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ARTICLE

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A Missing Deduction of the Clausius Equality and Inequality

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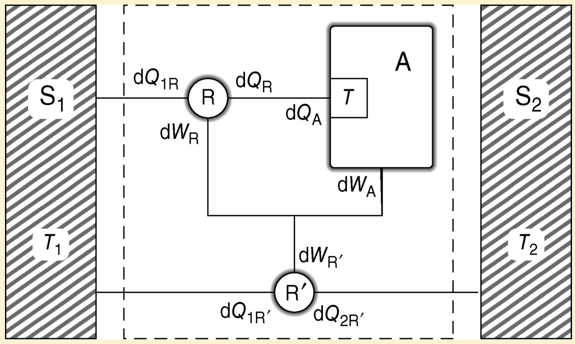
S Supporting Information



ABSTRACT: The two main statements of the second law of thermodynamics were given by Clausius, and Kelvin and Planck. Other statements followed well into the 20th century. It is known that the two main statements are not exactly equivalent, although their differences may never show outside academic environments or very specific areas of science. At negative absolute temperatures, a phenomenon studied mainly in connection to the constitution of matter and to its behavior under specific electromagnetic conditions, the non-equivalence of the two major statements, appears. Whereas the Kelvin–Planck statement must be modified to remain true, the Clausius statement remains true unaltered. This article proposes a deduction of the Clausius equality and inequality from the Clausius statement only, thus, inheriting its validity in the domain of negative absolute temperatures. The deduction developed here uses a simple arrangement of Carnot engines and a conceptualization of a system with very loose constraints. As a result, the level of generality achieved is high and includes both positive and negative absolute temperatures.

KEYWORDS: Upper-Division Undergraduate, Graduate Education/Research, Physical Chemistry, Interdisciplinary/Multidisciplinary, Textbooks/Reference Books, Misconceptions/Discrepant Events, Thermodynamics

Negative absolute temperatures (NAT) appear in rare and very specific conditions difficult to observe in practice. They were systematically treated by Ramsey[1] to explain experiments with nuclear spin systems.[2] There are two approaches to appreciate their physical meaning: the first is to conceive temperature as $T = (\partial U/\partial S)_V$[3] and the second is to reason according to statistical mechanics.[4] Both approaches lead to finding that negative absolute temperatures represent systems in which it is more probable to find particles at a high-energy level than at a low-energy level, which is opposite to the usual case.

Negative absolute temperatures have shown the necessity of revisiting fundamental aspects of thermodynamics to refine assumptions. The relationship between the concept of temperature and what we call "hot" and "cold" has been thoroughly analyzed; a revision can be found in ref 5 and refs 6 and 7 provide insight into the conditions of quasistatic adiabatic processes in the ∞^-, ..., 0^- and 0^+, ..., ∞^+ range of temperatures. Several discussions about the equivalence of the major statements of the second law can also be found in ref 8 which show the necessity of reformulating the Kelvin–Planck statement for systems at NAT.[1] The most general statement of the second law is the Clausius statement, which is valid both for negative and positive absolute temperatures. It must be noted that only some of its commonly used formulations hold.[9]

The implications of NAT and the partial findings shown by studies, such as these mentioned above, have triggered attempts to reformulate the conceptual framework of thermodynamics to increase its level of generality.[10,11] This generalization requires developing a deduction of the Clausius inequality from the Clausius postulate only, as opposed to the common hybrid Clausius–Kelvin–Planck approaches (see the Supporting Information). This deduction, however, has been found in the work of Clausius[12] and from a different point of view in an article by Muschik.[10] In Muschik's work, a formal, algebraic formulation is given based on rules of composition and set theory for connecting sources, engines, and processes. The Clausius inequality is derived by applying these mathematical rules to the particular case of two sources. Both approaches, however, are beyond the scope of undergraduate courses in thermodynamics because of their complexity[13] and, in the second case, for the lack of physical traceability of the reasoning (based exclusively in algebra).

A simple deduction of the Clausius inequality derived from the Clausius postulate is developed here, which holds for both positive and negative absolute temperatures. The deduction may be of conceptual and educational interest because, opposed to the complexity of the other sources, it is based on two bithermal Carnot engines. To make the discussion clearer, in the first part of the article we recapitulate the main issues related to the Clausius inequality: (i) the Kelvin–Planck and Clausius postulates and (ii) Carnot's theorem and some points related to the concept thermodynamic temperature. The second part of the article is dedicated to deducing the Clausius inequality starting

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from Carnot's theorem and the Clausius postulate in a way that explicitly shows its validity for NAT.

■ DISCUSSION OF TEMPERATURES AND THE CONCEPTS OF "WARMER" AND "COOLER"

Intuitively, we understand that a body at T_W is warmer than another body at T_C if the first delivers heat and energy to the second. In our everyday life, this happens if $T_W > T_C$. This is because at some point in the history of thermodynamics the function chosen to express temperature was T, but there is no conceptual reason behind it and the function could have been $1/T$, as it has been commented many times (for a full justification see ref 14). The main advantage of defining temperature as function T is, perhaps, a certain simplification of mathematical operations. However, it has the disadvantage of misleading when talking of NAT.

A system at a negative temperature is warmer than any system with a positive one because it would *deliver* energy, in accordance with the intuitive notion of "warmer" mentioned earlier.[1] This cannot be expressed with the usual $|T_W| > |T_C|$ because for some cases it is exactly the opposite. How do we express that a system at T_W is hotter than another at T_C in the case $T < 0$? Perhaps the simplest and general form is to say:

A system at T_W is warmer than one at T_C if

$$\frac{1}{T_W} < \frac{1}{T_C} \tag{1}$$

This criterion holds both for positive and negative temperatures. For example, a body at temperature $T_1 = -1$ K is warmer than one at $T_2 = -10$ K, because

$$\frac{1}{T_1} = \frac{1}{-1\text{ K}} = -1\text{ K}^{-1} < -0.1\text{ K}^{-1} = \frac{1}{-10\text{ K}} = \frac{1}{T_2}$$

In other words, at NAT, the warmer body is the one whose temperature has the smaller modulus (as in the example: $|T_1| < |T_2|$), the opposite to the positive temperatures case. In addition, and this is the actual justification of eq 1 instead of saying $T_W > T_C$ as a criterion for the word *warmer*, a body with any temperature lower than zero is always warmer than other with temperature higher than zero. The hottest body would thus be at 0^-, which would be warmer than any other body at any NAT, and a body at $-\infty$ would be warmer than any body at positive temperature, but cooler than any other at NAT.

Following this remark on the relation between "cooler" and "warmer" and temperatures, we change the notation in the text, indicating the warmer temperature by T_1 and the cooler by T_2.

■ CARNOT'S THEOREM

A Carnot engine is a system operating in cycles between two sources of heat, a warmer one, S_1 at T_1 and a cooler one, S_2, at T_2, to produce work. A cycle is composed by four reversible processes

Isothermal heat exchange with S_1 at T_1.
Adiabatic process from T_1 to the cooler T_2.
Isothermal heat exchange with S_2 at T_2.
Adiabatic process from T_2 to the initial state at T_1.

We indicate the heat interchanged with the sources Q_1 and Q_2, respectively, as seen from the engine. Thus, from the first law, it follows that the work produced by the engine in one cycle is $W = Q_1 + Q_2$. As all the processes of the cycle are reversible by definition, the operation of the machine can be inverted, absorbing work, $W < 0$, and reversing heat fluxes.

The Carnot theorem provides that the engine operates in such a way that the following relation holds:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{2}$$

Equation 2 is valid regardless the sign of T_1 and T_2. A bithermal reversible machine working between two NAT reservoirs would take heat from the cold reservoir ($Q_2 > 0$), and it would transfer the nonconverted work part to the hot reservoir ($Q_1 < 0$), with $|Q_1| < |Q_2|$.[a] A bithermal reversible machine working between a hot reservoir with NAT and a cold reservoir with positive T_2 would take heat from both reservoirs ($Q_1, Q_2 > 0$) and convert it integrally into work. These statements may make us feel uncomfortable owing to our intuition based on the Kelvin–Planck postulate. But it must be noted that it is only valid for the case of positive temperatures and fails in the rest of the cases, *contrarily to the case of Clausius's postulate*.

It follows from above that the efficiency of a Carnot engine, defined as $\eta = W/Q_1 = 1 + (Q_2/Q_1)$, is always $\eta = 1 - (T_2/T_1)$, regardless of its size or how it is built. This definition of efficiency would lead to negative values ($\eta < 0$) for the two-NAT bithermal machine and to greater than one values ($\eta > 1$) for the bithermal machine with one NAT source plus one positive T source. A new more general definition of the machine efficiency would be more useful for the case of NAT reservoirs. For example, $\eta = W/Q_{in}$ is proposed, where $Q_{in} = Q_1 + Q_2$ for the case of one NAT reservoir, $Q_{in} = Q_2$ for the case of two NAT reservoirs, and $Q_{in} = Q_1$ for the case of two positive temperature reservoirs.

■ CLAUSIUS AND KELVIN–PLANCK POSTULATES OF THE SECOND LAW

The previous sections have defined the conceptual basis for understanding the deduction of the Clausius equality and inequality. Developing the deduction from here requires a postulate of the second law that imposes the conditions to the heat and work flows in the arrangement of machines and sources used in the process. Only the Clausius postulate is used in this text; however, both this and the Kelvin–Planck statement are reiterated to fully understand the following sections and to allow the reader to clearly perceive the subtle differences between them.

- Clausius statement:[12] "Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time."
- Kelvin–Planck statement:[14] "It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat reservoir" or "it is impossible to transform heat into work with no other effect."

■ CLAUSIUS EQUALITY AND CLAUSIUS INEQUALITY

The Clausius equality and inequality apply to any system A that interchanges work, W_A, and heat, Q_A, with its environment. Work and heat are relative to system A carrying out a process that starts and ends at the same state,

$$\oint_{\text{rev}} \frac{dQ_A}{T} = 0$$
$$\oint_{\text{irr}} \frac{dQ_A}{T} < 0 \tag{3}$$

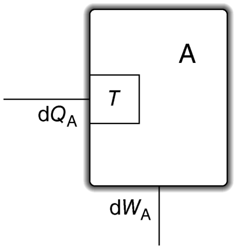

Figure 1. Conceptualization of a system. The part that interchanges heat is at a defined temperature T. $Q_A > 0$ if entering the system, $W_A > 0$ if done by the system.

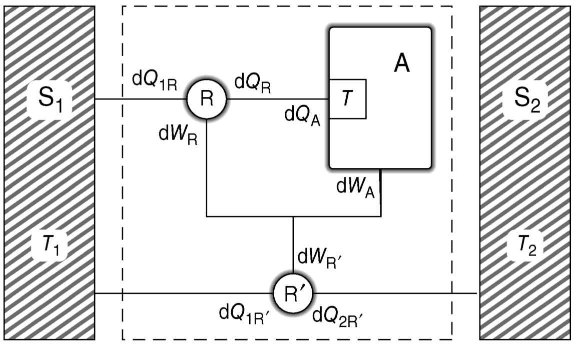

Figure 2. Array of Carnot engines for deducing the Clausius inequality.

where T is the temperature at which dQ_A is transferred at each intermediate state in the process. The Clausius equality and inequality lead to the definition of entropy current (J_S) and internal entropy generation (σ). It is derived from the Carnot theorem and from either of the postulates of the second law of thermodynamics applied to a generic system A.

Conceptualizing a Generic System

We consider system A as represented in Figure 1. The only restrictions applied to system A are (i) it is a closed system; (ii) there are no relativistic effects; and (iii) temperature, T, is defined in the area where the system interchanges heat with its environment. The sign criteria are $W_A > 0$ if done by the system and $Q_A > 0$ when it enters the system. We consider a single heat exchange for simplicity; enhancing the system for n heat exchanges at T_1, ..., T_n is straightforward. With these conventions, the first law is written as $\Delta U_A = Q_A - W_A$. No constraints are put on the operation of the system, so that it may be either reversible or irreversible. Both cases are examined.

Structuring the System−Environment Interaction

The Clausius postulate of the second law is formulated only in terms of heat flow between heat sources. Thus, to apply it to the operation of system A, an auxiliary array of Carnot engines must be connected, so that its heat and work interaction with the environment is reduced to heat only transfers between S_1 and S_2.

We propose the array indicated in Figure 2. It consists of two Carnot engines, R and R′, coupled to A in such a way that there exists no irreversibility in the heat transfer (dQ_A) on one side and that the work (dW_A) is transformed to an equivalent heat transfer on the other. As to R and R′, we impose no condition on them except that they operate for integer number of cycles in the intermediate stages of our analysis, so that we may assume $\Delta U_R = 0$ and $\Delta U_{R'} = 0$. With this, the presence of the Carnot engines does not affect the analysis either in terms of energy or irreversibility, and it is be possible to isolate the effects of the operation of system A. Hence, for the most part of the analysis, we analyze and extract results on the combined set of systems A, R, and R′, and we infer conclusions on A from them.

Considering eq 2 and the sign criteria previously mentioned, the following relations hold:

$$dW_{R'} = -dW_R - dW_A \tag{4}$$

$$dW_{R'} = dQ_{1R'} + dQ_{2R'} \tag{5}$$

$$dW_R = dQ_{1R} + dQ_R \tag{6}$$

$$dQ_R = -dQ_A \tag{7}$$

A point must be made about R, the Carnot engine operating between A and S_1. The system definition proposed for A does not require that T be constant. Thus, during a process, T could change, and thus R would be required to operate between T_1, fixed, and a variable T. There are a number of ways of overcoming this conceptual difficulty. We propose to understand R not as a single Carnot engine, but as a set of infinite *differential* Carnot engines, each of which would operate between T_1 and a value of T, producing dW_R and absorbing dQ_{1R} and dQ_R in one cycle.

Deducing the Clausius Equality and Inequality

For deducing the Clausius equality and inequality, eq 3, we analyze A, following a generic process between an initial state i and a final state f, and back to i, so that $\Delta U_A = 0$. With U_A, we indicate total energy: $U_A = E_A + E_{pA} + E_{kA}$ (internal, potential and kinetic). The analysis is done in two parts, first from i to f and then from f to i. We indicate the quantities in the reverse part of the process by the super-index "I":

$$\oint \frac{dQ_A}{T} = \int_i^f \frac{dQ_A}{T} + \int_f^i \frac{dQ_A^I}{T^I} \tag{8}$$

Carnot's theorem and first law to engines R and R′: Combining eq 2 with eqs 5, 6, and 7, the differential work of R′ can be expressed in terms of $dQ_{2R'}$ and dQ_A,

$$\begin{aligned} dW_R &= -dQ_A\left(1 - \frac{T_1}{T}\right) \\ dW_R^I &= -dQ_A^I\left(1 - \frac{T_1}{T^I}\right) \\ dW_{R'} &= dQ_{2R'}\left(1 - \frac{T_1}{T_2}\right) \\ dW_{R'}^I &= dQ_{2R'}^I\left(1 - \frac{T_1}{T_2}\right) \end{aligned}$$

where T^I indicates the temperature value along the line of the backward process, which may not coincide with that of the forward. Integrating these expressions gives

$$\begin{aligned} W_R &= -Q_A + T_1\int_i^f \frac{dQ_A}{T} \\ W_R^I &= -Q_A^I + T_1\int_f^i \frac{dQ_A^I}{T^I} \end{aligned} \tag{9}$$

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$$W_{R'} = Q_{2R'}\left(1 - \frac{T_1}{T_2}\right)$$
$$W^I_{R'} = Q^I_{2R'}\left(1 - \frac{T_1}{T_2}\right) \quad (10)$$

First law to A: According to eq 4:

$$\Delta U_A = Q_A - W_A = Q_A + W_R + W_{R'}$$

and it is possible to proceed to get the analogous one for the backward direction. Combining this equation with eqs 9 and 10, results in

$$\Delta U_A = T_1 \int_i^f \frac{dQ_A}{T} + Q_{2R'}\left(1 - \frac{T_1}{T_2}\right)$$
$$\Delta U^I_A = T_1 \int_f^i \frac{dQ^I_A}{T^I} + Q^I_{2R'}\left(1 - \frac{T_1}{T_2}\right)$$

Imposing the condition that A returns to i: If A returns to its initial state, whichever the process followed, the total increment of U must be zero:

$$\Delta U_A^{tot} = 0 = T_1 \oint \frac{dQ_A}{T} + \left(1 - \frac{T_1}{T_2}\right)(Q_{2R'} + Q^I_{2R'})$$

Consequently, we obtain

$$\oint \frac{dQ_A}{T} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)(Q_{2R'} + Q^I_{2R'}) \quad (11)$$

The sign of the integral depends on that of the two operands. However, according to eq 1

$$\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \geq 0$$

hence, the sign of the integral coincides with the sign of $Q_{2R'} + Q_{2R'}^{I}$. This operand is a net balance of the heat absorbed by the combined system of A, R, and R′ in the cyclical process i → f → i. According to the Clausius postulate, heat must always flow from the warmer to the cooler source in absence of work and in a cyclic process, so it must be: $Q_{2R'} + Q_{2R'}^{I} \leq 0$. Finally

$$\oint \frac{dQ_A}{T} \leq 0 \quad (12)$$

If the i → f process were reversible, system A may return to its initial state i by reversing its interchange of heat and work, which occurs by changing the original sign of dQ_A and dW_A. As a result, $dQ_A = -dQ_A^I$ and $dW_A = -dW_A^I$, inducing the same change of sign in the heats and works of R and R′. Thus, all increments in the forward direction would be compensated by the backward one, making eq 12 equal to zero. This case is known as the Clausius equality:

$$\oint_{rev} \frac{dQ_A}{T} = 0 \quad (13)$$

This result, however, is an exception to the general case, in which heat flux and work in one direction and the other do not compensate perfectly, leading to the Clausius inequality:

$$\oint_{irr} \frac{dQ_A}{T} < 0 \quad (14)$$

■ DISCUSSION

It is essential to understand the Clausius statement of the second law with its full level of generality for which it is necessary to describe a warmer system at T_1 and a cooler at T_2 as given by eq 1. This criterion allows discriminating the warmer and the cooler regardless the sign of T. The deduction of the Clausius equality and inequality proposed here has the highest level of generality. This is due to several points: (i) the level of the Clausius statement itself and (ii) the generality of the conceptualization of system as shown in Figure 1. The case of a single heat transfer has been considered in the text, but the extension to any number is immediate; the deduction is valid even the case of an adiabatic system.

Some more subtle points must be noted. As proposed in the text, the deduction is valid for any kind of process carried out by system A, whether it is reversible, quasistatic, or irreversible. This generality may easily be lost if eqs 9 and 10 are not integrated, with differential works considered instead, and thus dU_A instead of ΔU_A. Operating with differential quantities would implicitly assume a quasistatic process in A, thus, restricting the validity of the final result in eq 12.

A final comment must be made regarding temperatures and the validity of the deduction and eq 12. It could seem that for the expression to hold, T_1 and T_2 should have the same sign, to preserve the integrability of $\int_i^f dQ_A/T$ and the reverse from f to i, by avoiding the passing through $T = 0$. This is not so, however, because such passing would not occur. In case of $T_2 > 0$, $T_1 < 0$, the line of integration would pass from the positive to the negative and vice versa through $\pm\,\infty$. This is due to the distinction of warmer and cooler, which establishes the extremes of the temperature scale at 0^+ and 0^-, and $+\infty$ and $-\infty$ at the center. With respect to passing through $\pm\,\infty$, it must be remarked that it is possible only by nonstatic adiabatic processes.[6]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Derivation of the Clausius equality and inequality from the Kelvin−Planck postulate. This material is available via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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■ ADDITIONAL NOTE

[a]It may be of interest to remark that for NAT the interchangeability of heat and work is just the opposite of the usual one (Kelvin−Planck postulate), so work cannot be entirely converted into heat in a cyclical process. Therefore, the Clausius postulate is not possible to be violated converting the work produced by the bithermal machine into heat given to the hot reservoir.

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