Entropy Generation Rate in a Chemically Reacting System

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For a nonchemical-equilibrium state of an isolated system A *that has* r *constituents with initial amounts* $\mathbf{n}_a = \{n_{1a}, n_{2a}, \ldots, n_{ra}\}$, *and that is subject to* τ *chemical reaction mechanisms, temperature, pressure, and chemical potentials cannot be defined. As time evolves, the values of the amounts of constituents vary according to the stoichiometric relations* $n_i(t) = n_{ia} + \Sigma_{j=1}^{\tau} \nu_i^{(j)} \epsilon_j(t)$, *where* $\nu_i^{(j)}$ *is the stoichiometric coefficient of the* ith *constituent in the* j-*reaction mechanism and* $\epsilon_j(t)$ *the reaction coordinate of the* jth *reaction at time* t. *For such a state, we approximate the values of all the properties at time* t *with the corresponding properties of the stable equilibrium state of a surrogate system* B *consisting of the same constituents as* A *with amounts equal to* $n_i(t)$ *for* i = 1, 2, . . . , r, *but experiencing no chemical reactions. Under this approximation, the rate of entropy generation is given by the expression* $\dot{S}_{irr} = \dot{\epsilon} \cdot \mathbf{Y}$, *where* $\dot{\epsilon}$ *is the row vector of the* τ *rates of change of the reaction coordinates,* $\dot{\epsilon} = \{\dot{\epsilon}_1, \ldots, \dot{\epsilon}_\tau\}$, $\mathbf{Y}$ *the column vector of the* τ *ratios* $\mathcal{C}_j / T_{off}$ *for* j = 1, 2, . . . , τ, $\mathcal{C}_j = -\Sigma_{i=1}^{r} \nu_i^{(j)} \mu_{i,off}$, *that is, the* jth *affinity of the stable equilibrium state of the surrogate system* B, $\mu_{i,off}$ *and* T_{off} *are the chemical potential of the* ith *constituent and the temperature of the stable equilibrium state of the surrogate system. Under the same approximation, by further assuming that* $\dot{\epsilon}$ *can be represented as a function of* $\mathbf{Y}$ *only that is,* $\dot{\epsilon}(\mathbf{Y})$, *with* $\dot{\epsilon}(0) = 0$ *for chemical equilibrium, we show that* $\dot{\epsilon} = \mathbf{L} \cdot \mathbf{Y} + $ *(higher order terms in* $\mathbf{Y}$*), where* $\mathbf{L}$ *is a* $\tau \times \tau$ *matrix that must be non-negative definite and symmetric, that is, such that the matrix elements* L_{ij} *satisfy the Onsager reciprocal relations,* $L_{ij} = L_{ji}$. *It is noteworthy that, for the first time, the Onsager relations are proven without reference to microscopic reversibility. In our view, if a process is irreversible, microscopic reversibility does not exist.*

1 Introduction

In authoritative discussions [1–3] of chemical equilibrium among r constituents of a system A, the conditions of equilibrium in the presence of τ chemical reaction mechanisms is presumably shown to be

$$\sum_{i=1}^{r} \nu_i^{(j)} \mu_i (U,V,n_1,n_2, \ldots, n_r) = 0 \quad \text{for } j = 1,2, \ldots, \tau \quad (1)$$

where $\nu_i^{(j)}$, for i = 1, 2, . . . , r and j = 1, 2, . . . , τ, is the ith stoichiometric coefficient of the jth chemical reaction mechanism

$$\sum_{i=1}^{r} \nu_i^{(j)} A_i = 0 \quad (2)$$

A_i denotes the ith constituent, μ_i the chemical potential of the ith constituent, U the internal energy, V the volume, n_1, n_2, . . . , n_r are the amounts of constituents given by the relations

$$n_i = n_{ia} + \sum_{j=1}^{\tau} \nu_i^{(j)} \epsilon_j \quad \text{for } i = 1,2, \ldots, r \quad (3)$$

and n_{ia}, for i = 1, 2, . . . , r, is the amount of the ith constituent for which the values of the reaction coordinates ϵ_1, ϵ_2, . . . , ϵ_τ are all equal to zero.

For given values of U, V, n_{1a}, n_{2a}, . . . , n_{ra}, and $\nu_i^{(j)}$, for i = 1, 2, . . . , t and j = 1, 2, . . . , τ, the τ conditions (1) yield the values ϵ_{1o}, ϵ_{2o}, . . . , $\epsilon_{\tau o}$, for which the system is in a chemical equilibrium (stable equilibrium) state. Thus, at the chemical equilibrium state, the amounts of constituents are given by the relations

$$n_{io} = n_{ia} + \sum_{j=1}^{\tau} \nu_i^{(j)} \epsilon_{jo} \quad \text{for } i = 1,2, \ldots, r \quad (4)$$

and the corresponding mole fractions or composition by the relations

$$y_{io} = \frac{n_{ia} + \Sigma_{j=1}^{\tau} \nu_i^{(j)} \epsilon_{jo}}{n_a + \Sigma_{j=1}^{\tau} \nu^{(j)} \epsilon_{jo}} \quad \text{for } i = 1,2, \ldots, r \quad (5)$$

where $n_a = \Sigma_{i=1}^{r} n_{ia}$ for $\nu^{(j)} = \Sigma_{i=1}^{r} \nu^{(j)}$.

In the discussions just cited [1–3], it is also stated that conditions (1) result from the requirement that, for an isolated system, the value of the sum $\Sigma_{i=1}^{r} \mu_i (U, V, \mathbf{n}) \, dn_i$ at the chemical equilibrium state must be zero for any variations of the amounts of constituents compatible with the stoichiometries of the reaction mechanisms.

Even though experience shows that conditions (1) lead to results consistent with observations, their derivation and meaning are problematic. According to the second law [4], an isolated system with one or more chemical reactions, and given values of U, V, n_{1a}, n_{2a}, . . . , n_{ra} admits one and only one stable equilibrium state. This state is characterized by a unique composition. Any composition that deviates from that of the stable equilibrium state corresponds to a state that is not stable equilibrium, and, therefore, chemical potentials cannot be defined. So, what functions $\mu_i(U, V, n_1, n_2, . . . , n_r)$ should be used in conditions (1) in order to find the ϵ_{jo}s and the chemical equilibrium state?

We investigate this question in references [5 and 6] and find a satisfactory answer for any system A that is simple. For such a system, the chemical potentials appearing in conditions (1) are those of a surrogate simple system B, consisting of the same constituents as A, but experiencing no chemical reactions [5]. In this paper, we summarize our findings about system A and its surrogate system B because the ideas are not widely known yet.

Then we use the expression for the entropy of the stable equilibrium states of B, and estimate the rate of entropy generation in a simple system A with τ chemical reaction mechanisms. It turns out that, for states that are not too far from chemical equilibrium, the estimate is a quadratic form in the τ rates of change of the reaction coordinates.

Finally, we write the rate of change of each reaction coordinate as a function of the affinities. We show that the linear parts of these functions have coefficients that satisfy Onsager reciprocal relations. In contrast to other derivations, for the first time the proof of the reciprocal relations is achieved without use of the concept of microscopic reversibility. This is a confirmation of our view that irreversibility is a physical rather than a statistical phenomenon, and that mircoscopic reversibility does not apply to irreversible processes.

The paper is organized as follows: in Section 2 we provide a summary of the concept of a surrogate system, and the derivations of conditions (1); in Section 3 we express the rate of entropy generation in a system A with τ chemical reaction mechanisms in terms of the rates of change of the reaction coordinates; in Section 4 we express each rate of change of a reaction coordinate as a function of the affinities, and show that the linear parts of these functions have coefficients that satisfy Onsager reciprocal relations; in Section 5 we present our conclusions.

2 Chemical Equilibrium States of a Simple System

We define a system as simple [6] if it has volume as the only parameter, and if it satisfies the following two additional requirements:

(a) If in any of its stable equilibrium states it is partitioned into a set of contiguous subsystems in mutual stable equilibrium, the system is such that the effects of the partitions are negligible.

(b) In any of its stable equilibrium states, the instantaneous switching on or off of one or more internal reaction mechanisms, such as a chemical reaction, causes negligible instantaneous changes in the values of the energy, the entropy, the volume, and the amounts of constituents.

In general, either the introduction of partitions, or the instantaneous switching on or off of chemical reaction mecha-

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Nomenclature

A = system

A_i = ith constituent in chemical reaction mechanism

$\mathcal{C}_j$ = $-\Sigma_{i=1}^r \nu_i^{(j)} \mu_{i,\text{off}}$

A_ϵ = state of system A that has same values of energy, volume, and amounts of constituents as stable equilibrium state of surrogate system B having amounts $n_i = n_{ia} + \Sigma_{j=1}^\tau \nu_i^{(j)} \epsilon_j$ for $i = 1, 2, . . . , r$

A_{ϵ_o} = chemical equilibrium state of system A

B = surrogate system of A

$\mathbf{L}$ = $\tau \times \tau$ matrix with elements L_{ij}

L_{ij} = $(\partial \dot{\epsilon}_k / \partial Y_l)_{U,V,\mathbf{n}_a,\nu,\mathbf{Y}=0}$

$\mathbf{n} = \mathbf{n}(t)$ = $\{n_1, n_2, . . . , n_r\}$

$\mathbf{n}_a$ = $\{n_{1a}, n_{2a}, . . . , n_{ra}\}$

n_a = $\Sigma_{i=1}^r n_{ia}$

n_i, $n_i(t)$ = amount of ith constituent at time t

n_{ia} = amount of ith constituent for which values of all reaction coordinates are zero

n_{io}, $n_{io}(U, V, \mathbf{n}_a; \nu)$ = amount of ith constituent at chemical equilibrium state of system A

p_{off} = pressure of surrogate system B

r = no. of constituents

S, $S(t)$ = entropy of system A at time t

S_ϵ = entropy of state A_ϵ

S_{irr} = rate of entropy generation in system A

S_{off}, $S_{\text{off}}(U, V, \mathbf{n})$ = entropy of stable equilibrium states of surrogate system B

$S(U, V, \mathbf{n}_a; \nu)$ = entropy of chemical equilibrium states of A

t = time

T_{off} = temperature of surrogate system B

$\mathbf{Y}$ = column vector of τ ratios $\mathcal{C}_j / T_{\text{off}}$ for $j = 1, 2, . . . , \tau$

Y_j = $\mathcal{C}_j / T_{\text{off}}$

$\mathbf{Y}^t$ = row vector of τ ratios $\mathcal{C}_j / T_{\text{off}}$ for $j = 1, 2, . . . , \tau$

y_{io} = mole fraction of ith constituent of chemical equilibrium state of system A

U = internal energy

V = volume

$\epsilon = \epsilon(t)$ = $\{\epsilon_1, \epsilon_2, . . . , \epsilon_\tau\}$

$\dot{\epsilon}$, $\dot{\epsilon}(\mathbf{Y})$ = row vector of τ rates of change of reaction coordinates

ϵ_j, $\epsilon_j(t)$ = reaction coordinate of jth reaction mechanism at time t

$\dot{\epsilon}_j$ = rate of change of jth reaction coordinate

ϵ_{jo}, $\epsilon_{jo}(U, V, \mathbf{n}_a; \nu)$ = value of jth reaction coordinate for which system A is in chemical equilibrium state

ϵ_o = $\{\epsilon_{1o}, \epsilon_{2o}, . . . , \epsilon_{\tau o}\}$

μ_i, $\mu_i(U, V, \mathbf{n})$ = chemical potential of ith constituent

$\mu_{i,\text{off}}$ = chemical potential of ith constituent of surrogate system B

ν = $\{\nu_i^{(j)}$ for $i = 1, 2, . . . , r$ and $j = 1, 2, . . . , \tau\}$

$\nu_i^{(j)}$ = stoichiometric coefficient of ith constituent in jth chemical reaction mechanism

$\nu^{(j)}$ = $\Sigma_{i=1}^r \nu_i^{(j)}$

τ = no. of chemical reaction mechanisms

nisms, or both have definite effects on the system. These effects become less and less important, and negligible for all practical purposes, if the value of the amount of each constituent is larger than a small number. Hence, the definition of a simple system is applicable only to systems with large values of the amounts of constituents.

Now, let us consider a simple system A consisting of r constituents, and subject to τ chemical reaction mechanisms, and having given values U of the energy, and V of the volume, and values $n_1, n_2, \ldots, n_r$ of the amounts of constituents that are obtained from given values $n_{1a}, n_{2a}, \ldots, n_{ra}$, as a result of the τ reaction mechanisms. Such a system admits a very large number of states. But the second law requires that among all these states one and only one be stable equilibrium—the chemical equilibrium state. At this state, the values of the amounts of constituents, $n_{1o}, n_{2o}, \ldots, n_{ro}$, and the corresponding values of the reaction coordinates, ϵ_{jo} for $j = 1, 2, \ldots, \tau$, satisfy Eq. (4).

The values U, V, $\mathbf{n}_a = \{n_{1a}, n_{2a}, \ldots, n_{ra}\}$, and the stoichiometric coefficients $\nu = \{\nu_i^{(j)}$ for $i = 1, 2, \ldots, r$ and $j = 1, 2, \ldots, \tau\}$ determine uniquely the values of all the properties and quantities that characterize the chemical equilibrium state, including the values of the entropy, S, the reaction coordinates $\epsilon_o = \{\epsilon_{1o}, \epsilon_{2o}, \ldots, \epsilon_{\tau o}\}$, and each n_{io}. We write the dependences of the latter quantities in the forms

$$S = S(U, V, n_a; \nu) \tag{6}$$

$$\epsilon_{jo} = \epsilon_{jo}(U, V, \mathbf{n}_a; \nu) \quad \text{for } j = 1, 2, \ldots, \tau \tag{7}$$

$$n_{io} = n_{io}(U, V, \mathbf{n}_a; \nu) \quad \text{for } i = 1, 2, \ldots, r \tag{8}$$

In general, we cannot find the explicit functional forms of Eqs. (6) to (8). For simple systems, however, we can express chemical equilibrium properties in terms of stable equilibrium properties of a multiconstituent system in which the chemical reaction mechanisms are inhibited—switched off. To see how this is done, we proceed as follows [5].

First, we consider a simple system B consisting of the same r types of constituents as system A, but with all chemical reaction mechanisms inhibited—switched off. We call B the surrogate of A. Of course, A and B are different systems because they are subject to different internal forces and constraints. We assume that B is in a stable equilibrium state with values U of the energy, V of the volume, and $\mathbf{n} = \{n_1, n_2, \ldots, n_r\}$ of the amounts of constituents of its r constituents. We denote the entropy at that stable equilibrium state by S_{off}, where we use the subscript "off" to emphasize that the reaction mechanisms are switched off. By virtue of the state principle, S_{off} depends only on U, V, $\mathbf{n}$; that is,

$$S_{\text{off}} = S_{\text{off}}(U, V, \mathbf{n}) \tag{9}$$

Next, we assume that the chemical reaction mechanisms are instantly switched on, that is, the reactions defined by the stoichiometric coefficients ν are no longer inhibited. As a result, we obtain again system A.

By virtue of the definition of a simple system, switching on of the chemical reaction mechanisms causes negligible instantaneous changes in the values of entropy, energy, volume, and amounts of constituents. Accordingly, immediately after switching on the reaction mechanisms, the state of system A has the same values of S, U, V, $n_1, n_2, \ldots, n_r$ as the corresponding values of the stable equilibrium state of the surrogate system B. In general, however, this state of A is not stable equilibrium.

Among all the states of A that may be obtained from B in the manner just cited, we consider the subset that has given values U of the energy and V of the volume, and amounts of constituents that are compatible with given values $n_{1a}, n_{2a}, \ldots, n_{ra}$, in the sense that the values of the amounts of constituents satisfy the stoichiometric relations

$$n_i = n_{ia} + \sum_{j=1}^{\tau} \nu_i^{(j)} \epsilon_j \quad \text{for } i = 1, 2, \ldots, r \tag{10}$$

We denote the resulting state by A_ϵ. Among all the states A_ϵ, we can prove that the one with the highest entropy is the unique chemical equilibrium state with energy U, volume V, and amounts of constituents compatible with $\mathbf{n}_a$. We denote it by A_{ϵ_o}.

As a result of these observations, we see that we can express the entropy S_ϵ of a state A_ϵ in terms of the entropy $S_{\text{off}}(U, V, \mathbf{n})$ of the state of the surrogate system to which A_ϵ corresponds. Moreover, we can determine the chemical-equilibrium entropy $S(U, V, \mathbf{n}_a; \nu)$ (Eq. (6)) by maximization of the function

$$S_\epsilon = S_{\text{off}}(U, V, \mathbf{n}) = S_{\text{off}}(U, V, \mathbf{n}_a + \nu \cdot \epsilon) \tag{11}$$

where in writing the second part of Eq. (11), we substitute in $S_{\text{off}}(U, V, \mathbf{n})$ the shorthand notation $\mathbf{n}_a + \nu \cdot \epsilon$ for the set of Eq. (10). Indeed for A_{ϵ_o} to be the state of highest entropy among all the states A_ϵ with given U, V, $\mathbf{n}_a$, and ν, the values ϵ_o must be such that

$$\left(\frac{\partial S_\epsilon}{\partial \epsilon_j} \right)_{U, V, \mathbf{n}_a, \nu, \epsilon} = 0 \quad \text{for } j = 1, 2, \ldots, \tau \tag{12}$$

where the subscripts $\mathbf{n}_a$, ν and ϵ denote, respectively, that each of the amounts n_{ia}, each of the stoichiometric coefficients $\nu_i^{(j)}$, and each of the reaction coordinates that do not appear in the partial derivative are kept fixed. Using Eq. (11) in Eq. (12), we find

$$\left(\frac{\partial S_\epsilon}{\partial \epsilon_j} \right)_{U, V, \mathbf{n}_a, \nu, \epsilon} = \sum_{i=1}^{r} \left(\frac{\partial S_{\text{off}}}{\partial n_i} \right)_{U, V, \mathbf{n}} \left(\frac{\partial n_i}{\partial \epsilon_j} \right)_{\mathbf{n}_a, \nu, \epsilon}$$

$$= - \sum_{i=1}^{r} \frac{\mu_{i, \text{off}}}{T_{\text{off}}} \nu_i^{(j)} = 0 \quad \text{for } j = 1, 2, \ldots, \tau \tag{13}$$

where $\mu_{i, \text{off}}$ is the chemical potential of constituent i, and T_{off} the temperature of the stable equilibrium state of the surrogate system B. For finite values of T_{off}, we see from Eq. (13) that the necessary conditions that relate U, V, $\mathbf{n}_a$, ν, and ϵ_o at chemical equilibrium are

$$\sum_{i=1}^{r} \nu_i^{(j)} \mu_{i, \text{off}}(U, V, \mathbf{n}_a + \nu \cdot \epsilon_o) = 0 \quad \text{for } j = 1, 2, \ldots, \tau \tag{14}$$

They can be expressed also in terms of temperature, pressure, and composition of the surrogate system [5, 7]; that is,

$$\sum_{i=1}^{r} \nu_i^{(j)} \mu_{i, \text{off}}(T_{\text{off}}, p_{\text{off}}, y_{1o}, y_{2o}, \ldots, y_{ro}) = 0$$

$$\text{for } j = 1, 2, \ldots, \tau \tag{15}$$

where each y_{io} is given by Eq. (5). Moreover, we can show that the extremum determined by either Eq. (13) or Eq. (15) is a maximum.

For states other than chemical equilibrium, the expressions $\Sigma_{i=1}^{r} \nu_i^{(j)} \mu_{i, \text{off}}$ for $j = 1, 2, \ldots, \tau$ are well defined, but different from zero. The negative of each such expression has been called by de Donder the *affinity of the reaction*. It is noteworthy that this affinity cannot be expressed in terms of chemical potentials of system A because no such potentials can be defined for states of A that are not chemical equilibrium.

3 Entropy Generation Rate

In the course of chemical reactions in an isolated system A with r constituents and τ chemical reaction mechanisms, the system passes through a sequence of nonequilibrium states, and entropy is generated until the system reaches chemical equilibrium. At chemical equilibrium, all changes cease—the

rate of change of each reaction coordinate is zero—and, thereafter, the system remains in the stable equilibrium state.

The evaluation of the evolutions of the properties of the system as functions of time from any state that is not stable equilibrium to a chemical or stable equilibrium state, and, therefore, the entropy generation, are not possible at present. In principle, such an evaluation would require the solution of a general equation of motion that is still to be established. The discovery of the equation of motion remains one of the most challenging and outstanding problems at the frontiers of physics.

Despite this deficiency, we can derive an estimate of the rate of entropy generation in terms of the τ affinities of the surrogate system B of A, and the rates of change of the reaction coordinates of the τ chemical reaction mechanisms. We will see that this estimate is informative both about what might be considered as the driving forces of the reactions, and about whether the so-called principle of microscopic reversibility plays any role in entropy generation. To derive this estimate, we proceed as follows.

For given values U of the energy, and V of the volume, at an instant of time t the values of the amounts of the r constituents $\mathbf{n} = \mathbf{n}(t) = \{n_1, n_2, \ldots, n_r\}$ satisfy Eqs. (3), and, in general, are functions of time. Moreover, the entropy of A can be regarded as a function of time $S(t)$ because it depends on a large number of independent properties each of which is a function of time, except if it is a constant of the motion.

The value of $S(t)$ is smaller than the value $S_{\mathrm{off}}(U, V, \mathbf{n}(t))$ of the surrogate system B; that is,

$$S(t) \leq S_{\mathrm{off}}(U,V,\mathbf{n}(t)) = S_{\mathrm{off}}(U,V,\mathbf{n}_a + \nu \cdot \epsilon(t)) \quad (16)$$

where the equal sign applies only for the chemical equilibrium state. The justification of Eq. (16) is that, by definition, $S_{\mathrm{off}}(U, V, \mathbf{n}(t))$ corresponds to the entropy of a stable equilibrium state and the entropy of that state is larger than the entropy of any other state with the same values of U, V, $\mathbf{n}(t)$. Because at chemical equilibrium both $S(t)$ and $S_{\mathrm{off}}(U, V, \mathbf{n}(t))$ assume the same value, an estimate of the rate of entropy generation $\dot{S}_{\mathrm{irr}}$—the rate of entropy generated by irreversibility in the isolated system A—is obtained by assuming that A is always in one of the states A_ϵ defined in Section 2, so that the values of all the properties are equal to the corresponding properties of the stable equilibrium states of the surrogate system B.

Under the cited assumption

$$\dot{S}_{\mathrm{irr}} = \frac{dS_{\mathrm{off}}(U,V,\mathbf{n}_a + \nu \cdot \epsilon(t))}{dt} = \sum_{i=1}^{r} \left(\frac{\partial S_{\mathrm{off}}}{\partial n_i}\right)_{U,V,\mathbf{n}} \left(\frac{\partial n_i}{\partial t}\right)_{\mathbf{n}_a,\nu}$$

$$= -\sum_{i=1}^{r} \frac{\mu_{i,\mathrm{off}}}{T_{\mathrm{off}}} \sum_{j=1}^{\tau} \nu_i^{(j)} \dot{\epsilon}_j = \sum_{j=1}^{\tau} \sum_{i=1}^{r} \left(-\frac{\nu_i^{(j)}\mu_{i,\mathrm{off}}}{T_{\mathrm{off}}}\right) \dot{\epsilon}_j$$

$$= \sum_{j=1}^{\tau} Y_j \dot{\epsilon}_j = \dot{\epsilon} \cdot \mathbf{Y} \quad (17)$$

where $\dot{\epsilon}$ is the row vector of the τ rates of change of the reaction coordinates $\dot{\epsilon}_1, \dot{\epsilon}_2, \ldots, \dot{\epsilon}_\tau$, $\mathbf{Y}$ the column vector of the τ ratios $Y_j = \alpha_j / T_{\mathrm{off}}$ for $j = 1, 2, \ldots, \tau$, and $\alpha_j = -\Sigma_{i=1}^{r} \nu_i^{(j)} \mu_{i,\mathrm{off}}$, that is, the jth affinity of a stable equilibrium state of the surrogate system B.

From Eqs. (11) and (13), we see that each of the functions S_{off} and Y_j for $j = 1, 2, \ldots, \tau$ depends solely on the reaction coordinates ϵ_i for $i = 1, 2, \ldots, \tau$. Accordingly, we can write

$$\frac{\partial S_{\mathrm{off}}(U,V,\mathbf{n}_a + \nu \cdot \epsilon)}{\partial \epsilon_k} = -\sum_{i=1}^{r} \nu_i^{(k)} \frac{\mu_{i,\mathrm{off}}}{T_{\mathrm{off}}}$$

$$= Y_k(U,V,\mathbf{n}_a + \nu \cdot \epsilon) \quad (18)$$

$$\frac{\partial^2 S_{\mathrm{off}}(U,V,\mathbf{n}_a + \nu \cdot \epsilon)}{\partial \epsilon_l \partial \epsilon_k} = \frac{\partial^2 S_{\mathrm{off}}(U,V,\mathbf{n}_a + \nu \cdot \epsilon)}{\partial \epsilon_k \partial \epsilon_l} \quad (19a)$$

or, equivalently,

$$\left(\frac{\partial Y_k}{\partial \epsilon_l}\right)_{U,V,\mathbf{n}_a,\nu,\epsilon} = \left(\frac{\partial Y_l}{\partial \epsilon_k}\right)_{U,V,\mathbf{n}_a,\nu,\epsilon} \quad (19b)$$

Equation (19b) indicates that the $\tau \times \tau$ matrix with elements $a_{kl} = (\partial Y_k / \partial \epsilon_l)_{U,V,\mathbf{n}_a,\nu,\epsilon}$ is symmetric, that is, $a_{kl} = a_{lk}$ for all values of ϵ. Moreover, if we invert the relations

$$Y_k = Y_k(U,V,\mathbf{n}_a + \nu \cdot \epsilon) \quad \text{for } k = 1,2,\ldots,\tau \quad (20)$$

with respect to the variables $\epsilon_1, \epsilon_2, \ldots, \epsilon_\tau$, to obtain the relations

$$\epsilon_l = \epsilon_l(U,V,\mathbf{n}_a + \nu \cdot \epsilon) \quad \text{for } l = 1,2,\ldots,\tau \quad (21)$$

we can easily show using the properties of Jacobians that the matrix with elements $b_{kl} = (\partial \epsilon_k / \partial Y_l)_{U,V,\mathbf{n}_a,\nu,\mathbf{Y}}$ is symmetric also; that is,

$$\left(\frac{\partial \epsilon_k}{\partial Y_l}\right)_{U,V,\mathbf{n}_a,\nu,\mathbf{Y}} = \left(\frac{\partial \epsilon_l}{\partial Y_k}\right)_{U,V,\mathbf{n}_a,\nu,\mathbf{Y}} \quad (22)$$

for both zero and nonzero values of $\mathbf{Y}$.

Relations (19b) and (22) are among the many Maxwell relations that can be established for the stable equilibrium states of a multiconstituent system—here, the surrogate system B. Relation (22) implies that for the state of the surrogate system to remain a stable equilibrium state, of the four changes $d\epsilon_k$, $d\epsilon_l$, dY_k, dY_l, we can specify only three arbitrarily and independently. We use this result in the next section.

4 Dependences of $\dot{\epsilon}$ on Y

We proceed under the assumption-approximation that the state of the chemically reacting system A belongs at each instant of time to the family of states A_ϵ. For fixed values of U, V, $\mathbf{n}_a$ and ν, we regard $Y_1, Y_2, \ldots, Y_\tau$ as the independent variables of the family of A_ϵ states, and assume that the rate of change of each reaction coordinate is a sole function of the elements of vector $\mathbf{Y}$, so that

$$\dot{\epsilon} = \dot{\epsilon}(\mathbf{Y}) \quad (23a)$$

with

$$\dot{\epsilon}(0) = 0 \quad (23b)$$

Condition (23b) is necessary because at chemical equilibrium, all the Ys are zero (Eqs. (14)), and the rates of change of all the reaction coordinates are also zero.

Inspired by the Maxwell relations (22), we further assume that

$$\left(\frac{\partial \dot{\epsilon}_k}{\partial Y_l}\right)_{U,V,\mathbf{n}_a,\nu,\mathbf{Y}} = \left(\frac{\partial \dot{\epsilon}_l}{\partial Y_k}\right)_{U,V,\mathbf{n}_a,\nu,\mathbf{Y}} \quad (23c)$$

for $k = 1, 2, \ldots, \tau$ and $l = 1, 2, \ldots, \tau$. We conjecture that condition (23c) is equivalent to the condition that along the time evolution the surrogate system proceeds through stable equilibrium states, and so indeed system A proceeds through states A_ϵ. In any case, this condition is stated not only without any reference to microscopic reversibility, but also for all values of $\mathbf{Y}$, that is, even for states that are not chemical equilibrium.

Now, we can always expand each of the τ Eqs. (23a) into a Taylor series around the chemical equilibrium state at which $\mathbf{Y} = \mathbf{0}$. The expansions can be written in the form

$$\dot{\epsilon} = \mathbf{L} \cdot \mathbf{Y} + (\text{higher order terms in } \mathbf{Y}) \quad (24)$$

where $\mathbf{L}$ is a $\tau \times \tau$ matrix of coefficients, each defined by the relation

$$L_{kl} = \left(\frac{\partial \dot{\epsilon}_k}{\partial Y_l}\right)_{U,V,\mathbf{n}_a,\nu,\mathbf{Y}=0} \tag{25}$$

for $k = 1, 2, \ldots, \tau$ and $l = 1, 2, \ldots, \tau$.

Upon using Eq. (23c) in Eq. (25), we conclude that the matrix **L** is symmetric, that is, that the matrix elements L_{kl} obey the Onsager reciprocal relations $L_{kl} = L_{lk}$ for $k = 1, 2, \ldots, \tau$ and $l = 1, 2, \ldots, \tau$. Moreover, as we noted already, these Onsager relations are obtained without any reference to microscopic reversibility [8–9], or use of postulates in addition to those of thermodynamics, except the assumptions that the state of A proceeds through states A_ϵ, that $\dot{\epsilon}$ is a sole function of **Y**, for given values of U, V, $\mathbf{n}_a$ and ν, and that condition (23c) is assumed by analogy with relations (22). This is a very important conclusion because microscopic reversibility cannot and should not be the cause of entropy generation by irreversibility.

For small values of **Y**, that is, for states of A near the chemical equilibrium state, the linear term predominates in Eq. (24), and the rate of entropy generation becomes

$$\dot{S}_{\mathrm{irr}} \approx \mathbf{Y}' \cdot \mathbf{L} \cdot \mathbf{Y} \tag{26}$$

where $\mathbf{Y}'$ is the row vector of the ratios $\alpha_j / T_{\mathrm{off}}$ for $j = 1, 2, \ldots, \tau$. Because $\dot{S}_{\mathrm{irr}} \geq 0$ in general, and the right-hand side of Eq. (26) is a quadratic form, the matrix **L** must be positive semi-definite.

Our results can be interpreted in the customary manner of the so-called "thermodynamics of irreversible processes." Each Y_j, for $j = 1, 2, \ldots, \tau$, can be regarded as a driving force, and each rate of change of a reaction coordinate $\dot{\epsilon}_j$, for $j = 1, 2, \ldots, \tau$, as a flux that depends on all the forces, that is, forces and fluxes are coupled. If the fluxes are expressed as functions of the forces, the coefficients of the linear terms form a symmetric matrix, that is, obey Onsager reciprocal relations.

Conclusions

An approximate expression for the rate of entropy generation in a system A with τ chemical reaction mechanisms is derived in terms of the rates of change of the reaction coordinates and the affinities of a surrogate system without chemical reactions.

The rates of change of the reaction coordinates can be expressed in terms of the affinities, and the coefficients of the linear approximations of these expressions are shown to obey Onsager reciprocal relations. The reciprocal relations are valid both for states that are chemical equilibrium and for states that are not. This result and its derivation are novel to thermodynamics.

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