MINIMUM ENTROPY PRODUCTION
AND THE STEADY STATE

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In the study of thermodynamic systems, it has been found that a particularly simple way of characterizing the equilibrium state of these systems is to find the values of the thermodynamic variables associated with the systems for which the entropy is maximum. The next logical question which might be asked, then, is whether the steady state of a thermodynamic system might be characterized in some analogous manner. Is there some function associated with the system which can be used to determine the steady state of the system by, perhaps, finding an extremum of this function?

The purpose of this thesis is to answer this question, in part, from the standpoint of statistical mechanics. A specific system will be considered, and it will be shown that if the rate of production of entropy for the system is minimum, the system will be in the steady state. In the proof it will be necessary to make certain assumptions which limit the domain of validity of the proof, but which nevertheless do not diminish the insight which may be gained into the physical significance of the entropy production process.
I should like to take this opportunity to express my sincere appreciation to Professor Roald K. Wangsness for suggesting this problem, and for his valuable assistance in preparing this manuscript.

April, 1962

D. J. W.
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CHAPTER I
INTRODUCTION

In 1912, Paul Ehrenfest, in a footnote to an article in *Encyclopädie d. mathematischen Wissenschaften*\(^1\) which he wrote with his wife, asked if the steady state of a thermodynamic system might be characterized by stating that the time rate of change of a function which is a generalization of the entropy is minimum. The answer to this question is supplied, in part, by the principle of minimum entropy production, which may be stated as\(^2\): "The steady state is that state in which the rate of entropy production has the minimum value consistent with the external constraints which prevent the system from reaching equilibrium."

The principle of minimum entropy production was first formulated by Prigogine,\(^3\) on the basis of the Onsager


\(^3\)Ibid., citing Prigogine, *Etude Thermodynamique des Phénomènes irréversibles* (Editions Desoer, Liège, 1947), Chapter V.
reciprocal relations. S. R. de Groot\textsuperscript{4} also formulated the principle in a somewhat more generalized form on the basis of the Onsager relations.

In 1954, Klein and Meijer\textsuperscript{2} derived the principle of minimum entropy production from the standpoint of statistical mechanics by considering two identical containers, each in contact with separate heat reservoirs maintained at different temperatures. With the containers filled with an ideal gas and a capillary tube connecting them, they found that the principle does indeed hold, provided the temperatures of the two reservoirs were not far apart. Throughout their discussion, Boltzmann distributions were assumed for the energy levels of the molecules in the containers.

Klein\textsuperscript{5} later found that the steady state of the Overhauser Nuclear Polarization Process is the state which the minimum entropy production principle predicts. Meijer\textsuperscript{6} has since extended the principle to systems for which Bose-Einstein and Fermi-Dirac statistics are applicable. He has also considered systems with variable numbers of particles.


We shall now proceed to prove the validity of the principle of minimum entropy production for a system which is a generalization of Klein and Meijer's two-container system. Our development of the principle will closely follow that of Klein and Meijer. We shall generalize to a system of an arbitrary but finite number of containers; we shall, thus, answer Ehrenfest's question for a particular system.

In the balance of this chapter, the problem will be formulated in terms of the rates of change of the occupation probabilities of the energy levels in each of the containers. Chapter II will be devoted to the determination of the conditions for extremum entropy production, and in Chapter III we shall show the equivalence of the steady state and extremum entropy production. The extremum will then be shown to be a minimum.

Consider \( N \) identical containers of an ideal gas, all arranged in a line, and connected by capillary tubes. Suppose the molecules of the ideal gas in any given container are free to pass to and fro from the container to the next container in line, either preceding or following, but do so in such a way that they exchange no energy with the capillary tubes connecting the containers, nor do they exchange energy with each other while in a capillary tube. We shall assume the entire system to have a total number \( N \) of molecules.
Let each container be in contact with a heat reservoir maintained at a constant temperature, i.e., let, say, the $l$th container be in contact with a heat reservoir maintained at temperature $T_l$. Since all the molecules in the entire system are identical, we can denote the energy of the $i$th energy level available to any given molecule in any container by $E_i$.

The state of the system can now be specified at any particular time by giving all the occupation numbers for the levels in each container, i.e., by specifying all the numbers

$$n_i^{(1)}, n_i^{(2)}, \ldots, n_i^{(M)},$$

where $n_i^{(l)}$ is the number of molecules in the $i$th energy level in the $l$th container. In terms of the $n_i^{(l)}$, we can define the occupation probabilities as

$$p_i^{(l)} = \frac{n_i^{(l)}}{N}.$$  

At this point we should observe that since the total number $N$ of molecules in the entire system is constant,

$$\sum_{l=1}^{M} \sum_i n_i^{(l)} = N,$$

so that

$$\sum_{l=1}^{M} \sum_i p_i^{(l)} = 1.$$  \hspace{1cm} (1)
We now wish to determine the rates of change of the occupation probabilities \( \rho^{(l)}_i \), given by

\[
\frac{d\rho^{(l)}_i}{dt}.
\]

There are essentially two ways in which a molecule can enter or leave an energy level, thereby changing \( \rho^{(l)}_i \). While remaining in a given container, it can undergo an internal transition by going from a given energy level to another, or, alternatively, it may come into this particular energy level from some other level. On the other hand, it may leave the container for one adjacent to it, or come from an adjacent container into the container of interest, keeping the same energy while passing through the capillary tube. Since we have stipulated that the purpose of the capillary tubes is to conduct the molecules only so that no transitions take place within the tube, a molecule cannot leave one container with a certain energy and arrive at an adjacent container with a different energy.

In order to formulate these concepts quantitatively, we must define the transition probabilities associated with them. Let \( a_{ij}^{(l)} \) denote the probability per unit time that a molecule in the \( l \)th container undergoes a transition from energy level \( i \) to energy level \( j \), while remaining in the \( l \)th container, and let \( b_{i}^{(l)} \) denote the probability per unit time that a molecule in level \( i \) moves from the \( l \)th container to the \((l + 1)\)th. Then
\[
\frac{d\rho_i^{(l)}}{dt} = \sum_j \left( a_{ji}^{(l)} \rho_j^{(l)} - a_{ij}^{(l)} \rho_i^{(l)} \right) + b_{ii}^{(l-1)} \rho_i^{(l-1)} + b_{ii}^{(l)} \rho_i^{(l+1)} - b_{ii}^{(l)} \rho_i^{(l)} - b_{ii}^{(l-1)} \rho_i^{(l-1)} - b_{ii}^{(l-1)} \rho_i^{(l-1)}. \tag{2}
\]

This equation expresses quantitatively the rate of change of \( \rho_i^{(l)} \); 
\[
\sum_j a_{ji}^{(l)} \rho_j^{(l)},
\]
for example, is the sum of the probabilities per unit time of molecules coming into state \( i \) in the \( l \)th container from other states \( j \) in the same container; \( b_{ii}^{(l-1)} \rho_i^{(l-1)} \) is the probability per unit time of a molecule in the \((l-1)\)th container, in the \( i \)th state, coming into the \( l \)th container in the state \( i \).

For convenience in notation, we have implicitly assumed in writing (2) that 
\[
\rho_j^{(0)} = \rho_j^{(M+1)} = b_{ii}^{(M)} = b_{ii}^{(0)} = a_{ii}^{(l)} = 0
\]
for all \( l, i \) and \( j \). For instance, \( \rho_j^{(0)} \) is zero since there is no zeroth container; \( b_{ii}^{(M)} \) is zero since this would represent the probability of a molecule moving from the \( M \)th container to the non-existent \((M+1)\)th.

At this point it is convenient to derive an expression from (2) which will be of use in the later portions of
this analysis. Suppose the capillary tubes were not present, i.e., suppose the individual containers were isolated from each other, so that \( b_{ii}^{(l)} = 0 \), for all \( i \) and \( l \). In that case, (2) becomes simply

\[
\frac{d\rho_{ii}^{(l)}}{dt} = \sum_j (a_{ji}^{(l)} \rho_j^{(l)} - a_{ij}^{(l)} \rho_i^{(l)}),
\]

which indicates that \( \rho_{ii}^{(l)} \) changes via internal transitions only. But since each container is now independent, the \( l \)th container will come to a state of thermal equilibrium with its heat bath, and

\[
\frac{d\rho_{ii}^{(l)}}{dt} = 0,
\]

for all \( i \). This will be the case if

\[
a_{ji}^{(l)} \rho_j^{(l)} - a_{ij}^{(l)} \rho_i^{(l)} = 0,
\]

which is seen to be the condition for equilibrium, so that

\[
\frac{a_{ji}^{(l)}}{a_{ij}^{(l)}} = \frac{\rho_i^{(l)}}{\rho_j^{(l)}}.
\]

Now for an ideal gas, the \( \rho_i^{(l)} \) are proportional to the Boltzmann factor, so that

\[
\frac{\rho_i^{(l)}}{\rho_i^{(l)}} = \exp\left(-\frac{\varepsilon_i}{kT_l}\right) = \exp\left(-\frac{\varepsilon_j}{kT_l}\right)
\]

\[
\frac{\rho_i^{(l)}}{\rho_i^{(l)}} = \exp\left(-\frac{\varepsilon_j}{kT_l}\right)
\]
where, of course, $k$ is Boltzmann's constant, and we thus have the important result that

$$\frac{a_{ji}(t)}{a_{ij}(t)} = \frac{e^{-\frac{\varepsilon_i}{kT\xi}}}{e^{-\frac{\varepsilon_j}{kT\xi}}}.$$  \hspace{1cm} (4)

We now have the problem formulated in terms of the rates of change of the occupation probabilities. In the next chapter, we shall find the rate of production of entropy for the entire system, and find the conditions under which the rate of production of entropy shall be an extremum.
CHAPTER II
CONDITIONS FOR EXTREMEUM ENTROPY PRODUCTION

Entropy can be produced in this system in both the containers and the heat baths. If we denote the \( l \) th container by \( C_l \) and the \( l \) th heat bath by \( B_l \), we can write

\[
\frac{dS}{dt} = \sum_{l=1}^{M} \left[ \left( \frac{dS}{dt} \right)_{C_l} + \left( \frac{dS}{dt} \right)_{B_l} \right],
\]

and which we wish to evaluate explicitly. Let us first seek the total entropy of all the containers, so that a time derivative will yield the total rate of entropy production in all the \( C_l \). In terms of the occupation probabilities, the entropy of the \( l \) th container can be written as

\[
S_{C_l} = -Nk \sum_{i} \rho_{i}^{(l)} \ln \rho_{i}^{(l)},
\]

so that

\[
\sum_{l=1}^{M} S_{C_l} = -Nk \sum_{l=1}^{M} \sum_{i} \rho_{i}^{(l)} \ln \rho_{i}^{(l)}
\]

and

\[
\sum_{l=1}^{M} \left( \frac{dS}{dt} \right)_{C_l} = -Nk \sum_{l=1}^{M} \sum_{i} \rho_{i}^{(l)} \frac{d\rho_{i}^{(l)}}{dt},
\]

(6)
since

$$\sum_{\ell=1}^{M} \sum_{i} \frac{d \rho_{i}^{(\ell)}}{dt} = 0$$

by (1). Substituting from (2), then, we get

$$\sum_{\ell=1}^{M} \left( \frac{dS}{dt} \right)_{C_{\ell}} = -N k \sum_{\ell=1}^{M} \sum_{i} \frac{\ln \rho_{i}^{(\ell)}}{v} \left\{ \sum_{j} \left( a_{ij}^{(\ell)} \rho_{j}^{(\ell)} - a_{ji}^{(\ell)} \rho_{i}^{(\ell)} \right) 
+ b_{i}^{(\ell-1)} \left[ \rho_{i}^{(\ell-1)} - \rho_{i}^{(\ell)} \right] + b_{i}^{(\ell)} \left[ \rho_{i}^{(\ell+1)} - \rho_{i}^{(\ell)} \right] \right\}$$

which expresses the total rate of production of entropy in the containers in terms of the occupation and transition probabilities.

In the $\ell$th heat bath, entropy is being produced at the rate

$$\left( \frac{dS}{dt} \right)_{B_{\ell}} = \frac{1}{T_{\ell}} \left( \frac{dU}{dt} \right)_{B_{\ell}}$$

where $U_{B_{\ell}}$ is the energy of the heat bath. Since the $\ell$th heat bath exchanges energy only with the $\ell$th container, we can express

$$\frac{dU_{B_{\ell}}}{dt}$$

in terms of the changes in energy of the gas in the $\ell$th container produced only by interactions with the heat bath, which we call internal processes, i.e.,
\[
\left( \frac{d U}{d t} \right)_{B_{\ell}} = - \left( \frac{d U}{d t} \right)_{\text{C} \ell, \text{INTERNAL}}.
\]

Now \( U_{C \ell, \text{INTERNAL}} = N \sum_i \varepsilon_i \mathcal{P}_i^{(\ell)} \), so that
\[
\left( \frac{d U}{d t} \right)_{C \ell, \text{INTERNAL}} = N \sum_i \varepsilon_i \left( \frac{d \mathcal{P}_i^{(\ell)}}{d t} \right)_{\text{INTERNAL}},
\]
and
\[
\left( \frac{d U}{d t} \right)_{B_{\ell}} = -N \sum_i \varepsilon_i \left( \frac{d \mathcal{P}_i^{(\ell)}}{d t} \right)_{\text{INTERNAL}}. \tag{9}
\]

But by (3) we have
\[
\left( \frac{d \mathcal{P}_i^{(\ell)}}{d t} \right)_{\text{INTERNAL}} = \sum_j \left( a_{ij}^{(\ell)} \mathcal{P}_j^{(\ell)} - a_{ij}^{(\ell)} \mathcal{P}_i^{(\ell)} \right),
\]
and finally
\[
\left( \frac{d S}{d t} \right)_{B_{\ell}} = -N \sum_i \sum_j \frac{\varepsilon_i}{k T_{\ell}} \left( a_{ji}^{(\ell)} \mathcal{P}_j^{(\ell)} - a_{ij}^{(\ell)} \mathcal{P}_i^{(\ell)} \right). \tag{10}
\]

Using (7) and (10) in (5), we will have the total entropy production expressed as
\[
\frac{d S}{d t} = -Nk \sum_{\ell=1}^{M} \sum_i \mu \mathcal{P}_i^{(\ell)} \left\{ \sum_j \left( a_{ji}^{(\ell)} \mathcal{P}_j^{(\ell)} - a_{ij}^{(\ell)} \mathcal{P}_i^{(\ell)} \right) \right\}
\]
\[
- Nk \sum_{\ell=1}^{M} \sum_i \frac{\varepsilon_i}{k T_{\ell}} \left( a_{ji}^{(\ell)} \mathcal{P}_j^{(\ell)} - a_{ij}^{(\ell)} \mathcal{P}_i^{(\ell)} \right)
\]
\[
- Nk \sum_{\ell=1}^{M} \sum_i \mu \mathcal{P}_i^{(\ell)} \left\{ b_{ii}^{(\ell+1)} \left[ \mathcal{P}_i^{(\ell+1)} - \mathcal{P}_i^{(\ell)} \right] + b_{ii}^{(\ell)} \left[ \mathcal{P}_i^{(\ell+1)} - \mathcal{P}_i^{(\ell)} \right] \right\}.
\]
By rearranging this expression and replacing \( \ell \) by \( \ell + 1 \) in

\[
b_{ii}^{(\ell)} \left[ \rho_{ii}^{(\ell+1)} - \rho_{ii}^{(\ell)} \right],
\]

we can express the entropy production in the more convenient form

\[
\frac{dS}{dt} = -Nk \sum_{\ell=1}^{M} \left\{ \left[ \ln \rho_{ii}^{(\ell)} + \frac{\epsilon_{i}}{kT_{i}} \right] \sum_{j} \left( a_{ij}^{(\ell)} \rho_{ij}^{(\ell+1)} - a_{ij}^{(\ell)} \rho_{ij}^{(\ell)} \right) + b_{ii}^{(\ell)} \left( \ln \rho_{ii}^{(\ell)} - \ln \rho_{ii}^{(\ell+1)} \right) \left( \rho_{ii}^{(\ell+1)} - \rho_{ii}^{(\ell)} \right) \right\}.
\]

Equation (11) now gives the rate of production of entropy in terms of the occupation and transition probabilities. We now wish to find the conditions under which \( \frac{dS}{dt} \) shall be an extremum, subject to the constraint (1) that the total number of molecules in the system is constant. Anticipating our result, we shall find that \( \frac{dS}{dt} \) being an extremum is equivalent, provided the gas in each container is near equilibrium with its heat bath, to stating that

\[
\frac{d\rho_{ii}^{(\ell)}}{dt} = 0,
\]

for all \( i \) and \( \ell \), which will be recognized as the condition for the steady state.

In order to find the conditions under which \( \frac{dS}{dt} \) will be an extremum, we first find the derivatives of \( \frac{dS}{dt} \) with respect to the occupation probabilities. By direct evaluation, we have
\[\frac{\partial}{\partial \rho^{(m)}_n} \left( \frac{dS}{dt} \right) = -Nk \left\{ \sum_j \left[ a^{(m)}_{jn} \frac{\rho^{(m)}_j}{\rho^{(m)}_n} - a^{(m)}_{nj} \right] \right. \]

\[+ \sum_i \left[ \ln \rho^{(m)}_i + \frac{E_i}{kT_m} \right] a^{(m)}_{ni} \]

\[-\sum_j a^{(m)}_{nj} \left[ \ln \rho^{(m)}_n + \frac{E_n}{kT_m} \right] \]

\[+ b^{(m)}_{nn} \left[ \left( \frac{\rho^{(m+1)}_n}{\rho^{(m)}_n} - 1 \right) + \ln \frac{\rho^{(m+1)}_n}{\rho^{(m)}_n} \right] \]

\[+ b^{(m-1)}_{nn} \left[ \left( \frac{\rho^{(m-1)}_n}{\rho^{(m)}_n} - 1 \right) + \ln \frac{\rho^{(m-1)}_n}{\rho^{(m)}_n} \right] \} \quad (12) \]

We cannot yet set
\[\frac{\partial}{\partial \rho^{(m)}_n} \left( \frac{dS}{dt} \right) = 0,\]

in order to determine the extremum of dS/dt, for the \( \rho^{(m)}_j \) are not all independent, but are related by equation (1),

\[\sum_{\ell=1}^{M} \sum_j \rho^{(\ell)}_j = 1.\]

If we introduce a Lagrange multiplier \( \mu \), however, we have

\[\mu \left[ \sum_{\ell=1}^{M} \sum_j \rho^{(\ell)}_j - 1 \right] = 0,\]
and we can now set

$$\frac{d}{\partial p^{(m)}_n}\left(\frac{dS}{dt}\right) + \frac{\partial}{\partial p^{(m)}_n} \left\{ \mu \left[ \sum_{\xi=1}^{N} \sum_{j} p_{j}^{(\xi)} - 1 \right] \right\} = 0,$$

so that

$$\frac{d}{\partial p^{(m)}_n} \left(\frac{dS}{dt}\right) + \mu = 0$$

and the conditions for extremum entropy production can be expressed by the equations

$$\mu = Nk \left\{ \sum_{j} \left[ a_{j}^{(m)} \frac{p_{j}^{(m)}}{p^{(m)}_n} - a_{j}^{(m)} \right] + \sum_{i} \left[ \ln p_{i}^{(m)} + \frac{\varepsilon_i}{kT_m} \right] a_{i}^{(m)} \right\}$$

$$- \sum_{j} a_{j}^{(m)} \left[ \ln p^{(m)}_n + \frac{\varepsilon_j}{kT_m} \right]$$

$$+ b_{n\alpha}^{(m)} \left[ \left( \frac{p^{(m+1)}_{n}}{p^{(m)}_n} - 1 \right) + \ln \frac{p^{(m+1)}_{n}}{p^{(m)}_n} \right]$$

$$+ b_{n\alpha}^{(m-1)} \left[ \left( \frac{p^{(m-1)}_{n}}{p^{(m)}_n} - 1 \right) + \ln \frac{p^{(m-1)}_{n}}{p^{(m)}_n} \right] \right\} .$$

These can be rewritten in the form
\[
\mu = Nk \left\{ \sum_i a_{\alpha i}^{(m)} \left[ \ln \frac{p_i^{(m)}}{p_{\alpha}^{(m)}} \frac{\varepsilon_i}{e^{\frac{\varepsilon_i}{kT_m}}} + \left( \frac{a_{\alpha i}^{(m)}}{a_{\alpha i}^{(m)}} \frac{p_i^{(m)}}{p_{\alpha}^{(m)}} - 1 \right) \right] \right. \\
+ b_{\alpha \alpha}^{(m)} \left[ \left( \frac{p_{n}^{(m+1)}}{p_{n}^{(m)}} - 1 \right) + \ln \frac{p_{n}^{(m+1)}}{p_{n}^{(m)}} \right] \\
+ b_{\alpha \alpha}^{(m-1)} \left[ \left( \frac{p_{n}^{(m-1)}}{p_{n}^{(m)}} - 1 \right) + \ln \frac{p_{n}^{(m-1)}}{p_{n}^{(m)}} \right] \right\}.
\]

Since by (4) we have

\[
\frac{a_{\alpha i}^{(m)}}{a_{\alpha i}^{(m)}} = \frac{e^{-\varepsilon_i/kT_m}}{e^{e^{-\varepsilon_i/kT_m}}},
\]

we can write

\[
\mu = Nk \left\{ \sum_i a_{\alpha i}^{(m)} \left[ \ln \frac{p_i^{(m)}}{p_{\alpha}^{(m)}} \frac{\varepsilon_i}{e^{\frac{\varepsilon_i}{kT_m}}} + \frac{p_i^{(m)}}{p_{\alpha}^{(m)}} \frac{\varepsilon_i}{e^{\frac{\varepsilon_i}{kT_m}}} - 1 \right] \right. \\
+ b_{\alpha \alpha}^{(m)} \left[ \left( \frac{p_{n}^{(m+1)}}{p_{n}^{(m)}} - 1 \right) + \ln \frac{p_{n}^{(m+1)}}{p_{n}^{(m)}} \right] \\
+ b_{\alpha \alpha}^{(m-1)} \left[ \left( \frac{p_{n}^{(m+1)}}{p_{n}^{(m)}} - 1 \right) + \ln \frac{p_{n}^{(m-1)}}{p_{n}^{(m)}} \right] \right\}.
\]
The conditions on the \( p_i^{(m)} \) expressed by equations (13) above are exact; \( p_i^{(m)} \) such that (13) are satisfied must be those for which \( \frac{dS}{dt} \) is an extremum, subject to the constraint (1). We cannot proceed further without additional assumptions concerning the temperatures of adjacent heat baths and the difference between the actual container states and the equilibrium states. In the next chapter we shall complete the proof of the minimum entropy production theorem, by showing that (13) is equivalent to stating that all

\[
\frac{d p_i^{(m)}}{dt} = 0,
\]

provided the temperatures of adjacent heat baths differ by only a small amount, and the containers are near equilibrium with their respective heat baths.
We can formulate the assumption that each of the containers is near equilibrium with its heat bath as

\[
\frac{\rho_i^{(m)}}{\rho_n^{(m)}} \frac{\epsilon_i/kT_m}{\epsilon_n/kT_m} = 1 + \rho_{in}^{(m)},
\]

where the \(\rho_{in}^{(m)}\) are small compared to unity, and second order terms in these small quantities can be neglected. Physically, (14), in view of (4), corresponds to stating that the probability per unit time of a molecule in the mth container going from state \(r\) to state \(i\) differs by only a small factor from the probability per unit time of a molecule going from state \(i\) to the \(r\)th state, which would be expected if the mth container were near equilibrium with its heat bath.

The assumption that the temperatures of adjacent heat baths are not far apart can be expressed by

\[
\frac{\rho_n^{(m+1)}}{\rho_n^{(m)}} = 1 + \delta_n^{(m)}
\]

and
\[
\frac{\rho_n^{(m-1)}}{\rho_n^{(m)}} = 1 + \eta_n^{(m)},
\]

(16)

where the \( \delta_n^{(m)} \) and \( \eta_n^{(m)} \) are small compared to unity, for in that case we would expect that the occupation probabilities of the same energy state in adjacent containers would differ only by a small quantity.

Under the assumptions (14), (15), and (16) we can complete our proof with the aid of the relationship

\[
\ln(1 + x) \approx x, \quad |x| < < 1.
\]

Then,

\[
\ln \frac{\rho_i^{(m)} e^{E_i/kT_m}}{\rho_n^{(m)} e^{\varepsilon_n/kT_m}} \approx \frac{\rho_i^{(m)} e^{E_i/kT_m}}{\rho_n^{(m)} e^{\varepsilon_n/kT_m}} - 1,
\]

\[
\ln \frac{\rho_n^{(m+1)}}{\rho_n^{(m)}} \approx \frac{\rho_n^{(m+1)}}{\rho_n^{(m)}} - 1,
\]

\[
\ln \frac{\rho_n^{(m-1)}}{\rho_n^{(m)}} \approx \frac{\rho_n^{(m-1)}}{\rho_n^{(m)}} - 1,
\]

and (13) becomes

\[
\mu = 2Nk \left\{ \sum_i a_n^{(m)} \left[ \frac{\rho_i^{(m)} e^{E_i/kT_m}}{\rho_n^{(m)} e^{\varepsilon_n/kT_m}} - 1 \right] + b_n^{(m)} \left[ \frac{\rho_n^{(m+1)}}{\rho_n^{(m)}} - 1 \right] + b_{n-1}^{(m-1)} \left[ \frac{\rho_n^{(m-1)}}{\rho_n^{(m)}} - 1 \right] \right\}.
\]

(17)
Let us first prove that if the system is in the steady state, the rate of production of entropy is an extremum. In the steady state,
\[ \frac{d\rho^{(m)}_{\eta}}{dt} = 0 \]
for all \( r \) and \( m \), and consequently (2) becomes
\begin{equation}
\sum_{i} \left( a_{i}^{(m)} \rho^{(m)}_{i} - a_{i}^{(m)} \rho^{(m)}_{\eta} \right) = \frac{b^{(m-1)}_{\eta \eta}}{\rho^{(m)}_{\eta}} \left[ \rho^{(m)}_{\eta} - \rho^{(m-1)}_{\eta} \right] + \frac{b^{(m)}_{\eta \eta}}{\rho^{(m)}_{\eta}} \left[ \rho^{(m)}_{\eta} - \rho^{(m+1)}_{\eta} \right]. \tag{18}
\end{equation}
Dividing by \( \rho^{(m)}_{\eta} \) and using an expression of the form (11), we obtain
\[ \sum_{i} a_{i}^{(m)} \left( \frac{\rho^{(m)}_{i} \varepsilon_{i}/kT_{m}}{\rho^{(m)}_{\eta} \varepsilon_{\eta}/kT_{m}} - 1 \right) \]
\[ = -b^{(m)}_{\eta \eta} \left( \frac{\rho^{(m+1)}_{\eta}}{\rho^{(m)}_{\eta}} - 1 \right) - b^{(m-1)}_{\eta \eta} \left( \frac{\rho^{(m-1)}_{\eta}}{\rho^{(m)}_{\eta}} - 1 \right). \]
Substituting this result into (17), we obtain immediately
\( \mu = 0 \) for all \( r \) and \( m \), so that
\[ \frac{\partial}{\partial \rho^{(m)}_{\eta}} \left( \frac{dS}{dt} \right) \bigg|_{\text{STEADY STATE}} = 0, \]
and \( dS/dt \) is an extremum if the containers are in equilibrium with their heat baths.

Let us now suppose that \( dS/dt \) is an extremum. We
then wish to show that the values of all the \(\rho_n^{(m)}\) at the extremum are such that

\[
\frac{d\rho_n^{(m)}}{dt} = 0.
\]

When \(dS/dt\) is an extremum, (17) is satisfied, and if we multiply this expression by \(\rho_n^{(m)}\) and use an equation of the form (44), we have

\[
\mu \rho_n^{(m)} = 2Nk \left\{ \sum_i (a_{i,n}^{(m)} \rho_i^{(m)} - a_{i,n}^{(m)} \rho_n^{(m)}) + b_{n,n}^{(m)} (\rho_n^{(m+1)} - \rho_n^{(m)}) + b_{n,n}^{(m-1)} (\rho_n^{(m-1)} - \rho_n^{(m)}) \right\},
\]

or

\[
\mu \rho_n^{(m)} = 2Nk \frac{d\rho_n^{(m)}}{dt},
\]

by (2). Summing over all \(m\) and \(r\), we find

\[
\sum_{m=1}^{M} \sum_n \mu \rho_n^{(m)} = 2Nk \sum_{m=1}^{M} \sum_n \frac{d\rho_n^{(m)}}{dt} = 0,
\]

by (1), so that \(\mu = 0\), and in view of (19),

\[
\frac{d\rho_n^{(m)}}{dt} = 0,
\]

which, again, is the condition for the steady state.

Summarizing, we have now shown that under the
assumptions that the system is not far from equilibrium and the temperatures of adjacent heat baths are not far apart, a statement that the entropy production is an extremum is both a necessary and sufficient condition for the system to be in the steady state. We now wish to show that the extremum is, in fact, a minimum.

To do this, we shall first compute the change \( \delta (dS/dt) \) in the entropy production for a small change \( \delta (p_i^{(\ell)}) \) in each of the occupation probabilities from their steady-state values. Let us denote explicitly the values of the \( p_i^{(\ell)} \) at the steady state by \( \hat{p}_i^{(\ell)} \), so that

\[
\left( \frac{dS}{dt} \right) \bigg|_{p_i^{(\ell)}} = -Nk \sum_{\ell=1}^{M} \sum_i \left[ k \ln \hat{p}_i^{(\ell)} + \frac{\varepsilon_i - \varepsilon_j}{kT_{\ell}} \right] \sum_j (a_{ij}^{(\ell)} \hat{p}_j^{(\ell)} - a_{ij} \hat{p}_i^{(\ell)})
\]

\[
+ \delta_{i\ell} \left( k \ln \hat{p}_i^{(\ell)} - k \ln \hat{p}_i^{(\ell+1)} \right) \left( \hat{p}_i^{(\ell+1)} - \hat{p}_i^{(\ell)} \right),
\]

and since the change in \( dS/dt \) from its value at equilibrium can be written

\[
\delta \left( \frac{dS}{dt} \right) = \left( \frac{dS}{dt} \right) \bigg|_{\hat{p}_i^{(\ell)}} + \delta \hat{p}_i^{(\ell)} - \left( \frac{dS}{dt} \right) \bigg|_{\hat{p}_i^{(\ell)}},
\]

we can express \( \delta (dS/dt) \) by
\[
\frac{\delta (d \Delta s)}{d t} = -N\ k \sum_{l=1}^{M} \sum_{i} \left\{ \left[ \ln \rho_i^{(l)} + \ln \left( 1 + \frac{\delta \rho_i^{(l)}}{\rho_i^{(l)}} \right) + \frac{E_i}{kT_e} \right] \cdot \right.
\]
\[
\cdot \sum_{j} \left[ (a_{ij}^{(l)} \rho_j^{(l)} - a_{ij}^{(l)} \rho_i^{(l)}) + (a_{ii}^{(l)} \rho_j^{(l)} - a_{ii}^{(l)} \rho_i^{(l)}) \right]
\]
\[
+ b_{ii}^{(l)} \left[ \ln \rho_i^{(l)} + \ln \left( 1 + \frac{\delta \rho_i^{(l)}}{\rho_i^{(l)}} \right) - \ln \rho_i^{(l+1)} - \ln \left( 1 + \frac{\delta \rho_i^{(l+1)}}{\rho_i^{(l+1)}} \right) \right] \cdot
\]
\[
\cdot \left[ (\rho_i^{(l+1)} - \rho_i^{(l)}) + (\delta \rho_i^{(l+1)} - \delta \rho_i^{(l)}) \right]
\]
\[
- \left( \ln \rho_i^{(l)} + \frac{E_i}{kT_e} \right) \sum_{j} \left( a_{ij}^{(l)} \rho_j^{(l)} - a_{ij}^{(l)} \rho_i^{(l)} \right)
\]
\[
- b_{ii}^{(l)} \left( \ln \rho_i^{(l)} - \ln \rho_i^{(l+1)} \right) \left( \rho_i^{(l+1)} - \rho_i^{(l)} \right) \right) \right\}.
\]

Again, using the relationship
\[
\ln(1 + x) \approx x, \quad |x| << 1,
\]
and the fact that \( \delta \rho_i^{(l)} \) is a small quantity compared to \( \rho_i^{(l)} \), we can write the above as
\[
\delta \left( \frac{dS}{dt} \right) = -Nk \sum_{\ell=1}^{\infty} \sum_i \left\{ \sum_j \left( a_{ij}^{(\ell)} \tilde{\rho}_j^{(\ell)} - a_{ij}^{(\ell)} \tilde{\rho}_i^{(\ell)} \right) \frac{\delta \tilde{\rho}_i^{(\ell)}}{\tilde{\rho}_i^{(\ell)}} \right. \\
+ \left. \left( \ln \tilde{\rho}_i^{(\ell)} + \frac{\varepsilon_i}{kT_\ell} \right) \left( a_{ii}^{(\ell)} \delta \tilde{\rho}_i^{(\ell)} - a_{ii}^{(\ell)} \delta \tilde{\rho}_i^{(\ell)} \right) \right. \\
+ \left. b_{ii}^{(\ell)} \left[ \left( \frac{\delta \tilde{\rho}_i^{(\ell)}}{\tilde{\rho}_i^{(\ell)}} - \frac{\delta \tilde{\rho}_i^{(\ell+1)}}{\tilde{\rho}_i^{(\ell+1)}} \right) \left( \tilde{\rho}_i^{(\ell+1)} - \tilde{\rho}_i^{(\ell)} \right) \right. \\
+ \left. \left( \ln \tilde{\rho}_i^{(\ell)} - \ln \tilde{\rho}_i^{(\ell+1)} \right) \left( \delta \tilde{\rho}_i^{(\ell+1)} - \delta \tilde{\rho}_i^{(\ell)} \right) \right. \\
+ \left. \frac{\delta \tilde{\rho}_i^{(\ell)}}{\tilde{\rho}_i^{(\ell)}} \sum_j \left( a_{ij}^{(\ell)} \delta \tilde{\rho}_j^{(\ell)} - a_{ij}^{(\ell)} \delta \tilde{\rho}_i^{(\ell)} \right) \right. \\
+ \left. b_{ij}^{(\ell)} \left( \frac{\delta \tilde{\rho}_i^{(\ell)}}{\tilde{\rho}_i^{(\ell)}} - \frac{\delta \tilde{\rho}_i^{(\ell+1)}}{\tilde{\rho}_i^{(\ell+1)}} \right) \right\},
\]

which expresses the change in \(dS/dt\) in terms of first and second order terms in \(\delta \rho\), i.e., in terms of the \(\delta \rho_i\) and \(\delta \rho_j\). But since we are computing the change from a stationary state, the first order terms in the \(\delta \rho\) must vanish, leaving, after multiplying and simplifying,
\[
\dot{S}(\frac{dS}{dt}) = -Nk \sum_{\ell=1}^{M} \left\{ \sum_{i,j} \left( a_{ij}^{(\ell)} \frac{\delta p_{i}^{(\ell)} \delta p_{j}^{(r)}}{p_{i}^{(\ell)}} - a_{ij}^{(r)} \frac{(\delta p_{i}^{(s)})^2}{p_{i}^{(\ell)}} \right) \\
+ \sum_{i} b_{ii}^{(\ell)} \left[ - \frac{(\delta p_{i}^{(s)})^2}{p_{i}^{(\ell)}} - \frac{((\delta p_{i}^{(s)})^{2})}{p_{i}^{(\ell+1)}} \\
+ \left( \dot{p}_{i}^{(s)} + \dot{p}_{i}^{(s+1)} \right) \left( \frac{\delta p_{i}^{(s)} \delta p_{i}^{(s+1)}}{p_{i}^{(\ell)} p_{i}^{(\ell+1)}} \right) \right] \right\}.
\] (20)

We can now show that \( \dot{S}(dS/dt) \geq 0 \), and hence that the extremum is a minimum, by writing \( \dot{S}(dS/dt) \) as a sum of squares. If in equation (18) we replace \( i \) by \( j \), \( r \) by \( i \), and \( m \) by \( \ell \) and then solve for

\[
\sum_{j} a_{ij}^{(s)}
\]

we have

\[
\sum_{j} a_{ij}^{(s)} = \frac{\sum_{j} a_{ij}^{(s)} \dot{p}_{j}^{(s)} + b_{ii}^{(s+1)}(\dot{p}_{i}^{(s+1)} - \dot{p}_{i}^{(s)}) + b_{ii}^{(s)}(\dot{p}_{i}^{(s)})}{\dot{p}_{i}^{(s)}}
\]

in terms of the \( \dot{p} \) indicating explicitly the steady state values. Using this in (20), we obtain
\[
\mathcal{S}(\frac{dS}{dt}) = -\text{Nk} \sum_{\ell=1}^{M} \left\{ \sum_{i,j} a_{ij}^{(\ell)} \left( \frac{\delta \rho_{i}^{(\ell)}}{\hat{\rho}_{i}^{(\ell)}} \right)^{2} \hat{\rho}_{i}^{(\ell)} \\
+ \sum_{i,j} a_{ij}^{(\ell)} \frac{\delta \rho_{i}^{(\ell)}}{\hat{\rho}_{i}^{(\ell)}} \frac{\delta \rho_{j}^{(\ell)}}{\hat{\rho}_{j}^{(\ell)}} \hat{\rho}_{j}^{(\ell)} \\
- \sum_{i} b_{ii}^{(\ell-1)} \left[ \left( \frac{\delta \rho_{i}^{(\ell)}}{\hat{\rho}_{i}^{(\ell)}} \right)^{2} \hat{\rho}_{i}^{(\ell-1)} - \left( \frac{\delta \rho_{i}^{(\ell)}}{\hat{\rho}_{i}^{(\ell)}} \right)^{2} \hat{\rho}_{i}^{(\ell)} \right] \\
- \sum_{i} b_{ii}^{(\ell)} \left[ \left( \frac{\delta \rho_{i}^{(\ell)}}{\hat{\rho}_{i}^{(\ell)}} \right)^{2} \hat{\rho}_{i}^{(\ell+1)} + \left( \frac{\delta \rho_{i}^{(\ell+1)}}{\hat{\rho}_{i}^{(\ell+1)}} \right)^{2} \hat{\rho}_{i}^{(\ell+1)} \\
- \left( \hat{\rho}_{i}^{(\ell)} + \hat{\rho}_{i}^{(\ell+1)} \right) \left( \frac{\delta \rho_{i}^{(\ell)}}{\hat{\rho}_{i}^{(\ell)}} \frac{\delta \rho_{i}^{(\ell+1)}}{\hat{\rho}_{i}^{(\ell+1)}} \right) \right]\right\}. \tag{21}
\]

Now if, in (21), we replace \((\ell - 1)\) by \(\ell\) in the expression

\[
\sum_{i} b_{ii}^{(\ell-1)} \left[ \left( \frac{\delta \rho_{i}^{(\ell)}}{\hat{\rho}_{i}^{(\ell)}} \right)^{2} \hat{\rho}_{i}^{(\ell-1)} - \left( \frac{\delta \rho_{i}^{(\ell)}}{\hat{\rho}_{i}^{(\ell)}} \right)^{2} \hat{\rho}_{i}^{(\ell)} \right],
\]

and then add (21) to (20), after interchanging the roles of \(i\) and \(j\) in the term

\[
a_{ij}^{(\ell)} \frac{(\delta \rho_{i}^{(\ell)})^{2}}{\hat{\rho}_{i}^{(\ell)}}
\]

in (20), we find that
2 \delta \left( \frac{dS}{dt} \right) = Nk \sum_{\ell=1}^{M} \left\{ \sum_{ii} a_{ii}(\ell) \left[ \left( \frac{\rho_i(\ell)}{\rho_i^{(\ell)}} \right)^{1/2} \delta \frac{\rho_i^{(\ell)}}{\rho_i^{(\ell)}} - \frac{\delta \rho_i^{(\ell)}}{\rho_i^{(\ell)}} \right]^2 + \sum_i b_{ii}(\ell) \left( \frac{\rho_i(\ell)}{\rho_i^{(\ell)}} + \frac{\rho_i^{(\ell+1)}}{\rho_i^{(\ell+1)}} \right) \left( \frac{\delta \rho_i^{(\ell+1)}}{\rho_i^{(\ell+1)}} - \frac{\delta \rho_i^{(\ell)}}{\rho_i^{(\ell)}} \right)^2 \right\}.

so that

\delta \left( \frac{dS}{dt} \right) \geq 0,

and the extremum of dS/dt for the \( \rho_i^{(\ell)} \) is indeed a minimum.

This completes the proof of the principle of minimum entropy production for our particular system. In conclusion, we may make an interesting observation on the physical nature of the entropy production process. By (8) and (9), we have

\begin{align*}
\left( \frac{dS}{dt} \right)_{\text{rel}} = -Nk \sum_{i} \frac{\varepsilon_i}{kT_{\ell}} \left( \frac{d\rho_i^{(\ell)}}{dt} \right)_{\text{INTERNAL}},
\end{align*}

so that (5) becomes, with the help of (6),

\begin{align*}
\frac{dS}{dt} = -Nk \sum_{\ell=1}^{M} \sum_{i} \left[ \ln \rho_i^{(\ell)} \frac{d\rho_i^{(\ell)}}{dt} + \frac{\varepsilon_i}{kT_{\ell}} \left( \frac{d\rho_i^{(\ell)}}{dt} \right)_{\text{INTERNAL}} \right].
\end{align*}

Now in the steady state, the total rates of change of the \( \rho_i^{(\ell)} \) are zero, and the rates of change of the \( \rho_i^{(\ell)} \) due to internal transitions must be just balanced by their
rates of change due to molecules passing to or from the $\ell$th container. Since
\[
\left( \frac{d \rho_i^{(\ell)}}{dt} \right)_{\text{INTERNAL}} = \sum_j \left( a_{ij}^{(\ell)} \rho_j^{(\ell)} - a_{ji}^{(\ell)} \rho_i^{(\ell)} \right),
\]
we can write, by (2), since
\[
\frac{d \rho_i^{(\ell)}}{dt} = 0,
\]
\[
\left( \frac{d \rho_i^{(\ell)}}{dt} \right)_{\text{INTERNAL}} = -b_{ii}^{(\ell-1)} \left[ \rho_i^{(\ell-1)} - \rho_i^{(\ell)} \right] - b_{ii}^{(\ell)} \left[ \rho_i^{(\ell+1)} - \rho_i^{(\ell)} \right].
\]

Thus in the steady state, the entropy production can be written in terms of the transition probabilities of molecules passing between containers as
\[
\left( \frac{d S}{dt} \right)_{\text{STEADY STATE}} = N k \sum_{\ell=1}^M \sum_i \frac{\varepsilon_i}{k T_\ell} \left\{ b_{ii}^{(\ell-1)} \left[ \rho_i^{(\ell-1)} - \rho_i^{(\ell)} \right] + b_{ii}^{(\ell)} \left[ \rho_i^{(\ell+1)} - \rho_i^{(\ell)} \right] \right\}.
\]

By again replacing $(\ell - 1)$ by $\ell$ in the $b_{ii}^{(\ell-1)}$ terms, we can write
\[
\left( \frac{d S}{dt} \right)_{\text{STEADY STATE}} = -\sum_{\ell=1}^M \sum_i N b_{ii}^{(\ell)} \left( \rho_i^{(\ell)} - \rho_i^{(\ell+1)} \right) \left( \frac{\varepsilon_i}{T_\ell} - \frac{\varepsilon_i}{T_{\ell+1}} \right),
\]
which represents the sum over all containers of the net
entropy production due to molecules passing from the $l$th to the $(l+1)$th container, whether this number be positive or negative.

The term

$$N b_{ij}^{(l)}(\rho_i^{(l)} - \rho_i^{(l+1)})$$

represents the net number of molecules passing from the $l$th to the $(l+1)$th container, and this is then multiplied by the term

$$\frac{\epsilon_i}{T_l} - \frac{\epsilon_i}{T_{l+1}}$$

which can be interpreted as the entropy produced when energy $\epsilon_i$ is received at temperature $T_l$ and deposited at temperature $T_{l+1}$. We note that if $T_l > T_{l+1}$, the entropy production is positive, for then

$$\frac{\epsilon_i}{T_l} - \frac{\epsilon_i}{T_{l+1}} < 0.$$ 

Thus in the steady state, we may conclude that the containers effectively serve no purpose as far as the entropy production process is concerned, for the final steady state entropy production expression contains no explicit reference to the containers; the temperatures in the expression are, of course, the temperatures of the heat baths. The containers serve only as a mechanism for the exchange of energy but the processes within the containers do not participate in the entropy production.


