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Studies on equalities and inequalities of heat, work and ratio of work to temperature

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This research investigates relationships between resistances with heat and work. It is completely proven that the ratio of work to temperature for the realistic process is no less than that for the reversible process. The equalities and inequalities on the heat, work and ratio of work to temperature could be applied to the gravitational field and chemical reactions. The relationships between path functions and state functions are studied in the chemical reactions. Some criteria for spontaneous directions have been suggested such as the equalities and inequalities on the heat, work, and ratio of work to temperature, except the Clausius inequality and must be ordinarily obeyed in the spontaneous process.

Key words: First law of thermodynamics, Clausius inequality, thermodynamic functions, chemical reactions, gravitational field, resistances, ratio of work to temperature.

INTRODUCTION

The first law of thermodynamics was as a result of applying the conservation of energy to thermodynamics (Sandler and Woodcock, 2010). The Carnot theorem could be proven by the second law of thermodynamics. The Clausius inequality was derived from the Carnot theorem (Atkins and Paula, 2014; Nieto et al., 2011; Lee et al., 2015). In the gravitational field and chemical reactions, relations between the entropy or free energy with the kinetic, gravitational potential, and electrical energy was studied (DeVoe, 2013; Gislason and Craig, 2013; de Abreu and Guerra, 2012). The equalities and inequalities in regard to the work and ratio of work to temperature between the reversible process and irreversible process are entirely denied and neglected

in the fundamental theory; hence, they are seldom researched yet. The motion path of solids and liquids is only affected by external force, which is different from the gas. The application of the scopes of Clausius inequality will be enhanced by the equalities and inequalities on the work and the ratio of work to temperature.

In a reversible process, the first law of thermodynamics is given by:

$$dU_r(A) = \delta Q_r(A) + \delta W_r(A) \text{ or } \Delta U_r(A) = Q_r(A) + W_r(A) \qquad (1)$$

Where U_r, Q_r and W_r are the internal energy, heat, and work in a reversible path (A), respectively.

In an irreversible process, the resistances including

frictions or internal resistances must be considered. The first law of thermodynamics is given by:

$$dU_{real}(B) = \delta Q_{real}(B) + \delta W_{real}(B) \text{ or } \Delta U_{real}(B) = Q_{real}(B) + W_{real}(B) \quad (2)$$

where Q_{real} and W_{real} are the heat and work in a realistic path (B), respectively. Q_{resist} and W_{resist} are the heat and work generated by resistance in an irreversible path (B), respectively. The realistic process or path includes the reversible and irreversible process or path. The resistances are equal to zero in any reversible process. A process may have unlimited paths.

The heat and work are taken as positive if energy is transferred into the system and negative if energy is transferred out of the system. The heat and work are the path functions in a realistic process. U is the state function. "d" and "δ" are total differential symbols to the state function and path function, respectively. "Δ" expresses a change of quantity value.

In a reversible isothermal process, $Q_r = T\Delta S$, where T is the thermodynamic temperature, ΔS expresses the entropy change (state function). So that, in a reversible isothermal process, both Q_r and W_r are state functions (the temperature must be kept constant). In a reversible adiabatic process, W_r is the state function (the system must be kept adiabatic). In an isochoric process, Q_r is the state function (the volume must be kept constant). In a reversible isobaric process, Q_r and W_r are all the state functions (the pressure must be kept constant).

EQUALITIES AND INEQUALITIES OF HEAT, WORK, AND RATIO OF WORK TO TEMPERATURE

Equalities and inequalities of heat and work

In a process, we assume:

$$Q_{real}(B) = Q_r(B) + Q_{resist}(B), \quad (3)$$

$$W_{real}(B) = W_r(B) + W_{resist}(B). \quad (4)$$

In a spontaneous process, the following equations must be obeyed (Jin, 2016):

$$Q_r(A) \geq Q_{real}(B), \quad (5)$$

$$W_r(A) \leq W_{real}(B), \quad (6)$$

where the equality sign is the same for a reversible or irreversible process in which $W_{resist}(B) = 0$, whereas the sign of inequality is for an irreversible process. In a process or cycle, $\Delta U_r = \Delta U_{real}$, on the basis of

Equations 1 to 4, $Q_{resist}(B) = -W_{resist}(B)$ for a realistic path (B). According to Equations 5 and 6, $Q_r(B) \geq Q_{real}(B)$ and $W_r(B) \leq W_{real}(B)$ are also right; as such we could obtain:

$$W_{resist}(B) = -Q_{resist}(B) \geq 0 \quad (7)$$

where the sign of equality is the same for a reversible or irreversible process in which $W_{resist}(B) = 0$, while the sign of inequality is for an irreversible process.

Equations 5 and 6 were derived from the Clausius inequality and the Carnot theorem. Any reversible cycle could be simulated by the infinitesimal reversible Carnot cycles. When the area of infinitesimal reversible Carnot cycles is equal to that of the simulated reversible cycle, then they are the same work. Because their ΔU_r are all zero in arbitrary cycle, then they are also the same heat. Therefore, Equations 5 and 6 can be extended and applied to any reversible cycle.

Assuming that a realistic path (B) and its reversible path (A) with another reversible path (C) constitute both a realistic and a reversible cycle (Figure 1), then we can gain $\quad Q_r(A) - Q_r(C) \geq Q_{real}(B) - Q_r(C) \quad$ and $W_r(A) - W_r(C) \leq W_{real}(B) - W_r(C)$.   Thus, $Q_r(A) \geq Q_{real}(B)$ and $W_r(A) \leq W_{real}(B)$ in a process. Therefore, Equations 5 and 6 can be extended and applied to arbitrary process.

Complete derivation of the inequality on the ratio of work to temperature from the Clausius inequality

The Clausius inequality can be rewritten as follow:

$$\int_j^i \frac{\delta Q_r(A)}{T} - \int_j^i \frac{\delta Q_{real}(B)}{T_i} \geq 0, \quad (8)$$

where the sign of equality is for a reversible process and the sign of inequality is for an irreversible process. "∫" is integral symbol. The entropy change $\int_j^i \frac{\delta Q_r(A)}{T}$ is the ratio of heat to temperature in a reversible path (A). $\int_j^i \frac{\delta Q_{real}(B)}{T_i}$ is the ratio of heat to temperature in a realistic path (B). In a process, the state "j" expresses the initial state, the state "i" expresses the final state, T_j and T_i are the initial and final states thermodynamic temperature of the surroundings or reservoirs, respectively. If a complex process has many processes, T_i should include thermodynamic temperatures of many surroundings or reservoirs. T varies from T_j to T_i, which is
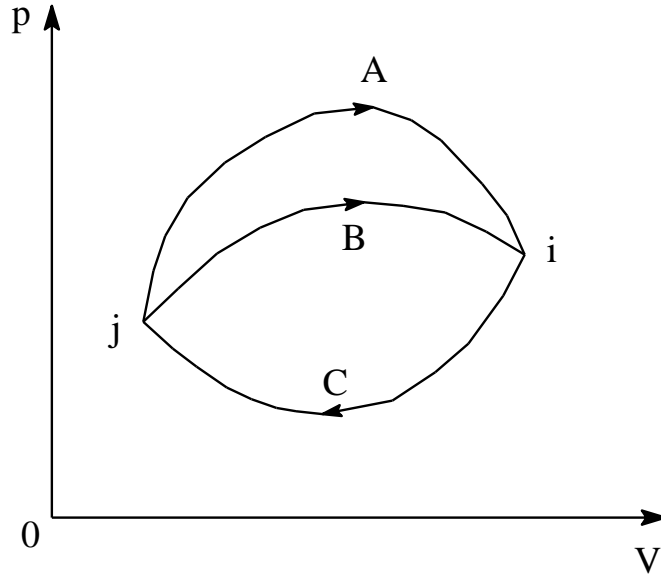
Figure 1. The reversible cycle "jAiCj" and realistic cycle "jBiCj".

different from the contact temperature (Muschik, 2014). In the reversible process, T_i and $Q_{real}(B)$ will be replaced by T and $Q_r(B)$ in Equation 8.

From Equations 1 and 2, we can obtain

$$\int_j^i \frac{dU_r(A)}{T} = \int_j^i \frac{\delta Q_r(A)}{T} + \int_j^i \frac{\delta W_r(A)}{T}$$ and

$$\int_j^i \frac{dU_{real}(B)}{T_i} = \int_j^i \frac{\delta Q_{real}(B)}{T_i} + \int_j^i \frac{\delta W_{real}(B)}{T_i}.$$ Thus, the following equation is given by:

$$\int_j^i \frac{dU_r(A)}{T} - \int_j^i \frac{dU_{real}(B)}{T_i} = \int_j^i \frac{\delta Q_r(A)}{T} - \int_j^i \frac{\delta Q_{real}(B)}{T_i} + \int_j^i \frac{\delta W_r(A)}{T} - \int_j^i \frac{\delta W_{real}(B)}{T_i},$$ (9)

where $\int_j^i \frac{dU_r(A)}{T}$ or $\int_j^i \frac{dU_{real}(B)}{T_i}$ are the ratio of internal energy change to temperature in a reversible path (A) or in a realistic path (B), respectively. $\int_j^i \frac{\delta W_r(A)}{T}$ or $\int_j^i \frac{\delta W_{real}(B)}{T_i}$ are the ratio of work to temperature in a reversible path (A) or in a realistic path (B), respectively.

If $\int_j^i \frac{dU_r(A)}{T} - \int_j^i \frac{dU_{real}(B)}{T_i} \geq 0$ and

$\int_j^i \frac{\delta W_r(A)}{T} - \int_j^i \frac{\delta W_{real}(B)}{T_i} > 0$, in accordance with Equation 9, we have

$$\int_j^i \frac{\delta Q_r(A)}{T} - \int_j^i \frac{\delta Q_{real}(B)}{T_i} \geq -(\int_j^i \frac{\delta W_r(A)}{T} - \int_j^i \frac{\delta W_{real}(B)}{T_i}),$$

where $-(\int_j^i \frac{\delta W_r(A)}{T} - \int_j^i \frac{\delta W_{real}(B)}{T_i})$ is negative value which violates the Clausius inequality. This is impossible.

So that, the equality and inequality on the ratio of work to temperature can be written as follow:

$$\int_j^i \frac{\delta W_r(A)}{T} - \int_j^i \frac{\delta W_{real}(B)}{T_i} \leq 0.$$ (10)

If $\int_j^i \frac{dU_r(A)}{T} - \int_j^i \frac{dU_{real}(B)}{T_i} \geq 0$, on the basis of Equations 9 and 10, we can obtain:

$$\int_j^i \frac{\delta Q_r(A)}{T} - \int_j^i \frac{\delta Q_{real}(B)}{T_i} \geq -(\int_j^i \frac{\delta W_r(A)}{T} - \int_j^i \frac{\delta W_{real}(B)}{T_i}) \geq 0,$$

This confirms the Clausius inequality. Therefore, Equation 10 is right in any case. Where the sign of equality should belong to the reversible process, the sign of inequality should belong to the irreversible process; otherwise, Equation 10 will be incorrect.

According to Equations 9 and 10, the inequality $\int_j^i \frac{dU_r(A)}{T} - \int_j^i \frac{dU_{real}(B)}{T_i} < 0$ violates the Clausius

inequality. Therefore, $\int_j^i \frac{dU_r(A)}{T} - \int_j^i \frac{dU_{real}(B)}{T_i} \geq 0$ is correct in any case.

The ideal gas equation of state is $pV = nRT$. By this (Borgnakke and Sonntag, 2014; Jacobs, 2013), we know that:

$$dU_r = C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p \right] dV = C_V dT ,$$

$$\delta W_r = -pdV = -\frac{nRTdV}{V} ,$$

where p is the pressure, V is the volume, R is the gas constant, and n is the amount of substance. Because $\oint \frac{dU_r}{T} = \oint \frac{C_V dT}{T} = 0$ and $\oint \frac{\delta W_r}{T} = -\oint \frac{pdV}{T} = -\oint \frac{nRdV}{V} = 0$, they are all state functions in the reversible process for ideal gas. It should be noted that the van der Waals equation of state is an approximate for the real gases and could not prove the aforementioned results. "∂" is partial differential symbol.

APPLICATIONS OF EQUALITIES AND INEQUALITIES ON HEAT AND WORK

Applications to the chemical reactions

The non-expansion work does not exist

If the chemical reactions could happen, Equations 5 to 8 and 10 must be obeyed. In the isothermal and isobaric process, we know that $W_{real} = W_{other} - p\Delta V$ and $W_r = W_{max} - p\Delta V$, where p$\Delta$V is the volume expansion work, W_{other} expresses the non-expansion work (namely that the other work) in the realistic process except W_{resist}, while W_{max} expresses other work in the reversible process. In the isothermal and isobaric process, $\Delta G = \Delta H - T\Delta S$, $\Delta H = \Delta U + p\Delta V$; where G is the free energy, H is the enthalpy. It should be noted that ΔU and ΔS are state functions in any process. ΔH is the state function in any isobaric process. In any isothermal and isobaric process, ΔG is the state functions.

If the non-expansion work does not exist in the chemical reactions, in the isothermal and isobaric reversible path (A), we can gain $W_r(A) = -p\Delta V(A)$, $\Delta H = Q_r(A) = T\Delta S$, $W_{resist}(A) = 0$, $W_r(A) = \Delta U - Q_r(A) = \Delta U - T\Delta S = -p\Delta V(A)$, namely $\Delta G(A) = 0$. Attention, the temperature must be kept constant in the isothermal and isobaric reversible path (A). In the isothermal and isobaric irreversible path (B), $W_{real}(B) = -p\Delta V(B)$. According to Equation 4, we have $W_{real}(B) = W_r(B) + W_{resist}(B) = \Delta U - Q_r(B) + W_{resist}(B) = -p\Delta V(B)$.

So, $Q_r(B) = \Delta U + p\Delta V(B) + W_{resist}(B) = \Delta H(B) + W_{resist}(B)$. On the basis of Equations 3 and 7, we obtain $Q_{real}(B) = Q_r(B) + Q_{resist}(B) = \Delta H(B)$. In the isothermal and isobaric process, Equation 5 can become

$Q_r(A) = T\Delta S \geq \Delta H(B)$ or $-\Delta G(B) \geq 0$.

In the isothermal and isobaric process, Equation 6 will vary:

$W_r(A) = \Delta U - Q_r(A) \leq W_{real}(B) = -p\Delta V(B)$ or $\Delta G(B) \leq 0$.

While the non-expansion work does not exist in the chemical reactions, $Q_{real}(B) = \Delta H(B)$ and $\Delta G(B) \leq 0$ are consistent with the actual facts. Equations 5 and 6 are confirmed.

The non-expansion work exist

If the other work exists in the chemical reactions, we can obtain $W_r(C) = \Delta U - Q_r(C) = \Delta U - T\Delta S = W_{max}(C) - p\Delta V(C)$ in the isothermal and isobaric reversible path (C), thus, $\Delta G(C) = W_{max}(C)$. In the isothermal and isobaric irreversible path (D), according to Equation 4, we will gain $W_{real}(D) = W_r(D) + W_{resist}(D) = \Delta U - Q_r(D) + W_{resist}(D) = W_{other}(D) - p\Delta V(D)$ namely that, $W_{other}(D) = \Delta H(D) - Q_r(D) + W_{resist}(D)$. According to Equations 3 and 7, we obtain $Q_{real}(D) = Q_r(D) + Q_{resist}(D) = \Delta H(D) - W_{other}(D)$.

In the isothermal and isobaric process, according to Equation 5, we have $Q_r(C) = T\Delta S \geq Q_{real}(D) = \Delta H(D) - W_{other}(D)$, then $-\Delta G(D) \geq -W_{other}(D)$. In isothermal and isobaric process, Equation 6 can be converted into $W_r(C) = \Delta U - Q_r(C) \leq W_{real}(D) = W_{other}(D) - p\Delta V(D)$, that is, $\Delta G(D) \leq W_{other}(D)$.

In the meantime, if the paths (C) and (D) exists, the result is $\Delta G = \Delta G(C) = \Delta G(D) = W_{max}(C)$. When the path (B) with the paths (C) and (D) exists in the meantime, the following equation will be given by:

$$\Delta G = \Delta G(B) = \Delta G(C) = \Delta G(D) = W_{max}(C) .$$

If the paths (B), (C), and (D) with the path (A) exists in the meantime, we have $\Delta G = \Delta G(A) = \Delta G(B) = \Delta G(C) = \Delta G(D) = 0$.

For electrochemical reaction, $\Delta G = W_{max}(C) = -nFV_{ele}$, where n is the number of electrons transferred per mole in cell reaction, F is the Faraday constant, V_{ele} is the cell potential when the electric current approaches zero namely $W_{resist}(C)=0$.

Applications to the gravitational field

In the gravitational field, mgΔh is the gravitational

potential energy change, m is the mass, g is the acceleration of gravity, and Δh is the elevation change. In the reversible process ($W_{resist} = 0$), according to the conservation of energy, we can obtain

$$\Delta U_r + \Delta E_{cal} + \int_j^i p dV + \Delta E_{ele} + mg\Delta h + \Delta E_{kin} = 0.$$

Where p is not the internal pressure (Marcus, 2013). ΔE_{cal} is the heat energy change of calorimeter in the reversible process, $Q_r = -\Delta E_{cal}$. ΔE_{ele} and ΔE_{kin} are electrical energy change and kinetic energy change in the reversible process, respectively. When compared with Equation 1, if $\int_j^i p dV$ and ΔE_{ele} are neglected, we find:

$$W_r = -mg\Delta h - \Delta E_{kin}. \tag{11}$$

In the realistic process, on the basis of the conservation of energy, we can gain

$$\Delta U_{real} + \Delta E_{cal}' + \int_j^i p dV + \Delta E_{ele}' + mg\Delta h + \Delta E_{kin}' = 0$$

, where $\Delta E_{ele}'$ and $\Delta E_{kin}'$ are electrical energy change and kinetic energy change in the realistic process, respectively, $Q_{real} = -\Delta E_{cal}'$. When compared with Equation 2, if $\int_j^i p dV$ and $\Delta E_{ele}'$ are neglected, we find:

$$W_{real} = -mg\Delta h - \Delta E_{kin}'. \tag{12}$$

The gravitational potential energy change is identical in the irreversible and reversible process. In accordance with Equation 6, we gain:

$$\Delta E_{kin} \geq \Delta E_{kin}'. \tag{13}$$

The falling matter and flowing river water have to obey Equation 13. Equation 13 is an approximate formula. When the mechanical energy want to keep the conservation, the changes of ΔU_r, ΔE_{cal}, $\int_j^i p dV$, and ΔE_{ele} are equal to zero or could be neglected.

Applications to free expansive ideal gas

The ideal gas in the adiabatic isochoric container was freely expanding to the adiabatic isochoric vacuum container; the temperature will be without any change. In the irreversible path (B), $W_{real}(B) = Q_{real}(B) = 0$ and $\Delta U = 0$. The reversible process is isothermal expansion in the path (A); the result is $Q_r(A) = -W_r(A) = \int_j^i \frac{nRTdV}{V} = nRT \ln \frac{V_i}{V_j} > 0$, where $V_i > V_j$. Therefore, Equations 5 to 7 are all obeyed. It should be noted that according to Equations 3, 4 and 7, we have $Q_r(B) = -Q_{resist}(B) > 0$ and $W_r(B) = -W_{resist}(B) < 0$.

Conclusion

If the work does not exist, $Q_r = Q_{real}$, the difference in temperature would cause the heat to be transferred. For example, the temperature either rises or falls in isochoric gas; Equations 6 and 10 are disobeyed, but Equation 8 is obeyed.

W_{real} is approximately equal to W_r in the He(II) superfluid, namely, that $W_{resist} \approx 0$. So the difference in temperature would cause the motion of the He(II) superfluid, but Equation 10 will be obeyed. If the He(II) superfluid is heated it will flow from low temperature to high temperature; on the basis of Equation 10 $W_{real} \approx W_r < 0$ (namely, $-\Delta E_{kin} - mg\Delta h \approx -\Delta E_{kin}' - mg\Delta h < 0$ or $\Delta E_{kin} \approx \Delta E_{kin}' > mg\Delta h$). Therefore, if $\Delta h \leq 0$, $\Delta E_{kin} \approx \Delta E_{kin}' > 0$. If $\Delta E_{kin} \approx \Delta E_{kin}' \leq 0$, $\Delta h > 0$. The aforementioned conclusion could not be obtained from other fluids.

If $\int_j^i \frac{\delta Q_r(A)}{T} - \int_j^i \frac{\delta Q_{real}(B)}{T_i} = X$, $X \geq 0$, where X is the entropy generation with ΔS_g (Grazzini et al., 2013). We will gain $\Delta S = X + \frac{Q_{real}(B)}{T_i} = \Delta S_g + \frac{Q_{real}(B)}{T_i}$, as the ratio of heat to temperature $\frac{Q_{real}(B)}{T_i}$ is entropy flow.

Equation 8 is the criteria for a spontaneous process and must be obeyed by the spontaneous process. Equations 5 to 7 are always the criteria for a spontaneous process except $W_{resist} = 0$. Equation 10 is always criteria for a spontaneous process except $W_r = W_{real} = W_{resist} = 0$. Equations 3 and 4 are well reasonable presumptions. Because the resistance exists, ΔG will change to zero when the chemical reaction reaches balance state in the isothermal and isobaric realistic path. The resistance should have relation to the rate and activation energy in the chemical reactions. In Equations 5, 6, and 13, the reversible process could not

be arbitrarily invented or fabricated. The reversible and irreversible paths generally have a distinction for gas.

CONFLICT OF INTERESTS

The author has not declared any conflict of interests.

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