New Method Proving Clausius Inequality*

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Abstract

It is impossible that proving the internal energy change has the relations with volume and pressure. About the second law of thermodynamics, many mistakes of formulations need to be put right and modified, and many new concepts are surveyed too. The equality and inequality on the ratios of internal energy change to temperature and work to temperature are discussed. The relation between the reversible paths and their realistic paths is also researched. In an isothermal process, the internal energy change for the gases is equal to zero, but the internal energy change is not equal to zero for the phase transition or chemical reaction. The Clausius inequality can be derived from the equation calculating the internal energy change in mathematics; it is the new method proving the Clausius inequality. These change laws of thermodynamics could be applied to the gravitational field and mechanical motion and so on.

Keywords

First Law of Thermodynamics, Clausius Inequality, Internal Energy Change, Chemical Reaction, Gravitational Field

1. Introduction

In text, the heat and work are taken as positive if the energy is supplied to the system and negative if the energy is lost out of the system. W_{other} expresses the other work (also called the non-expansion work), and $-p\mathrm{d}V$ indicates the pressure-volume work (namely the expansion work).

According to the first law of thermodynamics [1] [2] [3], if the expansion work doesn't exist, the internal energy change is equal to the non-expansion work in the adiabatic process. If any work doesn't exist, the internal energy change is equal to the heat in a constant volume process (namely that $\mathrm{d}U = C_V \mathrm{d}T$, where, C_V is

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the heat capacity at the constant volume). If the other work doesn't exist in a constant pressure process, the internal energy change is equal to $\Delta U = \Delta H - p\Delta V$ (where, $\Delta H = C_p \Delta T$, C_p is the heat capacity at the constant pressure, ΔH is the enthalpy change at the constant pressure). In a process, the heat, work, and internal energy change can transfer each other, but the relation of heat, work, and internal energy change has to obey the energy conservation law namely the first law of thermodynamics.

The difference on the ratios of work to temperature between a reversible process and its realistic process is no more than zero; simultaneously, the difference on the ratios of internal energy change to temperature between a reversible process and its realistic process is no less than zero. If the latent heat and chemical reactions do not exist, the internal energy change in an isothermal process will be zero [4]. In this paper, the new method proving the Clausius inequality will be investigated.

Attentively, "d" and "δ" are total differential symbols to the state function and path function, respectively. "Δ" expresses the change of quantity value. "∫" is integral symbol. "∂" is partial differential symbol. The internal energy change is the state function. The heat and work are the path functions in many processes. The enthalpy change at the constant pressure is the state function too.

2. New Concepts about the Ratios of Internal Energy Change to Temperature and Work to Temperature

In a spontaneous or realistic process, according to the first law of thermodynamics, we can obtain [4] [5]

$$
\begin{aligned}
&\int_i^f \frac{\mathrm{d}U_r(A)}{T} - \int_i^f \frac{\mathrm{d}U_{real}(B)}{T_{res}} \\
&= \int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}} + \int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}}
\end{aligned}
\tag{1}
$$

The criterion equation for a process is obeyed as the follows

$$
\int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}} \geq 0 .
\tag{2}
$$

In a spontaneous or realistic process, the following equations must be also obeyed

$$
\int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}} \leq 0 ,
\tag{3}
$$

$$
\int_i^f \frac{\mathrm{d}U_r(A)}{T} - \int_i^f \frac{\mathrm{d}U_{real}(B)}{T_{res}} \geq 0 .
\tag{4}
$$

where, the equality is usually for a reversible process, the inequality is for an irreversible process. (B) and (A) express the realistic path and reversible path, respectively. The realistic paths may include the reversible or irreversible paths. The friction does not exist in any reversible process. ΔS and $\int_i^f \frac{\delta Q_r(A)}{T}$ all

express the entropy change, that is, $\Delta S = \int_i^f \frac{\delta Q_r(A)}{T} \cdot \int_i^f \frac{\delta W_r(A)}{T}$ is indicated with ΔS_W, namely that $\Delta S_W = \int_i^f \frac{\delta W_r(A)}{T} \cdot \int_i^f \frac{dU_r(A)}{T}$ is expressed with ΔS_U, namely that $\Delta S_U = \int_i^f \frac{dU_r(A)}{T}$. In a process, T_i and T_f are the thermodynamics temperature of system in the initial state and final state, respectively. T expresses the thermodynamics temperature of system transforms from T_i to T_f. T_{res} is the thermodynamics temperature of surroundings or reservoirs, and T_{res} can vary or influence the thermodynamics temperature of system except the adiabatic system. Of course, T_{res} is the same as T in any reversible process or constant temperature process. T_{res} is not always considered as a constant in a realistic process. Any spontaneous or realistic process has to obey the Clausius inequality [6] [7] [8].

$\Delta S_g = \int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}}$, where, ΔS_g is called the entropy generation [9] [10] [11]. In a spontaneous or realistic process, we can gain $\Delta S_g \geq 0$. In the adiabatic process, ΔS_g is not equal to zero for an irreversible process.

$(\Delta S_W)_g = \int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}}$, where, $(\Delta S_W)_g$ is defined as the ratio of work to temperature generation. In a spontaneous or realistic process, we have $(\Delta S_W)_g \leq 0$. If any work doesn't exist, $(\Delta S_W)_g$ is equal to zero.

$(\Delta S_U)_g = \int_i^f \frac{dU_r(A)}{T} - \int_i^f \frac{dU_{real}(B)}{T_{res}}$, where, $(\Delta S_U)_g$ is defined as the ratio of internal energy change to temperature generation. In a spontaneous or realistic process, we shall obtain $(\Delta S_U)_g \geq 0$. In the isothermal process, $(\Delta S_U)_g$ is equal to zero. Equation (1) can be rewritten as $(\Delta S_U)_g = \Delta S_g + (\Delta S_W)_g$.

Certainly, the values of ΔS_g, $(\Delta S_W)_g$, and $(\Delta S_U)_g$ all will change into zero in the reversible process or equilibrium changeless state for the spontaneous or realistic processes. The ΔS_g, $(\Delta S_W)_g$, and $(\Delta S_U)_g$ are the path functions, not the state functions. According to Equations (1), (3), we know $\Delta S_g \geq (\Delta S_U)_g$.

$\int_i^f \frac{\delta Q_{real}(B)}{T_{res}}$ is the path functions called the entropy flow [12]. When the solids and liquids are cooled, it will release the heat and its temperature will fall, the entropy change is negative value which conforms to the Clausius inequality, it is very reasonable nature results, but the entropy generation is no less than zero in the processes, that is, $\Delta S_g \geq 0$. In a process, ΔS is unable to be varied by the entropy flow or path or energy like work and heat, since it is the state functions. The entropy generation could be changed from negative to positive by the entropy flow or path or energy. In the living things, the entropy generation in the glucose synthesized reaction will be changed from negative to positive. If there is not any energy supplied to system, the damage cells in the living things could not be repaired, and the life will end and die.

3. New Method Proving the Clausius Inequality

The internal energy change has to be equal to zero for the ideal and real gases in any isothermal process, namely that, $\left(\dfrac{\partial U}{\partial V}\right)_T = 0$ and $\left(\dfrac{\partial U}{\partial p}\right)_T = 0$ (where, the subscript T indicates constant temperature). In the Rossini and Frandsen experiment [4] [13], the high pressure gas slowly expands and enters the air through the valve and pipeline, the water heated by heater in trough will keep constant temperature, but the expansion gas is open will still do work to air, so the heat is unable to be accurately determined. Therefore, it is regretful that the Rossini and Frandsen experiment could not prove the internal energy change having a relation with the pressure and volume for the gas. In the Rossini and Frandsen experiment, the pressure-volume work is equal to $-\int_i^f p\,\mathrm{d}V$, which is approximately equal to $-p\Delta V$ (where, p is the constant pressure).

If the latent heat and chemical reactions do not exist, we can obtain [4]

$$\mathrm{d}U = C_V \mathrm{d}T . \tag{5}$$

The gases, solids and liquids all obey Equation (5). If the phase transition or chemical reactions exist in the constant temperature and constant pressure, the internal energy change will be given by

$$\Delta U = Q_V ,$$

$$\Delta U = \Delta H - p\Delta V .$$

where, the enthalpy change is the latent heat or chemical reaction heat in the constant temperature and constant pressure. Therefore, the internal energy change is the state functions for the phase transition or chemical reactions.

If the phase transition or chemical reactions does not exist for the closed system, we can obtain $\mathrm{d}U = \delta Q + \delta W_{other} - p\,\mathrm{d}V$ and $C_V \mathrm{d}T = T\mathrm{d}S + \delta W_{other} - p\,\mathrm{d}V$. Where, $\delta W_{real}(B) = \delta W_{other}(B) - p\mathrm{d}V(B)$, $\delta Q_{real}(B) = T\mathrm{d}S(B)$ (it is dependable, since $\mathrm{d}S(B) = \dfrac{\delta Q_{real}(B)}{T}$, $\int_i^f \dfrac{\delta Q_r(A)}{T} = \int_i^f \dfrac{\delta Q_{real}(B)}{T} = \Delta S$), $\delta Q_r(A) = T\mathrm{d}S(A)$, $\delta W_r(A) = \delta W_{other}(A) - p\mathrm{d}V(A)$, $p\mathrm{d}V(A) \neq p\mathrm{d}V(B)$. Attentively, T is often not the constant in the isothermal irreversible path (B), but $T_i = T_f = T_{res}$. T is the constant in the isothermal reversible path (A).

Thereinafter, using Equation (4) will prove the Clausius inequality is absolutely correct.

According to Equation (5), we can prove Equation (4) is absolutely right in mathematics. When $\mathrm{d}T \geq 0$, we find $T \leq T_{res}$ and $\dfrac{\mathrm{d}T}{T} \geq \dfrac{\mathrm{d}T}{T_{res}}$. If $\mathrm{d}T \leq 0$, we find $T \geq T_{res}$ and $\dfrac{-\mathrm{d}T}{T} \leq \dfrac{-\mathrm{d}T}{T_{res}}$, further, $\dfrac{\mathrm{d}T}{T} \geq \dfrac{\mathrm{d}T}{T_{res}}$. Hence, $\int_i^f \dfrac{\mathrm{d}T}{T} \geq \int_i^f \dfrac{\mathrm{d}T}{T_{res}}$. Thus, $\int_i^f \dfrac{\mathrm{d}U_r(A)}{T} \geq \int_i^f \dfrac{\mathrm{d}U_{real}(B)}{T_{res}}$.

If $\Delta S_g \geq 0$, that is, $\int_i^f \dfrac{\delta Q_r(A)}{T} - \int_i^f \dfrac{\delta Q_{real}(B)}{T_{res}} \geq 0$, on the basis of Equation (1),

we can obtain

$$\int_i^f \frac{\mathrm{d}U_r(A)}{T} - \int_i^f \frac{\mathrm{d}U_{real}(B)}{T_{res}} \geq \int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}}.$$

In order to guarantee that above-mentioned inequality is absolutely right, according to Equation (4), the value of $\int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}}$ must be no more than zero (namely that $\int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}} \leq 0$). If

$\int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}} < 0$, we can obtain

$$\int_i^f \frac{\mathrm{d}U_r(A)}{T} - \int_i^f \frac{\mathrm{d}U_{real}(B)}{T_{res}} < \int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}}.$$

On the basis of Equation (4), we have $\int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}} > 0$.

If $\int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}} > 0$, according to Equation (1), we can obtain

$$\int_i^f \frac{\mathrm{d}U_r(A)}{T} - \int_i^f \frac{\mathrm{d}U_{real}(B)}{T_{res}} > \int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}}.$$

In order to guarantee that aforesaid inequality is absolutely right, according to Equation (4), the value of $\int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}}$ must be no more than zero (that is, $\int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}} < 0$). If $\int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}} \leq 0$, we have

$$\int_i^f \frac{\mathrm{d}U_r(A)}{T} - \int_i^f \frac{\mathrm{d}U_{real}(B)}{T_{res}} \leq \int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}}.$$

Consequently, according to Equation (4), we can find

$$\int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}} \geq 0.$$

There are two results generated by Equation (4), but their conclusions are contrary. Which result should be selected? We need to eliminate a wrong answer from the next procedures.

When any work doesn't exist, we can gain $\int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}} = 0$.

According to Equation (1), we have

$$\int_i^f \frac{\mathrm{d}U_r(A)}{T} - \int_i^f \frac{\mathrm{d}U_{real}(B)}{T_{res}} = \int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}}.$$

Therefore, on the basis of Equation (4), we can get

$$\int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}} \geq 0.$$

Furthermore,

$$\left| \int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}} \right| \geq \left| \int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}} \right|. \qquad (6)$$

where, $| \ |$ expresses absolute value symbol of quantity. In the isothermal process, $\int_i^f \frac{\mathrm{d}U_r(A)}{T} - \int_i^f \frac{\mathrm{d}U_{real}(B)}{T_{res}} = 0$, we can gain

$$\int_i^f \frac{\delta Q_r(A)}{T} - \int_i^f \frac{\delta Q_{real}(B)}{T_{res}} + \int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}} = 0 .$$

Accordingly, we can confirm $\int_i^f \frac{\delta W_r(A)}{T} - \int_i^f \frac{\delta W_{real}(B)}{T_{res}} \leq 0$.

The aforementioned results prove the Clausius inequality is right. These Equations (2)-(6) are all the results of nature option. The other methods proving the Clausius inequality see the references [14] [15].

4. Results and Discussion

4.1. Relation between the Reversible Paths and Its Realistic Paths in the Gases and Chemical Reactions

In a spontaneous or realistic process, we would assume [4]

$$Q_{real}(B) = Q_r(A) + Q_{pf}(B), \qquad (7)$$

$$W_{real}(B) = W_r(A) + W_{pf}(B). \qquad (8)$$

where, $Q_r(A)$ and $W_r(A)$ do not contain $Q_{pf}(B)$ and $W_{pf}(B)$. Here, $W_{pf}(B)$ can cause the temperature change.

According to the first law of thermodynamics, in a process, the following equations are given by $\Delta U_r(A) = Q_r(A) + W_r(A)$, $\Delta U_{real}(B) = Q_{real}(B) + W_{real}(B)$, and $\Delta U_r(A) = \Delta U_{real}(B)$. Where, $\Delta U_r(A)$ and $\Delta U_{real}(B)$ are the internal energy change in a reversible path (A) and its realistic path (B), respectively. Because $\Delta U_r(A) = \Delta U_{real}(B)$, we can get

$$Q_{pf}(B) = -W_{pf}(B) \qquad (9)$$

Attentively, $W_r(A)$ and $W_{real}(B)$ can be calculated from p-V diagram for the gases (employing the gas equation of state or the state experiment datums). A reversible path and its irreversible path are distinction for the gases, otherwise, $W_{pf}(B)$ will be equal to zero.

In a reversible path (A) and its realistic path (B), the following equations have to be obeyed [5] [16], such as

$$Q_r(A) \geq Q_{real}(B), \qquad (10)$$

$$W_r(A) \leq W_{real}(B), \qquad (11)$$

$$Q_{pf}(B) = -W_{pf}(B) \leq 0. \qquad (12)$$

where, the equality is for the identical reversible paths (if any work doesn't exist, the equality is also for the irreversible paths), the inequality is for other irrevers-

ible paths. So that, the reversible path (A) and its realistic path (B) are not arbitrary.

If the other work doesn't exist for a chemical reaction, in an isothermal and constant volume process, we have $\Delta U_{TV} = Q_V$. Where, ΔU_{TV} is the internal energy change, Q_V is the chemical reaction heat at the constant volume, they are all the state function. In an isothermal and constant pressure process, we have $\Delta U_{Tp} = \Delta H - p\Delta V$. Where, ΔU_{Tp} is the internal energy change, and ΔH is the chemical reaction heat at the constant pressure, they are all the state function. In the same temperature for a chemical reaction, we can find $\Delta U_{TV} = \Delta U_{Tp}$, so that, we have $Q_V = \Delta H - p\Delta V$, where, p is the constant pressure.

When the chemical reaction and other work all do not exist at the non-constant pressure, on the basis of Equations (3), (11), the gases in the closed system obey $-\int_i^f p\mathrm{d}V(A) \leq -\int_i^f p\mathrm{d}V(B)$. Where, $W_r(A) = -\int_i^f p\mathrm{d}V(A)$, and $W_{real}(B) = -\int_i^f p\mathrm{d}V(B)$.

If the chemical reactions exist and any work does not exist in the constant pressure and isothermal process, according to Equations (2), (10), we have $\int_i^f T\mathrm{d}S(A) \geq \int_i^f T\mathrm{d}S(B)$. At the moment, even if any work does not exist, we still find $Q_{pf}(B) = -W_{pf}(B) \neq 0$. This result indicates us the internal friction resistance is existence namely that $W_{pf}(B) \neq 0$ for the chemical reactions in the irreversible path (B).

In the constant pressure and isothermal process for the unclosed system, if the chemical reaction exists and the other work does not exist, according to Equations (2), (10), we still obtain $\int_i^f T\mathrm{d}S(A) \geq \int_i^f T\mathrm{d}S(B)$. We know $-p\Delta V(A) = -p\Delta V(B)$, $W_r(A) = -p\Delta V(A)$, and $W_{real}(B) = -p\Delta V(A) + W_{pf}(B)$. On the basis of Equation (11), we have $W_{pf}(B) \geq 0$. According to Equations (2), (10), we can get

$$T\Delta S_g = Q_r(A) - Q_{real}(B) = -Q_{pf}(B) = T\Delta S(A) - \Delta U + W_{real}(B)$$
$$= T\Delta S(A) - \Delta U - p\Delta V(B) = T\Delta S(A) - \Delta H = -\Delta G \geq 0$$

thus, $T\Delta S_g \geq 0$ (where, T is the constant) or $\Delta G = Q_{pf}(B) \leq 0$, which are criterions without the other work in the constant pressure and isothermal chemical reactions.

If the chemical reaction and other work all exist in the constant pressure and isothermal process, we have
$W_r(A) = \Delta U - Q_r(A) = \Delta U - T\Delta S(A) = W_{other}(A) - p\Delta V(A)$, where,
$W_r(A) = W_{other}(A) - p\Delta V(A)$. Because $\Delta H = \Delta U + p\Delta V$ and $\Delta G = \Delta H - T\Delta S$ (where, ΔG is free energy change. In the constant pressure and isothermal process, ΔG is the state function), the result is $W_{other}(A) = \Delta G$. In the realistic process, we can find $W_{real}(B) = W_{other}(B) - p\Delta V(B)$, therefore,
$W_{real}(B) = \Delta U - Q_{real}(B) = W_{other}(B) - p\Delta V(B)$, further,
$Q_{real}(B) = \Delta H - W_{other}(B)$. On the basis of Equations (2), (10), we can gain
$T\Delta S_g = Q_r(A) - Q_{real}(B) = T\Delta S(A) - \Delta H + W_{other}(B) = W_{other}(B) - \Delta G \geq 0$, that is, $T\Delta S_g \geq 0$ (here, T is the constant), or $W_{other}(B) \geq \Delta G$ and

$W_{other}(B) \geq W_{other}(A)$, which are criteria when the other work exists in the constant pressure and isothermal chemical reactions (see **Figure 1**).

4.2. Maxwell Relations and Joule-Thomson Throttling Experiment

Maxwell [17] thought the thermodynamics functions obey the following relations, namely that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V,$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p,$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V,$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p.$$

They are all obtained by commutation relations, but these commutation relations are not always correct. Moreover, the both sides (namely that, the left side and right side) per Maxwell equality correspond to the different processes, their results for the gases are no-confidence. Simultaneously, the Maxwell relations are also not right for the unclosed system. Therefore, the Maxwell relations are not right and disobey the Clausius inequality.

The formula $dU = C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]dV$ [1] is error, and it disobeys the

Clausius inequality. The van der Waals gas equation of state does not obey the thereinbefore conclusions, furthermore, it is an approximate equation, but its availability values could not be denied.

The Joule-Thomson throttling experiment (the sketch sees **Figure 2**) [17] is an adiabatic process, so that, $Q = 0$, $\Delta U = W$. Thereby
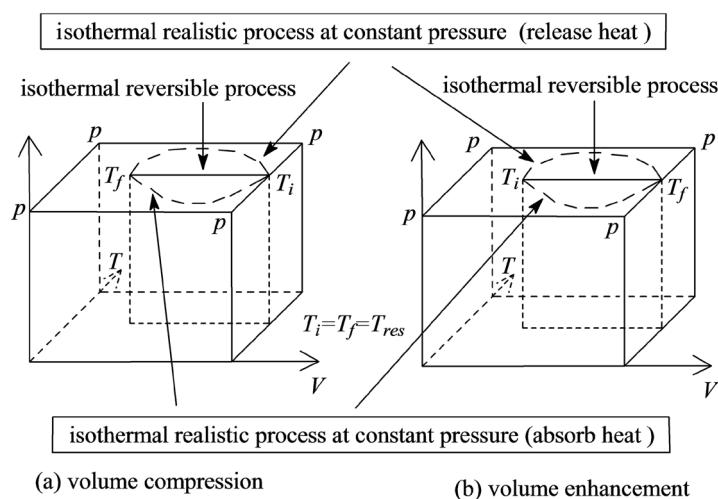
Figure 1. The unclosed system paths of chemical reactions in the constant pressure and isothermal process.
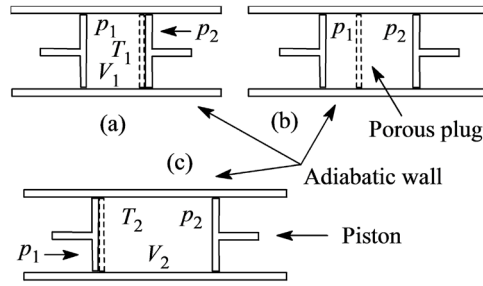
Figure 2. The Joule-Thomson throttling experiment. (a) is the initial state; (b) is the transition state; (c) is the final state.

$$W = -\sum \left(p_2 \mathrm{d}V_2 + p_1 \mathrm{d}V_1 \right) = -p_2 \left(V_2 - 0 \right) - p_1 \left(0 - V_1 \right) = -p_2 V_2 + p_1 V_1 \,.$$

Because the other work does not exist, hence, $\Delta H = 0$ (where, ΔH is the enthalpy change). We know $\Delta U = C_V \Delta T$, thus, the temperature change is given by

$$\Delta T = \frac{-p_2 V_2 + p_1 V_1}{C_V} \,. \tag{13}$$

So that, the average value of Joule-Thomson coefficient μ_{JT} is approximately equal to

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H \approx \frac{\Delta T}{\Delta p} = \frac{-p_2 V_2 + p_1 V_1}{C_V \left(p_2 - p_1 \right)} \,.$$

The Joule-Thomson throttling experiment is an irreversible process, thereof, μ_{JT} is not the state function. The temperature in the chamber 1 will raise since the work is done by surroundings. The temperature in the chamber 2 will fall since the gas does work to surroundings. Therefore, the formula (13) calculating the temperature change in the Joule-Thomson throttling experiment is an approximate equation.

4.3. Applying to the Earth Gravitational Field and Motional Body

In the gravitational field, $mg\Delta h$ is the gravitational potential energy change, m is the mass, g is the acceleration of gravity, Δh is the elevation change. In a process, the relations among the gravitational potential energy change, kinetic energy change, and internal energy change had been investigated [18] [19] [20]. Attentively, the motion path in the reversible process is the same as the realistic process. According to the conservation law of energy, we can get

$$\Delta U - Q - W = 0 \,, \tag{14}$$

$$\Delta U_r - Q_r + mg\Delta h + \Delta E_{kin} + \Delta E_{ele} + \int_i^f p\mathrm{d}V - W_b = 0 \,, \tag{15}$$

$$\Delta U_{real} - Q_{real} + mg\Delta h + \Delta E'_{kin} + \Delta E'_{ele} + \int_i^f p\mathrm{d}V - W_b = 0 \,. \tag{16}$$

where, p is the pressure between system and surroundings (it isn't internal pressure [21]). ΔE_{ele} and $\Delta E'_{ele}$ are the electrical energy change in a reversible and realistic process, respectively. ΔE_{kin} and $\Delta E'_{kin}$ are the kinetic energy change

in a reversible and realistic process respectively. Attentively, the positive or negative sign for the electrical energy, kinetic energy, and gravitational potential energy are all against the corresponding work. The kinetic energy and gravitational potential energy are called mechanical energy. For the motional body, W_b expresses the work done by the buoyancy or non-friction resistance. W_b does not belong to the mechanical work, electrical work, or friction work. It is obvious that the air buoyancy exists for the gravitational field in the irreversible process. W_b cannot cause the heat change directly, but it can influence the kinetic energy change. In a process, the absorbed heat is positive, the released heat is negative.

If the obtained energy including heat and work with the mechanical work could not be repeatedly calculated for the motional body, but they should be able to transform into the kinetic energy. For the closed gas, the mechanical work with the pressure-volume work is unable to be repeatedly calculated. For instance, the bullet and rocket could obtain the heat energy from the burned ammunition and fuel, but the obtained heat need to avoid repeating calculation with the mechanical work in Equations (15), (16) (see **Figure 3**). In the parachute, W_b has to be considered. In the pipeline system of fluid, the mechanical work and pressure-volume work have to be all considered.

Because $mg\Delta h$, ΔE_{kin}, ΔE_{ele}, and W_b all do not belong to the heat, therefore, they all belong to the work, we can gain

$$W_r = -mg\Delta h - \Delta E_{kin} - \Delta E_{ele} - \int_i^f p\mathrm{d}V + W_b, \tag{17}$$

$$W_{real} = -mg\Delta h - \Delta E'_{kin} - \Delta E'_{ele} - \int_i^f p\mathrm{d}V + W_b. \tag{18}$$

where, in a reversible process, $W_{other}(A) = -mg\Delta h - \Delta E_{kin} - \Delta E_{ele} + W_b$. In a realistic process, $W_{other}(B) = -mg\Delta h - \Delta E'_{kin} - \Delta E'_{ele} + W_b$.

The conservation law of mechanical energy disobeys on the earth system except the vacuum state. The equation of conservation law of mechanical energy is given by $mg\Delta h + \Delta E_{kin} = 0$. For a bulk condensed matter in the gravitational
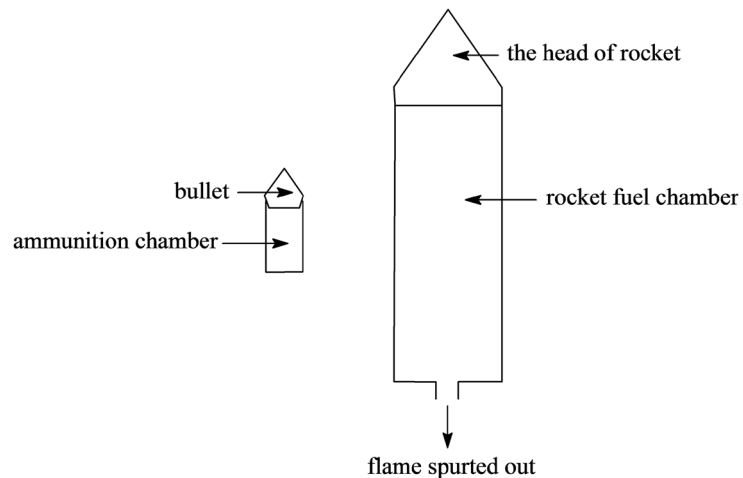
Figure 3. The processes of heat energy obtained from the burned ammunition and fuel in the bullet and rocket.

field of earth, if the influence of heat, internal energy change, pressure-volume work, electrical energy change, and W_b can be neglected, on the basis of Equation (11), we have $mg\Delta h + \Delta E_{kin} \approx 0$, W_{real} will be no less than zero, that is, $W_{real} = -mg\Delta h - \Delta E'_{kin} \geq 0$ or $mg\Delta h + \Delta E'_{kin} \leq 0$. If the bulk condensed matters are still namely that $\Delta E'_{kin} = 0$, we can obtain $\Delta h \leq 0$, namely that the bulk condensed matters such as the solid ball and rain will fall on earth's surface. The process obeys Equation (3) too.

For the particles and gases, the pressure-volume work, electrical energy change, and W_b can be all neglected in the unclosed earth atmosphere system. In altitudes, the temperature is low and the internal energy change will decrease. If the heat effect is not considered, or the process absorbs the heat, W_r and W_{real} will become negative, so that, $W_{real} = -mg\Delta h - \Delta E'_{kin} \leq 0$ or $mg\Delta h + \Delta E'_{kin} \geq 0$. If the particles are motionless namely that $\Delta E'_{kin} = 0$, we find $\Delta h \geq 0$ (namely that, the particles will raise on the open earth system), but the raising height will be limited according to Equation (3), where, T_{res} is less than T in the process.

In the wind, the friction resistance is generally small, therefore, W_r is approximately equal to W_{real}. According to Equation (3), if W_r and W_{real} are negative, the wind can easily spontaneously blow from low temperature to high temperature on the same altitude (if $\Delta h = 0$, $\Delta E'_{kin} \geq 0$). In this process, if the internal energy change keeps constant, the absorbed heat mostly converts into the work. In the heat wave, if W_r and W_{real} will easily become into positive, the heat wave will blow from high temperature to low temperature on the same altitude (but $\Delta E'_{kin} \leq 0$), the motional distances will be finite.

If the temperature varies little for the heated He(II) superfluid, the internal energy change will be very small. Because W_r and W_{real} are easily affected by the heat, W_r and W_{real} will all be negative value. Consequently, on the basis of Equation (3), it is easily the He(II) superfluid spontaneously flow from low temperature to high temperature, then, the heat will mostly convert into the kinetic energy change.

If the body could raise, the following equation will be obeyed besides Equation (3), and it is given by

$$mg\Delta h = Q_{real} - \Delta U_{real} - \Delta E'_{kin} - \Delta E'_{ele} - \int_i^f p\,dV + W_b \geq 0.$$

5. Conclusions

The Clausius inequality should be derived from Equation (4), the Carnot theorem can be proven by Kelvin and Clausius formulations of the second law of thermodynamics which are inconvenient compared with Equations (2)-(6). The Carnot theorem can be proven by the Clausius inequality.

In the equilibrium and changeless state, ΔU, Q, W, ΔS, ΔS_W, ΔS_U, ΔS_g, $(\Delta S_W)_g$, and $(\Delta S_U)_g$ are all equal to zero. In a reversible process, ΔS_g, $(\Delta S_W)_g$, and $(\Delta S_U)_g$ are all equal to zero, but ΔU, Q_r, W_r, ΔS, ΔS_W, and ΔS_U could not be all equal to zero simultaneously. Obviously, the change of $(\Delta S_U)_g$ will cause the temperature change.

In the isothermal process, Equation (4) is not the criterion. If any work doesn't exist, Equation (3) is not the criterion. It is not surprising the He(II) superfluid, particles, and gases disobey the conservation law of mechanical energy. The conservation law of mechanical energy is a bad conservation law. Equations (1)-(5), (10), (11) should be able to apply to a single particle or big object. The pressure-volume work of gases could be generated easily. In any case for a particle or big object, the friction work is all positive value, and the friction heat will be negative. The afore-mentioned function such as ΔS_W and ΔS_U are all the state function for the ideal gas in a reversible process. For the vacuum state, any irreversible process does not exist for the motional body.

For the whole unclosed system, the expansion work for the chemical reactions in the constant pressure and isothermal process is not equal to $-\int_i^f p\,dV$, but it is equal to $-p\Delta V$ in fact. The application scope of thermodynamics could not refuse the gravitational field and mechanical motion.

Altogether, for the organisms, all the processes including the biological chemical reactions obey the Clausius inequality. It is above comprehension that the organisms disobey the second law of thermodynamics. The sign of surroundings entropy is opposite to the system entropy, and the surroundings entropy is equal to negative value of the entropy flow ($\int_i^f \frac{\delta Q_{real}(B)}{T_{res}}$). Therefore, the system entropy may be less than zero sometime in the isolated system, but the entropy generation has to be no less than zero in the isolated system. The principle of entropy increase is not always right in the isolated system and non-isolated system.

The organisms are a type of heat engine, but they are controlled by the biological chemical reactions, DNA, and RNA etc. (not mechanism).

If assuming that the surroundings entropy or entropy flow are equal to zero, the entropy generation has to be equal to the entropy change. For the isolated system in a realistic path (B), the entropy change will become the entropy generation which is the non-state function except when $Q_{real}(B) = 0$. So that, the principle of entropy increase is an error for many cases. A reversible path (A) may contain a few processes in its realistic path (B), and a realistic path (B) may contain a few processes in its reversible path (A) too.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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