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A generalized and explicit conceptual statement of the principle of the second law of thermodynamics

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ABSTRACT

The Clausius Inequality, the fundamental statement of the second law of thermodynamics, focuses on the net entropy rejection by heat transfer out of a closed system operating in a cyclic manner. Recently, the Clausius Inequality was re-stated to correctly apply to systems regardless of the form of heat transfer, and in particular systems with radiative transfer. This is important for many engineering systems because all matter emits thermal radiation continuously due to non-zero temperature. Other statements of the second law also generally refer to heat transfer and heat engines. Of even greater importance, the focus is on equilibrium processes and relations, whereas actual engineering systems are overwhelmingly non-equilibrium by nature. Although not explicitly stated in the Clausius Inequality, the second law principle encompasses the universal approach to obtain uniformity or equilibrium, a state of maximum entropy or disorder. By nature this approach to equilibrium is through non-equilibrium processes that continuously produce entropy as they occur. This paper attempts to capture a more generalized conceptual statement of the second law, that explicitly states various aspects of the second law principle for the purposes of engineering education; a statement that applies to any scenario, system or process.

1. Introduction

Second law analysis is important in scientific and engineering analysis as it provides a number of benefits over energy analysis alone, including the basis for determining energy quality, understanding fundamental physical phenomena, and providing enhanced performance evaluation and optimization. All matter emits thermal radiation (TR) continuously and consequently radiation is an inherent part of physical systems. Radiative heat transfer is particularly important in engineering analysis whenever high temperatures are involved, cryogenic systems are considered, when radiation is being utilized as a source flux, or in particular, when radiative transfer is the primary mode of heat transfer.

The Clausius Inequality, the fundamental statement of the second law, focuses on the net entropy transfer by heat transfer out of a closed system operating in a cyclic manner. Wright (2007) re-stated the Clausius Inequality to correctly apply to any system, regardless of the form of heat transfer, including radiative transfer.

Other statements that imply the second law typically refer to heat transfer and heat engines, such as the Kelvin-Planck statement. This paper attempts to capture a more generalized conceptual statement of the second law, that explicitly states various aspects of the second law principle for the purposes of engineering education; a statement that applies to any

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Nomenclature

A	Surface area (m^2)
c	Speed of light = $(2.9979)10^8$ m/s
k	Boltzmann's constant = $(1.38)10^{-23}$ J/K
h	Planck's constant = $(6.626)10^{-34}$ J s
N_j	Number of bosons in quantum state j
q	Heat flux (W/m^2)
Q	Heat transfer (J)
q_{cc}	Heat flux by conduction and convection (W/m^2)
$đQ$	Infinitesimal heat transfer (J)
$đQ_{cc}$	Infinitesimal heat transfer by heat conduction and convection (J)
$đS$	Infinitesimal entropy transfer by radiation (W/K)
$đS_{Net,Rad}$	Infinitesimal net entropy transfer by radiation (W/K)
S	Entropy of a system (J/K)
ΔS_{12}	Entropy change of the system from state 1 to 2 (J/K)
T	Material emission temperature or the temperature at the system boundary (K)
T_S	Material emission temperature of incident radiation (K)
dt, Δt	Infinitesimal and finite time interval (s)
x	Non-dimensional group, hν/kT
Greek	
ε	Emissivity for gray radiation (GR)
ν	Frequency (s^{-1})
σ	Stefan-Boltzmann constant = $(5.67)10^{-8}$ W/m^2K^4
π	Mathematical constant, 3.14159…
Π	Entropy production (J/K)
Ω	Number of microstates of a system
Acronyms	
BR	Blackbody radiation
DBR	Diluted blackbody radiation
GR	Graybody radiation
NBR	Non-blackbody radiation
PLS	Principle of local state
TR	Thermal radiation

scenario, system or process, whether heat transfer is present or not, and under any circumstances, including non-equilibrium conditions.

2. Re-stating the Clausius inequality for any heat transfer scenario

The Clausius inequality for a cycle is expressed as,

$$\oint \frac{đQ}{T} \leq 0, \tag{1}$$

where $đQ$ represents an infinitesimal heat transfer into the system at the boundary where the temperature is T. The integration is carried out over the entire boundary and over a complete cycle. The symbol $đQ$ is specifically used to indicate that the heat transfer is path or process dependent. Physically, the Clausius[1] inequality is interpreted as there must be net transfer of entropy out of the system over the cycle, which is due to entropy production for real processes (zero for a cycle of reversible or ideal processes). If instead we look at a portion of the cycle, say between equilibrium states 1 and 2, then this inequality can be stated as,

$$\Delta S_{12} \geq \int_1^2 \frac{đQ}{T}. \tag{2}$$

This form of the inequality, indicates that the change in entropy of a closed system between two equilibrium states is greater than or equal to what can be accounted for due to entropy transfer by heat flow into the system during the process.

[1] The 'Clausius statement' (rather than inequality) states that "It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body". In other words, the spontaneous transfer of heat from a colder to a hotter body is not possible as this implies the destruction of entropy.