly described due to the different forms of the internal energy are not clearly distinguished, there has no an explicit equation that can be used to describe the energy conversion process between the different forms of the internal energy, for an example, we both know that Gibbs free energy will be reduced in a spontaneous chemical reaction, but can hardly confirm what the reduced Gibbs free energy converts into.

Another example is the production of heat by friction, a process of heat production different from heat flux $Q$. The concept of “the heat energy” is ill-defined in classical thermodynamics, and “the heat production” is also not well defined, therefore, this means that there has no a complete narrative for a process of energy conversion.

In order to overcome the above difficulties, a set of concepts of thermodynamic potentials are introduced, which are explained as the some parts of the internal energy that can be released in the form of work, continued the thinking patterns of the energy exchange between a system and its surroundings. The question is: in addition to Gibbs free energy, the concepts of thermodynamic potentials cannot distinguish the different forms of the internal energy, for example, the internal energy of an ideal gas and the elastic potential energy of a spring both are described as the parts of Helmholtz free energy, whereas, the two are so different.

The some parts of the internal energy that can be released in the form of work involve the two sources: 1. it can be directly released in the form of work, such as the elastic potential energy of a spring, 2. It is not the same form of energy with the released work, but can be converted into work in a release process, such as the internal energy of an ideal gas, which has two intensity variables $T$ and $p$, and can be released via the two paths: the heat transfer or the volume work, the volume work path corresponds to the energy conversion. The latter is not a true free energy in the storage state of the internal energy, therefore, the concepts of the free energy cannot exactly correspond to the state properties of the different forms of the internal energy.

In the second law, the physical meanings of the entropy now still can hardly be explained in thermodynamics even after more than a century of discussions, I. Prigogine wrote: “Now entropy is a very strange concept and without hoping to achieve a complete description”[1]. The second law establishes an inequality, but this inequality does not have a explicit total differential in mathematics. This limitation has been significantly improved due to the progress of non-equilibrium thermodynamics, but the question still has not been fully clarified, because in addition to the thermody-
namic processes that can be described by the concepts of “force” and “flux”, there are also thermodynamic processes that need to be described by the concepts of “force” and “production”. The “flux” means the process of transfer, and the “production” describes the energy conversion.

Due to the limitations of the classical theoretical framework, a series of deep problems in thermodynamics now still remain unsolvable, for more examples: the definition of thermodynamic entropy relies on Carnot cycle, the explicit function of the entropy is not made clear. $\delta Q/T$ is the calorimetric entropy; we cannot discuss the configurational entropy according to $\delta Q/T$, the fundamental equation can hardly distinguish energy transfer and energy conversion processes, the compensation mechanism of energy conversion are unclear, the entropy production and the second law do not have a total differential expression, etc, these problems are all originated from the limitations of the classical theoretical framework itself, it is impossible to clarify these deep problems within classical theoretical framework.

The unsolvable problems caused from the limitations of classical theoretical framework itself can only be clarified by extending of the theoretical framework. In classical theoretical framework, the classification of the different forms of energy are only limited to the energy exchange processes between a given system and its surroundings, we extend the classification of different forms of energy into the internal energy. We present a new state function to describe the energy of thermal motion, defined as the heat energy, combine with the known mechanical free energy and Gibbs free energy, we find that the internal energy can be classified into the three independent forms, thus, the limitations of classical theoretical framework will be broken.

In a new theoretical framework, we extend the equations of the first law of thermodynamics, introduce the concept of the conversion potential, distinguish the energy transfer and the energy conversion processes by the concepts of the flux and the production, we discuss the compensation relationships of the heat conversion, establish a complete narrative of energy conversion.

In a new theoretical framework, we first need to ascertain the state changes when the flux $\delta Q$ to be transferred into a thermodynamic system, then redefine the concept of the entropy according to these state changes of the system, which is the sum of the calorimetric entropy and the configurational entropy, a binomial function. We prove that the entropy is a state function in mathematics, it means that, the imaginary cycle of heat engine\cite{2} is not an essential requirement for the definition of the physical concept.

In a new theoretical framework, we discuss the total differential expression of the entropy production and the three sources of irreversibility, thermodynamic spontaneous processes are caused by different driving forces, the second law of thermodynamics is derived from such a fundamental principle: All of the gradients of the thermodynamic forces cannot be spontaneous recovery completely.

In a new theoretical framework, we discuss the relationship between dissipation and evolution, we find that the second law itself has already contained the mechanism of evolution, this point of view comes from such a fact, in a coupling process, we always have the total entropy production $d_i S \geq 0$, but the partial differentials of $d_i S$ can be less than zero, it implies that order and evolution can arise spontaneously, therefore, the second law is no longer thought to be only a dissipative law, it is also the law of evolution.

In a new theoretical framework, we establish a new foundation for discussing the relations between thermodynamics and dynamics, in the previous work, we have not found a similar theoretical framework of the second law that can be applied to dynamics. It seems, the master equations of dynamics only involves the conservation of energy, which correspond only to the first law of thermodynamics, it is destined to be a very difficult work in the previous time in that the theoretical framework of the two are different.

We believe, thermodynamics is a self-consistent theory, in a new theoretical framework, we will witness a profound change that will be brought into thermodynamics, in which, all of the concepts and principles are comprehensible.

“The fact that it is comprehensible is a miracle.”\cite{3}

**HEAT ENERGY: A NEW STATE FUNCTION**

In physics, thermal motion is a state property, and the energy of thermal motion is thought to be a form of energy, J.C.Maxwell\cite{4}, R.Feynman\cite{5} explicitly indicated that is the heat energy, and an earlier idea can also be found from D.Bernoulli book\cite{6}: “what we experience as heat is simply the kinetic energy of the great numbers of the particles motion”, as we know, this great numbers of the particles motion now is called as thermal motion.

Now, we consider how to define the energy of thermal motion in thermodynamics. For a given thermodynamic system, using the symbol $q$ denotes the energy of thermal motion, named as the heat energy, which involves all of the heat phenomena at different levels.

By our experience, the heat energy is a non-conserved quantity, so it has the two sources, the energy transfer and the energy conversion, as we have already known, $\delta Q$ is the heat transfer, and the another source of the energy of thermal motion, we named as the heat production, comes from the heat conversion, such as a mechanocaloric effect, the heat effects of chemical reaction or phase transition.

Using $d_s q$ denotes the heat transfer, where the subscript $e$ denotes the energy transfer, we have $d_s q = \delta Q$, using $d_i q$ denotes the heat production, we obtain

$$dq = d_s q + d_i q.$$  \(1\)

Eq.(1) express the changes in the heat energy for a given system: the total changes of the heat energy are equal to the sum of the heat transfer and the heat production.
Since the limitations of theoretical framework, in classical thermodynamics, the heat is only defined as a form of energy in transfer, but the heat production is ill defined.

Now we consider an example, for an ideal gas, all of the internal energy are the energy of thermal motion, therefore, by the first law, we have

$$dU = dq = \delta Q - pdV,$$

(2)

where $U$ is the internal energy, $Q$ is the heat exchange, $p$ is the gas pressure, $V$ is the gas volume, and $-pdV = \delta W$ is the reversible volume work.

Since the heat energy $q$ has the two intensity variables: temperature $T$ and pressure $p$, so it can be increased or decreased via the two different paths: heat transfer $\delta Q$ or heat conversion, the reversible volume work $-pdV$.

For an ideal gas, the pressure $p$ comes from thermal motion, so $-pdV$ denotes work done by the heat energy $q$, it signifies the heat energy of the gas to be converted into work, and then exchanged with its surroundings.

$$d_e,q = \delta Q,$$

(3)

$$d_i,q = -pdV.$$

(4)

For $pV$ work of an ideal gas, the work $-\delta W = pdV$ is the change in the surroundings, and $d_i,q$ is the change in the system, thus, the work done $-pdV$ denotes not only the energy exchange but also the energy conversion between the system and its surroundings.

In general, the pressure denotes a force acting per unit area, which involves different sources, including thermal motion and the interactions between the particles. Using $p$ represents the heat partial pressure which comes from thermal motion, using $p'$ represents the partial pressure when the other generalized force $Y$ is expressed as a force acting per unit area, the different sources of the total pressure therefore can be distinguished by

$$P = p + p',$$

(5)

where $P$ is the total pressure.

The first law thus becomes

$$dU = \delta Q - pdV + \frac{d}{dx} \left( Y \right) dx + \sum_j \mu_j' dN_j$$

$$= dq + \frac{d}{dx} \left( Y \right) dx + \sum_j \mu_j' dN_j,$$

(6)

where $Y$ is the generalized force, $dx$ is the generalized displacement, $-pdV$ includes $-p'dV$, $\mu_j'$ is the chemical potential of the type $j$ particles, and $N_j$ is the number of such particles, corresponds to $\mu_j' \neq 0$. The internal energy $U$ is the sum of the three independent forms of energies.

An interesting difference shows that “the pressure $p$ has different sign from other generalized force, if we increase the pressure, the volume increases, whereas if we increase the force, $Y$, for all other cases, the extensive variable, $x$, decreases”[7]. This is an interesting criterion that can be used to distinguish the heat partial pressure $p$ from other generalized force $Y$, by this criterion, the heat partial pressure $p$ will be different from other generalized force.

We find that $dq$ can be proven to be an exact differential. Consider $U=U(T,V,x,N_j)$, where $T, V, x$ and $N_j$ are the four independent state variables. Then we obtain[7]

$$dU = \left( \frac{\partial U}{\partial T} \right)_{V,x,N_j} dT + \left( \frac{\partial U}{\partial V} \right)_{T,x,N_j} dV + \left( \frac{\partial U}{\partial x} \right)_{T,V,N_j} dx + \sum_j \left( \frac{\partial U}{\partial N_j} \right)_{T,V,x,N_j} dN_j.$$  

(7)

By definition and compare Eq.(7) with Eq.(6), $q$ is the function of the two independent variables $T$ and $V$

$$dq = \left( \frac{\partial q}{\partial T} \right)_V dT + \left( \frac{\partial q}{\partial V} \right)_T dV.$$

(8)

Compare Eq.(7) with Eq.(8), we get

$$dq = \left( \frac{\partial q}{\partial T} \right)_V dT + \left( \frac{\partial q}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_{V,x,N_j} dT + \left( \frac{\partial U}{\partial V} \right)_{T,x,N_j} dV.$$  

(9)

Owing to the fact that $dU$ is an exact differential, by Eq.(7) and Eq.(9), the two partial derivatives of the internal energy satisfy the relation that

$$\left[ \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial T} \right) \right]_{V,x,N_j} = \left[ \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right) \right]_{T,x,N_j}$$

(10)

Such that

$$\left[ \frac{\partial}{\partial V} \left( \frac{\partial q}{\partial T} \right) \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial q}{\partial V} \right) \right]_V.$$  

(11)

Thus we have proven that $dq$ is an exact differential. Using the function $A$ denotes the mechanical free energy within a given system that

$$A = Yx.$$  

(12)

The equation of the first law becomes

$$dU = dq + dA + dG$$

$$= dq + d(Yx) + \sum_j d(\mu_j' N_j).$$

(13)

The internal energy $U$ is equal to the sum of the internal heat energy $q$, the internal mechanical free energy $A$ and the internal Gibbs free energy $G$.

In Eq.(13), $Y$ and $x$ both are the independent variables, we have $\left[ \frac{\partial}{\partial x} \left( \frac{\partial A}{\partial x} \right) \right]_y = \left[ \frac{\partial}{\partial y} \left( \frac{\partial A}{\partial y} \right) \right]_x = 1$, and similar for $G$, so $A$ and $G$ both are the state functions.

$A$ and $G$ are the two non-conserved quantities, we have the two equations similar to Eq.(1)

$$dA = d_e A + d_i A,$$

(14)

where $d_e A$ denotes the mechanical free energy flux, and $d_i A$ denotes the mechanical free energy production.
For Gibbs free energy we have

\[ dG = d_e G + d_i G, \quad (15) \]

where \( d_e G \) denotes Gibbs free energy flux, \( d_i G \) denotes Gibbs free energy production, similar to Eq.(14).

Thus the concepts “flux” and “production” can be used as a general method to distinguish the two processes: the energy transfer and the energy conversion.

The equation of the first law can be extended that

\[ dU = d_e q + d_i A + d_i G, \quad (16) \]

\[ d_i q + d_i A + d_i G = 0. \quad (17) \]

Eq.(17) gives the relation

\[ d_i q = -(d_i A + d_i G). \quad (18) \]

Eq.(18) denotes the relations of the energy conversion between the different energy forms, the heat production is equal to the negative free energy productions due to the energy is a conserved quantity.

Now, we consider some applications.

The first example we consider an equation combined with heat diffusion and heat conversion, which describes the changes of “the distribution of the heat”\[^8\].

\[ \frac{\partial q}{\partial t} = -\nabla \cdot J_q + 1 \frac{\partial q_o}{\partial t}, \quad (19) \]

\[ J_q = -k \nabla T, \quad (20) \]

where \( q_o \) is \( q \) per unit volume, \( J_q \) denotes the heat flux density, \( t \) is time, and \( k \) is the thermal conductivity.

The second example is the heat effects of chemical reaction or phase transition, the heat production

\[ d_i q = -d_i G. \quad (21) \]

Eq.(4) and Eq.(18) both are the equations of conservation of energy, we noticed, the state changes of the heat transfer and \( pV \) work done are different.

The driving force of heat into work comes from the heat partial pressure, the heat production is equal to \( d_i q \), another state change involves the heat partial pressure \( p \) and the volume \( V \), in a reversible conversion process, we have

\[ d_i q = -pdV. \quad (22) \]

Since the heat energy has the two intensity variables \( T \) and \( p \), it can be changed via different paths, \( -pdV \) implies an energy conversion path, and \( -pdV \) has the two meanings: (a) it equals to the volume work done in a reversible process, (b) the change of a conversion potential, the conversion of heat into work or free energy needs a compensation, which comes from the dissipation of the conversion potential, this is the internal causal mechanism of the heat conversion, and also the compensation mechanism of the conversion of heat into work or free energy.

In an reversible conversion process, the following equation describes the compensation relations between the heat production and the dissipation of the conversion potential.

\[ d_i q + pdV = 0. \quad (23) \]

In an irreversible conversion process, we have

\[ d_i q + pdV \geq 0. \quad (24) \]

In that \( pdV \) contains some spontaneous dissipation of the conversion potential, the free expansion of a gas is a simple example, the process has no work done.

**ENTROPY: EXACT DIFFERENTIAL**

In classical thermodynamics, the concept of the entropy was defined by the aid of Carnot cycle that

\[ \int_{rev} \frac{\delta Q}{T} = 0, \quad (25) \]

where \( rev \) denotes the reversible processes. It given a conditional definition with an additional restriction.

\[ dS = \left( \frac{\delta Q}{T} \right)_rev. \quad (26) \]

In Eq.(26), \( (\delta Q/T)_{rev} \) is reversible path dependent, in thermodynamics, it is an only exception to the principles of exact differential.

We now consider a new approach.

Consider the heat transfer \( \delta Q \), it is known as the change of an extensive quantity, and can be transferred only from higher temperature to lower temperature, this property shows us that the heat transfer \( \delta Q \) relates to the intensity distribution of temperature \( T \).

For the same \( \delta Q \), if its temperature distribution is different, the intensive property of \( \delta Q \) will be also different, thus, we can use the function \( \delta Q/T \) to measure \( \delta Q \) and its intensive property of temperature distribution, and then \( \delta Q/T \) may be named as the entropy of the heat flux \( \delta Q \).

\[ d_e S = \frac{\delta Q}{T}. \quad (27) \]

In Eq.(27), \( \delta Q/T \) is only a process variable. For a given system, we need to consider when \( \delta Q \) to be transformed into the internal energy of a given system, or the internal energy of the system to be transformed into the heat flux \( \delta Q \), how do we describe the state changes of the system.

Consider a reversible process, combined with Eq.(6) and Eq.(23), it follows that

\[ \frac{\delta Q}{T} \Rightarrow dU = Y dx - \sum \frac{\mu_j dN_j}{T} + pdV \Rightarrow dq + pdV. \quad (28) \]

When \( \delta Q/T \) to be transferred into the given system, the right hand side of the equation is the state changes.

Such that, we can define the state function according to the state changes of the given system.
Using a function denotes the state changes
\[ dS = \frac{dq}{T} + \frac{pdV}{T}. \] (28)

\( S \) is named as the entropy of the given system.
Eq.(28) is a binomial expression, the integral of \( dq/T \)
we named as the calorimetric entropy \( S_q \).
\[ dS_q = \frac{dq}{T}. \] (29)

The integral of \( pdV/T \) we named as the configurational
entropy \( S_c \), \( S_c \) is in relation to the density distribution of
the particles number.
\[ dS_c = \frac{pdV}{T}. \] (30)

By Eq.(8) and Eq.(28), \( S \) is the function of the two inde-
pendent variables \( T \) and \( V \). According to the mathematical
theory of exact differential, if the two partial derivatives of
the function \( S \) satisfy the equation
\[ \left[ \frac{\partial}{\partial V} \left( \frac{\partial S}{\partial T} \right) \right]_V = \left[ \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial V} \right) \right]_T. \] (31)
d\( S \) will be an exact differential.
We now prove this conclusion.
Using Eq.(8) in Eq.(28), it follows that
\[ dS = \frac{dq}{T} + \frac{p}{T} \ dV \]
\[ = \frac{1}{T} \left( \frac{dq}{\partial T} \right)_V dT + \frac{1}{T} \left( \frac{dq}{\partial V} \right)_T dV + \frac{p}{T} \ dV. \] (32)

By Eq.(32) we have
\[ \left[ \frac{\partial}{\partial V} \left( \frac{\partial S}{\partial T} \right) \right]_V = \left( \frac{\partial}{\partial V} \left( \frac{1}{T} \left( \frac{dq}{\partial T} \right)_V \right) \right)_T \]
\[ = \frac{1}{T} \left[ \frac{\partial}{\partial V} \left( \frac{dq}{\partial T} \right)_V \right]_T, \] (33)
and
\[ \left[ \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial V} \right) \right]_V = \left( \frac{\partial}{\partial T} \left( \frac{1}{T} \left( \frac{dq}{\partial V} \right)_T \right) + \frac{p}{T} \right)_V \]
\[ = \frac{1}{T} \left[ \frac{\partial}{\partial T} \left( \frac{dq}{\partial V} \right) \right]_T + \frac{1}{T^2} \left( \frac{dq}{\partial V} \right)_T \]
\[ + \frac{1}{T^2} \left[ T \left( \frac{dp}{\partial T} \right)_V \right] - p. \] (34)

Before we compare Eq.(33) with Eq.(34), we need to
prove a well known relation anew that
\[ \left( \frac{\partial q}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p. \] (35)
From Eq.(32) we have
\[ dS = \frac{1}{T} \left( \frac{dq}{\partial T} \right)_V dT + \frac{1}{T} \left[ \left( \frac{\partial q}{\partial V} \right)_T + p \right] dV. \] (36)

It follows that
\[ dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV. \] (37)
d\( q \) can be expressed as the follows
\[ dq = TdS - pdV, \] (38)
The pressure \( p \) and the volume \( V \) both are the state vari-
ables, so \( d(pV) \) is an exact differential, we consider
\[ pV = TS - q. \] (39)
\[ d(pV) = d(TS) - dq = TdS + SdT - dq. \] (40)

Using Eq.(38) in Eq.(40), we get
\[ d(pV) = d(TS) - dq = SdT + pdV. \] (41)

Where \( d(pV) \equiv d(pV)(T, V) \), we have from Eq.(41)
\[ \left[ \frac{\partial}{\partial V} \left( \frac{\partial(pV)}{\partial T} \right)_V \right]_T = \left( \frac{\partial S}{\partial V} \right)_T. \] (42)
and
\[ \left[ \frac{\partial}{\partial T} \left( \frac{\partial(pV)}{\partial V} \right)_V \right]_T = \left( \frac{\partial p}{\partial T} \right)_V. \] (43)

Since \( d(pV) \) is an exact differential, so that
\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V. \] (44)
Using Eq.(44) in Eq.(37), we get
\[ dS = \left( \frac{\partial S}{\partial V} \right)_V dT + \left( \frac{\partial p}{\partial T} \right)_V dV. \] (45)

Compare Eq.(45) with Eq.(36), the two partial derivati-
es satisfy the equation that
\[ \left( \frac{\partial p}{\partial T} \right)_V = \frac{1}{T} \left[ \left( \frac{\partial q}{\partial V} \right)_T + p \right]. \] (46)

It follows that
\[ \left( \frac{\partial q}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p. \] (47)
Thus we have proven the relation Eq.(35).
Using Eq.(47) in Eq.(34), we get
\[ \left[ \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial V} \right)_T \right]_V = \frac{1}{T} \left[ \frac{\partial}{\partial T} \left( \frac{\partial q}{\partial V} \right) \right]_V. \] (48)

Compare Eq.(33) and Eq.(48) with Eq.(11), we obtain the
following conclusion
\[ \left[ \frac{\partial}{\partial V} \left( \frac{\partial S}{\partial T} \right) \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial V} \right) \right]_T. \] (49)

Eq.(49) indicates that \( dS \) is an exact differential, \( S \) is a
state function. The conclusion perfectly obey the general
rules of exact differential, and does not need to depend on
an imaginary reversible cycle, therefore, there has no ex-
ception to the principles of exact differential.
As the conclusion of Eq.(49), the function changes $dS$ will be path-independent, the integral of $dS$ around an arbitrary closed path will be always equal to zero

$$\oint dS \equiv 0.$$  \hspace{1cm} (50)

In non-equilibrium thermodynamics, the changes in the entropy may be considered as the sum of the entropy flux $d_e S$ and the entropy production $d_i S$ that

$$dS = d_e S + d_i S.$$  \hspace{1cm} (51)

In this opinion, $\delta Q/T$ is really the entropy flux $d_e S$. The physical meaning of Clausius inequality is that

$$\oint d_e S = \oint \delta Q/T \leq 0,$$  \hspace{1cm} (52)

and the second law inequality is actually that

$$\oint (d_e S + d_i S) \geq \oint d_e S.$$  \hspace{1cm} (53)

In Eq.(53), $dS = \delta Q/T$ does not contain $d_i S$, and in Clausius inequality, $S$ is not an explicit function.

We now consider the two examples. The first example is a photon gas. Using $q = \alpha T^4 V, p = \alpha T^4/3$ in Eq.(32), where $\alpha$ is a constant, and then we get that

$$dS = d(\alpha T^4 V) = 4 \alpha T^3 V dT + \alpha T^4 dV.$$  \hspace{1cm} (54)

$$dS = \frac{1}{T} dq + \frac{p}{T} dV = \frac{1}{T} 4 \alpha T^3 V dT + \frac{1}{T} \alpha T^4 dV + \frac{1}{3T} \alpha T^4 dV = 4 \alpha T^2 V dT + \frac{4}{3} \alpha T^3 dV.$$  \hspace{1cm} (55)

We have from Eq.(55)

$$\left[ \frac{\partial}{\partial V} \left( \frac{\partial S}{\partial T} \right) \right]_{\alpha T} = \left[ \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial V} \right) \right]_{\alpha T} = 4 \alpha T^2.$$  \hspace{1cm} (56)

Thus the entropy of a photon gas is a state function.

The second example is an ideal gas. Using $dq = C_v dT$ and $pV = nRT$ in Eq.(32), where $C_v$ is the heat capacity at constant volume, $n$ is the number of moles, and $R$ is the gas constant. We have

$$dS = C_v \frac{1}{T} dT + \frac{p}{T} dV = C_v \frac{1}{T} dT + \frac{nRT}{V} dV,$$  \hspace{1cm} (57)

and

$$\left[ \frac{\partial}{\partial V} \left( \frac{C_v}{T} \right) \right] = \left[ \frac{\partial}{\partial T} \left( \frac{nRT}{V} \right) \right] = 0.$$  \hspace{1cm} (58)

Thus the entropy of an ideal gas is a state function.

For an ideal gas, $T = 2q/iNk, pV = NkT$, we get

$$dS = \frac{i}{2} \frac{Nk}{q} dq + \frac{Nk}{V} dV,$$  \hspace{1cm} (59)

where $i$ is the number of the degrees of freedom of the gas molecules, $N$ is the number of the gas molecules, and $k$ is Boltzmann constant.

For a photon gas, we have the photon gas equation

$$pV = \frac{\zeta(4)}{\zeta(3)} NkT = NR_{(p)} T,$$  \hspace{1cm} (60)

where $N$ is the number of the photons, $\zeta(3)$ and $\zeta(4)$ both are the Riemann zeta functions, $R_{(p)} = [\zeta(4)/\zeta(3)]k$ is the photon gas constant.

Consider $q = 3pV$ and $T = q/3NR_{(p)}$, combine Eq.(60) with Eq.(55), we get

$$dS = \frac{3NR_{(p)}}{q} dq + \frac{NR_{(p)}}{V} dV.$$  \hspace{1cm} (61)

All of the variables in Eq.(59) and Eq.(61) are extensive variables, where $iN/q$ refers to the average energy levels per degree of freedom of the particles, $N/V$ is the density function of the particles. In an earlier work[9], we presented a mathematical model to express the average degrees in the distribution of the extensive variables $q$ and $N$, for an ideal gas or a photon gas, the Nature of the Entropy is a binomial distributions function.

In Eq.(59) and Eq.(61), $dS$ has the same function form, it may be the primary equation of the entropy that

$$dS = \frac{\hat{a}}{q} NR_{(k)} dq + \frac{NR_{(k)}}{V} dV,$$  \hspace{1cm} (62)

where $\hat{a}$ denotes a factor, for an ideal gas $\hat{a} = i/2$, for a photon gas $\hat{a} = i$, and $R_{(k)}$ denotes the system constant, for an ideal gas $R_{(k)} = k$, for a photon gas $R_{(k)} = R_{(p)}$.

According to Eq.(49), Eq.(28) is a perfect definition of the state function in the usual sense, and the fundamental equation of thermodynamics is the equivalent equation of the definition of the entropy, so Eq.(28) has the same mathematical results as that can be derived by the fundamental equation, such that, the new approach does not change the mathematical results of the classical thermodynamics.

**THE SECOND LAW: THE TOTAL DIFFERENTIAL**

The classical equation of the second law is derived by the aid of heat engine cycle, it is expressed as the increment in the entropy of an isolated system $dS \geq 0$, and in non-equilibrium thermodynamics, the increment in the entropy of an isolated system has been substituted by the entropy production $d_e S$ and the inequality $d_S \geq 0$[10].

In classical thermodynamics, Clausius inequality does not have an explicit total differential formula, and in non-equilibrium thermodynamics, the compensation relationships of the heat conversion are unclear, the two both are in relation to the limitations of the theoretical framework.

By Eq.(13), for a given system, we have

$$dU = dq + dA + dG.$$  \hspace{1cm} (63)
The internal energy is equal to the sum of the internal heat energy \( q \), the internal mechanical free energy \( A \), and the internal Gibbs free energy \( G \).

By Eq.\((28)\), \( dq/T \) is the entropy of \( dq \), but \( dA/T \) and \( dG/T \) make no sense. The mechanical free energy \( A \) and Gibbs free energy \( G \) can be called by a joint name: the free energy. The difference with the heat energy is that the heat energy \( q \) has some quality losses, these quality losses can be measured by the entropy, the free energy has no quality loss, the entropy of which is equal to zero, only the heat energy makes contribution to the entropy.

That is why thermodynamics entropy can hardly to be continue discussed in the traditional theoretical framework, a perfect definition depends on such a fact: the heat energy has already been well defined.

Assume a given system in locals equilibrium, and some irreversible processes occurred between the two locals \( A \) and \( B \), the driving forces of the processes are the gradients of thermodynamic forces between the two locals. Using the subscript \( A \) and \( B \) denote the locals \( A \) and \( B \), the subscript \( AB \) denote the interactions between the locals \( A \) and \( B \), the changes in the internal energy of the processes can be expressed respectively as follows.

The heat flux driven by the gradient in temperature \( \Delta T \) between the two locals \( A \) and \( B \) satisfies the relation
\[
d_\epsilon q = d_\epsilon qb = -d_\epsilon qA. \tag{64}\]

The changes in the mechanical free energy
\[
d_\epsilon A_{AB} = -(Y_B - Y_A)dx = -\Delta Y dx, \tag{65}\]
where the driving force \( \Delta Y \geq 0 \) denotes a spontaneous process, and \( d_\epsilon A_{AB} \leq 0 \) represents the free energy loss.

The changes in Gibbs free energy
\[
d_\epsilon G_{AB} = -\sum_j (\mu_j^b - \mu_j^a) dN_j = -\sum_j \Delta \mu_j^d dN_j, \tag{66}\]
where the driving forces \( \Delta \mu_j^d \geq 0 \) denote a spontaneous process, and \( d_\epsilon G_{AB} \leq 0 \) represents the free energy loss.

If some independent processes arise only in the locals \( A \) or \( B \), using the subscripts \( a \) and \( b \) denote the independent changes of the locals \( A \) and \( B \), respectively, we have
\[
d_\epsilon A_A = -Y_A dx_a, \tag{67}\]
\[
d_\epsilon A_B = -Y_B dx_b, \tag{68}\]
and
\[
d_\epsilon G_A = -\sum_j \mu_j^a dN_{ja}, \tag{69}\]
\[
d_\epsilon G_B = -\sum_j \mu_j^b dN_{jb}. \tag{70}\]

Combine Eqs.\((65)\)–\((70)\), and sum the changes of the two locals \( A \) and \( B \), it follows that
\[
\sum_k d_\epsilon G_k = d_\epsilon G_{AB} + d_\epsilon G_A + d_\epsilon G_B
= -\sum_j (\mu_j^b - \mu_j^a) dN_j
= -\sum_j (\mu_j^b - 0) dN_{ja} - \sum_j (\mu_j^b - 0) dN_{jb}
= -\sum_k \sum_j \Delta \mu_j^d dN_j, \tag{72}\]
where, the subscript \( k \) denotes the process \( k \). Such that, we have
\[
-d_\epsilon A = -\sum_k d_\epsilon A_k = \sum_k \Delta Y dx, \tag{73}\]
\[
-d_\epsilon G = -\sum_k d_\epsilon G_k = \sum_k \sum_j \Delta \mu_j^d dN_j. \tag{74}\]

By Eq.\((18)\), we have the heat production \( d_\epsilon q \) that
\[
d_\epsilon q = -(d_\epsilon A + d_\epsilon G)
= \sum_k \Delta Y dx + \sum_k \sum_j \Delta \mu_j^d dN_j. \tag{75}\]

Now we consider the total entropy production, which involves the different sources of irreversibility.

Using Eq.\((1)\) in Eq.\((28)\), we get
\[
dS = d_\epsilon S + d_\epsilon S = dS_A + dS_B. \tag{77}\]

The increments in the entropies of the two locals \( A \) and \( B \) are equal to
\[
dS = d_\epsilon S + d_\epsilon S = dS_A + dS_B. \tag{77}\]

The increments in the entropy of the two locals that
\[
dS_A = \frac{d_\epsilon q_A}{T_A} + \frac{d_\epsilon q_A}{T_A} + \frac{p_A dV_A}{T_A}, \tag{78}\]
\[
dS_B = \frac{d_\epsilon q_B}{T_B} + \frac{d_\epsilon q_B}{T_B} + \frac{p_B dV_B}{T_B}. \tag{79}\]

Assume the external entropy flux \( d_\epsilon s = 0 \), and then the sum of the entropy productions of the two locals will be equal to that
\[
d_\epsilon S = dS_A + dS_B
= \left( \frac{d_\epsilon q_A}{T_A} + \frac{d_\epsilon q_B}{T_B} \right) + \left( \frac{d_\epsilon q_A}{T_A} + \frac{d_\epsilon q_B}{T_B} \right)
= \left( \frac{p_A dV_A}{T_A} + \frac{p_B dV_B}{T_B} \right). \tag{80}\]

In Eq.\((80)\), the heat fluxes satisfy the relation
\[
d_\epsilon q_B = -d_\epsilon q_A = d_\epsilon q. \tag{81}\]
It follows that
\[
\left( \frac{d_a q_A}{T_A} + \frac{d_b q_B}{T_B} \right) = \left( \frac{1}{T_B} - \frac{1}{T_A} \right) d_e q = \Delta \left( \frac{1}{T} \right) d_e q. \tag{82}
\]

By Eq.(75), we have
\[
\left( \frac{d_A q_A}{T_A} + \frac{d_B q_B}{T_B} \right) = \sum_k \frac{1}{T} \Delta Y dx + \sum_k \sum_j \frac{1}{T} \Delta \mu_j^i dN_j, \tag{83}
\]
where, \( T \) is the temperature of the heat conversion.

Using \( dV_r \) denotes the volume change of the reversible volume work between the two locals \( A \) and \( B \), using \( dV_a \) and \( dV_b \) represent the two independent volume changes caused by the pressures \( p_A \) and \( p_B \), respectively that
\[
dV_A = -dV_r + dV_a, \tag{84}
\]
\[
dV_B = dV_r + dV_b. \tag{85}
\]

Using Eq.(84) and Eq.(85) in Eq.(80), we get that
\[
\left( \frac{p_A dV_A}{T_A} + \frac{p_B dV_B}{T_B} \right) = \left( \frac{p_B}{T_B} - \frac{p_A}{T_A} \right) dV_r
+ \left( \frac{p_A}{T_A} - 0 \right) dV_a + \left( \frac{p_B}{T_B} - 0 \right) dV_b
= \sum_k \Delta \left( \frac{p}{T} \right) dV. \tag{86}
\]
The subscript \( k \) denotes the process \( k \).

Using Eqs.(82), (83) and (86) in Eq.(80), we obtain
\[
d_i S = dS_A + dS_B
= \Delta \left( \frac{1}{T} \right) dq + \sum_k \frac{1}{T} \Delta Y dx
+ \sum_k \sum_j \frac{1}{T} \Delta \mu_j^i dN_j + \sum_k \Delta \left( \frac{p}{T} \right) dV. \tag{87}
\]
The heat flux \( dq \) can be considered as a micro-quantity \( dq \), and the sum “\( k \)” can be simplified, thus we have
\[
d_i S = \Delta \left( \frac{1}{T} \right) dq + \frac{1}{T} \Delta Y dx
+ \sum_j \frac{1}{T} \Delta \mu_j^i dN_j + \Delta \left( \frac{p}{T} \right) dV. \tag{88}
\]

Compare with the known equations of the entropy production, the difference between the two is that \( \Delta Y dx \) and \( \Delta \mu_j^i dN_j \) denote the heat productions, therefore, the gradients do not include \( 1/T \).

For a non-equilibrium state, consider the spatial distribution of the gradients, it follows that
\[
d_i S = \nabla \left( \frac{1}{T} \right) dq + \frac{1}{T} \nabla Y dx
+ \sum_j \frac{1}{T} \nabla \mu_j^i dN_j + \nabla \left( \frac{p}{T} \right) dV. \tag{89}
\]

In Eq.(89), \( q \) is the heat flux, \( dV = dV_i e_i + dV_j e_j + dV_k e_k \), where \( e_i, e_j, e_k \) are the direction vectors.

Eq.(88) and Eq.(89) are the equations of the total entropy productions of arbitrary processes for a given system.

Now we continue discuss the second law.

In order to simplify the discussion, rewrite Eq.(88) by using Eq.(75), and simplify the sum “\( k \)”, as follows
\[
d_i S = \Delta \left( \frac{1}{T} \right) dq + \frac{1}{T} dq + \Delta \left( \frac{p}{T} \right) dV. \tag{90}
\]

We consider the independent processes first, it denotes that there is only one gradient of thermodynamic forces driving the spontaneous process, the driving forces of the heat production \( dq \) are \( \Delta Y \) or/and \( \Delta \mu_j^i \), the direction of the gradient of the thermodynamic force decides the direction of an independent spontaneous process.

(1). The first type of the independent process is the heat transfer, a micro-quantity of the heat energy \( dq \) is transferred between different temperatures, the driving force of the heat transfer is the gradient of the temperature, and the direction of the heat flux is determined by the gradient in the temperature \( \Delta T \), so, the heat energy can only be transferred from higher temperature \( T_h \) to lower temperature \( T_c \).

\[
dq(T_h) \rightarrow dq(T_c). \tag{91}
\]

We have the entropy production
\[
d_i S = \frac{1}{T_c} - \frac{1}{T_h} dq \geq 0. \tag{92}
\]

The heat transfer obeys such a principle: the gradient \( \Delta T \) or \( \Delta (1/T) \) spontaneously tend to zero, and the entropy production describes the dissipation of the driving force \( \Delta (1/T) \) or \( \Delta T \). In an independent process, the dissipation of the the driving force \( \Delta (1/T) \) or \( \Delta T \) cannot be spontaneous recovery completely.

(2). The second type is the independent process driven by the heat partial pressure \( p \). Consider a given system, the heat partial pressure \( p \) always points to the normal direction of the system’s surface, thus the volume change of the system always be positive definite in a spontaneous dissipation process of the conversion potential, so we have
\[
d_i S = \left( \frac{p}{T} - 0 \right) dV = \Delta \left( \frac{p}{T} \right) dV \geq 0. \tag{92}
\]

The spontaneous diffusion process driven by the heat partial pressure \( p \) obeys such a principle: the gradient \( \Delta p \), or \( \Delta (p/T) \) spontaneously tends to zero. In an independent process, the dissipation of the the driving force \( \Delta p \) or \( \Delta (p/T) \) cannot be spontaneous recovery completely.

(3). The third type of the independent processes is the energy conversion process, the free energy is converted into the heat energy directly without the volume work done.

The driving forces of the processes are \( \Delta Y \) and \( \Delta \mu_j^i \), the conversion processes obey the law of the conservation of energy, so \( d_i q \) cannot be less than zero, thus we get
\[
d_i q = \Delta Y dx + \sum_j \Delta \mu_j^i dN_j \geq 0. \tag{93}
\]
Since there has no volume work done, \(pdV \geq 0\) denotes only the dissipation of the conversion potential, the entropy production

\[
d_iS = \frac{1}{T} \Delta Y dx + \sum_j \frac{1}{T} \Delta \mu'_j dN_j + \Delta \left( \frac{p}{T} \right) dV \geq 0, \quad (94)
\]

where \(T\) is the temperature of the heat conversion.

Eq.(94) represents the free energy dissipations in the energy conversion processes. The free energy dissipations are derived from such a principle: the gradients \(\Delta Y\) and \(\Delta \mu'_j\) spontaneously tend to zero.

The three independent irreversible processes that we discussed above are the three different sources of irreversibility, the driving forces of the processes come from the gradients in the temperature \(\Delta(1/T)\), in the heat partial pressure \(\Delta p\), in the generalized force \(\Delta Y\) and in the chemical potential of the type \(j\) particles \(\Delta \mu'_j\), the dissipations of the gradients correspond to \(d\Delta(1/T) \leq 0, d\Delta(p/T) \leq 0, d\Delta Y \leq 0\) and \(d\Delta \mu'_j \leq 0\), the reverse processes cannot progress spontaneously in an independent process, a positive gradient production can only be driven by another gradient and in a coupling process.

In general, a thermodynamic coupling process involves two or more gradients of thermodynamic forces, and involves the two basic types: (1) the heat energy is converted into the free energy with some compensations; (2) the free energy is converted into the heat energy via the path of the volume work. The two coupling processes will be discussed below, respectively.

(1) The first type of the coupling processes is the conversion of heat into work, the heat energy is converted into the free energy via the path of the volume work

\[
dq \rightarrow \delta W_r(-pdV_r) \rightarrow Ydx + \sum_j \mu'_j dN_j
\]

where \(-pdV_r\) denotes the reversible volume work.

Consider an arbitrary coupling process, we have

\[
d_iq + pdV_r = \Delta Y dx + \sum_j \Delta \mu'_j dN_j + pdV_r, \quad (95)
\]

where we only consider a reversible process.

The conversion process obeys the law of the conservation of energy, so we have

\[
d_iq = \Delta Y dx + \sum_j \Delta \mu'_j dN_j = -pdV_r. \quad (96)
\]

Combine Eq.(95) and Eq.(96) with Eq.(88), we get

\[
d_iS = \frac{1}{T} \Delta Y dx + \sum_j \frac{1}{T} \Delta \mu'_j dN_j + \Delta \left( \frac{p}{T} \right) dV_r = 0. \quad (97)
\]

The driving forces of the process is derived from the gradient \(\Delta(p/T)\), according to Eq.(29) and Eq.(30), the entropy is the sum of the calorimetric entropy \(S_q\) and the configurational entropy \(S_v\), combine with Eq.(97) that

\[
d_iS = d_iS_q + d_iS_v = \frac{1}{T}dq + \frac{p}{T}dV_r = 0. \quad (98)
\]

Since \(d_iq \leq 0\), so in Eq.(98), we have

\[
d_iS_q = \frac{1}{T}dq \leq 0, \quad (99)
\]

and

\[
d_iS_v = \frac{p}{T}dV_r \geq 0. \quad (100)
\]

When the heat energy is converted into the free energy, the original quality loss will be retained in another form

\[
d_iS_q = \frac{1}{T}dq \rightarrow d_iS_v = \frac{p}{T}dV_r. \quad (101)
\]

Eq.(101) establishes a compensation mechanism, when the heat energy is converted into the free energy via the path of the volume work, the calorimetric entropy \(d_iq/T\) will be transformed into the configurational entropy \(pdV_r/T\), and never disappear. It shows an interesting fact, that the partial differential of the total entropy production can be less than zero.

(2) The second type of the coupling processes is the conversion of the free energy into the heat energy via the path of the volume work, including the case that the free energy partly be converted directly into the heat energy

\[
Ydx + \sum_j \mu'_j dN_j \rightarrow \delta W_r(-pdV_r) \rightarrow dq
\]

The driving forces of the processes come from the gradients in \(\Delta Y\) or/and \(\Delta \mu'_j\).

Since the free energy partly be converted directly into the heat energy, so we have

\[
d_iq = \Delta Y dx + \sum_j \Delta \mu'_j dN_j \geq -pdV_r, \quad (102)
\]

where \(-pdV_r\) denotes the reversible volume work.

Using Eq.(102) in Eq.(88), it follows that

\[
d_iS = \frac{1}{T} \Delta Y dx + \sum_j \frac{1}{T} \Delta \mu'_j dN_j + \Delta \left( \frac{p}{T} \right) dV_r = \frac{1}{T}dq + \frac{p}{T}dV_r \geq 0. \quad (103)
\]

Similar to Eq.(98), we have

\[
d_iS = d_iS_q + d_iS_v = \frac{1}{T}dq + \frac{p}{T}dV_r \geq 0. \quad (104)
\]

Since \(d_iq \geq 0\), so in Eq.(104) we have

\[
d_iS_q = \frac{1}{T}dq \geq 0. \quad (105)
\]
\[ d_iS_i = \frac{P}{T} dV_r \leq 0. \] (106)

In such a process, the configurational entropy \( p dV_r / T \) is transformed into the calorimetric entropy \( d_iq / T \).

\[ d_iS_q = \frac{P}{T} dV_r \rightarrow d_iS_q = \frac{1}{T} d_iq. \] (107)

In Eq.(98) and Eq.(104), the total entropy productions involve the two terms

\[ d_iS = d_iS_q + d_iS_v \geq 0, \] (108)

where \( d_iS_q \) denotes the calorimetric entropy production, and \( d_iS_v \) denotes the configurational or the density entropy production. In a coupling process, the total entropy production \( d_iS \geq 0 \), but the partial differentials of \( d_iS \) can be less than zero.

When some irreversible processes occurred between the two locals A and B, such as

\[ dq_A \rightarrow \delta W(v)(-p_A dV_A) \rightarrow \delta W(v)(-p_B dV_B) \rightarrow dq_B \]

where the subscripts A or B denote the locals A or B, and the heat flux between the locals A and B is equal to zero.

By Eq.(80), sum up the independent process Eq.(92) and the coupling processes Eq.(97), Eq.(103), we have

\[ d_iS = dS_A + dS_B \]

\[ = \left( \frac{d_iq_A}{T_A} + \frac{d_iq_B}{T_B} \right) + \left( \frac{p_A dV_A}{T_A} + \frac{p_B dV_B}{T_B} \right) \geq 0. \] (109)

Under more general situations, irreversible processes usually are the mixed behaviors of the above processes that we discussed respectively. Combine with Eqs.(91), (92), (94), (97), and (103), we obtain

\[ d_iS = \Delta \left( \frac{1}{T} \right) dq + \frac{1}{T} \Delta Y dX + \sum_j \frac{1}{T} \Delta \mu'_j dN_j + \Delta \left( \frac{P}{T} \right) dV \geq 0. \] (110)

There are three positive definite sources of the entropy production: (1). Heat transfer from higher temperature to lower temperature; (2). The independent process caused by the heat partial pressure; (3). Free energy is converted into the heat energy without compensation.

In an independent process, the direction of the gradient of the thermodynamic force decides the direction of a spontaneous process.

In an irreversible process, the total entropy production is always positive definite, we have \( d_iS \geq 0 \), but the partial differentials of which can be less than zero, the second law itself contains the mechanism of evolution, it implies that order and evolution can arise spontaneously.

In non-equilibrium thermodynamics, the increment in the entropy of an open system

\[ dS = d_eS + d_iS, \] (111)

has demonstrated that the total entropy of an open system can be reduced by the aid of the negative entropy flux \( d_eS \), it is an external mechanism of evolution. From Eq.(101) and Eq.(107), the second law itself has already contained the internal mechanism of evolution, in a coupling process

\[ d_iS = d_iS_q + d_iS_v \geq 0, \] (112)

the partial differential \( d_iS_q \) or \( d_iS_v \) can be less than zero.

As an explanation, \( pdV \) is defined as the change of the conversion potential related to the dissipative compensation, and by Eq.(62), \( pdV / T \) involves a density function or a configurational function, configuration means that the particles distribution has been frozen by the symmetry or asymmetry of the interactions.

For a non-equilibrium state, consider the spatial distribution of the gradients, it follows that

\[ d_iS = \nabla \left( \frac{1}{T} \right) dq + \frac{1}{T} \nabla Y dX \]

\[ + \sum_j \frac{1}{T} \nabla \mu'_j dN_j + \nabla \left( \frac{P}{T} \right) dV \geq 0. \] (113)

Eq.(112) and Eq.(113) are the total differential expressions of the second law of thermodynamics.

The second law indicates such a fundamental principle: all of the gradients of the thermodynamic forces spontaneously tend to zero, in an irreversible process, the dissipations of the gradients of the thermodynamic forces cannot be spontaneous recovery completely, the total entropy production \( d_iS \geq 0 \) is the results of the irreversible process.

DISCUSSION: A NEW FOUNDATION

Now, we are witnessing a profound change that has been bringing into thermodynamics, it is a deep change in the way of thinking, we expect to breakthrough the limitations of the traditional patterns of thinking, and establish a new theoretical framework. Start from the first law of thermodynamics, we need to re-consider thermodynamics, and answer those deep problems that can hardly continue to be discussed in the traditional theoretical framework.

In a new theoretical framework, we have ascertained the concept of the heat energy \( q \), the last one of the undefined form of the internal energy, combine with the known mechanical free energy and Gibbs free energy, we obtain

\[ dU = dq + d(Y x) + \sum_j d(\mu'_j N_j). \] (114)

The first law has been extended into

\[ dU = d_eq + d_eA + d_eG, \] (115)

\[ d_iq + d_iA + d_iG = 0. \] (116)

The energy transfer and the energy conversion can be easily distinguished by the different explicit equations.
From Eq.(28), we obtain a binomial expression, it is an explicit definition of the entropy
\[ dS = \frac{dq}{T} + \frac{p}{T} dV. \tag{117} \]

For an ideal gas or a photon gas, a primary equation of the entropy can be given by
\[ dS = \frac{\hat{a} NR(k)}{q} dq + \frac{NR(k)}{V} dV. \tag{118} \]

It is a binomial distribution function, and the entropy is proportional to the average degrees of the binomial distribution. Perhaps, it represents the real nature of the entropy.

For Eq.(118), an interesting inference can be made
\[ T \rightarrow \frac{1}{R(k)} \frac{q}{\hat{a} N}, \quad p \rightarrow \frac{q}{\hat{a} V}, \quad \left( q = \sum_{j=1}^{N} \epsilon_j \right) \]
where \( \epsilon_j \) is the kinetic energy of the particle \( j \).

Temperature \( T \) is the function of the average heat energy per degrees of freedom of the particles, and the heat partial pressure \( p \) is the function of the density of the heat energy.

For Eq.(113), an interesting inference can be made
\[ \frac{\hat{a} NR(k)}{q} dq \rightarrow R(k) \sum_{j=1}^{N} \sum_{s=1}^{s} \frac{\hat{a}}{i} d \ln \epsilon_{j(s)}, \]
where \( s \) denotes the degrees of freedom of the particles.

We find that this is a differential of a distribution function, but without any probability factor, which can be used to describe the average degree of the distribution of the extensive quantity \( q \), and when \( \hat{a} \) is a constant, we obtain a logarithmic relationship.

In Eq.(113), the driving forces of the spontaneous processes come from the different gradients of the thermodynamic forces that
\[ \nabla \left( \frac{1}{T} \right), \quad \nabla Y, \quad \nabla \mu_j, \quad \nabla \left( \frac{p}{T} \right). \]

In an independent spontaneous process, the direction of the gradient of the thermodynamic force decides the direction of the spontaneous process.

The second law of thermodynamics is derived from a fundamental principle: the gradients of the thermodynamic forces spontaneously tend to zero, and in an irreversible process, the dissipations of the gradients of the thermodynamic forces cannot be spontaneous recovery completely. In a coupling process, the dissipation of one gradient can drive the production of another gradient; it implies, the second law itself contains the mechanism of evolution.

Thermodynamics involves the two main lines, one is the law of conservation and conversion of energy, the other one involves evolution and dissipation, as a macroscopic theory, it involves the total of the microscopic dynamical processes, it should be a self-consistent theory, and should be mutually consistent with dynamics.

The master equations of dynamics are established on a fundamental principle: the law of conservation of energy, and the first law of thermodynamics is the total of these master equations, since the present dynamics involves only one main line, the law of conservation of energy, so it can hardly discuss irreversibility, similar to discuss the same problems only according to the first law of thermodynamics. In the present dynamics, we have not found a similar theoretical framework of the second law.

This theme depends on such a foundation: the physical content of the entropy has been made clear, we can verify whether a similar theoretical framework that can be found in a real dynamic process, before that, no solutions to the problems. Now, we are approaching to this foundation.

In a new theoretical framework, we might be able to find a new conclusion that is similar to the relations between chemical dynamics and chemical thermodynamics, and meanwhile, we tend to regard the second law as a law of evolution, and the total entropy productions \( dS \geq 0 \) as the spending of the evolution processes [9,11,12].

Such an attempt may be the beginning of a new study, perhaps, the primary structure of theoretical physics might be distinguished into the two main lines according to the different laws [9,12], one being the first law physics, the another one being the second law physics [9]. We can do, or cannot do, that is the problem.

**[tangsuye@hotmail.com]**

[1] I.Prigogine What is entropy? Naturwissenschaften, Vol. 76, 1. (1989)
[2] R.Clausius Ann. Phys. Chem. 125 353 (1865)
[3] A.Einstein Physics and Reality (1936)
[4] J.C.Maxwell Theory of Heat. (London: Longmans Green, 1872)
[5] R.Feynman Lectures on Physics, Vol. I. (Addison-Welsey, 1963)
[6] D.Bernoulli Hydrodynamica. (1738)
[7] L.E.Reichl A Modern Course in Statistical Physics, 2nd ed. (New York: John Wiley & Sons Inc, 1997) pp. 23.
[8] J.Fourier The Analytical Theory of Heat. (London: Cambridge University Press, 1878)
[9] Tang Suye Tackling a Century Mystery: Entropy, 2nd ed. (Hefei: University of Science & Technology of China, 2008)
[10] I.Prigogine Science. 201 4358 (1978)
[11] I.Prigogine Structure, Dissipation and Life. Theoretical Physics and Biology, Versailles, 1967, (Amsterdam: North-Holland Publ. Company 1969)
[12] I.Prigogine From Being to Becoming: Time and Complexity in the Physical Sciences. (New York: W.H.Freeman, 1980)