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An exploration for the macroscopic physical meaning of entropy

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The macroscopic physical meaning of entropy is analyzed based on the exergy (availability) of a combined system (a closed system and its environment), which is the maximum amount of useful work obtainable from the system and the environment as the system is brought into equilibrium with the environment. The process the system experiences can be divided in two sequent sub-processes, the process at constant volume, which represents the heat interaction of the system with the environment, and the adiabatic process, which represents the work interaction of the system with the environment. It is shown that the macroscopic physical meaning of entropy is a measure of the unavailable energy of a closed system for doing useful work through heat interaction. This statement is more precise than those reported in prior literature. The unavailability function of a closed system can be defined as T_0S and p_0V in volume constant process and adiabatic process, respectively. Their changes, that is, $\Delta(T_0S)$ and $\Delta\,(p_0V)$ represent the unusable parts of the internal energy of a closed system for doing useful work in corresponding processes. Finally, the relation between Clausius entropy and Boltzmann entropy is discussed based on the comparison of their expressions for absolute entropy.

entropy, macroscopic physical meaning, exergy, heat interaction

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1 Introduction

The concept of entropy is a state function in thermodynamics with great significance. It was first proposed in the early 1850s by Clausius to illuminate Carnot cycle and the second law of thermodynamics in a mathematical format. Its differential form is

$$\mathrm{d}S = \left(\frac{\delta Q}{T}\right)_{\mathrm{rev}}, \tag{1}$$

where dS is the differential form of entropy, δQ is the heat exchange between the system and its environment (everything external to the system), T is the temperature of heat reservoir or environment which is also equal to the system temperature in reversible processes and the subscript, rev, represents that the heat is supplied or extracted reversibly. It can be proved that entropy is a state function since $\oint \mathrm{d}S = \oint\left(\frac{\delta Q}{T}\right)_{\mathrm{rev}} \equiv 0$ for an arbitrarily reversible process.

The concept of entropy provides a way to describe the second law of thermodynamics mathematically, that is, the entropy of an isolated system will always increase in a spontaneous process ($\mathrm{d}S_{\mathrm{iso}} > 0$). Notice that all the variables in the definition of entropy shown in eq. (1) are macroscopic properties of a thermodynamic system and they make no reference to the microscopic nature of matter. Hence, the entropy definition by Clausius appears so

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*Corresponding author (email: jingwu12@gmail.com) straightforward that it is widely used in thermodynamic especially engineering thermodynamic literature to discuss or calculate entropy change of thermodynamic processes. In spite of this, it is still difficult to understand “what entropy is” to some extent for the reason that eq. (1) only provides the differential form of entropy rather than a direct definition of the absolute entropy.

By now, a clearer explanation for the physical meaning of entropy is mainly based on the microscopic definition of entropy developed in 1870s by Boltzmann:

$$S = k \ln \Omega, \tag{2}$$

where Ω is the number of microscopic states in Boltzmann’s kinetic theory of gases, and k is known as Boltzmann constant. In contrast to the Clausius entropy defined in terms of macroscopic quantities, Boltzmann entropy is referred to as the microscopic definition of entropy.

According to the entropy definition by Boltzmann, the physical meaning of entropy can be stated as entropy is a measurement of the disorder or randomness of a system. Since the definition of entropy in microscopic form and its physical meaning on microscopic level were established, the concept of entropy has been widely used in other fields of study to describe many phenomena beyond the strict limits of thermodynamics, although it was originally derived in classical thermodynamics. For example, in information theory, the Shannon entropy [1] or information entropy is a measure of uncertainty associated with random variable. In economics, the term “thermoeconomics” was coined by Tribus and developed by Georgescu-Roegen [2] and the concept of entropy is a central construct to the modeling of human economic activities. All these applications of entropy above are far from the initial research background and scope of Clausius entropy.

However, the interpretation of “disorder” on microscopic level is not adequate to show the essential of entropy for engineers and researchers who are more interested in the macroscopic application of entropy such as the efficiencies of heat to work conversion in heat engines and the irreversibility analysis in heat transfer process. Moreover, the shroud of mystery surrounding the concept of entropy has not uncovered even though there is an interpretation of “disorder” about entropy.

As one of the famous physical scientists, Feng [3] said that entropy is an extremely important physical quantity but it is well-known for its difficulty in comprehension. In Harken’s viewpoint[4], even physical scientists are considerably confused when they encounter the concept of entropy. Prigogine[5], the Nobel Prize winner, who developed the theory of minimum entropy production, has indicated that “…entropy is a very strange concept without hoping to achieve a complete description…”. Maybe the following interesting story [6] about information entropy will deliver the idea vividly that entropy is a shadowy kind of concept. In 1948, Shannon, who was named as “the father of information theory”, mathematically quantified the statistical nature of “lost information” in the field of information, but he had no idea about what to call this new quantity. He said, “My greatest concern was what to call it. I thought of calling it ‘information’, but the word was overly used, so I decided to call it ‘uncertainty’”. In 1949, however, he happened to visit Neumann, one of the foremost mathematicians of the 20th century. Neumann told him that he could call it entropy for the important reason that “…nobody knows what entropy really is, so in a debate you will always have the advantage.”

At present, to explore the essence of entropy is a challenging work and whether the result is convinced and accepted is still difficult to predict. This paper intends to obtain a simple and straightforward explanation of the macroscopic physical meaning of entropy based on the analysis of availability of a combined system without chemical reactions. Furthermore, some discussions about the consistency between Clausius entropy and Boltzmann entropy are also included.

2 Exergy (availability)

The concept of exergy or availability is commonly used in thermodynamic analysis. The exergy transfer accompanying heat transfer is the maximal possible conversion of the amount of a heat transfer Q to useful work by supplying the heat transfer to a reversible Carnot heat engine operating between the body releasing heat at temperature T and the environment at temperature $T_0(T>T_0)$. The exergy transfer accompanying heat transfer, Q_a, is in the amount of

$$Q_a = Q\left(1-\frac{T_0}{T}\right). \tag{3}$$

The part of heat transfer that cannot be transformed to useful work is called the unavailability transfer accompanying heat transfer

$$Q-Q_a = \frac{T_0}{T}Q. \tag{4}$$

The exergy of a system is the maximum useful work obtainable during a process that brings the system into equilibrium with the environment. Its relation with other properties of the system is

$$W_{\max} = U-U_0-p_0\left(V_0-V\right)-T_0\left(S-S_0\right), \tag{5}$$

where $W_{\max}$ denotes the exergy of the system, U, V, and S are the internal energy, volume, and entropy of the system at the given state, respectively, U_0, V_0, and S_0 are the corresponding properties of the system at the dead state (a state in equilibrium with the environment), T_0 is the temperature of the environment, and p_0 is its pressure.

It is noted (ignored or not pointed in some textbooks) that the maximum useful work possible may come from not only the energy of the closed system (control mass), but also partially or even all the energy of the environment for some conditions. Accordingly, the concept of "combined system [7]" needs to be emphasized when discussing the exergy of the system. That is, the maximum useful work $W_{\max}$ in eq. (5) should be referred to as the exergy of a combined system. As shown in Figure 1, a combined system consists of a closed system and its environment. According to the definition of adiabatic system in thermodynamics, the combined system can also be considered as an adiabatic system.

The exergy of a combined system equals the change of its internal energy [7], that is,

$$W_{\max} = -\underbrace{\left(U_0 - U\right)}_{\Delta U} - \underbrace{\left[p_0\left(V_0 - V\right) + T_0\left(S - S_0\right)\right]}_{\Delta U^0}, \tag{6}$$

where ΔU and ΔU^0 represent the changes in internal energy of the closed system and its environment, respectively.

From eq. (6), we can see that the exergy of a combined system is a measure of the departure of the state of the closed system from that of the environment and is independent of the particular processes selected to evaluate it. That is, when the parameters of the environment (p_0, T_0) and the state of the closed system are given, the exergy of the combined system is identified. The exergy always has a positive value no matter the temperature T of the closed system is greater than or less than the temperature T_0 or the pressure p of the system is greater than or less than p_0 [7].

Consider a closed system with a given state located in the shaded domain in Figure 2, namely, $S > S_0$ and $V < V_0$. Substituting these inequalities into eq. (6) yields $\Delta U^0 > 0$, which means that the internal energy of the environment increases. In this case, one part of the decreased internal energy of the closed system will convert into the internal energy of the environment, while the other part of it will convert into the useful work when the closed system proceeds from the given state to the dead state. Therefore, the useful work derived from the combined system comes solely from the energy reduction of the closed system rather than the environment. In this case ($S > S_0$ and $V < V_0$), the exergy of the combined system is actually "the exergy of a closed system". In contrast, if a closed system with an initial state located outside the shaded domain in Figure 2, (point a or point b, for example), the useful work will partially or even all come from the energy of environment. For convenience, only the conditions when the state of the closed system located in the shaded domain are discussed in this paper.

3 Heat interaction and work interaction

For the system reversibly brought into equilibrium with the environment the process can be divided into two sequent sub-processes, as shown in Figure 3: (i) process at fixed volume i–a from its given state to the in-between state and (ii) adiabatic process a–o from the in-between state to the dead state.

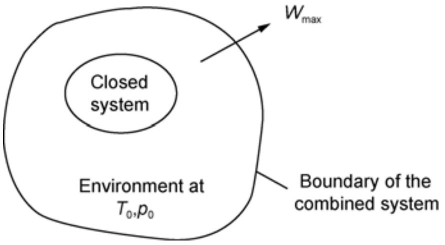


Figure 1 The sketch of combined system.

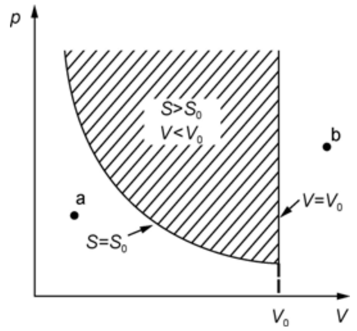


Figure 2 The domain of $S > S_0$ and $V < V_0$ of a closed system.

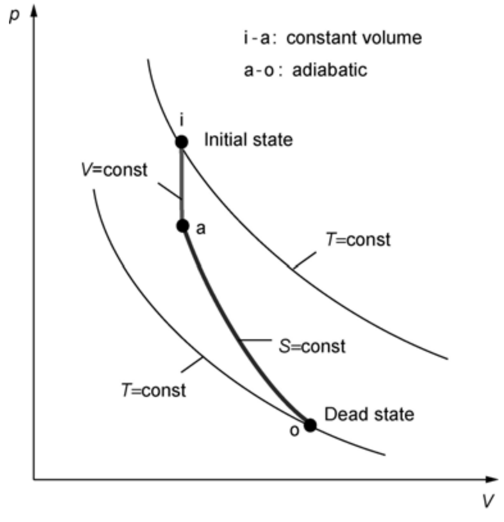


Figure 3 Two sequent sub-processes from the given state to the dead state.

3.1 Heat interaction

In the isovolumetric process i-a, the volume of the closed system is kept constant, which means that there is only heat transfer but no work transfer at the system boundary. Thus, the isovolumetic process represents the heat interaction [7] between the system and the environment. Work can be derived from the combined system when the heat transfer is effected through numerous heat engines operating, as shown in Figure 4.

The contribution of this process to the total work is

$$W_{\max 1}=\int_{\mathrm{i}}^{\mathrm{a}}\left(\frac{T_0}{T}-1\right)\delta Q, \tag{7}$$

where $W_{\max 1}$ is the useful work extracted through heat interaction between the closed system and the environment. In the condition as shown in Figure 4, the temperature of the closed system is more than that of the environment and heat is received from the closed system and discharged into the environment, which means $T > T_0$, $\delta Q < 0$ and $W_{\max 1} > 0$. In this process, the useful work is converted from the transferred heat by Carnot engine but not derived directly by the expansion of the closed system. Thus, the work done through heat interaction is named as "direct work".

In the process of heat interaction (doing work indirectly), the heat released to the environment is

$$Q_0=-\int_{\mathrm{i}}^{\mathrm{a}}T_0\frac{\delta Q}{T}. \tag{8}$$

According to the definition of entropy $\mathrm{d}S=(\delta Q/T)_{\mathrm{rev}}$ and $S_{\mathrm{a}}=S_0$ for isentropic process a-o, we can get

$$\int_{\mathrm{i}}^{\mathrm{a}}\frac{\delta Q}{T}=S_0-S. \tag{9}$$

Substituting eq. (8) into eq. (9) yields

$$Q_0=T_0\left(S-S_0\right). \tag{10}$$

The equation above shows that the term $T_0\left(S-S_0\right)$ in eq. (5) represents the amount of the exchanged heat Q_0 between the system and the environment in the process of heat interaction as shown in Figure 5(a).

3.2 Work interaction

In the adiabatic process as shown in Figure 3, there is no heat exchange but work exchange between the closed system and the environment. Thus, the adiabatic process represents the wok interaction [7] between them and the useful work in this process is derived by the expansion of the closed system. In contrast to the term of "indirect work" in the isovolumetric process, the work done during the adiabatic process is referred to as "direct work".

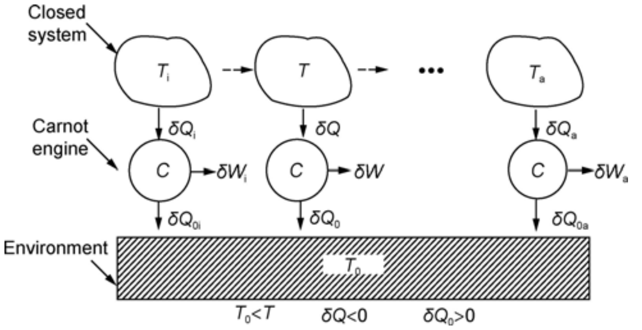
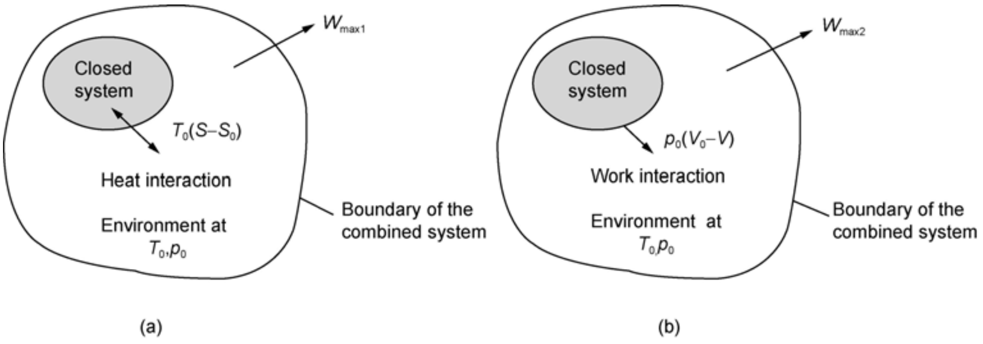


Figure 4 Heat interaction between the closed system and the environment in the isovolumetric process and work derived through Carnot heat engines.



(a) (b)

Figure 5 The sketch of energy exchange during the interaction between the system and the environment. (a) Heat interaction; (b) work interaction.

In the process of work interaction, the magnitude of work performed by the closed system is

$$W=\int_{\mathrm{a}}^{\mathrm{o}} p\mathrm{d}V. \tag{11}$$

Meanwhile, the magnitude of the work done upon the environment by the closed system is

$$W_0=p_0\left(V_0-V\right), \tag{12}$$

where W_0 is referred to as the useless work and it represents the amount of work the closed system has to pay for during its expansion against the environment.

By combining eq. (11) and eq. (12), the contribution of this adiabatic process to the total work can be expressed as

$$W_{\max2}=\int_{\mathrm{a}}^{\mathrm{o}} p\mathrm{d}V-p_0\left(V_0-V\right), \tag{13}$$

where $W_{\max2}$ is the useful work obtained through work interaction as shown in Figure 5 (b).

4 The macroscopic physical meaning of entropy

For the isovolumetric process i-a, the same reasoning as in Section 3.1 gives

$$W_{\max1}=\int_{\mathrm{i}}^{\mathrm{a}}\left(\frac{T_0}{T}-1\right)\delta Q=T_0\left(S_0-S\right)-Q. \tag{14}$$

Since $Q=U_{\mathrm{a}}-U_{\mathrm{i}}$ (from the equation of energy conservation) eq. (14) can be rewritten as

$$Q=U_{\mathrm{a}}-U_{\mathrm{i}}=U_{\mathrm{a}}-U, \tag{15}$$

or

$$T_0(S-S_0)=(U-U_{\mathrm{a}})-W_{\max1}, \tag{16}$$

where $U-U_{\mathrm{a}}$ represents the reduction in internal energy of the closed system through heat interaction, and $W_{\max1}$ is the useful work which can be extracted in this process. Thus, the term, T_0 $(S–S_0)$ is the part of the internal energy of a closed system that cannot be transformed to useful work. From the analysis above, we can define the term T_0 $(S–S_0)$ as the unavailable energy of a closed system through heat interaction when it passes from a given state to the dead state, namely

$$E_{\mathrm{un1}}=T_0\left(S-S_0\right), \tag{17}$$

where E_{un1} is the symbol of unavailable energy.

Eq. (17) can then be rewritten as

$$S=\frac{E_{\mathrm{un1}}}{T_0}+S_0. \tag{18}$$

In general, the values for p_0 and T_0 are taken as typical environment conditions, such as 1 atm and 25°C. In addition, for a closed system with designated composition, its entropy at the dead state, S_0, is a fixed value. In the conditions above, the entropy of a closed system, S, is proportional to the unavailable energy, E_{un1}. Accordingly, eq. (18) reveals that the macroscopic physical meaning of entropy can be explained as a measure of the unavailable energy of a closed system for doing useful work through heat interaction. The more entropy is, the more unavailable energy will be through heat interaction.

It is noticed that there are some descriptions, though limited, which are present in some literature[8–12] in an effort to explain the macroscopic physical meaning of entropy. For example, Liu et al. [8] indicated that the entropy change is a measure of the change in “non-work ability” for a system. However, this interpretation is kind of abstract due to the obscure concept of “non-work ability”. Moreover, entropy is explained as a measure of the unavailability of a system’s thermal energy for conversion into mechanical work [12]. This explanation, on the one hand, can verify the conclusion presented in this paper to a certain extent, that is, entropy is a measure of the unavailability of a system. On the other hand, however, it is not definite for the reason that the influence of entropy on the unavailability of a closed system displays only in the process of heat interaction between the system and the environment. Thus, entropy is a measure of unavailability in heat interaction rather than work interaction. These two processes are independent of each other and need to be discussed separately when considering the physical meaning of entropy.

5 Unavailability (anergy) and unavailability functions

In the reversible isovolumetric process i-a, the entropy change of the closed system is equal to the flow of entropy, namely $\mathrm{d}S=\delta Q/T$. In addition, the law of energy conservation gives $\delta Q=\mathrm{d}U$. Therefore, we can get

$$\mathrm{d}S=\frac{\delta Q}{T}=\frac{\mathrm{d}U}{T}. \tag{19}$$

We multiply eq. (19) by the environment temperature T_0 as follows

$$T_0\mathrm{d}S=\delta Q\frac{T_0}{T}=\mathrm{d}U\frac{T_0}{T}, \tag{20}$$

where the term $\delta Q T_0/T$ represents the unavailability transfer accompanying heat transfer δQ, that is, the part of heat transfer which can not be transformed to useful work.

This equation allows us to get the conclusion that when an amount of heat, δQ, transfers from a high temperature to a low one, there is an associated flow of unavailable energy, $\delta Q T_0/T$, as shown in Figure 6. The amount of unavailable energy is increased due to $T_1 > T_2$.

Integrating eq. (20) from the initial state i to the in-between state a of the closed system, we can obtain

$$T_0\left(S - S_0\right) = T_0 \int_{T_\mathrm{a}}^{T} \frac{C_\mathrm{v}}{T}\,\mathrm{d}T, \tag{21}$$

where C_v is the heat capacity of the closed system at constant volume and T_a is the temperature at the in-between state a.

Let us assume that the heat capacity at constant volume is fixed over the temperature range of $[T_\mathrm{a}, T]$. Then the internal energy can be expressed as $U = C_\mathrm{v} T$. The integral result of eq. (21) can be written as

$$T_0\left(S - S_0\right) = U \frac{T_0}{T} \ln \frac{T}{T_\mathrm{a}}, \tag{22}$$

where the term $UT_0/T \ln\left(T/T_\mathrm{a}\right)$ can be regarded as the unavailable energy of the internal energy of the closed system through heat interaction. It is similar to the form of unavailability transfer accompanying heat transfer, QT_0/T. Both of them are the product of an amount of energy and a dimensionless parameter except that the expression of the unavailable energy of the internal energy has an extra logarithmic factor of ln (T/T_a) due to the function relation between the internal energy U and the temperature T.

Apart from the unavailable energy of $T_0\left(S - S_0\right)$ through heat interaction, there is another kind of unavailable energy through work interaction. The work done by the closed system in the adiabatic process a-o is

$$\int_\mathrm{a}^\mathrm{o} p\,\mathrm{d}V = U_\mathrm{a} - U_0. \tag{23}$$

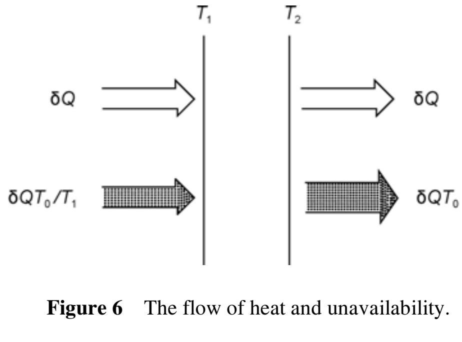


Figure 6 The flow of heat and unavailability.

Combining eq. (23) and eq. (13) gives

$$p_0\left(V_0 - V\right) = U_\mathrm{a} - U_0 - W_{\max 2}, \tag{24}$$

where $U_\mathrm{a} - U_0$ represents the reduction in internal energy of the closed system during the process of work interaction with the environment, and $W_{\max 2}$ is the useful work extracted in this process. Their difference, $p_0\left(V_0 - V\right)$, is the part of the internal energy of the closed system that cannot be transformed to useful work through work interaction. It can be defined as the unavailable energy of the closed system in this process, namely

$$E_{\mathrm{un}2} = p_0\left(V_0 - V\right). \tag{25}$$

Substituting eqs. (17) and (25) into eq. (6), we can obtain

$$W_{\max} = \underbrace{U - U_0}_{-\Delta U} - \underbrace{T_0\left(S - S_0\right)}_{E_{\mathrm{un}1}} - \underbrace{p_0\left(V_0 - V\right)}_{E_{\mathrm{un}2}}. \tag{26}$$

According to eq. (26), the physical signification of the exergy of a combined system can be explained from the viewpoint of unavailable energy. It shows that the exergy of a combined system is the internal energy left in this system after the deduction of the unavailable energy through heat interaction and work interaction as the closed system is brought into equilibrium with the environment.

In thermodynamics, potential functions [13] are introduced based on the state function such as internal energy U, enthalpy H and entropy S as the criterion of spontaneous reaction. One of the potential functions is the Helmholtz function, A=U–TS. When a closed system changes its thermodynamic state, the change in Helmholtz function, $\Delta A = A_1 - A_2$, measures the useful work obtainable from the system at a constant volume and temperature. Another main potential function is the Gibbs function with the definition of G=H–TS and the change in it, $\Delta G = G_1 - G_2$, represents the useful work obtainable from an isothermal, isobaric thermodynamic system. These two potential functions are commonly used in thermodynamics, especially in the chemical thermodynamics of reactions. Notice that the changes in Helmholtz function and Gibbs function, ΔA and ΔG, can be deduced in an arbitrary process. But only in specified conditions, namely, ΔA for a system at a constant volume and temperature and ΔG for a system at a constant pressure and temperature, ΔA and ΔG represent the maximum useful work done by the system, respectively.

By analogy of Helmholtz function and Gibbs function, we introduce a new thermodynamic potential function for a closed system and coin it unavailability function. In the isovolumetric process, its expression is $T_0 S$ and its change, $T_0\,(S_1$–$S_2)$, determines the amount of unavailable energy of the closed system in this process, that is, the unusable part of the internal energy for doing useful work in a process at constant volume. In the adiabatic process, the unavailability function is defined as p_0V and its change, in the same manner, $\Delta\left(p_0V\right)=p_0\left(V_2-V_1\right)$, is the amount of unavailable energy of the closed system in this process.

Same as the Helmholtz function and Gibbs function, unavailability functions are also state functions of a closed system and their changes, $\Delta\left(T_0S\right)$ and $\Delta\left(p_0V\right)$, can be calculated in any process. However, they represent the unavailable energy only in their associated volumetric and adiabatic processes, respectively and hence they have no physical meanings in other conditions. Moreover, note that unlike Helmholtz function or Gibbs function which is the combination of system's state functions, the unavailability functions consist of the parameters of the system and its environment, namely, the entropy S or volume V of the closed system, together with the environmental temperature T_0 or its pressure p_0. This means that when the temperature of the environment approaches to zero, there is no unavailable energy for a closed system through heat interaction, and its internal energy can be totally transformed to the useful work through heat interaction between the system and the environment. Similarly, when the pressure of the environment approaches to zero (vacuum for instance), the internal energy can be converted to work with 100% efficiency through work interaction.

6 The definition of absolute entropy

In 1905, German physical chemist and physicist, Nernst found a new rule by applying thermodynamic theory to the low temperature phenomena and chemical reactions. It can be stated as follows. In an isothermal reversible transformation between two stable states of a condensed substance, the change in entropy vanishes as the absolute temperature tends to zero. In 1911, Planck proposed to put S=0 at T=0, namely,

$$\lim_{T\to 0} S=S_0=0. \tag{27}$$

After the definition of entropy at a temperature of absolute zero, the absolute entropy of a substance at any state can be calculated by integrating the differential definition of Clausius entropy in eq. (1). In chemical thermodynamics, most chemical reactions occur at constant pressure and hence, the absolute entropy of a mole of a substance at one standard atmosphere is [8]

$$S_{\mathrm{m}}=\int_0^{T_{\mathrm{mel}}}\frac{C_{\mathrm{p,m,s}}\mathrm{d}T}{T}+\frac{\Delta H_{\mathrm{mel}}}{T_{\mathrm{mel}}}+\int_{T_{\mathrm{mel}}}^{T_{\mathrm{b}}}\frac{C_{\mathrm{p,m,l}}\mathrm{d}T}{T}+\frac{\Delta H_{\mathrm{b}}}{T_{\mathrm{b}}}+\int_{T_{\mathrm{b}}}^{T}\frac{C_{\mathrm{p,m,g}}\mathrm{d}T}{T}, \tag{28}$$

where the subscripts, mel and b, denote melting point and boiling point, respectively, s, l, and g represent solid, liquid and gas, respectively, m is mole, and $C_{\mathrm{p,m}}$ is the molar heat capacity at constant pressure.

Suppose that at an extremely low temperature, the molar heat capacity at a constant pressure of a substance satisfies the relation of

$$C_{\mathrm{p,m}}=233.8R\left(\frac{T}{\theta_{\mathrm{D}}}\right)^3, \tag{29}$$

where θ_{D} is the Debye temperature. The absolute entropy of one mole of substance can be determined by[8]

$$S_{\mathrm{m}}=\frac{1}{3}\left[233.8R\left(\frac{T^*}{\theta_{\mathrm{D}}}\right)^3\right]+\int_{T}^{T_{\mathrm{mel}}}\frac{C_{\mathrm{p,m,s}}\mathrm{d}T}{T}+\frac{\Delta H_{\mathrm{mel}}}{T_{\mathrm{mel}}}+\int_{T_{\mathrm{mel}}}^{T_{\mathrm{b}}}\frac{C_{\mathrm{p,m,l}}\mathrm{d}T}{T}+\frac{\Delta H_{\mathrm{b}}}{T_{\mathrm{b}}}+\int_{T_{\mathrm{b}}}^{T}\frac{C_{\mathrm{p,m,g}}\mathrm{d}T}{T}, \tag{30}$$

where T^* generally refers to a certain temperature lower than 20 K.

In some circumstance, eq. (30) can be further simplified. We assume that the temperature of a substance is much higher than its boiling point T_{b} and that the molar heat capacity at constant pressure $C_{\mathrm{p,m}}$ is fixed. So that eq. (30) can be rewritten as the simplified form

$$S_{\mathrm{m}}\approx C_{\mathrm{p,m}}\ln T. \tag{31}$$

It shows that when some additional assumptions are introduced, the logarithmic connection between entropy and temperature of a substance can be obtained based on the macroscopic definition of entropy by Clausius. It looks similar to the Boltzmann's definition of entropy, $S=k\ln\Omega$. In this sense, the connection between the macroscopic and microscopic expression of entropy is set up to some extent.

7 Conclusions

(i) For the system reversibly brought into equilibrium with the environment the process can be divided into two sequent sub-processes: an isovolumetric process and an adiabatic process. The isovolumetric process represents the heat interaction of the closed system with the environment, that is, to develop work and release heat to the environment through reversible heat engines. The adiabatic process represents the work interaction of the closed system with the environment, that is, to develop work through the volume change of the closed system as well as the environment. The macroscopic physical meaning of entropy can be stated as a measurement of unavailable energy through heat interaction between a system and its environment. This statement is more precise than those in the literature due to the added condition of "through heat interaction".

(ii) Same as Helmholtz function and Gibbs function, unavailability functions are defined. One is the product of the environment temperature and the system entropy, T_0S, the other is the environment pressure multiplied by the system volume, p_0V. The changes in them, $\Delta(T_0S)$ and $\Delta(p_0V)$, represent the unusable parts of the internal energy of the closed system in the volumetric process and adiabatic process, respectively.

(iii) After the comparison of the expressions for Boltzmann entropy and Clausius entropy in integrated form under some approximate conditions, we found that both of them have a logarithmic form and hence the relation between these two expressions are set up to some extent.

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