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Extension of the Statistical Proof of the Minimum Entropy Production Theorem*

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Klein and Meijer gave a proof of the minimum entropy production in the steady state based on the principles of statistical mechanics, making use of a simple model of a nonequilibrium system. In the first part of this paper it is shown how such a proof has to be modified in case we are dealing with particles that obey Fermi-Dirac or Bose-Einstein statistics. It is found that the constraint that the total number of particles has to be constant does not have to be made. The second part of the paper describes a different generalization, *viz.* to systems in which the total number of particles is variable. Both results will serve as a description for models less restrictive than that used in the paper mentioned above.

I. INTRODUCTION

A STATE in which the entropy production is smaller than in any other state that obeys the same external contraints is identical with the steady state. This minimum principle in irreversible thermodynamics, originally formulated by Prigogine, has been studied by several authors.[1,2] A derivation by the methods of classical statistical mechanics has been given by Klein and Meijer[3] for the case of two containers filled with an ideal gas which are connected through a narrow capillary tube. Each container is kept in contact with a heat bath. One has the temperature T_1 and the other the temperature T_2.

Klein and Meijer showed that in case the relation $2(T_1-T_2)/(T_1+T_2)\ll 1$ is fulfilled, the state steady is identical with the state of minimum entropy production; this condition is consistent with Prigogine's results.[4] Klein has applied similar considerations to the Overhauser effect.[5]

The criterion of minimum entropy production as expressed in terms of statistical mechanics is certainly less practical [compare Eq. (18) in reference 3] than expressing the condition for a steady state. The latter is the statement that the time derivatives of the occupation probabilities of the different levels have to be constants, excluding oscillatory systems for the time being. However, the study of this relationship may reveal possible generalizations of the minimum-entropy principle. In order to formulate the proof for a more general situation involving, for instance, radiation quanta, lattice vibrations, or multicomponent systems, two generalizations are necessary.

The modification for particles obeying Fermi-Dirac or Bose-Einstein restrictions,[6] a situation commonly referred to as "quantum statistics," is given in Sec. II. In order to develop the expression for the entropy production, the restriction that the total number of systems is constant does not have to be used. One is free either to impose or not to impose this condition, giving only a slight modification in the later steps of the proof. The second possibility is, of course, only realized in case we deal with photons.

In order not to begin with too complicated formulas, this section starts by considering a single isolated container, a microcanonical ensemble, then describes a single container connected with a heat bath, a microcanonical ensemble. For such a system, minimum entropy (or free energy) production implies that the

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[1] I. Prigogine, *Etude Thermodynamique des Phenomenes Irreversibles* (Editions Desoer, Liege, 1947), Chap. V.
[2] S. R. de Groot, *Thermodynamics of Irreversible Processes* (North Holland Publishing Company, Amsterdam, 1951), Chap. X.
[3] M. J. Klein and P. H. E. Meijer, Phys. Rev. 96, 250 (1954).
[4] I. Prigogine, Physica 5, 272 (1949).
[5] M. J. Klein, Phys. Rev. 98, 1736 (1955).
[6] Compare, e.g., E. Schrodinger, *Statistical Thermodynamics* (University Press, Cambridge, 1952), p. 44.

system is in thermodynamic equilibrium.[7] Finally, the case of two coupled containers is considered. As a secondary result some attention is paid to the fact that the hypothesis employed by Thomsen seems to be inadequate in "quantum statistics." The much narrower assumption of microscopic reversibility, or its equivalent for a canonical ensemble, has to be used.

The next section, in which the proof of the minimum-entropy theorem is developed for a grand canonical ensemble, consists of two parts. The first deals again with a single system. This means that the container which we are considering is connected with a large particle supply that tends to keep the number of particles near a given equilibrium value. Both systems, the container and its supply, are kept at a constant temperature by a large heat bath. In the second part of this section, two such systems with slightly different temperatures and slightly different densities are connected and the entropy production calculated.

II. "QUANTUM STATISTICS"

a. Single System

The usual derivation of the distribution functions in "quantum statistics" starts out by granting Z_i levels to the energy eigenvalue ϵ_i. Z_i can either be considered as the degeneration of a discrete level or as the number of levels between ϵ_i and $\epsilon_i+d\epsilon_i$ in case the levels are continuously distributed. The latter, of course, is the case in the statistical mechanics of a many-particle system. In spite of this we will use the discrete concept because of its simplicity, and assume as usual that the results will hold in the other case too.[8]

Let us consider first a single isolated system. The description of such a system is equivalent to Thomson's proof[7] of the second law, but now modified for "quantum statistics." The equation for the rate of change of the occupation numbers, as well as the definition of the entropy, have to be modified. The first can be written[3]

$$\frac{dN_i}{dt}=\sum_i[A_{ji}N_j(Z_i+\alpha N_i)-A_{ij}N_i(Z_j+\alpha N_j)], \quad \text{(II.1)}$$

where $\alpha=0,\ 1,\ -1$ represents the Boltzmann, Bose-Einstein, and Fermi-Dirac cases. In the first case, $A_{ji}Z_i$ stands for the transition probability from the jth level to all the i levels, A_{ji} being the transition probability to one of them and Z_i the number of them.

In the Fermi-Dirac case, the number of levels has to be replaced by the number of empty levels Z_i-N_i. In the Bose-Einstein case, it is difficult to give a short argument that makes the factor Z_i+N_i plausible. We postpone a rigorous analysis until the introduction of a temperature bath.

The definition of the entropy can be written in the following form[9]:

$$S/k=\ln W=\sum_i[(N_i+\alpha Z_i)\ln(\alpha+Z_i/N_i) -\alpha Z_i\ln(Z_i/N_i)]. \quad \text{(II.2)}$$

Differentiation with respect to the time gives the entropy production

$$dS/kdt=\sum_i \dot{N}_i[\ln(\alpha+Z_i/N_i) +(1-\alpha^2)/(1-\alpha N_i/Z_i)]. \quad \text{(II.3)}$$

In the case of "quantum statistics" the last term is zero, and the restriction that the total number of particles is constant does not have to be made at this moment. Substitution of (II.1) in (II.3) expresses dS/dt as a function of the N_i's. The minimum entropy production is found if the derivatives of this function with respect to the N_i's are all equal to zero. If the total number of particles is constant an additional term, $\kappa(N-\sum_i N_i)$ should be added to the entropy production. In this case all derivatives must equal the Lagrangian multiplier κ. The terms in the resulting expression will be written out in two groups:

$$(\partial/\partial N_r)(\dot{S}/k)=\sum{}'+\sum{}''=\kappa,$$

$$\begin{aligned}\sum{}'&=-\sum_i \ln(\alpha+Z_i/N_i)(\partial/\partial N_r)\dot{N}_i\\ &=\sum_i[A_{ri}(Z_i+\alpha N_i)-\alpha A_{ir}N_i]\\ &\qquad\times\ln\frac{N_i(Z_r+\alpha N_r)}{N_r(Z_i+\alpha N_i)}, \quad \text{(II.4a)}\end{aligned}$$

$$\begin{aligned}\sum{}''&=-\sum_i \dot{N}_i(\partial/\partial N_r)\ln(\alpha+Z_i/N_i)\\ &=\sum_i\{A_{ir}(N_i/N_r)Z_r\\ &\qquad -A_{ri}Z_r(Z_i+\alpha N_i)/(Z_r+\alpha N_r)\}. \quad \text{(II.4b)}\end{aligned}$$

Under the assumption of microscopic reversibility,

$$A_{ir}=A_{ri}, \quad \text{(II.5)}$$

Eqs. (II.4) can be written in the following form:

$$\sum{}'=\sum_i A_{ri}Z_i\ln\frac{N_i(Z_r+\alpha N_r)}{N_r(Z_i+\alpha N_i)}, \quad \text{(II.4a')}$$

$$\sum{}''=\sum_i A_{ri}\frac{Z_i+\alpha N_i}{Z_r+\alpha N_r}Z_r\left[\frac{N_i(Z_r+\alpha N_r)}{N_r(Z_i+\alpha N_i)}-1\right]. \quad \text{(II.4b')}$$

This form enables us to show that

$$p_i\equiv N_i/(Z_i+\alpha N_i)=\text{constant for all } i \quad \text{(II.6)}$$

is the unique solution of (II.4).[10] This finally leads

[7] Compare J. S. Thompson, Phys. Rev. **91**, 1263 (1953), theorems 1–3.

[8] The matrix elements A_{ij} used here would have continuous varying indices and the determination of the minimum would need a functional derivative.

[9] D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, New York, 1954), p. 77.

[10] For practical reasons we repeat the arguments: Suppose the p_i's are unequal. Then there must be at least one which is the biggest $p_b=P$ and at least one which is the smallest $p_s=p$. In case we write down the Eq. (4′) for $r=b$, we find that $\kappa<0$ because the

through (II.2) to the statement that all $\dot{N}_r$ are zero (steady state).

The somewhat broader "λ hypothesis" which Thomson, Feller, and Frechet[11] used instead of Eq. (II.5), *viz.*,

$$\sum_j A_{ij}=\sum_j A_{ji}, \tag{II.5$'$}$$

does not seem to accomplish this result, as A_{ri} in Eq. (II.4b) is multiplied by $Z_i+\alpha N_i$ inside the summation sign. We do not see at present whether such a narrowing has any implication as far as physical interpretation goes. For Boltzmann statistics the λ hypothesis can be maintained by using $\sum_j A_{ij}Z_j=\sum_j A_{ji}Z_i$ instead of (II.5$'$).

For a system coupled to a temperature bath the relationship

$$A_{ij}\exp(-\mu\epsilon_i)=A_{ji}\exp(-\mu\epsilon_j),\quad (\mu=1/kT) \tag{II.7}$$

for a macrocanonical ensemble has to be used.[3,12] The result is that (II.4b) can be written

$$\sum{}''=\sum_i A_{ir}\frac{Z_i+\alpha N_i}{Z_r+\alpha N_r}\times Z_r\left[\frac{N_i(Z_r+\alpha N_r)\exp(\mu\epsilon_i)}{N_r(Z_i+\alpha N_i)\exp(\mu\epsilon_r)}-1\right]. \tag{II.4b$''$}$$

A second modification, which has to be made, is to take into account the entropy exchange between the heat bath and our system. The additional entropy production, being

$$\dot{S}/k=-(kT)^{-1}\sum_i \epsilon_i\dot{N}_i,$$

adds another term to $\sum'$, giving

$$\sum{}'=-\sum_i \ln[(\alpha+Z_i/N_i)\exp(\mu\epsilon_i)](\partial/\partial N_r)\dot{N}_i$$
$$=\sum_i[A_{ri}(Z_i+\alpha N_i)-\alpha A_{ir}N_i]\times\ln\frac{N_i(Z_r+\alpha N_r)\exp(\mu\epsilon_i)}{N_r(Z_i+\alpha N_i)\exp(\mu\epsilon_r)}. \tag{II.4a$''$}$$

A different formulation of this step would be to say that, for a macrocanonical ensemble, the free-energy production has to be minimized. One starts out with the equation

$$-\mu F=\ln W-\mu\sum_i N_i\epsilon_i \tag{II.8}$$

and goes through the same procedure. Either way the minimum condition for the total (i.e., internal plus external) entropy or the free-energy production for a macroscopic ensemble is expressed by the following set of equations

$$\kappa=\sum_i A_{ir}\frac{Z_i+\alpha N_i}{Z_r+\alpha N_r}Z_r\left[\frac{N_i(Z_r+\alpha N_r)\exp(\mu\epsilon_i)}{N_r(Z_i+\alpha N_i)\exp(\mu\epsilon_r)}-1\right]$$
$$+\sum_i[A_{ri}(Z_i+\alpha N_i)-\alpha A_{ir}N_i]\times\ln\frac{N_i(Z_r+\alpha N_r)\exp(\mu\epsilon_i)}{N_r(Z_i+\alpha N_i)\exp(\mu\epsilon_r)},\quad (r=1,2,3\cdots). \tag{II.9}$$

We introduce the quantity

$$p_i=[N_i/(Z_i+\alpha N_i)]\exp(\mu\epsilon_i), \tag{II.10}$$

and we see that: $p_i=$constant, say λ (for all i), is a possible solution, making the right-hand side of the equation equal to zero for every value of r. The result

$$N_i/Z_i=1/(\lambda^{-1}e^{\mu\epsilon_i}-\alpha) \tag{II.11}$$

shows us that λ, the so-called absolute activity, has to be a positive quantity. We shall restrict ourselves to the group of solutions for which $p_i>0$, i.e., $Z_i-N_i>0$ in the Fermi-Dirac case. Actually this is nothing but the convention that only those initial conditions shall be given for which $Z_i>N_i$. One sees that the "equations of motion" (II.1) are unable to transfer distributions for which $N_i(t_1)<Z_i$ into those for which $N_i(t_2)>Z_i$ and reverse.

We now want to show that our solution is unique. For $\alpha=0$ or -1, we may go through the same type of argument that unequal p_i's lead to a contradiction. For $\alpha=1$, the proof has to be modified as follows. Equation (II.9) can be written as

$$\kappa+\sum_i A_{ir}N_i\ln(p_i/p_r)=\sum_i A_{ir}\frac{Z_i+\alpha N_i}{Z_r+\alpha N_r}Z_r\left(\frac{p_i}{p_r}-1\right)+\sum_i A_{ri}(Z_i+\alpha N_i)\ln(p_i/p_r).$$

sums contain only terms which are negative or zero. In case of $r=s$, however, we find $\kappa>0$, which leads to a contradiction as κ is independent of r. Because we assumed that the coefficients of the logarithm and the square bracket are positive, the restriction $Z_i>N_i$ has to be made. This point is discussed later in the paper.

[11] Reference 7, note 10.

[12] To show the relationship (II.7) as well as the factor $Z+\alpha N$ in Eq. (II.1), we take Eq. (A1.706) of ter Haar[9] and interpret the states k and l as applying to a reservoir with Boltzmann distribution ($\alpha=0$) and the states i and j as applying to the system in consideration, which is either Bose-Einstein or Fermi-Dirac depending on α. Thus we obtain

$$\frac{dN_i}{dt}=\sum_{jkl}A_{kilj}\{N_lN_jZ_k(Z_i+\alpha N_i)-N_kN_iZ_l(Z_j+\alpha N_j)\}.$$

Making the substitutions

$$N_l=BZ_l\exp(-\mu\epsilon_l),$$
$$N_k=BZ_k\exp(-\mu\epsilon_k),$$

we find (II.1), where

$$A_{ji}=B\sum_{kl}A_{kilj}Z_lZ_k\exp(-\mu\epsilon_l),$$

$$A_{ij}=B\sum_{kl}A_{kilj}Z_kZ_l\exp(-\mu\epsilon_k).$$

Under the assumption that energy is conserved in the transition processes, $\epsilon_l-\epsilon_k=\epsilon_i-\epsilon_j$, (II.7) follows from this result.

I would like to thank Dr. Callen for this derivation.

For $r=b$, we have

$$\kappa+\sum_i A_{ib}\ln(p_i/P)<0,$$

with the result that $\kappa<0$ because the terms in the sum on the left hand side are all negative or zero. In the same way one can show $\kappa>0$, and we see again that the supposition of unequal p_i's leads to a contradiction.

We would like to make again a side remark on the necessary condition (II.7). In case of Boltzmann statistics it can be shown that

$$\sum_j A_{ij}Z_j\exp(-\mu\epsilon_i)=\sum_j A_{ji}Z_j\exp(-\mu\epsilon_j) \quad \text{(II.7}')$$

is sufficient, but in F.D. and B.E. statistics this restriction is too narrow. We did not investigate whether (II.7) is a sufficient condition.

We would like to remark that the quantum statistical case is not a modification of the Boltzmann case in the sense that the proof can be obtained by a simple transformation of the proof already given. If one substitutes p_i instead of N_i with the help of (II.6) or (II.10) into the equations of motion (II.1) and the entropy definition (II.2), the result is neither equal nor analogous to the Boltzmann case.

b. Coupled Systems

The equations of motion for two coupled systems at slightly different temperatures T_1 and T_2 are

$$\begin{aligned}\frac{dN_i}{dt}-\left(\frac{dN_i}{dt}\right)_{\text{internal}} &=B_{ii}\{M_i(Z_i+\alpha N_i)-N_i(X_i+\alpha M_i)\}\\ &=B_{ii}(M_iZ_i-N_iX_i),\\ \frac{dM_i}{dt}-\left(\frac{dM_i}{dt}\right)_{\text{internal}} &=B_{ii}\{N_i(X_i+\alpha M_i)-M_i(Z_i+\alpha N_i)\}\\ &=B_{ii}(N_iX_i-M_iZ_i).\end{aligned} \quad \text{(II.1}')$$

N_i is the number of particles in the ith energy level of the first system, M_i the same of the second system, Z_i and X_i the degeneracies of the levels in the first and second systems, respectively. Minimizing the entropy production under the condition that the total number of particles is kept constant, leads to

$$\begin{aligned}\kappa=\sum_i A_{ri}\frac{Z_i+\alpha N_i}{Z_r+\alpha N_r}Z_r\left(\frac{p_i}{p_r}-1\right) &+\{A_{ri}(Z_i+\alpha N_i)-\alpha A_{ir}\}\ln\frac{p_i}{p_r}\\ &+B_{rr}X_r\ln\frac{(Z_r+\alpha N_r)M_r}{(X_r+\alpha M_r)N_r}\\ &+B_{rr}Z_r\left(\frac{M_r}{N_r}-\frac{X_r+\alpha M_r}{Z_r+\alpha N_r}\right),\end{aligned} \quad \text{(II.12)}$$

and a second set of equations in which Z_i is replaced by X_i, N_i by M_i and A_{ij} by C_{ij}, the internal transition probabilities of the second system. The important difference between A and C is that in the symmetry relationship (7) the temperature T has the value T_1 in the first case and T_2 in the second case. We have introduced as a shorthand

$$p_i=N_i\exp(\mu_1\epsilon_i)/(Z_i+\alpha N_i),$$
$$q_i=M_i\exp(\mu_2\epsilon_i)/(X_i+\alpha M_i).$$

In order to show the sufficiency of our theorem, we first remark that in the steady state $(dN_i/dt=dM_i/dt=0)$ the first group of terms plus the last one equal zero. This result is trivial as these terms originate from

$$\sum_i(dN_i/dt)(\partial/\partial N_r)\ln(\alpha+Z_i/N_i)=Z_r(dN_r/dt)/(Z_r+\alpha N_r)N_r.$$

We will show that the remaining terms are approximately equal to the ones just mentioned, and so their sum is also equal to zero, at least in first approximation. We make the assumptions that $p_i=p_r+\rho_{ir}$ (and a similar equation for q: $q_i=q_r+\sigma_{ir}$), where ρ and σ are small compared to p and q. This is a consequence of our considerations in Sec. IIa, in which we showed that the equation $p_i=$ constant holds for thermodynamic equilibrium, and the fact that our coupled system is near equilibrium: $2(T_1-T_2)/(T_1+T_2)\ll 1$. As a result, we find for the second term

$$\begin{aligned}\sum_i(Z_i+\alpha N_i)A_{ri}\{1-\alpha(p_r+\rho_{ir})\exp(-\mu_1\epsilon_r)\}&\times\ln(1+\rho_{ir}/p_r)\\ &\approx\sum_i\frac{Z_i+\alpha N_i}{Z_r+\alpha N_r}A_{ri}Z_i\{(p_i/p_r)-1\}.\end{aligned}$$

In order to make the last two terms of (12) equal to each other, the assumptions $Z_r=X_r$ and $N_r=M_r+\delta_r$ have to be made. The result is that all the equations can be satisfied with $\kappa=0$.

The necessity part of the proof makes use of the same considerations to show that (II.12) can be written as

$$\begin{aligned}\kappa(Z_i+\alpha N_i)N_i/Z_i&=2(dN_i/dt),\\ \kappa(Z_i+\alpha M_i)M_i/Z_i&=2(dM_i/dt).\end{aligned} \quad \text{(II.13)}$$

The sum of all these equations is

$$\sum_i\{N_i+M_i+\alpha(M_i^2+N_i^2)/Z_i\}\kappa=0.$$

The coefficients of κ could only be zero in the Fermi-Dirac case, but our restriction to distributions with $Z_i>N_i$ prevents this. So κ must be zero, and that implies the steady state according to (II.13).

III. GRAND CANONICAL ENSEMBLE

A. Single Systems

In considering a variable number of particles, as for instance the case in a thermal-diffusion process, we encounter two complications. The first is the fact that a state, which in the microcanonical case gets merely a label, and which in the macrocanonical ensemble has a label that characterizes the energy value, now has to be described by at least two indices. One indicates the energy value and a second, say α, represents the number of particles N_α in that state. So most of the sums will be double sums, as for instance in the equations of motion, which become in the Boltzmann case (dealing only with one type of particles):

$$dp_{i\alpha}/dt=\sum_{j\beta}(A_{j\beta,\,i\alpha}p_{j\beta}-A_{i\alpha,\,j\beta}p_{i\alpha}), \qquad \text{(III.1)}$$

where $p_{i\alpha}$ is the probability that the particle has the energy ϵ_i and is part of a system containing N_α particles in total. A second point of consideration is the fact that the entropy cannot be defined for an undetermined number of particles. The number of particles is not, however, completely arbitrary because there is a tendency towards an equilibrium number of particles and this tendency should be expressed in our formulas.

A macrocanonical grand ensemble can be looked upon as a part of a bigger ensemble consisting of a large number M of repetitions of the original one. The $(M-1)$ repetitions form the particle supply that tends to keep the number of particles near a given equilibrium value. The total number of particles of this large system is constant and the probability for finding N_α particles in a subdivision is given by $W_\alpha \propto \lambda^{N_\alpha}$, which gives

$$\ln W_\alpha = N_\alpha \ln\lambda + \text{const.}$$

We will postulate now that the entropy contribution is found by taking the weighted sum over all configurations,

$$\Delta S/k=\sum_\alpha p_\alpha \ln W_\alpha=\sum_\alpha p_\alpha N_\alpha \ln\lambda, \qquad \text{(III.2)}$$

where $p_\alpha=\sum_i p_{i\alpha}$ is the probability for a particular configuration. The quantity λ is called the activity and the symbol $\nu=\ln\lambda$ will be introduced. The large supply system, which tries to maintain the equilibrium concentration has been called an activity bath[13] in comparison with a temperature bath. This analogy is quite close, as kT is equal to the total energy of system plus bath divided by the number of copies [compare Appendix of reference 3] and the activity is equal to the total number of particles divided by the number of copies: $\lambda=M\bar{N}/M=\bar{N}$.

A different way to establish (III.2) is to look for the generalization of Eq. (II.8). The quantity to minimize for macrocanonical grand ensembles will be Kramers' grand potential[14]:

$$q=\ln W-\mu\sum_i N_i\epsilon_i+\nu' N. \qquad \text{(III.3)}$$

The use of N as a label and as the number of particles may cause confusion later, and we change to the probability notation used in reference 3:

$$\ln W=-\sum_{i\alpha}\bar{N}p_{i\alpha}\ln(\bar{N}p_{i\alpha})$$
$$=-\bar{N}\sum_{i\alpha}p_{i\alpha}\ln p_{i\alpha}+\text{const},$$
$$N_{i\alpha}=\bar{N}p_{i\alpha};\quad N=\sum_{i\alpha}p_{i\alpha}N_\alpha.$$

Now we can rewrite (III.3) as follows:

$$q=-\bar{N}\sum_{i\alpha}p_{i\alpha}(\ln p_{i\alpha}+\mu\epsilon_i-\nu N_\alpha);\quad \nu=\nu'/\bar{N}. \qquad \text{(III.3}')$$

The q production or the total entropy production should be minimized. The derivative of $\dot{q}$, using (III.2) is

$$\frac{\partial\dot{q}}{\partial p_{r\rho}}=\bar{N}\left[\sum_{i\alpha}\left(A_{j\beta,\,i\alpha}\frac{p_{i\alpha}}{p_{r\rho}}-A_{r\rho,\,j\beta}\right)\right.$$
$$\left.+\sum_{i\alpha}A_{r\rho,\,i\alpha}\ln\frac{p_{i\alpha}\exp(\mu\epsilon_i-\nu N_\alpha)}{p_{r\rho}\exp(\mu\epsilon_r-\nu N_\rho)}\right]. \qquad \text{(III.4)}$$

We are able to prove the second law along the same lines, if we use a relation similar to (II.7),[15] *viz.*,

$$A_{i\alpha,\,j\beta}\exp(-\mu\epsilon_i+\nu N_\alpha)$$
$$=A_{j\beta,\,i\alpha}\exp(-\mu\epsilon_j+\nu N_\beta), \qquad \text{(III.5)}$$

the minimum being obtained for a distribution

$$p_{i\alpha}\exp(\mu\epsilon_i-\nu N_\alpha)=C, \qquad \text{(III.6)}$$

where C is a constant. If we impose the condition that $p_{i\alpha}$, summed over all i:

$$\sum_i p_{i\alpha}=p_\alpha=C\sum_i e^{-\mu\epsilon_i}\exp(\nu N_\alpha)=CZ\exp(\nu N_\alpha),$$

and over all configurations:

$$\sum_{\text{conf}}p_\alpha=\sum\frac{p_\alpha}{N_\alpha!}=CZ\sum_N\frac{\exp(\nu N_\alpha)}{N_\alpha!}=CZ\exp(e^\nu),$$

should be equal to one, the constant in (III.6) is

$$1/C=Z\exp(\bar{N}\lambda).$$

B. Coupled Systems

In order to prove the minimum entropy production in the steady state for two coupled systems, we will proceed along the same lines as in reference 3. The

[13] See reference 9, Chap. VI, Sec. 1.

[14] H. A. Kramers, *Collected Scientific Papers* (North Holland Publishing Company, Amsterdam, 1956), p. 738 [Proc. Acad. Sci. Amsterdam **41**, 10 (1938)].

[15] This relation has also been established by ter Haar, reference 9, Appendix II, Eq. (A2.113).

equations of motion (III.1) are now

$$dp_{i\alpha}/dt=\sum_{j\beta}(A_{j\beta,\,i\alpha}p_{j\beta}-A_{i\alpha,\,j\beta}p_{i\alpha})+\sum_{\gamma}(B_{i\gamma,\,i\alpha}q_{i\gamma}-B_{i\alpha i\gamma}p_{i\alpha}),\quad \text{(III.7a)}$$

$$dq_{i\alpha}/dt=\sum_{j\beta}(C_{j\beta i\alpha}q_{j\beta}-C_{i\alpha,\,j\beta}q_{i\alpha})+\sum_{\gamma}(B_{i\gamma i\alpha}p_{i\gamma}-B_{i\alpha i\gamma}q_{i\alpha}),\quad \text{(III.7b)}$$

with the difference that the B's are not entirely diagonal. In case of the petit ensemble the b's were chosen diagonal, accounting for the fact that there would be no energy loss or gain during transfer from one vessel to the other. With regard to the second index, however, the situation is such that the initial state in the other container may have a different number of particles. Also $B_{i\alpha i\gamma}=B_{i\gamma i\alpha}$ will be assumed, which means that there are no other "forces" besides temperature gradient and activity difference.

The entropy production is, apart from the terms for each separate system, mentioned in (III.3′):

$$\Delta(\dot{S}/k)=(\dot{S}/k)-(\dot{S}/k)_{\text{system I}}-(\dot{S}/k)_{\text{system II}}=\sum_i[\sum_{\alpha\gamma}(\ln q_{i\gamma}-\ln p_{i\alpha})B_{i\alpha,\,i\gamma}p_{i\alpha}+\sum_{\alpha\gamma}(\ln p_{i\gamma}-\ln q_{i\alpha})B_{i\alpha,\,i\gamma}q_{i\alpha}],\quad \text{(III.8)}$$

and extra terms in the derivative due to the coupling are

$$\frac{\partial}{\partial p_{r\rho}}\left(\frac{\Delta\dot{S}}{k}\right)=\sum_{\gamma}B_{r\gamma r\rho}\left(\frac{q_{r\gamma}}{p_{r\gamma}}-1\right)+\sum_{\gamma}B_{r\rho r\gamma}\ln\frac{q_{r\gamma}}{p_{r\gamma}},\quad \text{(III.9)}$$

and the same type of expression for $q_{r\rho}$.

The assumptions that the temperatures and ν_1 and ν_2 are nearly the same, and that both systems are nearly in equilibrium, lead to the equations

$$\frac{p_{i\alpha}\exp(\mu_1\epsilon_i-\nu_1N_\alpha)}{p_{j\beta}\exp(\mu_1\epsilon_j-\nu_1N_\beta)}=1+\rho_{i\alpha,\,j\beta},\quad \text{(III.10a)}$$

$$\frac{q_{i\alpha}\exp(\mu_2\epsilon_i-\nu_2N_\alpha)}{q_{j\beta}\exp(\mu_2\epsilon_i-\nu_2N_\beta)}=1+\sigma_{i\alpha,\,j\beta},\quad \text{(III.10b)}$$

$$q_r/p_r=1+\delta_r.\quad \text{(III.10c)}$$

Under these restrictions, it is possible to rewrite the equations of motion (III.7) for the steady state (that is the state in which all time derivatives are zero) in the form

$$\sum_{j\beta}A_{i\alpha j\beta}\ln\frac{p_{j\beta}\exp(\mu_1\epsilon_j-\nu_1N_\beta)}{p_{i\alpha}\exp(\mu_1\epsilon_i+\nu_1N_\alpha)}=-\sum_{\gamma}B_{i\alpha i\gamma}\ln\frac{q_{i\gamma}}{p_{i\alpha}}.$$

Substituting this and (III.9) into the conditions for minimum entropy production

$$\partial\dot{S}/\partial p_{r\rho}=\kappa;\quad \partial\dot{S}/\partial q_{r\rho}=\kappa,$$

we find that these are satisfied for all r and ρ with $\kappa=0$.

The proof of the reverse, i.e., given the state of minimum entropy production then the state will be steady, can also be given along the same lines.

C. Entropy Production

Finally we will determine the amount of entropy produced in this state. With the help of (III.8) and the time derivative of (III.3′), we find

$$\dot{S}/k=-\bar{N}[\sum_{i\alpha}\dot{p}_{i\alpha}\ln p_{i\alpha}+\dot{q}_{i\alpha}\ln q_{i\alpha}+(\mu_1\epsilon_i-\nu_1N_\alpha)(\dot{p}_{i\alpha})_{\text{int}}+(\mu_2\epsilon_i-\nu_2N_\alpha)(\dot{q}_{i\alpha})_{\text{int}}],\quad \text{(III.11)}$$

where $(\dot{p}_{i\alpha})_{\text{int}}$ is given by (III.1) and $(\dot{q}_{i\alpha})_{\text{int}}$ by an equation similar to (III.1). Substituting the steady-state conditions $\dot{p}_{i\alpha}=0$, $\dot{q}_{i\alpha}=0$, gives with the help of (III.7)

$$\dot{S}/k=\bar{N}\sum_{i\alpha}[(\mu_1\epsilon_i-\nu_1N_\alpha)\sum_{\gamma}B_{i\gamma i\alpha}(q_{i\gamma}-p_{i\alpha})+(\mu_2\epsilon_i-\nu_2N_\alpha)\sum_{\gamma}B_{i\gamma i\alpha}(p_{i\gamma}-q_{i\alpha})].\quad \text{(III.12)}$$

An interpretation of this equation can be given, if we make some restrictions on the B's. It is clear that (III.12) now is the generalization of a well-known thermodynamical expression for the entropy production[16]:

$$S=\bar{W}\,\text{grad}(1/T)-J\,\text{grad}(g/T)=\sum_{i=1,2}J_iX_i.\quad \text{(III.13)}$$

Suppose $B_{i\alpha,\,i\gamma}=\delta_{\alpha\gamma}C$, where C is independent of i or α; we find

$$\dot{S}/k=B\sum_{i\alpha}(\bar{N}q_{i\alpha}\epsilon_i-\bar{N}p_{i\alpha}\epsilon_i)(\mu_1-\mu_2)-B\sum_{i\alpha}(q_{i\alpha}N_\alpha-p_{i\alpha}N_\alpha)(\nu_1'-\nu_2')=B[(\bar{\epsilon})_1-(\bar{\epsilon})_2](\mu_1-\mu_2)-B[(\bar{N})_1-(\bar{N})_2](\nu_1'-\nu_2').\quad \text{(III.14)}$$

In case we use the picture of two containers connected with a narrow tube, B can be considered a transition probability per unit area and $B(\epsilon_1-\epsilon_2)$ can be interpreted as an energy current $\bar{W}$ (flux J_1). In the same way the coefficient of $\nu_1'-\nu_2'$ can be read as a particle current J (flux J_2). The "forces" or affinities X_1 and X_2 are grad$(1/T)$ and grad(g/T) after multiplication of (III.14) with the Boltzmann constant. ($g=kT\nu'$ is the thermal potential.)

[16] K. G. Denbigh, *The Thermodynamics of the Steady State* (Methuen and Company, Ltd., London, 1951), p. 57.