

An Alternative Presentation of the Second Law of Thermodynamics

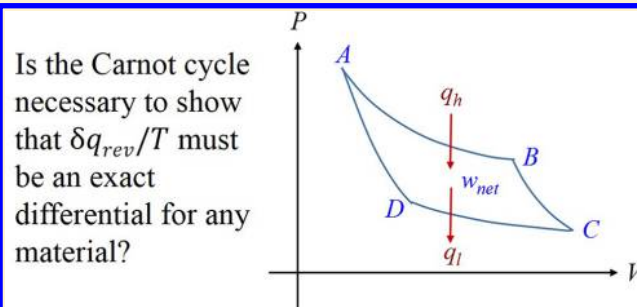
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S Supporting Information

ABSTRACT: We present an elementary, but still quite rigorous derivation of the Clausius inequality, which sheds a new perspective on the second law. Unlike the classical approach, our derivation does not employ the Carnot cycle. The Clausius inequality follows in a straightforward way from the first law and thermodynamic stability conditions without invoking the Clausius or the Kelvin–Planck statement of the second law. The background knowledge required for this article is the same as that for the usual textbook presentation of the second law. The new presentation of the second law is, therefore, appropriate for an introductory thermodynamics course.

KEYWORDS: Second-Year Undergraduate, Upper-Division Undergraduate, Physical Chemistry, Textbooks/Reference Books, Thermodynamics



The second law of thermodynamics has more formulations than any other physical law. There is a vast quantity of literature on the second law, and attempts to clarify the second law would continue to remain of interest.¹

In most physical chemistry textbooks,^{2–5} the presentation of the second law of thermodynamics is based on the Clausius or the Kelvin–Planck statement, which is used to validate the Carnot’s principle: “No heat engine can be more efficient than a reversible heat engine when both engines work between the same pair of hot and cold heat reservoirs” (ref 2, p 81). Then the efficiency of a heat engine performing the Carnot cycles with the ideal gas as the working substance is calculated, which leads to the definition of entropy. This description of the second law requires the knowledge of the first law, thermodynamic changes in the reversible processes of ideal gas, the concept of an exact differential, and so on.

Another popular approach to the second law is to start with a purely mathematical axiom as first formulated by Carathéodory.^{1,6,7} For example, the Born’s version of the Carathéodory’s theorem states that “In every neighborhood of a representative point of system in phase space there exist neighboring points that cannot be reached through any adiabatic process” (ref 7, p. 38). However, this approach has two disadvantages. First, the physical content of such a mathematical axiom can be understood only after learning the geometric aspects of thermodynamic equations. Second, the required mathematical background knowledge is too advanced for most college students.

In this article, we show that the second law, as expressed by the Clausius inequality, can be presented more economically without resort to the Carnot engine and even without the Clausius or the Kelvin–Planck statements. Specifically, we show that the derivation of the Clausius inequality requires just

the thermodynamic stability conditions (e.g., the positivity of compressibility). The derivation is general; it holds for any closed system of arbitrary materials involving any kinds of work. The required background knowledge is the same as that required for the usual textbook presentation of the second law described above.

For engineering students, the classical approach may still be preferred since the basic concepts on heat engines can also be gained. However, such materials can be covered quickly based on the Clausius inequality as shown in the Supporting Information.

■ INTRODUCING THE ENTROPY BASED ON IDEAL GAS PROCESSES

First, we introduce a new state function, called the entropy. The material in this section was first presented in ref 8 and may also be found in several textbooks,^{3,5} but it is included to make the article self-contained.

For an ideal gas, the internal energy U is a function of temperature only so that

$$dU = C_V(T) dT \quad (1)$$

where C_V is also a function of T only. From eq 1 and the first law, the heat transfer associated with a reversible, small change in temperature T and volume V of an ideal gas is given by

$$\begin{aligned}
 \delta q_{\text{rev}} &= dU - \delta w_{\text{rev}} \\
 &= C_V(T) dT + P dV \\
 &= C_V(T) dT + \frac{nRT}{V} dV
 \end{aligned}
 \quad (2)$$

where the subscript “rev” designates a quantity associated with a reversible process. δq_{rev} is an inexact differential; since $[\partial C_V(T)/\partial V]_T \neq [\partial(nRT/V)/\partial T]_V$, it does not satisfy the Euler’s criterion for an exact differential. Since the heat transfer depends on the temperature, one may multiply eq 2 by $1/T$ as an integrating factor. This gives

$$\frac{\delta q_{\text{rev}}}{T} = \frac{C_V(T)}{T} dT + \frac{nR}{V} dV \quad (3)$$

Since $[\partial(C_V/T)/\partial V]_T = [\partial(nR/V)/\partial T]_V = 0$, $\delta q_{\text{rev}}/T$ is an exact differential. In fact, we can rewrite the differential relation, eq 3, as

$$\frac{\delta q_{\text{rev}}}{T} = d \left[\int^T dT' \frac{C_V(T')}{T'} + \int^V dV' \frac{nR}{V'} + \text{constant} \right] \quad (4)$$

The quantity within the square bracket is a state function, that is, a function of T and V , which will be denoted by S and called the entropy.

■ GENERALIZING THE RELATION TO ARBITRARY MATERIALS

We have just seen that $\delta q_{\text{rev}}/T$ is an exact differential for an ideal gas system, but it holds for any systems made up of arbitrary materials. To show this, consider a composite system made up of two subsystems A and B, of which A is an ideal gas, while B consists of any arbitrary material (see Figure 1). The

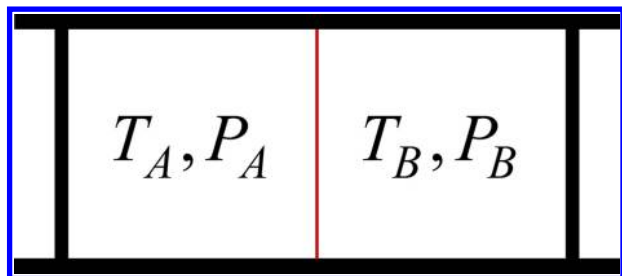


Figure 1. A composite system made up of two subsystems A and B. The subsystem A is an ideal gas, while the subsystem B consists of any arbitrary material. The whole system is insulated but the two subsystems may exchange work between them as well as with surroundings.

whole system is insulated but the inner wall separating the two subsystems conducts heat, so that the two subsystems may exchange heat with each other but not with the surroundings. However, works may be involved between the two subsystems as well as between them and surroundings. Although the ideal gas system A involves only the volume-expansion work, the subsystem B may involve various kinds of work via the coupling with surroundings.

Suppose now that the composite system undergoes a reversible cyclic process. Since the whole system is insulated, $\delta q_{\text{rev},B} = -\delta q_{\text{rev},A}$ at every moment during the process. For the process to be reversible, thermal equilibrium must be maintained between the two subsystems so that $T_A = T_B$ at

every instant. If the inner wall is movable, we must also have $P_A = P_B$, but this is not the necessary condition. Therefore, we have

$$\oint \frac{\delta q_{\text{rev},B}}{T_B} = - \oint \frac{\delta q_{\text{rev},A}}{T_A} = 0 \quad (5)$$

which indicates that $\delta q_{\text{rev},B}/T_B$ is also the exact differential of a state function, that is, S_B . Therefore, for any system,

$$dS = \frac{\delta q_{\text{rev}}}{T} \quad (6)$$

■ THE CLAUSIUS INEQUALITY AND THE SECOND LAW

The material in this section has been presented in ref 3. However, it is included to make the article self-contained. Let us first consider a system in which only the volume-expansion work is possible. When such a P – V – T system undergoes an infinitesimal change from a state with internal energy U and volume V to a neighboring state with $U + dU$ and $V + dV$, the first law states that

$$dU = \delta q + \delta w = \delta q - P_{\text{ex}} dV \quad (7)$$

This relation is valid for both reversible and irreversible processes. Now if the same change in the state is carried out reversibly, eq 7 becomes

$$dU = \delta q_{\text{rev}} - P dV \quad (8)$$

U is a state function, so that its change calculated from eq 8 must be equal to that calculated from eq 7. We thus have

$$\delta q_{\text{rev}} - \delta q = (P - P_{\text{ex}}) dV \quad (9)$$

Now, if $P - P_{\text{ex}} > 0$, the system must expand ($dV > 0$) as required by the thermodynamic stability condition. On the other hand, if $P - P_{\text{ex}} < 0$, we must have $dV < 0$. In either case, $(P - P_{\text{ex}}) dV > 0$ and it follows that $\delta q_{\text{rev}} > \delta q$. Since $T > 0$, we then obtain the Clausius inequality, which is the mathematical statement of the second law,

$$dS = \frac{\delta q_{\text{rev}}}{T} > \frac{\delta q_{\text{irrev}}}{T} \rightarrow dS \geq \frac{\delta q}{T} \quad (10)$$

where in the second relation, the equality applies only to a reversible process. Finally, we note that the above argument can be extended to the processes involving any other types of work.^{5,7}

■ ASSOCIATED CONTENT

§ Supporting Information

A short analysis on the efficiency of the Carnot engine with arbitrary working substance is given based on the Clausius inequality. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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