

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231368246>

# Minimum Entropy Production by Equipartition of Forces in Irreversible Thermodynamics

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · SEPTEMBER 2000

Impact Factor: 2.59 · DOI: 10.1021/ie0006920

---

CITATIONS

3

---

READS

18

3 AUTHORS, INCLUDING:



[Signe Kjelstrup](#)

Norwegian University of Science and Techno...

316 PUBLICATIONS 3,705 CITATIONS

[SEE PROFILE](#)



[Dick Bedeaux](#)

Norwegian University of Science and Techno...

305 PUBLICATIONS 5,477 CITATIONS

[SEE PROFILE](#)

# Minimum Entropy Production by Equipartition of Forces in Irreversible Thermodynamics

Signe Kjelstrup,<sup>\*,†</sup> Dick Bedeaux,<sup>†</sup> and Erik Sauar<sup>‡</sup>

Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan, and Solenergy AS, P.O. Box 301, N-1324 Lysaker, Norway

*Sir:* We are happy for the opportunity to explain the details of our principle of equipartition of forces. We understand that Haug-Warberg disagrees with our findings for the following reasons:

1. He states that the variational analysis of Schechter,<sup>1</sup> which gives minimum entropy production in a constrained system only if the transport coefficients are constant, is sufficient to disprove our result.

2. He constructs an example that he thinks is according to the premises for application of our principle and finds that equipartition of forces does not give minimum entropy production.

We argue below that Schechter's results are not at variance with ours; in fact, we agree with them. Schechter does not address our problem, however. Furthermore, we will show that the example chosen by Haug-Warberg does not meet criteria set by irreversible thermodynamics and, therefore, cannot be used as a counterexample to our principle of equipartition of forces.

We repeat first the essential parts of the proof for equipartition of forces to show that Schechter's problem is different from ours. The principle for equipartition of forces was originally found<sup>2</sup> using reasoning from economic theory. In cost–benefit analysis,<sup>3</sup> the typical problem is as follows: Given that we want to produce a given amount of product and have at our disposal several locations of production, where in the system should we produce in order to obtain the wanted product with the smallest costs? The principle of equipartition of forces was found as a solution to an analogous problem: Where do we want to transfer heat, mass, or charge (or other things) in a system with many *parallel* pathways, with a minimum in the total entropy production? The proof was presented on a discrete form in ref 4. We repeat it here on a continuous form to shed more light on the critical steps. For simplicity, we use only one type of force and flux, as does Haug-Warberg.

Consider heat transfer in the  $x$  direction across the area  $A$ . The rate of entropy production for heat transport along the paths ("streamlines") of length  $s(y,z)$  is

$$\frac{d\Sigma}{dt} = \int_A \int_0^1 \sigma(x,y,z) dx dy dz = \int_A \int_0^{s(y,z)} J_q(x,y,z) \frac{\partial}{\partial x} \left[ \frac{1}{T(x,y,z)} \right] dx dy dz \quad (1)$$

where we used  $\mathbf{J}_q(x,y,z) = (J_q(x,y,z), 0, 0)$ . In view of the assumed stationarity of the problem, we furthermore have  $J_q(x,y,z) = J_q(y,z)$ . We can, therefore, integrate over

$x$  to obtain

$$\frac{d\Sigma}{dt} = \int_A J_q(y,z) \left[ \frac{1}{T(s(y,z),y,z)} - \frac{1}{T(0,y,z)} \right] dy dz \equiv \int_A J_q(y,z) X(y,z) dy dz \quad (2)$$

The corresponding linear force–flux equation can be written as

$$J_q(y,z) = L(y,z) X(y,z) \quad (3)$$

or on the inverse form

$$X(y,z) = \frac{1}{L(y,z)} J_q(y,z) \equiv R(y,z) J_q(y,z) \quad (4)$$

In the context of standard nonequilibrium thermodynamics, the linear coefficient can be an arbitrary function of  $y$  and  $z$  and of the temperature  $T(0,y,z)$ . The linear coefficient may not depend on either the heat flux  $J_q(y,z)$  or the force  $X(y,z)$ , however. It follows from this condition that the linear coefficient may not depend on both  $T(0,y,z)$  and  $T(s(y,z),y,z)$ , because any such function can be written as a function of  $T(0,y,z)$  and  $X(y,z)$  and, as a consequence, depends on the force. We note here that, because of the fact that the heat flux is independent of  $x$ , the entropy production can be reduced to this simplified form, which is local in the  $y$  and  $z$  directions but which is not local in the  $x$  direction. These matters will be important in our analysis of Haug-Warberg's example below.

The duty of the heat exchanger is

$$J = \int_A J_q(y,z) dy dz \quad (5)$$

The smallest entropy production for a given duty is now given by<sup>5</sup>

$$\frac{\delta}{\delta J(z)} [\Sigma + \lambda J] = \frac{\delta}{\delta J(z)} \int_A [R(y',z) J_q^2(y',z) + \lambda J_q(y',z)] dy' dz' = 0 \quad (6)$$

where we have chosen a derivation which makes the analogy to economic theory more evident. When  $R$  is independent of  $J_q$ , the functional derivative gives

$$\frac{d}{dJ(y,z)} [R(y,z) J_q^2(y,z) + \lambda J_q(y,z)] = 2R(y,z) J(y,z) + \lambda = 0 \quad (7)$$

with the solution

$$R(z) J(z) = X(z) = -\frac{\lambda}{2} \quad (8)$$

This is the solution that we presented as the principle of equipartition of forces. (In retrospect, we should have

\* To whom correspondence should be addressed. Permanent address: Department of Chemistry, Norwegian University of Science and Technology, 7491 Trondheim, Norway.

<sup>†</sup> Kyoto University.

<sup>‡</sup> Solenergy AS.

chosen the word "theorem" rather than "principle".) The assumptions leading to this result have been clearly outlined above. We are now in a position to address the two points raised by Haug-Warberg.

Schechter<sup>1</sup> does not address the practical issue of where the system's production should take place to have the most energy-efficient total production. In particular, he does not consider the case sketched above, where the entropy production is first integrated over given parallel flux lines and then optimized with respect to moving flux from one flux line to another. Instead, he examines the set of partial differential equations to be solved for a system, given local flux equations, and seeks a variational formulation. The so-called *principle of minimum entropy production* was put forward by Prigogine and Glansdorff (see Schechter for further references) as such a variational principle. It gives balance equations describing the stationary state. All authors addressing this problem concluded that the only balance equations that are *compatible* with minimum entropy production in a stationary state, not only have constant linear coefficients throughout the system, but are also *fully linearized for the total system*. (Schechter adds that convective terms be negligible.) The local balance equations for the three-dimensional system is the result in the variational analysis.<sup>1</sup> We do not question this finding and agree with the analysis of Prigogine and others completely. The principle of minimum entropy production, as discussed by Schechter, does not address the optimization problem considered by us and cannot be used to argue that our principle is only valid for constant phenomenological coefficients, as Haug-Warberg does.

We return to the particular example for which an explicit proof of the principle of equipartition of forces was given above. Haug-Warberg's example is a special case of this where there are only two parallel paths of heat exchange. Our expression for the entropy production rate above then reduces to

$$\begin{aligned} \frac{d\Sigma}{dt} &= A_1 J_{q,1} \left[ \frac{1}{T_1(s_1)} - \frac{1}{T_1(0)} \right] + A_2 J_{q,2} \left[ \frac{1}{T_2(s_2)} - \frac{1}{T_2(0)} \right] \\ &= A_1 J_{q,1} X_1 + A_2 J_{q,2} X_2 \end{aligned} \quad (9)$$

where  $A_1$  and  $A_2$  are the surface areas in the two paths. The resulting linear laws are

$$\begin{aligned} A_1 J_{q,1} &= L_1 \left[ \frac{1}{T_1(s_1)} - \frac{1}{T_1(0)} \right] = L_1 X_1 \\ A_2 J_{q,2} &= L_2 \left[ \frac{1}{T_2(s_2)} - \frac{1}{T_2(0)} \right] = L_2 X_2 \end{aligned} \quad (10)$$

The principle of constant force now says that for a given duty  $J = A_1 J_{q,1} + A_2 J_{q,2}$  the entropy production rate is minimal if  $X_1 = X_2$ . Haug-Warberg disputes this and has an example to prove this. In his example

$$\begin{aligned} L_{HW,1} &= \frac{\kappa}{s_1} T_1(s_1) T_1(0) \\ L_{HW,2} &= \frac{\lambda_2}{s_1} \end{aligned} \quad (11)$$

His first coefficient can be written as

$$\begin{aligned} L_{HW,1} &= \frac{\kappa}{s_1} T_1^2(0) [1 + X_1 T_1(0)]^{-1} = \\ &T_1(0) \left[ \frac{\kappa}{s_1} T_1(0) - A_1 J_{q,1} \right] \end{aligned} \quad (12)$$

and is, therefore, a clear function of the force or alternatively the heat flux. Our principle of constant thermodynamic force is then not applicable. As such, we agree with Haug-Warberg's conclusion. Using eq 7, one may differentiate also  $R = 1/L$  with respect to the flux, and one then obtains as an optimization criterion

$$X_1 + \frac{1}{2} T_1(0) X_1^2 = X_2 = -\frac{\lambda}{2} \quad (13)$$

The forces are most clearly unequal. It is, however, no counterexample because it does not satisfy the basic assumption of nonequilibrium thermodynamics for the case presented. Equation 13 together with the equation for the given duty,  $J = L_{HW,1} X_1 + L_{HW,2} X_2$ , reproduces eq 16 for the optimum solution in Haug-Warberg's comment, if one introduces his dimensionless variables. This underlines again the fact that he uses force (or flux)-dependent heat-transfer coefficients. One is, of course, free to use these coefficients, but one should then take into account the variation of these coefficients if one changes the forces.

Haug-Warberg uses nonequilibrium thermodynamics on the more detailed three-dimensional level correctly. The problem is, however, that the integration over  $x$  of a temperature-dependent  $\lambda$ , from  $J_q = \lambda \partial T^{-1} / \partial x$  then leads to such problems (he uses  $\lambda_1 = \kappa T^2$  along his first path). We may thus conclude that force-independent  $L$ 's on the two-dimensional level are only found when the  $\lambda$ 's are in sufficiently good approximation constant along the path of integration from  $x = 0$  to  $x = s$ . One may dislike that a three-dimensional description in the context of nonequilibrium thermodynamics gives, upon integration along the flux lines, a two-dimensional description, which violates the analogous requirements on this level. This as such has, however, nothing to do with our principle. The conditions for its validity have been stated clearly.

We, therefore, conclude regarding the points raised in the beginning that the reference to Schechter is irrelevant in the present context and that the example taken by Haug-Warberg does not use force-independent transport coefficients, as required for validity of the principle.

It is next interesting to see how our principle deals with temperature-dependent coefficients. The coefficient must depend on only one temperature,  $T(0,y,z)$  in the above example, in order not to depend on the force. The optimization procedure gives a constant force solution, with such a coefficient, for the realistic case of continuous heat exchange.<sup>5</sup> By repeating the question for different heat exchanger areas, we obtain solutions with corresponding values of force and area. In other words, we obtain an isoforce operating curve and can analyze the tradeoff between area (cost) and energy efficiency for the heat exchange. While the optimum mode of operation is an isoforce line, this may not be realizable in practice. With knowledge of the optimum mode of operation, one can modify a system in the optimum direction, however. This was demonstrated to be beneficial for distillation columns<sup>6,7</sup> and has been found useful in control theory<sup>8</sup> and for batch reactors.<sup>13</sup> A large

group of chemical reactors that operate near maximum rate or close to equilibrium also follow an isoforce line.<sup>7,9</sup>

We have further discussed cases for which the principle of constant force is no longer strictly valid, like for chemical reactions.<sup>10–12</sup> Deviations from the principle when the coefficient depends on the force are often small. The reason for this was clarified by our analysis of Haug-Warberg's example above. Equation 13 shows for that case that the difference between the two forces is of second order. Its relative order of magnitude is the temperature difference across the heat exchanger divided by the absolute temperature. This explains why Haug-Warberg obtained a deviation of only 6% for relatively large forces. The fact that deviations are of second order make the principle useful as a rule of thumb in the cases when it does not apply in a strict sense. It seems that there are many fruitful practical applications yet to be explored.

### Literature Cited

- (1) Schechter, R. S. *The Variational Method in Engineering*; McGraw-Hill: New York, 1967; Chapter 4.
- (2) Kjelstrup Ratkje, S.; Sauar, E.; Hansen, E.; Lien, K. M.; Hafskjold, B. Analysis of entropy production rates for design of distillation columns. *Ind. Eng. Chem. Res.* **1995**, *34*, 3001–3007.
- (3) Park, C. S.; Sharp-Bette, G. P. *Advanced Engineering Economics*; Wiley: New York, 1990.
- (4) Sauar, E.; Kjelstrup Ratkje, S.; Lien, K. M. Equipartition of forces: A new principle for process design and optimization. *Ind. Eng. Chem. Res.* **1996**, *35*, 4147–4153.
- (5) Nummedal, L.; Kjelstrup, S. Equipartition of forces as a lower bound on the entropy production in heat exchange. *Int. J. Heat Mass Transfer*, in press.
- (6) Sauar, E. Energy efficient process design by equipartition of forces. With applications to distillation and chemical reaction. Doctoral Thesis No. 77, Department of Physical Chemistry, Norwegian University of Science and Technology, Trondheim, Norway, 1998.
- (7) Sauar, E.; Rivero, R.; Kjelstrup Ratkje, S.; Lien, K. M. Diabatic column optimization compared to isoforce columns. *Energy Convers. Manage.* **1997**, *38*, 1777–1783.
- (8) Farschman, C. A.; Viswanath, K. P.; Ydstie, B. E. Process systems and inventory control. *AIChE J.* **1998**, *44*, 1841–1857.
- (9) Sauar, E.; Ydstie, B. E. The temperatures of the maximum reaction rate and their relation to the equilibrium temperatures. *J. Phys. Chem. A* **1998**, 8860–8864.
- (10) Bedeaux, D.; Standaert, F.; Hemmes, K.; Kjelstrup, S. Optimization of processes by equipartition. *J. Non-Equilib. Thermodyn.* **1999**, *24*, 242–259.
- (11) Kjelstrup, S.; Sauar, E.; Bedeaux, D.; van der Kooi, H. The driving force distribution for minimum lost work in chemical reactors close to and far from equilibrium. 1. Theory. *Ind. Eng. Chem. Res.* **1999**, *38*, 3046–3050.
- (12) Kjelstrup, S. J.; Island, T. V. The driving force distribution for minimum lost work in chemical reactors close to and far from equilibrium. 2. Oxidation of SO<sub>2</sub>. *Ind. Eng. Chem. Res.* **1999**, *38*, 3051–3055.
- (13) Sauar, E.; Kjelstrup Ratkje, S.; Lien, K. M. Equipartition of forces—extensions to chemical reactors. *Comput. Chem. Eng.* **1997**, *21*, Suppl., 29–34.

IE0006920