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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.

Keywords: Equipartition; energy efficiency; entropy generation minimization

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 kWh
w	Specific work, kWh/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

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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

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.

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 variation 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:

$$\Xi \equiv \frac{S_{\text{gen},e}}{S_{\text{gen}}} \qquad (1)$$

where the subscript e denotes to 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:

$$S_{\text{gen}} = \iint Lf^2 \, dV \, dt \qquad (2)$$

where f is defined as (see, e.g. [17])

$$f \equiv \nabla \left(\frac{\partial S}{\partial X} \right) \qquad (3)$$

and X is the quantity being transported. For example, when $X = U$, the internal energy, in a nonflowing system j is heat flux q, and the force-flux relationship is written as $j = Lf = kT^2\nabla(1/T)$. Noting that the driving force[1] is by definition uniform in an equipartitioned system, using Eq. (2), the equipartition factor

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[1]The theory of equipartition applies when the driving force is defined by Eq. (3). This thermodynamic driving force, or affinity, does not always have the same form as the driving force implied by phenomenological force-flux relationships. For example, in the case of conduction heat flux, Fourier's law takes the form $q = kT^2\nabla(1/T)$ rather than $q = -k\nabla T$. However, in the cases considered herein for which gradients are relatively small (see Sec. 3), the phenomenological driving force is within an approximately constant factor of the thermodynamic driving force and may be used in the evaluation of Eq. (2).

may be written

$$\Xi = \frac{\bar{f}^2 V \tau}{\iint f^2 \, dV \, dt} \qquad (4)$$

where $\bar{f}$ is the mean thermodynamic driving force associated with any arbitrary distribution of thermodynamic driving force f, V is the system volume, and τ is the elapsed time. Defined in this way, the equipartition factor has clear limits. A system that is perfectly equipartitioned has $\Xi = 1$; for a highly non-equipartitioned system, $S_{\text{gen}} \gg S_{\text{gen},e}$ and $\Xi \to 0$. In addition, the expression limits correctly for a reversible system: $\Xi = 1$ as the numerator and denominator of Eq. (4) each approach zero.

Because the local driving force, f, may be written as the sum of a mean driving force and a local deviation, as done by Tondeur and Kvaalen [4], the equipartition factor is related to the variance of the dimensionless driving force within the system:

$$\Xi = \frac{1}{1 + \text{Var}(f/\bar{f})} \qquad (5)$$

Furthermore, the equipartition factor is easily related to second law efficiency. Second law efficiency is defined as the ratio of reversible work done to the sum of reversible and irreversible work, where irreversible work is represented by the product of entropy generation and the dead state temperature. That is,

$$\eta \equiv \frac{W_{\text{rev}}}{W_{\text{rev}} + T_0 S_{\text{gen}}} \qquad (6)$$

Making use of Eq.(1) and Eq. (4), the second law efficiency may be described in terms of reversible work, the entropy generation in an equipartitioned system, and the equipartition factor:

$$\eta = \frac{W_{\text{rev}}}{W_{\text{rev}} + T_0 S_{\text{gen},e}/\Xi} = \frac{W_{\text{rev}}}{W_{\text{rev}} + T_0 L \bar{f}^2 V \tau/\Xi} \qquad (7)$$

Written in this manner, we see that the second law efficiency of any system may be described by the second law efficiency of its equipartitioned equivalent and its equipartition factor. Thus, conversely, the potentially achieveable gain in second law efficiency for any system is defined by its second law efficiency and its equipartition factor, that is,

$$\eta_e = \frac{\eta_{ne}}{\Xi(1 - \eta_{ne}) + \eta_{ne}} \qquad (8)$$

where ne denotes a non-equipartitioned system. A plot of Eq. (8) shows a key feature of equipartition: the greatest potential for efficiency gain is found in systems with low equipartition factors *and* low second
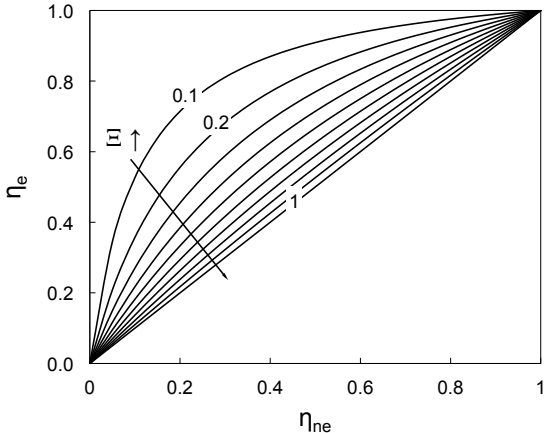
Figure 1: Second law efficiency of an equivalent, equipartitioned system as a function of non-equipartitioned second law efficiency and the equipartition factor

law efficiencies, the upper left corner of Fig. 1. The converse is also significant. If a non-equipartitioned design is preferable (e.g., significantly more economical, or easier to manufacture), it is clear that less is sacrificed in terms of energetic performance if the system has high Ξ and η_{ne}. The intuition behind these two observations is that by redistributing driving forces in space or time, only the irreversible portion of the work input may be affected. Thus, if the system is already highly efficient, irreversibility is small and any reduction in irreversibility will also have a small effect.

In summary, the equipartition factor quantifies the portion of irreversibility associated with driving force variance. In defining second law efficiency, the equipartition factor makes clear efficiency may be improved by two means. The first, involving a decrease in mean driving force, requires the trade-off of increased system size to achieve the same productivity[2]. The second is to redesign the system to reduce variance while holding the system size or process duration fixed. The most significant improvements may be achieved while still maintaining a given system extent and productivity are in the case of low Ξ and low η.

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[2]Here, the word productivity is used in a broad sense to mean a matched overall rate process or the same desired output, e.g., heat transfer in a heat exchanger or fresh water production in a water treatment system

3 Application of the equipartition factor

To illustrate the utility of the equipartition factor, we first apply it abstractly in a class of systems where the mathematical modeling is simple, but the representation is broad and the interpretation of results is abundantly clear: lumped capacitance systems. Concepts gleaned from this analysis are then extended to two, more practical representations of real-life systems.

3.1 Lumped-capacitance systems

In a lumped-capacitance model, the state of the system and the phenomenological driving force required to change that state may be described by the same variable Y. Spatial gradients in Y are captured in a measure of resistance, and the system is defined by some constant measure of capacitance. In the case of a simple RC circuit, for example, Y is a non-dimensional voltage difference. Other systems are shown in Table 1. Consider the case in which the time rate change of the system state is proportional to the driving force such that

$$\frac{dY}{dt} = -\kappa Y \qquad (9)$$

If the system is exposed to a step change from an initial state 0 to a state s, the result is the characteristic exponential change in state, $Y(t) = \exp(-\kappa t)$ common to electrical, thermal, and diffusive mass transfer transients. For any lumped-capacitance system characterized by Eq. (9), and for which the affinity f can be linearized such that it is proportional to Y (i.e., purely resistive), the equipartition factor can be written as [cf. Eq. (4)]

$$\Xi = \frac{\left(\int_0^\tau Y\,dt\right)^2}{\tau \int_0^\tau Y^2\,dt} = \frac{\tanh(\kappa\tau/2)}{\kappa\tau/2} \qquad (10)$$

where τ is the time elapsed from initial to final system states. From Eq. (10), it is clear that a redesign of the change in boundary conditions is necessary to achieve equipartition: otherwise only in the limit as the dimensionless charging time $\kappa\tau$ approaches zero does Ξ approach unity. The equipartition factor, and thus the second law efficiency, is otherwise always sub-optimal for systems characterized by Eq. (9).

By replacing the system with its equipartitioned equivalent, one in which the time-rate change of the system is constant, the second law efficiency can be improved. In terms of the lumped-capacitance systems characterized by the variables shown in Table 1,

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Table 1: Phenomenological laws, thermodynamic driving forces, generalized system state variables Y, and characteristic times $1/\kappa$ for lumped-capacitance systems

System	Phenomenological Law	f	Y	κ
Heat Transfer	$q = -k\nabla T$	$\nabla(1/T)$	$\dfrac{T - T_s}{T_0 - T_s}$	hA/mc
Electrical Circuit	$i = -\sigma\nabla\phi$	$\nabla(\phi F/T)$	$\dfrac{V_s - V_c}{V_s - V_0}$	$1/RC$
Mass Diffusion	$m'' = -D\nabla\rho_i$	$-\nabla(\mu/T)$	$\dfrac{\rho_i - \rho_{i,s}}{\rho_{i,0} - \rho_{i,s}}$	$h_m A/V$

this is equivalent to: (1) charging the capacitor with a constant current rather than a constant voltage; (2) heating or cooling with a uniform heat flux rather than a uniform source temperature; and (3) allowing mass to diffuse at a uniform rate, rather than from a uniform source concentration. In these redesigned cases, the equipartition factor is identically one.

For these lumped-capacitance systems and their equipartitioned equivalents, the achievable gains resulting from a redesign are completely quantifiable. Fig. 2 shows a plot the second law efficiency of the redesigned, equipartitioned system as a function of the non-equipartitioned second law efficiency, with contours for the dimensionless charging time $\kappa\tau$. For systems with the low dimensionless charging times *and* low Second Law efficiencies, the gain in efficiency from equipartition is most significant; for systems with short charging times and/or high efficiencies, the gain least significant. This observations mirror those found in Sec. 2. Systems with very short charging times approach constant flux processes, as the state of the system and the driving force do not have time to change. Thus, the equipartition factor is close to unity and the potential to improve efficiency small. At longer charging times, the equipartition factor approaches zero (see Eq. (10)) the driving force changes throughout the process and thus equipartition can bring about greater improvements in efficiency.

Although they are not lumped-capacitance systems, the following two examples illustrate this finding in models representative of practical systems.

3.2 Equipartition in a building heating system

Consider a simple model of a thermal storage heating system. For some portion of the night, an electrically driven heat pump warms a ceramic brick with heat capacity $(mc)_b = (\rho V c)_b$ from an initially uniform temperature T_0. At other times the brick cools, releasing stored heat to warm the building. Typically,
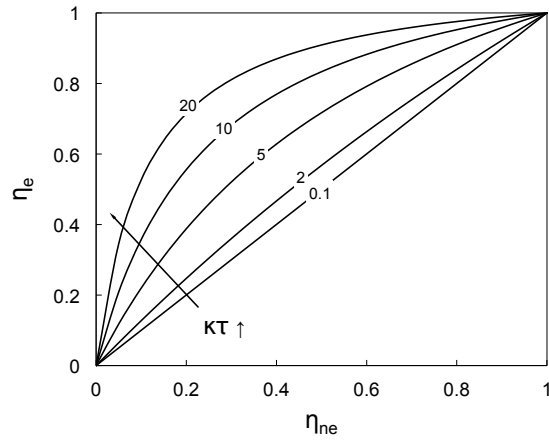

Figure 2: Second law efficiency for an equivalent, equipartitioned system as a function of non-equipartitioned second law efficiency and dimensionless time $\kappa\tau$

during the heating process, heat is transferred to the brick from a constant temperature source. We will compare this case to an improved design where we maintain a constant heat flux while heating the brick.

The heat pump is characterized by a second law efficiency η_{HP} (taken as unity to isolate the effect of equipartition), and has heat input Q_{in} from a sink at T_L and work input W_{in}. We consider two modes of operation for the heating of the brick: (I) the heat pump rejects heat at a constant temperature T_H (i.e., the brick is heated by a constant temperature heat source); (II) the heat pump rejects heat at a constant rate (i.e., the brick is heated by a constant flux heat source). The two modes are shown schematically in Figure 3. In the first case, the work requirement for the heat pump is $W_{\mathrm{in}} = Q_{\mathrm{out}}(1 - T_L/T_H)/\eta_{\mathrm{HP}}$. In the second, redesigned case, the work requirement for the heat pump is $W_{\mathrm{in}} = [Q_{\mathrm{out}} - T_L S_{\mathrm{trans}}]/\eta_{\mathrm{HP}}$, where S_{trans} is the entropy transferred out of the heat
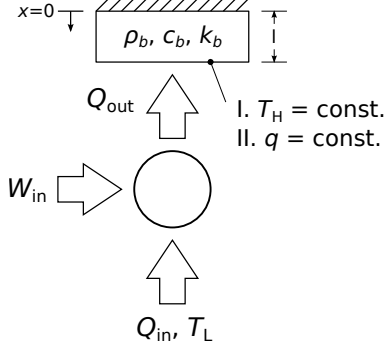
Figure 3: Schematic diagram of a simple model of a thermal storage heating system

pump and into the brick. The reversible work for the entire system (heat pump and brick) is $W_{rev} = Q_{out} - (mc)_b T_L \ln(T_H/T_0)$.

The heat transfer process within the brick is modeled as transient, one-dimensional heat conduction through a slab. The slab has width l and frontal area A. During the heating process, the brick has a diabatic boundary at $x = l$ and an adiabatic boundary at $x = 0$; heat loss to the ambient during the charging process is taken to be negligible. Immediately after the charging process, the diabatic boundary is thoroughly insulated, and the block equilibrates[3].

In each case, the heat pump provides the same amount of heat to the brick, Q_{out} over the same time period τ. In both cases the brick traverses from an initial state T_0 to a final state T_H. Thus, in both cases, the block undergoes the same average rate process and goes from the same initial state to the same final state. The change in internal energy of the block is the same, as is the block's entropy change. The path by which this change occurs, however, is different.

As our design case, we choose a typical $95\,\mathrm{m}^2$ house with a heating requirement of 7.64 kW, as discussed in [18], yielding a required 'charge' of $Q_{out} = 440$ MJ for a system that charges for 8 hours in a 24 hour period. The sink temperature, $T_L = 10\,^\circ\mathrm{C}$, and the intial and final brick temperatures are $T_0 = 20\,^\circ\mathrm{C}$ and $T_H = 100\,^\circ\mathrm{C}$, respectively. Other inputs are shown in Table 2. The temperature distribution within the slab facilitates a comparison of the transient rate processes and the resultant states. Details of the solution of the heat equation for uniform heat flux and for uniform wall temperature boundary conditions are clas-

sical and may be found, e.g., in [19, 20]. In terms of the general variables defined in Section 2, we are interested in the flux of heat, the temperature driving force, and the average driving force, respectively:

$$j = q \tag{11}$$

$$f = \frac{\partial(1/T)}{\partial x} \approx \frac{\Delta T}{l T_w^2} \tag{12}$$

$$\bar{f} = \frac{1}{\tau l} \int_0^\tau \int_0^l \frac{\partial(1/T)}{\partial x} \, dx \, dt \tag{13}$$

where q is heat flux, k is thermal conductivity, and w indicates the quantity is evaluated at the wall, i.e., at $x = l$. In both cases, as shown by Eq. (12), a good measure of the affinity for heat transfer is the familiar phenomenological driving force ΔT, the difference between the wall temperature and the mass-averaged temperature, $\overline{T}$. For this system, the equipartition factor, Eq. (5), is thus

$$\Xi = \frac{\left\{ \int_0^\tau \int_0^l [\partial(1/T)/\partial x] \, dx \, dt \right\}^2}{\tau l \int_0^\tau \int_0^l [\partial(1/T)/\partial x]^2 \, dx \, dt} \tag{14}$$

A plot of dimensionless[4] wall and average temperature for both cases, as shown in Figure 4a, reveals the expected trend: a uniform wall flux displays a more uniform distribution of driving temperature difference. The result is confirmed by a consideration of the instantaneous rate at which entropy is produced over time, calculated as $\dot{S}_{gen} = \int_0^l \frac{k}{T^2} \left(\frac{\partial T}{\partial x} \right)^2 \, dx$.

Comparing Figure 4b, entropy generation rate versus time to Figure 4a, which shows temperature differences in the two cases, the concept of equipartition presented graphically is immediately clear. The area under the entropy generation rate curve in the redesigned case—the net entropy production—is much smaller than in the base case. The boundary condition of uniform heat flux creates a more uniform heating disequilibrium, and thus a lower entropy production rate. The result is a nearly 22% reduction in work required by the heat pump, an increase in the equipartition factor from 0.34 to nearly unity, and an increase in the Second Law efficiency from 60.6% to 77.3%. Because the equipartition factor is low, significant gains in second law efficiency are achievable with equipartition. The results are summarized in Table 2.

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[3]Obviously the system will not reach true equilibrium in finite time; however, in the example presented here, entropy generated in the rundown to equilibrium may be shown to be negligible compared to the entropy generated in the heating process.

[4]The dimensionless temperatures are defined in the usual way: for the uniform wall temperature case it is $\theta = (T - T_0)/(T_w - T_0)$; for the uniform heat flux case, it is $\theta = (T - T_0)/(q_w L/k)$.

Table 2: Summary of the heat transfer system inputs and results

Variable	Symbol	Units	Base Case	Redesign Case
Total Heat Capacity	$(mc)_b$	MJ/K	5.5	5.5
Building Heat Load	Q_{out}	MJ	440	440
Equipartition Factor	Ξ	–	0.34	0.98
Work Input	W_{in}	MJ	106	83.1
Second Law Efficiency	η	–	60.6 %	77.3%
Entropy Generation in the Brick	$S_{\text{gen},b}$	kJ/K	148	66.6

(a) Dimensionless temperature profiles as a function of the dimensionless time, Fo $= \alpha t/l^2$

(b) Entropy generation rate profiles

Figure 4: Temperature and entropy generation profiles in the brick

3.3 Equipartition in water treatment systems
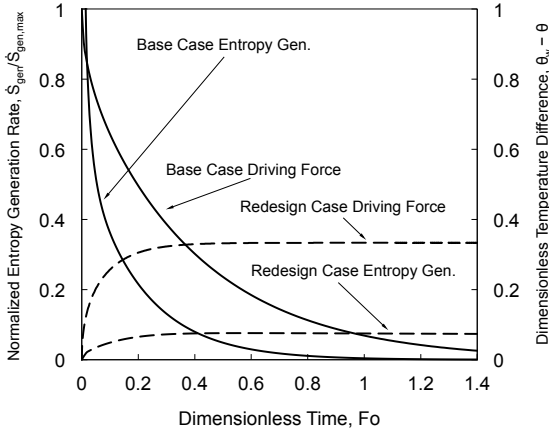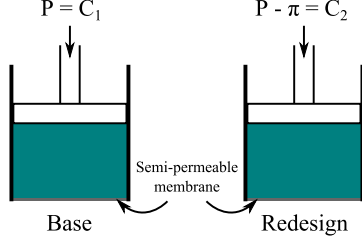
3.3.1 Reverse osmosis

Reverse osmosis systems account for the majority of the world's desalination capacity [21]. Reverse osmosis desalination (or more accurately, dewatering) involves the application of hydraulic pressure to the feed solution on one side of a semi-permeable membrane. The membrane is permeable to water but impermeable to salt. The hydraulic pressure applied must be sufficient to overcome the osmotic pressure of the feed, a measure of the tendency for water to naturally flow from lower salinity to higher salinity streams.

Consider a simple piston-cylinder model of a reverse osmosis system, as shown in Fig. 5. The piston pushes saline water through a semi-permeable membrane at the bottom of the cylinder in a predescribed, transient manner. Two simple batch processes of desalination are considered: in the base case (I), constant hydraulic pressure is applied to the feed; in the redesigned case (II), hydraulic pressure is increased throughout the process to maintain a constant difference between hydraulic and osmotic pressure. In the both the base case and the redesign, the membrane permeability and the total permeate produced are maintained constant (and consequently the average driving force is also constant, Eq. (17)). All resistance is confined to the membrane.

The force and flux variables of interest in this example are pure water flux and driving a pressure difference. Water flux through the membrane is modelled as being proportional to the difference in hydraulic pressure and osmotic pressure of the feed; $\bar{f}$ is a time-averaged driving force. In terms of the generalized variables, we have

$$j = A_m(p_f - \pi_f) \qquad (15)$$

$$f = -\nabla\left(\frac{\mu_w}{T}\right) = -(\bar{v}_w/T)\nabla(p - \pi) = \frac{\bar{v}_w}{Tl}(p_f - \pi_f) \qquad (16)$$

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Figure 5: Batch reverse osmosis processes

$$\bar{f} = \frac{1}{\tau} \int_0^\tau \frac{\bar{v}_w}{Tl} \left[p_f(t) - \pi_f(t) \right] dt \qquad (17)$$

where A_m is the membrane permeability coefficient, μ_w is the chemical potential of pure water, $\bar{v}_w$ is the partial molar volume of pure water, l is the membrane thickness, p_f is the applied pressure (gauge), and π_f is the osmotic pressure. Because the system is isothermal, the affinity f varies linearly with the phenomenological driving force $(p_f - \pi_f)$.

Treating the membrane as perfectly impermeable to salt, the mass of salt contained within the brine stream is conserved, so

$$y_f m_f = y_b m_b \qquad (18)$$

where y is salinity expressed as a mass fraction, and m is the mass of the feed, f, and the brine, b. The work required per unit volume of product (fresh) water, p, is thus

$$w = \frac{1}{m_p|_\tau} \int_0^\tau p_f A_m (p_f - \pi_f) A \, dt \qquad (19)$$

where A is the area of the membrane. Equations (15), (18), and (19) are calculated numerically. The equipartition factor is

$$\Xi = \frac{\left[\int_0^\tau (p_f - \pi_f) \, dt \right]^2}{\tau \int_0^\tau (p_f - \pi_f)^2 \, dt} \qquad (20)$$

Reversible work done, required in the calculation of the second law efficiency, is computed considering the change in Gibbs free energy of solutions from their initial to final states, as outlined by Mistry et al. [5].

Figures 6 illustrates the evolution of the hydraulic and osmotic pressures as a function of time in the base and the redesigned cases. The reduction in variance of the driving force (hydraulic minus osmotic pressure) in the redesigned case is immediately apparent. Table 3 summarizes the input parameters and results obtained. The equipartition factor in the base case is less than one, indicating that through redesign
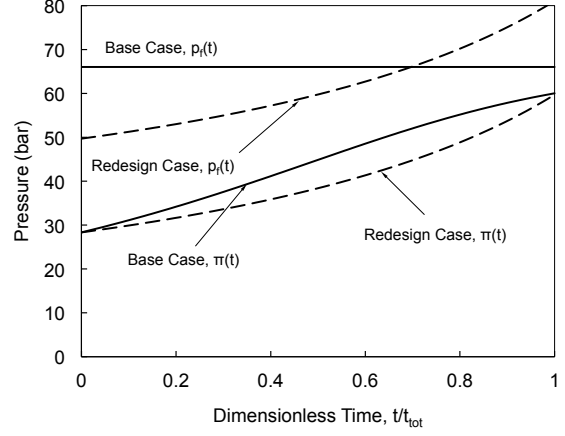

Figure 6: Hydraulic and osmotic pressures as a function of time

entropy generation can be reduced without compromising system productivity. The redesigned process has an equipartition factor of almost one, indicating the optimality of the process for fixed productivity. The small improvement in efficiency of dewatering, from 61.1% to 65.4% is in line with the predictions of Eq (8). The reverse osmosis system already operates at reasonable efficiency *and* its equipartition is close to one, so only a small improvement in efficiency is possible. (From the perspective of operating cost, this improvement in efficiency is nevertheless commercially important.)

In industry, more equipartitioned reverse osmosis systems have been achieved either through the staging of pressures—placing a booster pump between two membrane stages—or, more recently, by running the process in semi-batch mode [22]—somewhat like the process illustrated in Fig. 6. That the improvement in efficiency, obtained solely via the reduction of variance, is small, demonstrates that the direct benefit of equipartition is only a small factor motivating such redesigns. However, equipartition has the spillover benefit of allowing a reduction of the mean driving force for transport—allowing efficiency to be traded off against system size, where in previous reverse osmosis systems the driving force could only be reduced to a point where the hydraulic and osmotic pressures are equal at the end of the process (Fig. 6). Thus, in the case of reverse osmosis, the benefits of a reduction in variance are far weaker than the benefits of a reduction in mean driving force, as quantitatively asserted by the high equipartition factor.

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Table 3: Reverse osmosis base and redesign case results

Variable	Symbol	Units	Base Case	Redesign Case
Feed Salinity	y_f	g/kg	35	35
Brine Salinity	y_b	g/kg	70	70
Recovery Ratio	$\dot{m}_p/\dot{m}_f$	–	50%	50%
Permeate Flux	$\dot{m}_p''$	kg/m^{2}h	8.6	8.6
Mean Phenomenological Driving Force	$\overline{p_f - \pi_f}$	bar	21.6	21.6
Membrane Permeability	A_m	kg/m^{2}h bar	0.4	0.4
Equipartition Factor	Ξ	–	0.83	1
Second Law Efficiency	η	–	61.1%	65.4%
Energy Consumption (per unit volume product)	w	kWh/m^3	1.83	1.71
Entropy Generation (per unit volume product)	$s_{\text{gen,RO}}$	kJ/K-m^3	8.6	7.1

3.3.2 Humidification-dehumidification

The general concepts behind equipartition have also been applied to heat and mass exchangers used in a thermally-driven desalination system, the humidification-dehumidification (HDH) system [23]. In HDH desalination, a heated saline feed is brought into direct contact with dry air in a counterflow humidifier; pure water evaporates and moistens the air stream. This moist air stream is then sent to a dehumidifier, where it is cooled by the incoming feed and the pure water vapor condensed to produce the fresh product water. A heater provides the heat input at the top of the cycle.

As is the case with most thermal desalination systems, effective recovery of the heat given off during condensation to provide part of the heat for further evaporation is the crux of maximizing the system's energy efficiency. Several works [11, 24–27] have explored ideas to equalize the effective capacity rates of the humidifier and dehumidifier so as to optimize heat recovery between the two components, including extracting a portion of the flow of the air or the water stream from one component and injecting it into the other. The particular difficulty in applying the theory of equipartition to an HDH system results from the thermodynamics of a saturated air-water mixture: temperature and humidity are not independent and are nonlinearly related. Thus, in a standard, counterflow heat and mass exchanger, it is impossible to achieve a uniform distribution of both heat and mass transfer driving forces [11]. If the humidifier or dehumidifier is operated in a region where entropy generation from either heat or mass transfer is dominant, however, designing for a uniform distribution of the driving force associated with the dominant source of entropy production can provide a good approximation to the true minimum.

In [11], for example, a simple tube-in-tube dehumidifier is analyzed under conditions representative of a typical HDH system. When the mass flow rate ratio MR, of liquid to air, is adjusted to achieve a more uniform distribution of mass transfer driving force, an approximate minimum in entropy production is found, while still achieving the same overall heat and mass transfer rates over the same component size. Although it is impossible to perfectly equipartition the dehumidifier without the ability to change the mass flow rate ratio along the length of the component, an approximate value of Ξ can be calculated using Eq. (1) or Eq. (5). Using Eq. (1), the numerator is approximated as the entropy generation of the nearly equipartitioned case (MR $\approx$ 1 to 3, depending on the temperature range); using Eq. (5), f is the mass transfer driving force, as mass transfer is the dominant source of entropy generation. The equipartition factor for the dehumidifier increases from about 0.5–0.6 at very high mass flow rate ratios (MR = 100) to unity or near unity at the optimal mass flow rate ratio (MR $\approx$ 1 to 3).

Several other works on HDH systems [24–27] have successfully applied the central idea behind equipartition—designing for a more uniform distribution of driving forces—but have compared systems with different boundary conditions such that the computation of equipartition factors for cases in these works may not provide a meaningful comparison (i.e., the systems may not have fixed average driving forces or fixed sizes, and thus may achieve performance gains from a combination of effects, only one of which is equipartition). Nevertheless, HDH is a significant example of real-world performance gains achieved [25] in part by application of the ideas behind equipartition.

4 Conclusions

For systems characterized by linear force-flux laws of transport, irreversibility is caused both by a finite mean driving force for transport but also by a spatial or temporal variance in the driving force. In this work, the equipartition factor is introduced to quantify the extent to which driving force variance is directly responsible for irreversibility. Defined as the ratio of entropy generation in an equivalent equipartitioned (zero variance) system to entropy generation in the actual system, the equipartition factor tends towards zero as the variance tends to infinity and equals unity when the system is equipartitioned. Expressing the second law efficiency in terms of the equipartition factor illustrates how systems with low equipartition factors and low second law efficiencies stand to gain most from an equipartitioned redesign of the system. In the case of lumped capacitance systems with constant resistance and capacitance, an analytical expression is available for the equipartition factor, and thus efficiency, in terms of the dimensionless charging time for the process. Processes with long dimensionless charging times exhibit the lowest equipartition factors. Thus, we further conclude that charging processes with low second law efficiency and long dimensionless charging times provide the best opportunity for achieving improvement through redesign.

The equipartition factor is calculated for two simple models of practical systems to assess the improvement achievable by redesigning for reduced driving force variance while maintaining equal productivity and system extent. A significant improvement is achieved in the thermal storage heater, owing to its low equipartition factor. In contrast, the reverse osmosis system achieves only a small improvement through the redesign, owing to the relatively high equipartition factor of the base case.

The equipartition factor provides a simple, quantitative measure distinguishing the causes of irreversibility within diverse systems. Ultimately, it is intended to provide insight into when a redesign for reduced driving force variance can benefit the efficiency of real systems.

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