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Thermodynamic equipartition for increased second law efficiency

Gregory P. Thiel [a], Ronan K. McGovern [a,1], Syed M. Zubair [b], John H. Lienhard V [a,*]

[a] Rohsenow Kendall Heat Transfer Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA
[b] Department of Mechanical Engineering, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

HIGHLIGHTS

- Efficiency gains from equipartition to minimize entropy generation are quantified.
- The equipartition factor $(\varXi)$ quantifies the variance of thermodynamic affinities.
- Systems with low $(\varXi)$ and low efficiency gain most when redesigned for equipartition.
- For lumped capacitance systems long normalized charging times correlate with low $(\varXi)$.

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ABSTRACT

In this work, a clear distinction is drawn between irreversibility associated with a finite mean driving force in a transport process and irreversibility associated with variance in the spatial and/or temporal distribution of this driving force. The portion of irreversibility associated with driving force variance is quantified via a newly defined dimensionless quantity, the equipartition factor. This equipartition factor, related to the variance in dimensionless driving force throughout the system, is employed to formulate an expression for second law efficiency. Consequently, the equipartition factor may be employed to identify the improvement in efficiency achievable via system redesign for a reduction in driving force variance, while holding fixed the system output for fixed system dimensions in time and space. It is shown that systems with low second law efficiency and low equipartition factor will have the greatest benefit from a redesign to obtain equipartition. The utility of the equipartition factor in identifying situations where efficiency can be increased without requiring a spatial or temporal increase in system size is illustrated through its application to several simple systems.

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1. Introduction

Growing population, rapid advancement in the developing world, and an increasingly technological lifestyle are all driving an increasing demand for energy. The rate of increase in demand can be moderated by improved energy efficiency in processes of all types. There exists a fundamental trade-off between size of a system (or extent, whether spatial or temporal) and its second law efficiency. Only in infinite time can a hot object reach absolute equilibrium with its surroundings; only with infinite size can a heat exchanger transfer a finite amount of heat with an infinitesimal temperature difference. The literature on entropy generation minimization and finite time thermodynamics investigates these ideas in great detail (see, e.g., [1–3]).

An important, but little explored subset of the field of entropy generation minimization is that of equipartition, first studied by Tondeur and Kvaalen [4]. Their work indicates that the trade-off between size and efficiency is not direct. Independent of component size or process duration, irreversibility—and thus efficiency—is also influenced by the spatial and temporal distributions of entropy generation rates, and a component's entropy generation is minimized when these local rates are uniformly distributed, or equipartitioned. For processes with constant force-flux coefficients, this equipartition of entropy production is equivalent to the equipartition of the thermodynamic driving force. A corollary of the theory is that only when entropy generation rates are uniformly distributed in space and time, or equipartitioned, does total irreversibility (or efficiency) depend directly upon the absolute component size or upon the duration of the process. Equipartition thus provides a general framework for reducing entropy generation without sacrificing system output and without requiring an increase in system size or process duration. Whereas many entropy generation analyses focus on understanding which components in a system are most irreversible (see, e.g., [5,6]), equipartition provides insight into a possible next step: how a component could be redesigned to reduce entropy generation.

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[*] Corresponding author. Tel.: +1 617 253 3790.
E-mail address: lienhard@mit.edu (J.H. Lienhard V).
[1] Joint first author.

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Nomenclature

Roman symbols

A	area, m ^{2}
A_m	membrane permeability, kg/m^2 h bar
C	electrical capacitance, F
c	specific heat capacity, J/kg K
D	mass diffusivity, m^2/s
F	faraday constant, C/mol
f	affinity, or thermodynamic driving force
Fo	fourier number, $\alpha t/l^2$
h	heat transfer coefficient, W/m^2 K
h_m	mass transfer coefficient, m/s
i	current density, A/m^2
j	flux
k	thermal conductivity, W/m K
L	generalized force-flux coefficient
l	length, m
m	mass, kg
m''	mass flux, kg/m^2 s
MR	mass flow rate ratio, $\dot{m}_{\text{coolant}}/\dot{m}_{\text{moist air}}$
p	pressure, bar
Q	charge, C; or heat transfer, J
$\dot{Q}$	heat transfer rate, W
q	heat flux, W/m^2
R	resistance, Ω
S_{gen}	entropy generation, J/K
$\dot{S}_{\text{gen}}$	entropy generation rate, W/K
S_{trans}	entropy transferred, J/K
T	temperature, °C or K
t	time, s
U	internal energy, J
V	volume, m^3; or voltage, V
$\bar{v}_w$	partial molar volume of water, m^3/mol
W	work, J or kW h
w	specific work, kW h/m^3
Y	generalized system state
y	salinity, kg/kg

Greek symbols

α	thermal diffusivity, m^2/s
Δ	change
η	second law efficiency
θ	dimensionless temperature difference
κ	characteristic inverse time, 1/s
μ	chemical potential, J/mol
Ξ	equipartition factor
π	osmotic pressure, bar
ρ	density, kg/m^3
ρ_i	partial density of species i, kg/m^3
σ	electrical conductivity S/m
τ	characteristic time, s
ϕ	electrical potential, V

subscripts

0	dead state, initial state
b	brine; or brick
c	capacitor
e	equipartitioned
f	feed
H	high
HP	heat pump
L	low
ne	non-equipartitioned
p	product
rev	reversible
RO	reverse osmosis
s	source
w	wall; or water

Indeed, there are several innovations that can be explained with or have capitalized on the theory of equipartition. For example, although the minimization of entropy generation in heat exchangers has been widely studied (see, e.g., [2]), the distinction between reducing irreversibility through reduced driving force variance or reduced average driving force is not often made. The application of equipartition to make this distinction in heat exchangers has been examined by [7–9]. The optimization of effective capacity rate ratios to achieve minimum entropy production in heat and mass exchangers has also been studied [10], where it has been shown [11] that under certain conditions, designing for equipartition of the mass transfer driving force is superior to designing for a uniform heat transfer driving force. In a diabatic distillation column [4,12,13], equipartition has been used to show how adding heat along the length of the column results in a more uniform distribution of driving force and thus higher efficiency. Further discussion of the literature on equipartition is given in the references [14–16].

Although the prior studies have made it clear that the variance in entropy generation rates is itself responsible for a portion of total entropy generation, it is less clear what portion of the total entropy generation this variance accounts for, and under what conditions a reduction of variance would lead to significant improvement in overall efficiency. In this work, we define an equipartition factor and relate it to the second law efficiency, in order to provide quantitative answers to these questions. The broad applicability of this approach is illustrated through simple examples.

2. Design for equipartition

The presence of a finite driving force implies the presence of irreversibility within a process. For a system of fixed size (spatial or temporal), and with a linear force-flux relationship, Tondeur and Kvaalen [4] demonstrated that the driving force variance itself is responsible, in part, for irreversibility.

The amount of irreversibility associated with driving force variance is quantified by comparing entropy generation within a given system to the entropy generation within an equivalent system with zero driving force variance and the same mean driving force, i.e., an equipartitioned system. The equivalent system maintains the same output, or productivity (e.g., heat transfer, fresh water production), and is of the same size and operates over the same time period. The equipartition factor is the fraction of total entropy production associated with the equivalent, equipartitioned system:

$$\Xi \equiv \frac{S_{\text{gen},e}}{S_{\text{gen}}} \tag{1}$$

where the subscript e denotes the equivalent, equipartitioned system.

If the relationship between the thermodynamic driving force or affinity f and the flux j is linear, $j = Lf$, and the constant of proportionality L is uniform across the system, entropy generation is described by the integral over space and time of the force-flux coefficient multiplied by the square of the driving force:

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