J. Phys. Chem. A **2005,** *109,* 10607−10612

Exact Solutions for the Entropy Production Rate of Several Irreversible Processes

John Ross*,† and Marcel O. Vlad†,‡

Department of Chemistry, Stanford University, Stanford, California 94305-5080, and Institute of Mathematical Statistics and Applied Mathematics, Casa Academiei Romane, Calea Septembrie 13, 76100 Bucharest, Romania

Received: August 8, 2005; In Final Form: September 23, 2005

We investigate thermal conduction described by Newton's law of cooling and by Fourier's transport equation and chemical reactions based on mass action kinetics where we detail a simple example of a reaction mechanism with one intermediate. In these cases we derive exact expressions for the entropy production rate and its differential. We show that at a stationary state the entropy production rate is an extremum if and only if the stationary state is a state of thermodynamic equilibrium. These results are exact and independent of any expansions of the entropy production rate. In the case of thermal conduction we compare our exact approach with the conventional approach based on the expansion of the entropy production rate near equilibrium. If we expand the entropy production rate in a series and keep terms up to the third order in the deviation variables and then differentiate, we find out that the entropy production rate is not an extremum at a nonequilibrium steady state. If there is a strict proportionality between fluxes and forces, then the entropy production rate is an extremum at the stationary state even if the stationary state is far away from equilibrium.

I. Introduction

The entropy production rate in an irreversible process is a measure of the dissipation in that process.[1] A popular 'principle' in the literature is that if a stationary state is close enough to equilibrium, then the entropy production rate has an extremum at the steady state.[1] This 'principle' is mathematically correct if the relation between the thermodynamic fluxes and forces is strictly linear and the matrix of proportionality coefficients is symmetric[2] ("Stationary non-equilibrium states have the important property that, under certain conditions, they are characterized by a *minimum of the entropy production*, compatible with the external constraint imposed on the system. This property is valid only if the phenomenological coefficients are supposed to be *constants*".[2]). Later on, Glansdorff and Prigogine[3] restated the theorem with the thought that close to equilibrium the proportionality between fluxes and forces becomes nearly true ("It is easy to show that if the steady states occur *sufficiently* close to equilibrium states they may be characterized by an extremum principle according to which *the entropy production has* its minimum value at the steady-state compatible with the prescribed conditions (constraints) to be specified in each case."[3]). Unfortunately this incorrect statement has been repeated many times, especially in connection with biochemical and biological applications. There is a tendency, especially in biochemistry and biology, to present the principle of minimum entropy production in even vaguer terms, as a fundamental law of nature, which is supposed to be valid for any evolution equations, which is not correct. For example, Voet and Voet,[4] in a widely used text, mention that "Ilya Prigogine, a pioneer in the development of irreversible thermodynamics, has shown that a steady state produces the maximum amount of useful work for a given energy expenditure under the prevailing conditions. *The steady state of an open system is therefore its state of* maximum thermodynamic efficiency."

In earlier work[5] we presented a critique of the restated version[3] of the principle of minimum entropy production rate. The principle was shown to be based on a mathematical error[5] due to the unrecognized noncommutativity of two operations: 1. the differentiation of the entropy production rate to obtain an extremum and 2. the approach close to equilibrium. If 2. is done first, as in ref 5, then the principle is obtained; if 1. is done first then the principle is false. This critique was contested in ref 6 but this work was shown to be without merit.[7] Nonetheless references to this principle appear regularly, the original critique being unknown or neglected.

In this paper we go a step further: instead of using approximations based on series expansions, we present exact solutions of the entropy production rate for two empirical laws of thermal conduction and for chemical reactions obeying mass action kinetics. In the case of thermal conduction with Newton's law of cooling, we show, without any approximations, that the entropy production rate in a stationary state is never an extremum, whether that state is far from, or close to, equilibrium; an extremum occurs if and only if the stationary state is a state of thermodynamic equilibrium. This result is extended for nonuniform systems, described by Fourier's transport equation.

We also study the connections between the exact method introduced in this paper and the expansion approach. We expand the entropy production rate in variables that are small for systems close to equilibrium. If we first differentiate the entropy production rate and then keep only the lowest order terms in those variables, then the extremum is not at the stationary state, regardless of how close the system is to equilibrium. If, however, we keep in the entropy production only the lowest terms in these variables, all square terms, and subsequently differentiate, then the extremum is at the stationary state for given constraints. At equilibrium, of course, the entropy production rate vanishes and is an extremum. If and only if there is a strict proportionality

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* Corresponding author phone: (650)723-9203; fax: (650)723-4817; e-mail: john.ross@stanford.edu.

† Stanford University.

‡ Casa Academiei Romane.

10.1021/jp054432d CCC: $30.25

between fluxes and forces, then, and only then, the entropy production rate is an extremum at the stationary state. This requirement does not hold in general for transport processes or chemical kinetics without making approximations. We provide two examples of thermal conduction for which such proportionality is assumed to hold.

We also consider a general formulation of chemical reaction rates based on mass action kinetics. We write the entropy production rate and evaluate its differential. The differential of the entropy production rate is made up of two additive terms: the first term is always zero for a steady state, whereas the second term is in general different from zero. For an example we take a reaction mechanism with a single intermediate and show that the entropy production rate at the single stationary state of this system is never an extremum, except at chemical equilibrium.

II. Exact Solutions for Thermal Conduction

A. Newton's Cooling Law. We consider an example of thermal conduction, which we shall analyze exactly, without approximations. We consider a macroscopic, homogeneous system, with cylindrical shape of length l and cross-sectional area A, at temperature T, which generally is time-dependent. The system is in interaction with two thermal baths which are maintained at two different constant temperatures, T_1 and T_2, respectively; we assume, without restriction, that $T_1 > T_2$. The entropy production rate is

$$\sigma = Alk.\frac{T_1 - T}{l}\cdot\frac{1}{l}\left(\frac{1}{T} - \frac{1}{T_1}\right) + Alk.\frac{T_2 - T}{l}\cdot\frac{1}{l}\left(\frac{1}{T} - \frac{1}{T_2}\right) = \frac{kA}{TT_1T_2l}[T^2(T_1 + T_2) - 4T_1T_2T + T_1T_2(T_1 + T_2)] \geq 0 \quad (1)$$

Here the heat flux is $J = k\Delta T/l = \epsilon Al\rho c\Delta T$, the conjugated force is $\Delta(T^{-1})/l$, k is the thermal conductivity, c is the mass specific heat capacity of the system, which is assumed to be constant, ρ is the density of the system, which is also assumed to be constant, and $\epsilon = k/(\rho cAl^2)$ is the rate of temperature decay. Note that the flux is not proportional to the force. The transport equation of the process is a combination of two Newton's laws, which describe the interaction with the two thermal baths

$$lA\rho c\frac{dT}{dt} = k\left(\frac{T_1 - T}{l}\right) + k\left(\frac{T_2 - T}{l}\right) \quad (2)$$

The solution of eq 2 is

$$T(t) = T_{st} + [T_0 - T_{st}]\exp[-2\epsilon t] \quad (3)$$

where the relaxation rate is $2\epsilon = 2k/(\rho cAl^2)$ and $T_{st} = (T_1 + T_2)/2$. For long times, $t >> 1/(2\epsilon)$, the system reaches a stationary state for which

$$\lim_{t\to\infty} T = T_{st} = (T_1 + T_2)/2 \quad (4)$$

The derivative of the entropy production rate with respect to temperature is given by

$$\frac{d}{dT}\sigma(T) = \frac{Ak(T^2 - T_1T_2)(T_1 + T_2)}{lT^2T_1T_2} \quad (5)$$

and at the steady state ($T = T_{st}$) we have

$$\sigma(T_{st}) = Ak(T_1 - T_2)^2/2lT_1T_2 \quad (6)$$

$$\frac{d}{dT}\sigma(T_{st}) = \frac{Ak(T_1 - T_2)^2}{lT_1T_2(T_1 + T_2)} \quad (7)$$

Thus the entropy production rate is never an extremum at the stationary state, neither close to nor far from equilibrium; it is an extremum at a stationary state if and only if the system is at equilibrium, at $T_1 = T_2$. The entropy production rate has an extremum, which is a minimum, for $T_{extr} = \sqrt{T_1T_2}$. Since $T_{st} - T_{extr} = (\sqrt{T_1} - \sqrt{T_2})^2/2 > 0$, $T_1 \neq T_2$, it follows the extremal temperature T_{extr} is lower than the stationary temperature T_{st}.

We notice that the dimensionless ratio

$$\left[\frac{\sigma(T)/T}{d\sigma(T)/dT}\right]_{T=T_{st}} = 1 > 0 \quad (8)$$

is positive for any nonequilibrium steady state ($T_1 \neq T_2$). At equilibrium ($T_1 = T_2 = T_{eq}$) this ratio is zero

$$\left[\frac{\sigma(T)/T}{d\sigma(T)/dT}\right]_{T=T_{eq}} = \left[\frac{T - T_{eq}}{T + T_{eq}}\right]_{T=T_{eq}} = 0, \quad \text{for } T_1 = T_2 = T_{eq} \quad (9)$$

B. Fourier Equation. By extending Newton's cooling law to a continuous distribution of temperatures we obtain Fourier's law of heat conduction. The heat flux is given by $\mathbf{J} = -k\nabla T$ and the corresponding to thermodynamic force is ∇T^{-1}; once again, the flux is not proportional to the force. By inserting the flux $\mathbf{J} = -k\nabla T$ into the balance equation $\rho c(\partial T/\partial t) + \nabla\cdot\mathbf{J} = 0$ we obtain the Fourier law

$$\partial T/\partial t = \lambda\nabla^2 T \quad (10)$$

where $\lambda = k/\rho c$ is the thermal diffusivity. Fourier's law is the continuous analogue of the Newton's cooling law. A simple constraint which leads to the evolution of the system toward a nonequilibrium steady state is to impose a constant heat flux on the system $\mathbf{J} = \mathbf{J}_0$, constant. The stationary distribution of temperature $T_{st}(\mathbf{r})$ can be obtained by solving the equation

$$\mathbf{J}_0 = -k\nabla T_{st}(\mathbf{r}) \quad (11)$$

with suitable boundary conditions. In particular, for unlimited space

$$T_{st}(\mathbf{r}) = T_0(\mathbf{r}_0) - \mathbf{J}_0\cdot(\mathbf{r} - \mathbf{r}_0)/k \quad (12)$$

where $T_0(\mathbf{r}_0)$ is the stationary temperature at the reference position $\mathbf{r}_0$. For $\mathbf{J}_0 = \mathbf{0}$ there are no constraints, and the system evolves toward a state of thermodynamic equilibrium characterized by a uniform temperature $T_{eq} = T_0$, constant. Otherwise, for a nonequilibrium steady state at least one of the components of the flux $\mathbf{J}_0 = \mathbf{0}$ is different from zero, $|\mathbf{J}_0| > 0$ and the stationary temperature varies with position.

The entropy production rate for the whole system, $\sigma[T(\mathbf{r})]$, which is a functional of the temparature field $T(\mathbf{r})$, is given by

$$\sigma[T(\mathbf{r})] = \int \mathbf{J}\cdot\nabla T^{-1}d\mathbf{r} = k\int\frac{[\nabla T(\mathbf{r})]^2}{[T(\mathbf{r})]^2}d\mathbf{r} \geq 0 \quad (13)$$

To check if the entropy production rate has an extremum for the stationary state corresponding to a constant heat flux $\mathbf{J}_0$ we evaluate its functional derivative with respect to the temperature field:

$$\frac{\delta}{\delta T(\mathbf{r}')}\sigma[T(\mathbf{r})] = 2k\int\left[\left(\frac{1}{T(\mathbf{r})}(\nabla_{\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}'))\cdot(\nabla \ln T(\mathbf{r})) - \frac{\delta(\mathbf{r}-\mathbf{r}')}{T(\mathbf{r})}(\nabla \ln T(\mathbf{r}))^2\right)\right]d\mathbf{r} = 2k\left[\frac{(\nabla T(\mathbf{r}'))^2}{(T(\mathbf{r}'))^3} - \frac{\nabla^2 T(\mathbf{r}')}{(T(\mathbf{r}'))^2}\right] \quad (14)$$

For a stationary state $\partial T_{st}(\mathbf{r})/\partial t = 0$ and the Fourier eq 9 reduces to a Laplace equation

$$\nabla^2 T_{st}(\mathbf{r}) = 0 \quad (15)$$

We insert the stationarity condition 11 into eqs 13 and 14 and use the Laplace eq 15, resulting in

$$\sigma[T_{st}(\mathbf{r})]|_{st} = \frac{|\mathbf{J}_0|^2}{k}\int\frac{d\mathbf{r}}{[T_{st}(\mathbf{r})]^2} = \begin{cases} = 0 \text{ if } |\mathbf{J}_0| = 0 \\ > 0 \text{ if } |\mathbf{J}_0| > 0 \end{cases} \quad (16)$$

and

$$\frac{\delta}{\delta T(\mathbf{r}')}\sigma[T(\mathbf{r})]|_{st} = \frac{2|\mathbf{J}_0|^2}{k(T_{st}(\mathbf{r}'))^3} = \begin{cases} = 0 \text{ if } |\mathbf{J}_0| = 0 \\ > 0 \text{ if } |\mathbf{J}_0| > 0 \end{cases} \quad (17)$$

that is, the entropy production rate for the whole system is an extremum if and only if the stationary state is a state of thermodynamic equilibrium.

In conclusion, in this section we have shown that for a thermal conduction law described by Newton's cooling law the entropy production rate is an extremum if and only if the system is at thermodynamic equilibrium. This conclusion can be easily extended to space-dependent systems, described by Fourier's equation. These results are exact and not based on any series expansions. Nevertheless, the study of the connections between the exact method and the expansion approach will clarify the physical meaning of our conclusions. For details, see section IV.

III. Chemical Reactions

We consider a general network of elementary reactions which obey ideal mass-action law kinetics

$$\sum_{u=1}^{S_a}\alpha_{uw}^{+}A_u + \sum_{u=1}^{S_x}\beta_{uw}^{+}X_u \rightleftharpoons \sum_{u=1}^{S_a}\alpha_{uw}^{-}A_u + \sum_{u=1}^{S_x}\beta_{uw}^{-}X_u \quad (18)$$

where the forward and backward extensive reaction rates are given by

$$r_w^{\pm}(\mathbf{a},\mathbf{x}) = Vk_w^{\pm}\left[\prod_{u=1}^{S_a}(a_u)^{\alpha_{uw}{}^{\pm}}\right]\left[\prod_{u=1}^{S_x}(x_u)^{\beta_{uw}{}^{\pm}}\right] \quad (19)$$

Here $A_u, u = 1,...,S_a$ are stable species whose concentrations $a_u, u = 1,...,S_a$ are kept constant by interaction with a set of reservoirs connected to the system, which act as buffers, and $X_u, u = 1,...,S_x$ are reaction intermediates with variable concentrations $x_u, u = 1,...,S_x$ and V is the volume of the system. The system can be kept away from equilibrium by controlling the concentrations $a_u, u = 1,...,S_a$ of the stable species $A_u, u = 1,...,S_a$.

The entropy production rate can be expressed in the following form (see Appendix A)

$$\sigma(\mathbf{a},\mathbf{x}) = k_B\sum_{w=1}^{R}[r_w^{+}(\mathbf{a},\mathbf{x}) - r_w^{-}(\mathbf{a},\mathbf{x})]\ln\left[\frac{r_w^{+}(\mathbf{a},\mathbf{x})}{r_w^{-}(\mathbf{a},\mathbf{x})}\right] \geq 0 \quad (20)$$

where k_B is Boltzmann's constant. We notice that the entropy production rate does not depend directly on time, only on concentrations. The differential of $\sigma(\mathbf{a},\mathbf{x})$ can be easily evaluated by using the expression 19 for the forward and backward rates of the reaction 18. After some computations we come to

$$\delta\sigma(\mathbf{a},\mathbf{x}) = \sum_{u=1}^{S_x}\delta \ln x_u\frac{\partial}{\partial \ln x_u}\sigma(\mathbf{a},\mathbf{x}) = \sum_{u=1}^{S_x}\tilde{r}_u(\mathbf{a},\mathbf{x})\delta \ln x_u + \sum_{u=1}^{S_x}\mathscr{B}_u(\mathbf{a},\mathbf{x})\delta \ln x_u \quad (21)$$

where $\tilde{r}_u(\mathbf{a},\mathbf{x})$ are the net reaction rates of the species $X_u, u = 1,...,S_x$

$$\tilde{r}_u(\mathbf{a},\mathbf{x}) = \sum_{w=1}^{R}[r_w^{+}(\mathbf{a},\mathbf{x}) - r_w^{-}(\mathbf{a},\mathbf{x})](\beta_{uw}^{+} - \beta_{uw}^{-}) \quad (22)$$

and

$$\mathscr{B}_u(\mathbf{a},\mathbf{x}) = \sum_{w=1}^{R}[\beta_{uw}^{+}r_w^{+}(\mathbf{a},\mathbf{x}) - \beta_{uw}^{-}r_w^{-}(\mathbf{a},\mathbf{x})]\ln\left[\frac{r_w^{+}(\mathbf{a},\mathbf{x})}{r_w^{-}(\mathbf{a},\mathbf{x})}\right] \quad (23)$$

Notice that for a steady state $\mathbf{x} = \mathbf{x}^{st}$ the net reaction rates of the active species $X_u, u = 1,...,S_x$ are equal to zero $\tilde{r}_u(\mathbf{a},\mathbf{x}^{st}) = 0, u = 1,...,S_x$, and the sum $\sum_u\tilde{r}_u(\mathbf{a},\mathbf{x})\delta\ln x_u$ in eq 21 is equal to zero. The second sum, $\sum_u\mathscr{B}(\mathbf{a},\mathbf{x})\delta \ln x_u$, however, is in general different from zero; as expected, it is zero at thermodynamic equilibrium, where detailed balance ($r_w^{+}(\mathbf{a},\mathbf{x}) = r_w^{-}(\mathbf{a},\mathbf{x})$) holds.

For reaction systems of the type

$$\nu A \rightleftharpoons X\nu,\ \nu X \rightleftharpoons \nu B \quad (24)$$

where all reaction rates are identical $k_1^{\pm} = k_2^{\pm} = k$ it is easy to show that the term $\sum_u\mathscr{B}_u(\mathbf{a},\mathbf{x})\delta \ln x_u$ is zero if and only if the system is at thermodynamic equilibrium. This counterexample is sufficient for invalidating the minimum entropy production rate principle. There is a single physically significant stationary state for which

$$x = x^{st} = \left\{\frac{1}{2}[(a)^{\nu} + (b)^{\nu}]\right\}^{1/\nu} \quad (25)$$

For $a \neq b$ the stationary state is a nonequilibrium state, and for $a = b = x^{st}$ the stationary state is a state of thermodynamic equilibrium. The variation of the entropy production rate at the steady state $x = x^{st}$ is given by

$$\delta\sigma(a,b,x^{st}) = (\delta \ln x^{st})Vk_B\nu k\frac{1}{2}[(a)^{\nu} + (b)^{\nu}]\ln\left(\frac{[(a)^{\nu} + (b)^{\nu}]^2}{4a^{\nu}b^{\nu}}\right) \quad (26)$$

From the algebraic inequality

$$\frac{[(a)^{\nu} + (b)^{\nu}]^2}{4a^{\nu}b^{\nu}} = \begin{cases} 1 \text{ for } a = b \\ > 1 \text{ for } a \neq b \end{cases} \quad (27)$$

it follows that

$$\frac{\delta\sigma(a,b,x^{st})}{\delta \ln x^{st}} = \begin{cases} 0 \text{ for } a = b \\ > 0 \text{ for } a \neq b \end{cases} \quad (28)$$

and thus the entropy production rate has an extremum if and only if the system is at thermodynamic equilibrium. For nonequilibrium steady states, no matter how close to equilibrium, the entropy production rate does not have an extremum.

IV. Connections with Prior Work

In this section we try to make a connection between our exact approach and prior work based on the use of expansions and approximations. We also consider alternative models derived from linear nonequilibrium thermodynamics. For simplicity we only study thermal conduction

A. Expansions and Approximations. Now we consider again the discrete problem of thermal conduction studied in section II.A but make approximations; when and where the approximations are made is crucial.

We introduce two new variables

$$T_1 = T_2(1 + \delta),\ T = T_2(1 + \delta_T) \tag{29}$$

where δ is a measure of the deviation of the system from equilibrium, and δ_T is a measure of the deviation of the temperature T from the steady-state value T_{st}. If the entropy production rate is a quadratic function in δ_T, we expect that it is an extremum at the steady state. However, we start by considering a higher-order approximation for σ, say, up to cubic terms

$$\sigma = \frac{Ak}{l}\cdot\frac{\delta^2 - 2\delta\delta_T + (2 + \delta)(\delta_T)^2}{(1 + \delta)(1 + \delta_T)} = \frac{Ak}{l}[\delta^2 - 2\delta\delta_T + 2(\delta_T)^2 - \delta^3 + \delta^2\delta_T + \delta(\delta_T)^2 - 2(\delta_T)^3] + \mathcal{O}[(\delta_T)^4] \tag{30}$$

and differentiate with respect to δ_T we obtain

$$\frac{\partial}{\partial\delta_T}\sigma = \frac{Ak}{l}[-2\delta + 4\delta_T + \delta^2 + 2\delta\delta_T - 6(\delta_T)^2] + \mathcal{O}[(\delta_T)^3] \tag{31}$$

which at the stationary state, $(\delta_T)_{st} = \delta/2$, is

$$\frac{\partial}{\partial\delta_T}\sigma((\delta_T)_{st}) = \frac{kA}{2l}\delta^2 + \mathcal{O}[(\delta)^3] \tag{32}$$

and definitely not zero.

The ratio

$$\left[\frac{\sigma(\delta_T)}{d\sigma(\delta_T)/d\delta_T}\right]_{\delta_T=(\delta_T)_{st}} = 1 > 0 \tag{33}$$

is not zero, regardless of how close the system is to equilibrium.

On the other hand, if the temperatures of the two thermal baths are identical, we have $T_1 = T_2 = T_{eq}$, $\delta = 0$, and the system tends toward thermodynamic equilibrium for which $\delta_T = (\delta_T)_{eq} = 0$ and $\{\sigma(\delta_T)/[d\sigma(\delta_T)/d\delta_T]\}_{\delta_T=0} = 0$, a result which is consistent with eq 9.

If we approach conditions close to equilibrium, that is keep only square terms in δ and δ_T, then the entropy production rate is

$$\sigma = \frac{kA}{l}[\delta^2 - 2\delta\delta_T + 2(\delta_T)^2] + \mathcal{O}[(\delta_T)^3] \tag{34}$$

which upon differentiation with respect to δ_T leads to

$$\frac{\partial}{\partial\delta_T}\sigma = \frac{2kA}{l}[2\delta_T - \delta] + \mathcal{O}[(\delta_T)^2] \tag{35}$$

If we neglect the terms $\mathcal{O}[(\delta_T)^2]$ in eq 35 ($\mathcal{O}[(\delta_T)^3]$ in eq 34), it follows that the entropy production rate has an extremum at

$$(\delta_T)_{extr} = \delta/2, \text{ or } T_{extr} = T_{st} = (T_1 + T_2)/2 \tag{36}$$

that is at the stationary state, in contradiction to the exact solution, eq 7, in section II.A.

The error which leads to the invalid principle of minimum entropy production rate comes from first approximating the entropy production rate to lowest order in deviation from equilibrium and then differentiating to find an extremum, instead of the reverse procedure. The reverse procedure leads to the same result as that obtained from the exact solution, that is without any approximations or expansions.

B. Alternative Model To Newton Cooling. We stated in the Introduction that if there is a strict proportionality between a flux and a force, then the entropy production rate is an extremum at the stationary state. As an illustration of this point consider another example of thermal conduction carried out as discussed in section II.A. Now we assume the validity of linear nonequilibrium thermodynamics, that is, the heat flux J is proportional to the conjugated force $\Delta(T^{-1})/l$

$$J = \chi\Delta(T^{-1})/l \tag{37}$$

where χ is a phenomenological coefficient. The entropy production rate is

$$\sigma = Al\chi\left[\frac{1}{l}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right]^2 + Al\chi\left[\frac{1}{l}\left(\frac{1}{T} - \frac{1}{T_2}\right)\right]^2 = \tag{38}$$

We differentiate eq 37, resulting in

$$\frac{d\sigma}{dT} = -\frac{4A\chi}{lT^2}\left[\frac{1}{T} - \frac{1}{2}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)\right] \tag{39}$$

and thus the entropy production rate has a minimum for

$$T_{extr} = \frac{2T_1T_2}{T_1 + T_2} \tag{40}$$

Although we assume the validity of linear nonequilibrium thermodynamics, the evolution equation for the temperature is nonlinear

$$lA\rho c\frac{dT}{dt} = \frac{\chi}{l}\left(\frac{1}{T} - \frac{1}{T_1}\right) + \frac{\chi}{l}\left(\frac{1}{T} - \frac{1}{T_2}\right) \tag{41}$$

Eq 41 is a nonlinear equation which can be solved analytically. Its solution can be represented in an implicit form

$$T(t) = T_{extr} + [T_0 - T_{extr}]\exp\left(-\frac{T(t) - T_0}{T_{extr}}\right)\exp[-\lambda t] \tag{42}$$

where

$$\lambda = 2\chi/(l^2A\rho c(T_{extr})^2) \tag{43}$$

is an effective decay rate. From eq 42 it follows that for large times, $t \gg 1/\lambda$, the temperature tends toward a stationary value T_{st} which is the same as the extremum temperature T_{extr}

$$\lim_{t\to\infty} T = T_{st} = T_{extr} = \frac{2T_1T_2}{T_1 + T_2} \tag{44}$$

Due to the proportionality of the flux to the force there are only ‘square terms’ in $\Delta T^{-1}/l$ in the entropy production rate and at the stationary state the entropy production rate is an extremum. In, and only in, such cases the principle of minimum entropy production rate holds.

C. Alternative Model to Fourier Conduction. The alternative model of discrete heat transport can be easily extended to continuous (Fourier type) transport. According to linear nonequilibrium thermodynamics, we assume strict proportionality between the heat flux vector **J** and the corresponding to thermodynamic force ∇T^{-1}; we have

$$\mathbf{J} = \chi \nabla T^{-1} \tag{45}$$

and the Fourier law (10) is replaced by

$$\partial T/\partial t = -\zeta \nabla^2 (T^{-1}) = \zeta T^{-3}[T\nabla^2 T - 2(\nabla T)^2] \tag{46}$$

where $\zeta = \chi/\rho c$ is a nonlinear temperature diffusion coefficient with dimension $[\text{length}]^2[\text{temp.}]^2[\text{time}]^{-1}$. Similar to the linear Fourier model, a constraint which leads to the evolution of the system toward a nonequilibrium steady state is to impose a constant heat flux on the system $\mathbf{J} = \mathbf{J}_0$ constant. The stationary distribution of temperature $T_{st}(\mathbf{r})$ can be obtained by solving the equation similar to eq 11

$$\mathbf{J}_0 = -\chi \nabla (T_{st}(\mathbf{r}))^{-1} \tag{47}$$

with suitable boundary conditions. For unlimited space,

$$T_{st}(\mathbf{r}) = \frac{\chi T_0(\mathbf{r}_0)}{\chi - T_0(\mathbf{r}_0)\mathbf{J}_0 \cdot (\mathbf{r} - \mathbf{r}_0)} \tag{48}$$

where $T_0(\mathbf{r}_0)$ is the stationary temperature at the reference position $\mathbf{r}_0$. If $\boldsymbol{J}_0 = \mathbf{0}$ there are no constraints, and the system evolves toward a stare of thermodynamic equilibrium characterized by a uniform temperature $T_{eq} = T_0$ constant. For a nonequilibrium steady state $|\mathbf{J}_0| > 0$ and the stationary temperature varies with position.

The entropy production rate for the whole system, $\sigma[T(\mathbf{r})]$, and its functional derivative with respect to the temperature field are equal to

$$\sigma[T(\mathbf{r})] = \chi \int [\nabla T^{-1}(\mathbf{r})]^2 d\mathbf{r} = \chi \int \frac{[\nabla T(\mathbf{r})]^2}{[T(\mathbf{r})]^4} d\mathbf{r} \geq 0 \tag{49}$$

and

$$\frac{\delta}{\delta T(\mathbf{r}')}\sigma[T(\mathbf{r})] = -2\chi \int d\mathbf{r}'' \frac{\delta(\mathbf{r}'' - \mathbf{r}')}{[T(\mathbf{r}'')]^2} \int (\nabla_{\mathbf{r}} \delta(\mathbf{r}'' - \mathbf{r})) \cdot (\nabla T^{-1}(\mathbf{r}''))d\mathbf{r} = \frac{2\chi \nabla^2 T^{-1}(\mathbf{r}')}{[T(\mathbf{r}')]^2} \tag{50}$$

For a stationary state we have $\partial T_{st}(\mathbf{r})/\partial t = 0$, and the stationary temperature field $T_{st}(\mathbf{r})$ is the solution of a modified Laplace equation

$$\nabla^2 [T_{st}(\mathbf{r})]^{-1} = 0 \tag{51}$$

By combining eqs 49−51 we obtain

$$\sigma[T_{st}(\mathbf{r})]|_{st} = \frac{|\mathbf{J}_0|^2}{\chi} \int \frac{d\mathbf{r}}{[T_{st}(\mathbf{r})]^4} \tag{52}$$

and

$$\frac{\delta}{\delta T_{st}(\mathbf{r}')}\sigma[T_{st}(\mathbf{r})]|_{st} = 0, \quad \text{for any } |\mathbf{J}_0| \tag{53}$$

That is, for a stationary system obeying linear nonequilibrium thermodynamics for any value of the temperature field the entropy production rate is an extremum no matter how far the stationary state is from equilibrium. We also notice that a linear nonequilibrium thermodynamic relation between fluxes and forces leads (eq 45) leads to a nonlinear transport equation (eq 46).

V. Conclusions

In this paper we presented two exactly solvable counterexamples, which show that the entropy production rate does not have an extremum for a steady state, not even in the vicinity of thermodynamic equilibrium. These examples are complementary to and extend our initial critique of the theorem of minimum entropy production rate.[5,7] The theorem of minimum entropy production rate is an artifact produced by ignoring the noncommutativity of two different operations, the truncation of a Taylor series for the entropy production rate in terms of a set of parameters which express the distance from equilibrium and the differentiation of entropy production rate in search for an extremum.

In the literature the theorem of minimum entropy production rate is frequently presented as a fundamental law of nature with a deep meaning, even in recent textbooks of biochemistry and molecular biology.[4] Our analysis shows that this is incorrect.

Acknowledgment. This project was supported in part by the National Science Foundation.

Appendix A

We use the extents ξ_w, $w = 1,2,...$ of reaction 17 as progress variables. We have

$$dN_{X_u} = \sum_u (\beta_{uw}^- - \beta_{uw}^+) d\xi_w \tag{A.1}$$

where dN_{X_u} is the total variation of the number of molecules X_u. The affinity of the reaction u is given by

$$\mathcal{A}_w = -\frac{\partial}{\partial \xi_w} G = k_B T \ln\left[\frac{1}{K_w^{eq}}[\prod_{u=1}^{S_a}(a_u)^{\alpha_{uw}{}^+ - \alpha_{uw}{}^-}][\prod_{u=1}^{S_x}(x_u)^{\beta_{uw}{}^+ - \beta_{uw}{}^-}]\right] \tag{A.2}$$

where K_w^{eq}, $w = 1,2,...$ the equilibrium constants of reaction 17 are equal to

$$K_w^{eq} = [\prod_{u=1}^{S_a}(a_u^{eq})^{\alpha_{uw}{}^+ - \alpha_{uw}{}^-}][\prod_{u=1}^{S_x}(x_u^{eq})^{\beta_{uw}{}^+ - \beta_{uw}{}^-}] = \frac{k_w^+}{k_w^-} \tag{A.3}$$

where a_u^{eq} and x_u^{eq} are the equilibrium concentrations of the species A_u and X_u, respectively. We insert eq A.3 into eq A.2 and use eq 18; we obtain

$$\mathcal{A}_w = k_B T \ln[r_w^+(\mathbf{a},\mathbf{x})/r_w^-(\mathbf{a},\mathbf{x})] \tag{A.4}$$

The entropy production rate $\sigma(\mathbf{a},\mathbf{x})$ for the reaction system can be expressed in terms of the reaction rates

$$d\xi_w/dt = r_w^+(\mathbf{a},\mathbf{x}) - r_w^+(\mathbf{a},\mathbf{x}) \tag{A.5}$$

and of the reaction affinities $\mathcal{A}_w$. We have

$$\sigma(\mathbf{a},\mathbf{x}) = \frac{1}{T}\sum_w \mathcal{A}_w \frac{d}{dt}\xi_w \tag{A.6}$$

We insert eq A.4 and eq A.5 into eq A.6, resulting in eq 19.

References and Notes

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