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TECHNICAL NOTE

Minimum heat to environment and entropy

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1. INTRODUCTION

As a fundamental thermodynamic property, entropy plays a prominent part in the second-law analysis of engineering devices and serves as a valuable tool in physics and science. From microscopic perspective, entropy can be viewed as: (1) a measure of molecular disorder or molecular randomness [1–3], and (2) an inverse measure of information [3, 4]. The former comes from statistical thermodynamics and the latter stems from information theory. However, it is difficult to give a macroscopic physical description of entropy from its classical (macroscopic) definition. In fact, the question 'What is entropy?' is frequently raised with the implication that no one really knows [1, 5].

The entropy S was defined as a differential [1, 5]:

$$dS \equiv \left(\frac{\delta Q}{T}\right)_{\text{int,rev}}.$$

That is to say, the infinitesimal decrease of the entropy of a body in any internally reversible process is equal to its infinitesimal output of heat δQ divided by its absolute temperature T. This classical definition was first introduced by Clausius in 1865 [1] and comes from the Clausius inequality, a corollary or a consequence of the second law of thermodynamics [1, 5]. While the notation of entropy has been broadened by the advent of statistical mechanics and has been still further broadened by the later advent of information theory [3, 4], the classical definition offers no physical interpretation. Indeed, our understanding and appreciation of entropy only rely on studying its uses in commonly encountered processes and systems [1, 5].

The present work addresses the macroscopic definition and physical meaning of entropy. Application of both first and second laws of thermodynamics to thermodynamic processes reveals that the heat to the environment during totally reversible processes between two specified end states represents the change of a property. This leads to a new definition of entropy with a clear physical meaning and some practical implications. The classically defined entropy is recovered when the constant in the new definition is specified as the inverse of environment temperature T_0.

2. HEAT TO THE ENVIRONMENT

Consider a mass system A undergoing a process from state 1 to state 2 in Fig. 1(a). The work directly delivered by the system is termed the internal work W_i^{12}. The work produced by auxiliary cyclic devices is called external work W_e^{12} $(=\Sigma_{i=1}^{n} W_{ei}^{12})$. Such auxiliary cyclic devices are required to ensure external reversibility [1] in any heat exchanges between the system and its environment for a general process 1–2. The sum of W_i^{12} and W_e^{12} is termed total work W_t^{12}. Note that the process in the auxiliary devices is cyclic. The change in the total energy of the combined system A^+, comprising A and the auxiliary cyclic devices, is thus equal to that for the system A alone. The W_t^{12} and Q_0^{12} $(=\Sigma_{i=1}^{n} Q_{0i}^{12})$ are the work and heat interactions between the system A^+ and its surroundings, respectively.

A process is called internally reversible if no irreversibilities occur within the boundaries of the system during the process. A process is termed externally reversible if no irreversibilities occur outside the system boundaries during the process. A process is called totally reversible if it involves no irreversibilities within the system or its surroundings. For the process 1–2 undergone by the system A in Fig. 1(a), the total reversibility requires no irreversibilities in both the system A and the auxiliary cyclic devices. A striking feature of Q_0^{12} can be revealed by applying both first and second laws of thermodynamics to the system A^+, and is summarized as the following theorem.

Theorem: *For a system exchanging heat with a single thermal reservoir (the environment at temperature* T_0 *in particular), the heat exchanged is the same for all totally reversible processes between the same specified end states* 1 *and* 2, *which is termed the minimum heat symbolized with* Q_{0R}^{12}. *During any irreversible process between these same specified end states, the heat exchanged* Q_{0I}^{12} *is always larger than* Q_{0R}^{12}.

Proof: To prove this theorem, consider two processes R and I between 1 and 2, as shown in Fig. 1(b). One process (R) is totally reversible, and the other (I) is irreversible. The amount of total work produced during the totally reversible process R is W_{tR}^{12}, and the amount produced during the irreversible one is W_{tI}^{12}. The heat exchanged with the environment during the totally reversible process R is Q_{0R}^{12}, and the heat to the environment during the irreversible one I is Q_{0I}^{12}.

In violation of the theorem, we assume that $Q_{0I}^{12} < Q_{0R}^{12}$ and thus $W_{tI}^{12} > W_{tR}^{12}$ by the first law of thermodynamics. Now let the reversible process be reversed as a process R' from 2 to 1. This process will receive a work input W_{tR}^{12} from the surroundings and a heat input Q_{0R}^{12} from the environment.

Now considering the R' and I together as a cycle [Fig. 1(c)], we have an engine that produces a net work in the amount of $W_{tI}^{12} - W_{tR}^{12}$ while exchanging heat with a single reservoir in the amount of $Q_{0R}^{12} - Q_{0I}^{12}$, a violation of the Kelvin–Planck statement of the second law of thermodynamics. Therefore we conclude that

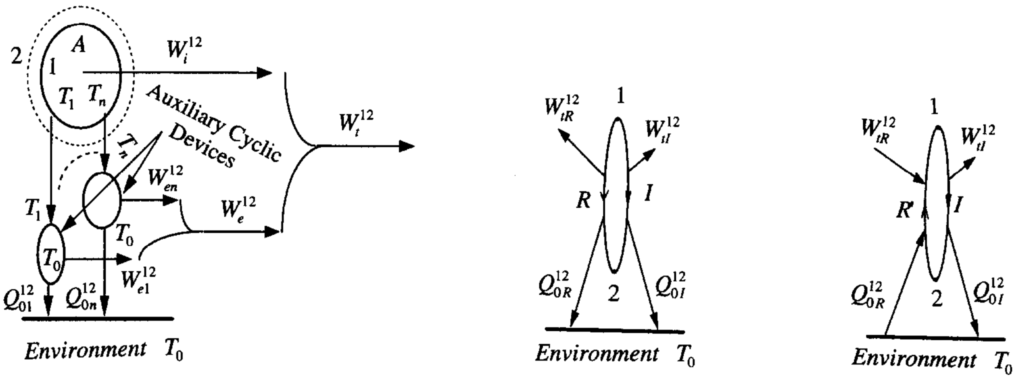
$$Q_{0I}^{12} \geqslant Q_{0R}^{12}. \tag{1}$$

However, if the equality holds in equation (1), the process I must be reversible as the process R' could then also act as the erasing process of I. This is certainly against the initial assumption. Consequently, we have

$$Q_{0I}^{12} > Q_{0R}^{12}. \tag{2}$$

NOMENCLATURE

C	positive constant
E, $\mathrm{d}E$	total energy, infinitesimal energy decrease
Q	heat, positive for the heat transfer from a system
Q_0^{12}	heat to environment during process 1–2
Q_{0I}^{12}	heat to environment during irreversible process 1–2
Q_{0R}^{12}	minimum heat to environment during process 1–2
S, $\mathrm{d}S$	entropy, infinitesimal entropy decrease
T	thermodynamic temperature
T_0	environment temperature
W	work, positive for the work done by the system
W_e^{12}	external work during process 1–2
W_i^{12}	internal work during process 1–2
W_t^{12}	total work during process 1–2
W_{tI}^{12}	total work during irreversible process 1–2
W_{tR}^{12}	total work during reversible process 1–2.



(*a*) (*b*) (*c*)

Fig. 1. Totally reversible process and proof of theorem.

Since both processes R and I are arbitrarily chosen as the totally reversible and irreversible, respectively, this is the proof that heat exchanged during an irreversible process is always larger than that during a totally reversible process.

Now we replace I and R by two arbitrarily chosen totally reversible processes R_1 and R_2, respectively. Equation (1) leads to

$$Q_{01}^{12} \geqslant Q_{02}^{12}.$$

Similarly, if I and R are replaced by R_2 and R_1, respectively, equation (1) yields

$$Q_{02}^{12} \geqslant Q_{01}^{12}.$$

As both expressions are true, to satisfy them simultaneously, we must have

$$Q_{01}^{12} = Q_{02}^{12}.$$

However, R_1 and R_2 are any two totally reversible processes between the specified end states 1 and 2, so that we conclude

$$Q_{01}^{12} = Q_{02}^{12} \equiv Q_{0R}^{12}. \tag{3}$$

This and equation (2) together establish the above-stated theorem. Furthermore, the first law of thermodynamics leads to

$$Q_{0R}^{12} = (E_1 - E_2) - W_{tR}^{12} \tag{4}$$

where E is the total energy of the system A.

It should be noted that the theorem is not valid for the internal work output as, with variable temperature of the system A, we cannot find a single thermal reservoir to ensure the reversible heat transfer.

3. ENTROPY AND ITS PHYSICAL MEANING

While heat is generally dependent on the characteristics of process, Q_{0R}^{12} is uniquely-valued for all totally reversible processes between two specified end states 1 and 2. Therefore, it must represent the change of a state property which will be shown to be entropy, a term first named by Clausius in 1865 [1]. Then we may define entropy S, at arbitrary state 1, as

$$S_1 \equiv CQ_{0R}^{10} \tag{5}$$

where state 0 is the reference state whose energy and entropy are assigned zero values, and C is a positive constant which will be determined later to recover the classical definition. The entropy decrease can thus be written as

$$\mathrm{d}S = C\mathrm{d}Q_{0R} = C(\mathrm{d}E - \mathrm{d}W_t)_R \tag{6}$$

and

$$S_1 - S_2 = CQ_{0R}^{12}. \tag{7}$$

The introduction of C is to recover the classical definition. However, it is more convenient and desirable for illustrating the physical meaning of entropy and performing entropy analysis to make C as 1. The entropy S at any state is, thus, an unavailable portion of the system energy E at that state which cannot be converted into work. An increase of the system entropy will decrease the availability of the system energy. This is the macroscopic physical meaning of entropy.

4. ENTROPY CHANGE OF SUBSTANCE SYSTEMS AND DETERMINATION OF *C*

After the constant C is specified, we may use the definition of equation (5) to obtain the value of entropy at any state 1. This consists of applying the first and the second laws of thermodynamics to obtain heat exchanged with the environment during a totally reversible process bringing the system from the specified state 1 to the reference state 0. As demonstrated below, only entropy changes are calculated here as they are more important than the absolute values and are usually required in applications [1, 5].

4.1. *Entropy change of a thermal reservoir*

As a hypothetical system, a thermal reservoir is defined as a body to which or from which heat can be transferred indefinitely without change in its temperature. The process within the thermal reservoir is reversible. Application of the first law of thermodynamics to a process undergone by the thermal reservoir shows that the energy decrease $\mathrm{d}E$ is equal to the heat δQ from the reservoir at temperature T during the process. With referring to Fig. 2(a),

$$\mathrm{d}W_{tR} = \delta W_{iR} + \delta W_{eR} = 0 + \left(1 - \frac{T_0}{T}\right)\delta Q.$$

Thus, equation (6) gives the entropy decrease $\mathrm{d}S$

$$\mathrm{d}S = C\,\mathrm{d}Q_{0R} = C(\mathrm{d}E - \mathrm{d}W_t)_R$$

$$= C\left[\delta Q - \left(1 - \frac{T_0}{T}\right)\delta Q\right] = C\frac{T_0}{T}\delta Q.$$

If let $C = 1/T_0$, the entropy decrease of the thermal reservoir becomes

$$\mathrm{d}S = \frac{\delta Q}{T}$$

which is identical to the classical definition of entropy.

4.2. *Entropy change of a work reservoir*

For a work reservoir, another hypothetical system in which the process is reversible, the energy decrease $\mathrm{d}E$ is equal to the work $\mathrm{d}W_{iR}$ from the work reservoir during the process. Also, $\mathrm{d}W_{tR} = \mathrm{d}W_{iR}$ for this case. Thus, equation (6) yields

$$\mathrm{d}S = C(\mathrm{d}E - \mathrm{d}W_t)_R = 0$$

which is also identical to that from the classical definition.

4.3. *Entropy change of a general system*

For a reversible, infinitesimal process by a general thermodynamic system A in Fig. 2(b),

$$\mathrm{d}E = \delta Q + \delta W_{iR}$$

$$dW_{tR} = \delta W_{iR} + \delta W_{eR} = \delta W_{iR} + \left(1 - \frac{T_0}{T}\right)\delta Q.$$

Equation (6), thus, leads to

$$\mathrm{d}S = C\,\mathrm{d}Q_{0R} = C[\mathrm{d}E - \mathrm{d}W_t]_R = C\frac{T_0}{T}\delta Q$$

which is again identical to that from the classical definition if C is specified as $1/T_0$.

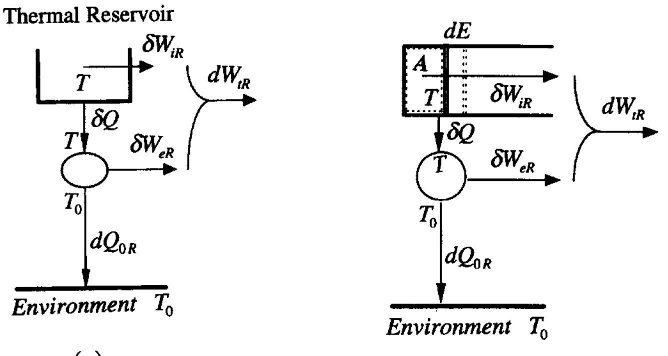
It is interesting to note that the new definition not only offers a clear physical meaning of entropy, but also simplifies the derivation of the Clausius inequality, the principle of the increase of entropy, and the relation between entropy creation and loss of available energy. With C as 1, the entropy defined in the present work is the unavailable portion of the system energy E. An entropy analysis can thus uncover the change of energy structure for various thermodynamic processes, a task which cannot be done by the classical entropy analysis as pointed out in [6].

5. CONCLUDING REMARKS

The first and second laws of thermodynamics are employed to show that the heat exchanged between the environment and a system undergoing a totally reversible process represents the change of a state property. This leads to a definition of entropy which uncovers the nature of entropy as the unavailable portion of the system energy. The calculation of entropy change of substance systems concludes that the new definition is identical to the classical one by choosing the constant C as the inverse of the environment temperature.

REFERENCES

1. Cengel, Y. A. and Boles, M. A., *Thermodynamics*. McGraw-Hill, New York, 1994.
2. Fast, J. D., *Entropy*. Macmillan, London, 1970.
3. Denbigh, K. G. and Denbigh, J. S., *Entropy in Relation to Incomplete Knowledge*. Cambridge University Press, Cambridge, 1985.
4. Kapur, J. N., *Measures of Information and Their Applications*. Wiley, New York, 1994.
5. Van Wylen, G. J., Sonntag, R. E. and Borgnakke, C., *Fundamentals of Classical Thermodynamics*. Wiley, New York, 1994.
6. Yang, D. H., *Exergy Analysis and Energy-Order Analysis*. Sciences, Beijing, 1986.



(*a*) (*b*)

Fig. 2. Entropy change of a thermal reservoir and a general system.