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# Equipartition of Forces: A New Principle for Process Design and Optimization

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This paper presents the general proof for a new design principle: the principle of equipartition of forces. The principle has been derived for coupled transports of heat, mass, and charge using irreversible thermodynamics combined with Cauchy–Lagrange optimization procedures. The principle says that the best trade-off between energy dissipation and transfer area is achieved when the thermodynamic driving forces are uniformly distributed over the transfer area. A new strategy for the design of energy optimal transfer processes follows. Practical problems in applications of the principle are discussed.

## Introduction

Process design is often described as a series of alternating synthesis and analysis steps, where synthesis means creation of a set of process alternatives, and analysis means evaluation of the set. Over the past few years, the increase in computational speed offered by standard computing hardware has been enormous, and our ability to numerically analyze process alternatives has increased accordingly. Thus, the synthesis step, the creation of a promising set of process alternatives in a systematic manner, is more and more clearly becoming the bottleneck in process design.

Several approaches to solving various parts of the synthesis problem exist, including combinatorial optimization of superstructures (Grossmann and Kravanja, 1995), structured procedures using heuristics and design guidelines (Douglas, 1988), and targeting procedures based on thermodynamic insights (Linnhoff and Hindmarch, 1983; El-Halwagi and Manousiouthakis, 1989; Westerberg, 1985). The present approach uses the laws of irreversible thermodynamics. More precisely, it is a method aimed at reducing the entropy production of a total system, given a specified flux (transfer duty) and a specified contact or transfer area in the apparatus.

Already in 1948, Tolman and Fine concluded that an increase in the internal entropy of a system reduced the maximum available work. This followed the work of Onsager (1931a,b) and Prigogine (1947) on minimum entropy production rates in stationary states. Since then, many authors have drawn attention to the need for reduction of the entropy production rates (King, 1971; Fonyo, 1974; Kjelstrup Ratkje and de Swaan Arons, 1995). The principle of minimum entropy generation or entropy production rate [as described by Bejan (1982)] can be viewed as a more engineering-oriented version of the work of Tolman and Fine. For precise formulations of the entropy production rate, the reader is referred to de Groot and Mazur (1962) and Førland et al. (1988).

For a process with constant transport coefficients, Tondeur and Kvaalen (1987) show that the entropy production rate of an energy optimal process should have a uniform distribution along the space and/or time variables of the process. We have shown for the distillation of a binary mixture (Kjelstrup Ratkje et al.,

1995; Sauar et al., 1995) that equipartition of driving forces rather than equipartition of entropy production rates should be applied to obtain a specified separation (i.e., mass fluxes). On this background, Sauar et al. (1995) suggested the use of isoforce operating lines in McCabe–Thiele diagrams [see King (1971)] as a tool for the design of distillation columns. This proposal has been supported by recent simulations (Rivero, 1995) of a diabatic stripping column. After minimizing the exergy (or energy) losses in a binary separation, Rivero concluded that a uniform distribution of the losses did not give minimum exergy loss. Minimum losses were rather obtained with an operating line more parallel to the equilibrium line in the McCabe–Thiele diagram, which means that the driving forces along the column were close to being equal.

We shall see in this work that it is possible to show on general grounds that equipartition of forces is indeed the situation that gives minimum exergy loss. We therefore propose a new design principle for optimization, the principle of equipartition of forces. The principle puts the knowledge referred to above (Tondeur and Kvaalen, 1987; Bejan, 1982; Kjelstrup Ratkje et al., 1995; Sauar et al., 1995; Rivero et al., 1995) and elsewhere [Szwast and Sieniutycz (1995) and Baclic and Seculic as reviewed by Sieniutycz and Shiner (1994)] into a systematic framework and has been derived from irreversible thermodynamics and Cauchy–Lagrange optimization procedures. The theory of irreversible thermodynamics is built on the assumption of local equilibrium everywhere in the system, an assumption of strong validity (Hafskjold and Kjelstrup Ratkje, 1995). The principle does not assume that the phenomenological coefficients are constant over the space variables in the process. Since most processes do have such varying phenomenological coefficients, we believe that the new principle can be successfully applied in process design. For constant phenomenological coefficients, our results reduce to those of Tondeur and Kvaalen (1987). Before we give the general proof, however, we shall discuss some limit cases to illustrate the physical mechanisms involved.

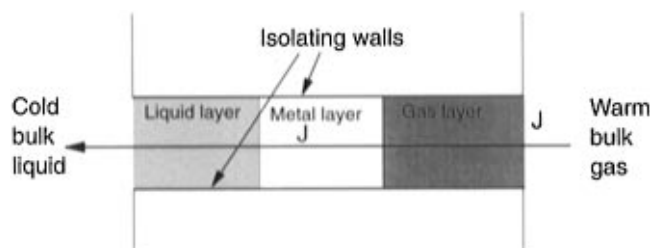
## Principle of Equipartition of Forces

**Introductory Comments.** Consider first the transport of heat, mass, or charge across a series of different materials (see Figure 1). The flux,  $J$ , is driven by one force,  $X$ , in the example, and for simplicity reasons we consider a one-dimensional problem only. The  $x$ -com-

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**Figure 1.** Flux through different phases defines a path. The cross-sectional area may vary along the path.

ponents of the vector flux and force are then of interest. The streamline of the flux is our path of transport, and the real paths we are dealing with refer to this definition. An example of such a path is the path going through a gas film, a metal layer, and another liquid film, as is typical in many heat exchangers (see Figure 1). The relation between the flux and the force everywhere in the system is given in irreversible thermodynamics (Onsager, 1931a,b) by

$$J = LX \quad (1)$$

Here  $L$  is a phenomenological coefficient that depends on the intensive thermodynamic variables of the system (the pressure, temperature, etc.) but not on the force. Equation 1 can be regarded as a representation of Fick's law for diffusion, Fourier's law for heat conduction, or Ohm's law for electric conduction. The coefficients  $L$  are then conductance coefficients. The entropy production rate per unit volume of the system is

$$\theta = JX = LX^2 \quad (2)$$

The entropy production rate is always positive according to the second law of thermodynamics. This means that  $L$  is positive.

The value of  $L$  is different in the different phases of Figure 1. We see from eq 1 that constant  $J$  can be maintained along the path by decreasing  $X$  when  $L$  increases. This leads to a decrease in the local entropy production rate,  $\theta$ , in eq 2, since the product  $LX$  remains constant while  $X$  decreases. The relationship between the relative changes can be found by differentiation of eq 1 keeping  $J$  constant:

$$(dX)_J = -\frac{J}{L^2} dL \quad (3)$$

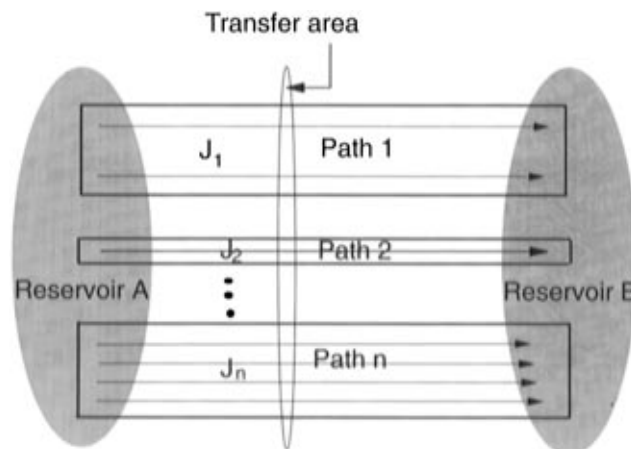
For constant  $J$ , the total entropy production of the system,  $\Theta$ , is obtained by integrating eq 2 over the volume of the process,  $V$ , and over time:

$$\Theta = \int^V \int^t \theta dV dt = J^2 \int^V \int^t \frac{1}{L} dV dt \quad (4)$$

A lower value of  $\Theta$  for constant  $J$  is obtained for increasing values of  $L$  along the path. Equation 3 shows that the greatest relative reduction of  $X$ , and hence  $\theta$ , can be achieved in those parts of the transport path where  $L$  is small, i.e., in the rate-limiting parts.

When both  $L$  and  $J$  are constant along the path however,  $X$ ,  $\theta$ , and  $\Theta$  are also constants, and there is no optimization problem. The conduction of electricity in a metal wire of constant diameter is an example of this situation. The electric field is constant for constant conductivity and electric current.

When  $L$  and  $J$  are not constant in space, and in particular when more fluxes and forces are present, an



**Figure 2.** Parallel transport paths from one reservoir (A) to another, (B). The two reservoirs may for instance be two process streams. The cross section of the paths constitutes the transfer area.

optimum solution for the entropy production rate exists, different from that of constant  $\theta$  and  $\Theta$ . We shall find this solution for two cases of constant total flux. In the first case, the total flux is composed of several contributions like eq 1. We call these contributions simple contributions, as the fluxes do not interact. In the next and more general case, the total flux is composed of coupled flux equations. In this case, eq 1 is replaced by equations of the general form

$$J_i = \sum_j L_{ij} X_j \quad (5)$$

Each single flux,  $J_i$ , is then coupled to all forces,  $X_j$ . The coefficients  $L_{ij}$  are coupling coefficients, with  $L_{ii}$  similar to the coefficients of eq 1.

**One Total Flux with Simple Contributions.** Consider next the system illustrated in Figure 2. By a transfer area,  $A$ , we mean the cross-sectional area given by a collection of non-intersecting paths. Each path represent a flux or a streamline. The non-intersecting streamlines may be located in different places in an apparatus. Separate trays in a distillation column are therefore examples of such paths. Assume that we want to achieve a specified total flux for a given transfer area. The flux of path number  $n$  is given by

$$J_n = L_n X_n \quad (6)$$

The flux in eq 6 may, for instance, be a mass flux or a heat flux like in eq 1. The entropy production rate for path number  $n$  is

$$\theta_n = J_n X_n = L_n X_n^2 \quad (7)$$

The total flux  $J$  has contributions from all single  $J_n$ . Since the paths are separate, we have

$$J = \sum_n J_n \quad (8)$$

and the total entropy production rate:

$$\Theta = \sum_n \theta_n \quad (9)$$

where the summation is carried out over all  $n$  and accounts for all paths in the process under consideration. The optimization problem is now

$$\text{minimize } \Theta = \sum_n \theta_n = \sum_n L_n X_n^2$$

$$\text{with } \sum_n J_n = \sum_n L_n X_n = \text{constant} \quad (10)$$

We require that the sum (eq 8) of the simple contributions, but not the single contributions themselves (eq 6) is constant. The Cauchy–Lagrange method of constant multipliers can be applied. We have only one  $\lambda$  and obtain

$$\frac{\partial \sum_m \theta_m}{\partial X_n} + \lambda \frac{\partial}{\partial X_n} \sum_m J_m = 2L_n X_n + \lambda L_n = 0 \quad (11)$$

so that

$$X_n = -\frac{1}{2}\lambda \quad (12)$$

Substitution of the constant total current determines the multiplier and results in

$$\lambda = \frac{-2J}{\sum_n L_n} \quad (13)$$

As a consequence

$$J_n = \frac{L_n J}{\sum_n L_n} \quad (14)$$

and

$$X_n = \frac{J}{\sum_n L_n} \quad (15)$$

Equation 15 implies that for a given total flux and a given transfer area, minimum entropy production is obtained when the driving force is equal for all  $n$  paths and given by eq 15. One can choose  $J$  and calculate the optimum corresponding forces for the process from eq 15. According to linear duality theory (Edgar and Himmelblau, 1989), the result of the optimization will be the same if we maximize the total flux for a given constant entropy production rate.

The number of paths  $n$  (which constitute the transfer area) and the force to be applied in the real system is a matter of a global trade-off between energy and area costs in the system. A well-known illustration of the result (eq 15) is the optimum temperature profile for heat exchangers, which shows constant temperature gradients over all heat exchange areas [Bacic and Seculic as reviewed by Sieniutycz and Shiner (1994)]. Also in drying processes (Szwast and Sieniutycz, 1995) and distillation columns (Rivero et al., 1995; Sauar et al., 1995), it was found that the optimum distribution of driving forces seemed to be the uniform ones for the  $n$  paths in the process. A condition for the validity of the result is that the  $L_n$ 's are independent of the distribution of forces. This may not always be fulfilled.

**Average Forces and Coefficients.** In practice, the phenomenological coefficient and the driving force are unknown in all parts of the apparatus. In order to

circumvent this problem, consider a real physical path of length  $l$ . Equation 6 applies to any point on the path. The flux  $J_n$  is constant, but the conductivity  $L_n$  varies in space along the path. The average resistance of the path,  $R_n$ , is the integral of the inverse of  $L_n$ :

$$R_n = \int_0^l \frac{1}{L_n} ds \quad (16)$$

The result obtained for  $R_n$  can then be used to find the average conductivity,  $L_n$ . The average force is then the force which obeys

$$X_n = R_n J_n \quad (17)$$

With this average procedure, the total entropy production rate in the stationary state will be the same whether the average forces and coefficients are used directly in the description or whether the local forces and coefficients are used, and the integration is performed over  $Ads$ . In a system with two fluxes, we have for the first force:

$$X_{1,n} = R_{11,n} J_{1,n} + R_{12,n} J_{2,n} \quad (18)$$

and a similar expression for the other (Kirkwood, 1954). This means that the optimization problem can be formulated also for average forces and coefficients in the stationary state. We shall continue the analysis with the local formulation, but the reader may keep in mind that in the stationary state the results are equally valid for average forces and coefficients.

**One Total Flux with Contributions from Coupled Fluxes.** Irreversible thermodynamics introduces interaction or coupling between fluxes in a system (de Groot and Mazur, 1962; Førland et al., 1988). When two forces give rise to two fluxes in path number  $n$ , we have the following flux equations from eq 5:

$$J_{1,n} = L_{11,n} X_{1,n} + L_{12,n} X_{2,n} \quad (19)$$

$$J_{2,n} = L_{21,n} X_{1,n} + L_{22,n} X_{2,n} \quad (20)$$

The matrix of phenomenological coefficients was proven symmetric by Onsager (1931a,b),  $L_{12,n} = L_{21,n}$ . The optimization problem for two coupled fluxes, which occur simultaneously along several paths is to minimize the total entropy production:

$$\Theta = \sum_n \theta_n = \sum_n (L_{11,n} X_{1,n}^2 + 2L_{12,n} X_{1,n} X_{2,n} + L_{22,n} X_{2,n}^2) \quad (21)$$

for constant total fluxes:

$$J_1 = \sum_n J_{1,n} = \sum_n (L_{11,n} X_{1,n} + L_{12,n} X_{2,n}) \quad (22)$$

$$J_2 = \sum_n J_{2,n} = \sum_n (L_{21,n} X_{1,n} + L_{22,n} X_{2,n}) \quad (23)$$

We use the Cauchy–Lagrange method for all paths  $n$

$$-\frac{\partial}{\partial X_{1,n}} \sum_m \theta_m = \lambda_1 \frac{\partial}{\partial X_{1,n}} \sum_m J_{1,m} + \lambda_2 \frac{\partial}{\partial X_{1,n}} \sum_m J_{2,m} \quad (24)$$

and

$$-\frac{\partial}{\partial X_{2,n}} \sum_m \theta_m = \lambda_1 \frac{\partial}{\partial X_{2,n}} \sum_m J_{1,m} + \lambda_2 \frac{\partial}{\partial X_{2,n}} \sum_m J_{2,m} \quad (25)$$

where  $\lambda_1$  and  $\lambda_2$  are Lagrange multipliers. We know from eqs 19 and 20 that

$$\frac{\partial}{\partial X_{1,n}} \sum_m J_{1,m} = L_{11,n} \quad (26)$$

$$\frac{\partial}{\partial X_{1,n}} \sum_m J_{2,m} = L_{21,n} \quad (27)$$

$$\frac{\partial}{\partial X_{2,n}} \sum_m J_{1,m} = L_{12,n} \quad (28)$$

$$\frac{\partial}{\partial X_{2,n}} \sum_m J_{2,m} = L_{22,n} \quad (29)$$

From eq 21, we have using also eqs 19 and 20:

$$\frac{\partial}{\partial X_{1,n}} \sum_m \theta_m = 2J_{1,n} \quad (30)$$

$$\frac{\partial}{\partial X_{2,n}} \sum_m \theta_m = 2J_{2,n} \quad (31)$$

By substituting the terms of eqs 24 and 25 with the right side of eqs 26–31, we have

$$-2J_{1,n} = \lambda_1 L_{11,n} + \lambda_2 L_{12,n} \quad (32)$$

and

$$-2J_{2,n} = \lambda_1 L_{21,n} + \lambda_2 L_{22,n} \quad (33)$$

for any path. Comparing the last two equations with eqs 19 and 20 gives the result:

$$X_{1,n} = -\frac{\lambda_1}{2} \quad X_{2,n} = -\frac{\lambda_2}{2} \quad (34)$$

Explicit expressions for  $\lambda_1$  and  $\lambda_2$  in terms of  $J_1$  and  $J_2$  can be found by substituting eqs 32 and 33 into eqs 19 and 20. Increasing the number of forces and fluxes will simply add more terms to eqs 32 and 33 but will give the same result (eq 34). Such generalizations are thus straight forward and will not be written out in detail.

It is also interesting to note that we have not given criteria for the nature of the fluxes in eqs 19 and 20. Since coupling does not take place between tensors of different order, this means that the proof for equipartition of forces is valid separately for scalar fluxes and forces and for vectorial fluxes and forces. Chemical reactions are scalar phenomena, which can couple to the normal component of vectorial fluxes at interfaces (Bedeaux, 1986). This property may allow for a treatment of chemical reactions within the present scheme.

We thus conclude that minimum entropy production is obtained for a given set of fluxes and a given transfer area, when the independent forces are equipartitioned over the different paths. This is a general result. The strengths and weaknesses of the result are pointed out in the Discussion section. Before we start the discussion however, we shall give two particularly interesting subcases in more detail.

**Only One Coupled Flux Is of Economic Importance.** In many industrial processes, the fluxes in equations like 19 and 20 are not equally interesting from an economical point of view. In separations, for instance, usually only one or two mass fluxes are of interest. An interesting question to ask therefore is "Does a combination of two forces give a lower entropy production than one force alone for the same separation duty?" For instance, can mass transport be better promoted by a combination of a concentration gradient and a thermal gradient or by a concentration gradient alone? This question is relevant for an evaluation of different separation processes (Humphrey and Siebert, 1992).

By taking away the constraint eq 23, we have a mathematical formulation of this problem. In eqs 24 and 25, the last terms disappear and eqs 32 and 33 reduce to

$$-2J_{1,n} = \lambda_1 L_{11,n} \quad (35)$$

and

$$-2J_{2,n} = \lambda_1 L_{21,n} \quad (36)$$

for any path. Elimination of  $\lambda_1$  and using eqs. 19 and 20 gives

$$\frac{L_{22,n}}{L_{21,n}} X_{2,n} = \frac{L_{12,n}}{L_{11,n}} X_{2,n} \quad (37)$$

with the solution:

$$X_{2,n} = 0 \quad (38)$$

Hence, eq 37 shows that only one force,  $X_{1,n}$ , should be applied to create the flux  $J_{1,n}$ . In the special case that

$$L_{11,n} L_{22,n} = L_{12,n}^2 \quad (39)$$

eqs 19 and 20 give fluxes that are linearly dependent [ $J_{1,n} = C J_{2,n}$  or strict coupling; Førland et al. (1994)]. In that case  $J_2 = J_1/C$  is also constant, and one has again the case with two constant total fluxes discussed above. The forces  $X_{2,n}$  should be equal but can be different from zero. Such strict coupling can occur in ion exchange membrane processes.

We conclude this section as follows: The principle of equipartition of forces is in the outset valid for optimization problems with the same number of independent fluxes and forces. When the number of independent forces exceeds the number of fluxes of interest, the forces conjugate to the wanted fluxes should be equipartitioned, and the others should be minimized.

## Discussion

**Characteristics of the Principle of Equipartition of Forces.** The principle of equipartition of forces is a general principle. In its simplest form, it can be applied to engineering problems without calculating or measuring either the entropy production rate or the phenomenological coefficients. Equipartition of forces can be done without such knowledge. Compared to most former applications of irreversible thermodynamics, this is a major advantage.

Equipartition of forces gives minimum entropy production rates only when independent forces are chosen to describe the transports. The thermodynamic forces

of the system are always linked by Gibbs–Duhem's equation, which should be used to eliminate one of the dependent forces. The practical situation is decisive for which variable one chooses to eliminate.

The assumption of local equilibrium does not restrict application of the principle in normal engineering contexts (Hafskjold and Kjelstrup Ratkje, 1995). The extra condition given by local equilibrium may turn out to be useful in reacting systems (Kjelstrup Ratkje and de Swaan Arons, 1995). Reaction rates are scalar rates and do not couple to vectorial processes of the bulk. At a phase boundary like a catalyst surface however, chemical reactions may couple to transport (Bedeaux, 1986). Independent of the question of coupling or not, chemical reactions will always affect the local chemical potentials of the system. If local chemical equilibrium can be assumed in the bulk or at the surface, further reductions of the number of variables can be done. Slow chemical reactions, however, may not allow for the elimination of variables and may require special treatment. It will be important in the future to find out how the principle of equipartition of forces can be extended for chemical reactions. Viscous flow is another dissipative process that should be further studied and included into the analysis.

The mathematical derivation of the principle uses a given set of parallel paths (a given transfer area) as a starting point. In its present form, the principle of equipartition of forces cannot be used to analyze process alternatives with different transfer areas. We conclude that the principle applies to coupled transports of heat, mass, and charge in bulk phases (vectorial transport) and for the same transports across interfaces (scalar transport).

**Implementation of the Principle of Equipartition of Forces.** The theoretical result was clear from the above analysis: In an energy optimal system, the force distribution is uniform over the transfer area. In practice, this situation can be difficult to achieve. It is then useful to realize that the importance of having equal forces is not the same for all paths. The effect of equalizing the driving forces is relatively larger for the entropy production rate and flux in paths with high or potentially high conductances. Such paths are therefore the primary target for equipartition of forces. Here the largest improvements of the efficiency may be obtained by a minimum number of apparatus modifications.

**Numerical and Empirical Support for Equipartition of Forces.** A formal mathematical proof has been given for a new design principle, the principle of equipartition of forces. Fortunately, there is already numerical and empirical evidence in the literature that supports the theoretical result. As has already been mentioned, the optimum temperature profile in heat exchangers derived by Baclic and Beculic [as reviewed by Sieniutycz and Shiner (1994)] conforms with eq 15.

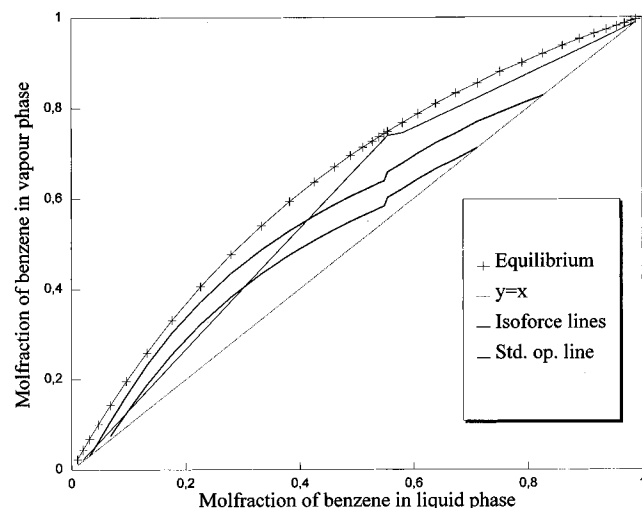
Szwast and Sieniutycz (1995) have provided examples from heating (cooling) and drying fluidized processes. They made mathematical models of multistage cross-current processes, assuming equilibrium on each stage and applying a discrete optimization algorithm to find the process designs with minimum exergy losses. Their results showed that the processes characterized by the same driving force (here temperature difference) for every stage of cascade gave the lowest energy loss, also in agreement with eq 15.

For a stripping column separating ethanol and water, Rivero (1995) used exergy analysis of different separa-

tion models to obtain a similar conclusion. Rivero varied the driving forces by replacing the reboiler and condenser in classical distillation, normally located at the bottom and at the top of the column, with heat exchangers integrated inside the column. This is commonly known as diabatic distillation and has also been described elsewhere (King, 1971; Fonyo, 1974; Kaiser and Gourelia, 1985; Rivero et al., 1991). Evaluating different optimization principles, Rivero (1995) compared three cases: uniform distribution of heat, uniform distribution of exergy losses, and a numerically found case representing minimum exergy losses. Although he made no explicit formulation of the driving forces in the column, Rivero found that "the equipartition of exergy losses" in a diabatic stripping column was not optimal. His optimal distribution depended mainly on the shape of the operating curve and on its departure from the equilibrium curve. By plotting the results in a McCabe–Thiele diagram, Rivero concluded that "for a given number of trays, there is a minimum distance between the operating and the equilibrium curves, which corresponds to the exergy optimum". The results of Rivero and co-workers also support the result in eq 15. Our first simple application of the principle was presented by Kjelstrup Ratkje et al. (1995). By deriving and using the principle of equipartition of forces for this special case, we managed to reduce the entropy production rate in a column separating benzene and toluene by 7%, with minimum changes in the apparatus.

The principle of equipartition of forces was derived for paths that do not intersect in space. Paths may also be distributed in time. The optimization problem is then to distribute the driving forces over time in order to minimize the total entropy production for a specified transfer duty. Because the mathematical formulation of the optimization problem remains unchanged, the conclusions derived above are still valid, meaning that the optimum operation of a continuous process is a stationary state operation with time-independent driving forces. Prigogine (1947) showed that the stationary state was a state of minimum entropy production for the special case of fully linearized transport equations considered also by us. Our result adds to this stationary state condition: It specifies which of several stationary states is the best for obtaining a total flux. Exceptions to the result may be found when the conductivities of the transport paths vary with time or when convection occurs. We conclude that there is ample material in the literature that can be taken as special cases of the principle of equipartition of forces and that the general nature of the principle was not realized until now.

**Equipartition of Entropy Production.** Our derivation of the principle of equipartition of forces was inspired by the work of Tondeur and Kvaalen (1987). According to these authors, the total entropy produced in a contacting or separation device involving a given transfer area and achieving a specified duty is minimum when the local rate of entropy production is uniformly distributed (equipartitioned) along the space and/or time variables. The result was obtained by assuming the phenomenological coefficients,  $L_{ij}$ , to be independent of  $n$  and minimizing the entropy production rate subject to constant fluxes. From eq 18, we have that constant fluxes and constant coefficients  $R_{ij}$  give constant forces automatically. Hence, when the  $L_{ij,n}$ 's are the same, a uniform distribution of forces and entropy production along the transport path is not only an optimum solution, it is the only possible solution. In the general



**Figure 3.** Illustration of the equipartition of forces principle. Isoforce operating lines in a McCabe–Thiele diagram for the separation of benzene–toluene (Saur et al., 1995).

situation, it is therefore not correct to seek uniform distribution of the entropy production rate.

**Versatility of the Design Method.** In the derivation of the principle, we started with the simplest example, which can be used to describe binary distillation. It is interesting that, even for this well-known example, the principle has proven useful already at first try. Saur et al. (1995) used the principle of equipartition of forces to specify, calculate, and draw isoforce operating lines in a McCabe–Thiele diagram (see Figure 3). According to the principle of equipartition of forces, these isoforce operating lines represent various optimum trade-offs between energy costs (operation) and area costs (investments). How to adjust these isoforce lines to boundary conditions like product specifications and maximum reflux ratios however remains to be done.

The largest potential for applications of the new principle will most probably be in predicting new designs or operation modes for new and/or more advanced processes. The equipartition of forces principle is for instance easily applicable to coupled processes with two or more local degrees of freedom. These can be processes with coupling between mass and heat transfer (as in distillation, reactions, drying processes, etc.) with coupling between heat, mass, and charge transport (like in electrolysis and fuel cells) or with coupling between mass and charge transport (batteries, fuel cells).

One potential for future application may be reactive distillation. In reactive distillation, the chemical reaction and separation of products take place simultaneously. The degrees of freedom will increase compared to ordinary distillation, and more forces can be optimized. Since such systems are not yet fully understood, there should be a potential for improving both the energy use and the investment costs in them.

The fact that a tedious and often impossible calculation of local entropy production rates can be omitted breaks the ground for a more widespread use of the principle of equipartition of forces. The process designer can concentrate on improving kinetics and equipartition forces over the different transport paths (e.g., the transfer area) in the prediction of new designs. Then, according to the new principle, an optimum trade-off between area and energy costs is approached. The evaluation of the suggested designs, however, must also be carried out by other techniques such as exergy

analysis, simulations, cost estimations, etc. The motivation for process improvements of course increases with the potential optimization profits and hence with the size of the process streams.

**Extended Optimization Strategy.** The principle of equipartition of forces can be used for the design of new process equipment but also for finding out whether the operation of existing equipment should be changed. In both cases, most process modifications will usually have effects on more than one variable. A first process improvement may lead to unwanted side effects that have to be compensated for afterwards. The order of process modifications is therefore important. It is probably difficult to do microscale optimization after macroscale optimization without having to return to macroscale optimization again. Hence, we suggest to start with microscale optimization.

We suggest to begin the optimization task by looking for paths with high conductivities. Find those parts of these transport paths where most of the resistance is located, and try to increase the conductivities in these regions. The conductivities vary with temperature, pressure, composition, etc. When the conductivities have been maximized, and in particular these well-conducting paths, the independent driving force(s) should be equipartitioned.

## Conclusions

A new principle has been derived for optimum production of a given set of fluxes with minimum dissipation of energy. The principle is called the equipartition of (thermodynamic driving) forces and applies to diffusion and heat and charge transfer. Empirical evidence for special cases of the theoretical result exists. The principle may prove valuable in process design because it is able to focus on the location for improvement, it gives easy-to-apply guidelines for complex process units, and covers three of the most important phenomena in process industry. Some future potentials of the design method have been pointed out.

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## List of Symbols

$A$  = transfer area  
 $C$  = constant  
 $j$  = local flux  
 $J_n$  = flux through transport path  $n$   
 $J_{i,n}$  = flux of  $i$  through transport path  $n$   
 $L_{ij}$  = phenomenological coefficient  
 $R_{ij}$  = generalized resistance  
 $s$  = path length  
 $T$  = temperature  
 $V$  = volume  
 $X$  = driving force  
 $\theta$  = entropy production rate per unit volume  
 $\Theta$  = total entropy production rate of a system  
 $\lambda, \lambda_1, \lambda_2$  = Lagrange multipliers

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