Stochastic thermodynamics and entropy production of chemical reaction systems

Tânia Tomé and Mário J. de Oliveira
Instituto de Física, Universidade de Sào Paulo
Rua do Matão, 1371, 05508-090 Sào Paulo, SP, Brazil
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We investigate the nonequilibrium stationary states of systems consisting of chemical reactions among molecules of several chemical species. To this end we introduce and develop a stochastic formulation of nonequilibrium thermodynamics of chemical reaction systems based on a master equation defined on the space of microscopic chemical states, and on appropriate definitions of entropy and entropy production. The system is in contact with a heat reservoir, and is placed out of equilibrium by the contact with particle reservoirs. In our approach, the fluxes of various types, such as the heat and particle fluxes, play a fundamental role in characterizing the nonequilibrium chemical state. We show that the rate of entropy production in the stationary nonequilibrium state is a bilinear form in the affinities and the fluxes of reaction, which are expressed in terms of rate constants and transition rates, respectively. We also show how the description in terms of microscopic states can be reduced to a description in terms of the numbers of particles of each species, from which follows the chemical master equation. As an example, we calculate the rate of entropy production of the first and second Schlögl reaction models.

I. INTRODUCTION

Chemical reaction systems are understood as systems in which one or more chemical reactions take place [1–3]. A chemical reaction can be as simple as a unimolecular reaction in which one molecule of a chemical species transforms into another molecule of a distinct chemical species, or it can be a complex process in which molecules of distinct species dissociate and recombine producing molecules of other species. In the process, a certain amount of energy is absorbed or released. A relevant feature of reactions taking place in a vessel is their intrinsic stochastic nature which give rise to random fluctuations on the quantities that describe the reactive system. An appropriate approach that takes into account this feature is the description of the time evolution of reactive systems by a continuous time Markov process [4–6]. That is, one assumes that the time evolution of the system is governed by a master equation and that the reaction rates are identified as the transition rates defining the stochastic process.

Usually the stochastic description of reactive systems is made in terms of the numbers of particles of each species, identified as stochastic variables, and the stochastic process is understood as a stochastic trajectory in the space spanned by the numbers of particles of each species. The process is a birth and death process in several variables and the corresponding master equation is called chemical master equation [4–14]. Here we consider a more general stochastic approach in which the state of the system consists of the set of microscopic states such as that used in stochastic lattice models [4]. The idea of using microscopic states [15] is not new but here we consider a more complete and explicit treatment by the use of a microscopic description in terms of microscopic chemical states, defined by the set of variables that denote the chemical species of each molecule. Under some circumstances, as we shall see, it is possible to pass from the microscopic description to the description in terms of the number of particles.

Our general stochastic approach is fully connect to thermodynamics and in this sense it can be understood as a stochastic thermodynamics of reactive systems. Stochastic thermodynamics [11–31] assumes that the time evolution of a system is a Markovian process, such as that described by a master equation or by a Fokker-Planck equation, and is based on two assumptions concerning entropy. The first is that the entropy has the Gibbs form and the second is that the production of entropy is related to the probabilities of the direct and reverse trajectories. This definition of entropy production is explicitly tied to the dynamics and, at first sight, seems to have no reference to the energetics, in contrast to thermodynamics [13]. However, from the definition of entropy production it is in fact possible, as we will show below, to connect the heat flux, the flux of energy plus the flux of work, to the flux of entropy, providing the consistency of stochastic thermodynamics [16–19].

Here we will be concerned mainly with the steady state, which might be an equilibrium or a nonequilibrium state. In the latter case each reaction taking place in a vessel will be in general either shifted to the products or to the reactants, a situation in which entropy is continuously being generated and fluxes of several types such as the flux of particles and the flux of entropy are occurring. In the case of equilibrium all fluxes vanish, including the entropy flux, a result that is the hallmark of what is meant by thermodynamic equilibrium. The vanishing of fluxes is a direct consequence of the microscopic reversibility which, in the present approach, is accomplished by the detailed balance condition.

Our approach to nonequilibrium thermodynamics assumes that certain quantities used in equilibrium thermodynamics continues to be well defined quantities, whereas
other quantities, such as temperature and chemical potential, cannot always be assigned to a nonequilibrium system. One assumes, for instance, that it is possible to assign an entropy and an energy to the system. According to this assumption, to each microscopic chemical state, one associates an energy. When a reaction occurs, the microscopic chemical state changes causing an increase or decrease in the energy of the system. This variation in energy is understood as the energy of activation. In the case of a system in contact with a heat reservoir, which is the case of the present approach, the variation in energy is due to the energy exchange with the reservoir and the rate of reaction is proportional to the Arrhenius factor. The coupling with reservoirs usually is in accordance with the hypothesis of local equilibrium, that is, the thermodynamic relations remain valid at a coarse-grained level, as considered, for example, in reference [15] for the mesoscopic stochastic formulation of nonequilibrium thermodynamics.

The present approach assumes that a closed reactive system will be found in thermodynamic equilibrium when it reaches the steady state, which amounts to say that the transition rates associated to the reactions obey the detailed balance condition in closed system. It is implied here that the presence of a reaction means that its reverse is also present. One way of taking the system out of equilibrium, so that the reactions will be unbalanced, even in a steady state, is to place the system in contact with particle reservoirs in which case the system is open. This is what we do in the present approach by representing the contact with a particle reservoir by a chemical reaction. Therefore, in addition to the set of ordinary chemical reactions, another set of chemical reactions will be considered in order to describe the contact with the particle reservoirs.

If the open system, in contact with particle reservoirs, reaches equilibrium, it will be described by the grand canonical Gibbs distribution. However, the equilibrium will not happen if the rates of reactions do not obey detailed balance with respect to the grand canonical distribution. In this case the system will be in a nonequilibrium situation and there will be fluxes of particles between the system and the particle reservoirs, and in general each reactions will be shifted either to the products or to the reactants. A flux of entropy from the system to the reservoirs will also occur due to the continuous production of entropy.

We demonstrate that in the nonequilibrium stationary state, the rate of entropy production is a sum of bilinear terms in the affinities and the fluxes of reaction. In addition, we show that the affinity is written in terms of the rate constants and the flux of reaction in terms of the transition rates. The derivation of the bilinear form was possible due to our use of an appropriate form of the transition rates associated to the chemical reactions and to the contact of the reaction system with the particle reservoirs.

**II. MICROSCOPIC REPRESENTATION**

Our object of study is an open chemical system consisting of molecules of several chemical species, or particles of various types, that react among themselves. The system is in contact with a heat reservoir and also in contact with several particle reservoirs, one for each type of particle. We assume that the system is described by a continuous time Markov process defined on a discrete microscopic space of states. A stochastic trajectory in the microscopic space of states is determined by the transition rate $W(\eta, \eta')$ from state $\eta'$ to state $\eta$, a quantity that plays a fundamental role in the present approach in the sense that a specific system is considered to be fully characterized when these transition rates are given. In other words, all the microscopic processes taking place inside the system, specifically, the chemical reactions, as well as the contact of the system with the reservoirs are embodied in the transition rates $W(\eta, \eta')$. Given the transition rates $W(\eta, \eta')$, we set up the master equation

$$\frac{d}{dt} P(\eta, t) = \sum_{\eta'} \{ W(\eta, \eta') P(\eta') - W(\eta', \eta) P(\eta) \}, \quad (1)$$

which governs the time evolution of the probability $P(\eta, t)$ of state $\eta$ at time $t$.

For long times the system eventually reaches a stationary state, meaning that the probability distribution $P(\eta, t)$ approaches a final stationary distribution. The final stationary state may or may not be an equilibrium state depending on the transition rates. If the transition rates obey the microscopic reversibility, that is, if they obey detailed balance with respect to the final probability distribution, then we say that the system has reached thermodynamic equilibrium and the equilibrium probability distribution will be a Gibbs probability distribution.

According to our assumptions, an energy $E(\eta)$ is always associated to the system. Given the transition rates, this quantity cannot be an arbitrary function but should be related to the transition rates. If, for a certain set of values of the parameters defining the transition rates, these obey detailed balance with respect to a Gibbs probability distribution, then this distribution should involve $E(\eta)$. That is, in equilibrium, the transition rates fulfill detailed balance with respect to a Gibbs probability distribution involving this quantity. At this point, however, what we wish to say is that, from the master equation, it is possible to obtain the time evolution of the average $U$ of the energy,

$$U = \sum_{\eta} E(\eta) P(\eta). \quad (2)$$

Taking the time derivative of both sides of this equation, and using the master equation, we immediately find the time evolution of $U$, that is,

$$\frac{dU}{dt} = \sum_{\eta, \eta'} W(\eta, \eta') P(\eta') [E(\eta) - E(\eta')]. \quad (3)$$
From the master equation we can in fact obtain the time evolution of any quantity that is an average of a state function. This is the case of the number of particle of each species. The average number of particles $N_i(\eta)$ of type $i$ is

$$N_i = \sum_\eta n_i(\eta)P(\eta),$$

(4)

where $n_i(\eta)$ stands for the number of particle of state $\eta$. In an analogous fashion we get from the master equation the time evolution of $N_i$, that is,

$$\frac{dN_i}{dt} = \sum_{\eta,\eta'} W(\eta,\eta')P(\eta')[n_i(\eta) - n_i(\eta')].$$

(5)

Together with the energy $U$ and the number of particles $N_i$ of each species, a relevant thermodynamic quantity that characterizes the system is the entropy. The entropy is not the average of a state function and is defined by the Gibbs expression

$$S = -k_B \sum_\eta P(\eta) \ln P(\eta),$$

(6)

assumed to be valid in equilibrium as well as in nonequilibrium situations, where $k_B$ is the Boltzmann constant. Its time evolution can be obtained from the master equation and is given

$$\frac{dS}{dt} = k_B \sum_{\eta,\eta'} W(\eta,\eta')P(\eta') \ln \frac{P(\eta')}{P(\eta)}. $$

(7)

The right-hand side of equation (7) represents the total variation of entropy, which is understood of consisting of two parts. One part is the flux of entropy from the environment, denoted by $\Phi$, and the other is the rate of production or generation of entropy, denoted by $\Pi$. The variation of the entropy of the system and these two quantities are related by (8)

$$\frac{dS}{dt} = \Pi + \Phi.$$

(8)

This fundamental relation was advanced by Prigogine [32 33], who wrote it as $dS = dS_i + dS_e$, and was founded on the ideas of De Donder [37 38] and Clausius [40] about the "uncompensated heat".

To develop a stochastic approach to thermodynamics we need a microscopic definition of either $\Pi$ or $\Phi$ since the sum $\Pi + \Phi$ is given by the right-hand side of equation (7). The definition of the rate of entropy production $\Pi$ should meet two conditions: it should be nonnegative and should vanish in equilibrium, that is, when detailed balance is obeyed. This is provided by the Schnakenberg expression (11)

$$\Pi = k_B \sum_{\eta,\eta'} W(\eta,\eta')P(\eta') \ln \frac{W(\eta,\eta')}W(\eta',\eta)P(\eta),$$

(9)

which can easily be shown to be semi-positive defined, that is, $\Pi \geq 0$. The entropy flux $\Phi$ is obtained by replacing expressions (4) and (7) into (8). The result is

$$\Phi = -k_B \sum_{\eta,\eta'} W(\eta,\eta')P(\eta') \ln \frac{W(\eta,\eta')}{W(\eta',\eta)}.$$

(10)

The equations we have introduced in this section define the stochastic thermodynamics for equilibrium and nonequilibrium systems. However, the transition rates were not yet specified.

### III. TRANSITION RATES

Now we wish to set up the transition rates related to the several chemical reactions occurring inside the system among $q$ chemical species. The reactions are described by the chemical equations

$$\sum_{i=1}^q \nu_{ij} B_i \leftrightarrow \sum_{i=1}^q \nu_{ij}^{+} B_i, \quad j = 1, 2, \ldots, r,$$

(11)

where $B_i$ denotes the chemical formula of species $i$, and $\nu_{ij} \geq 0$ and $\nu_{ij}^{+} \geq 0$ are the stoichiometric coefficients of the reactants and products, respectively, and $r$ is the number of reactions. Equation (11) tells us that when the $j$-th reaction occurs from left to right (forward reaction) then $\nu_{ij}$ molecules of type $i$ disappear and $\nu_{ij}^{+}$ molecules of type $i$ appear so that the number of molecules of type $i$ varies by $\nu_{ij} = \nu_{ij}^{+} - \nu_{ij}$. If the reaction occurs from right to left (backward reaction) the number of molecules of type $i$ varies by $-\nu_{ij} = \nu_{ij}^{+} - \nu_{ij}$. The set of reactions are assumed to be linearly independent, which means to say that no reaction is a linear combination of the others.

The description that we consider here takes into account only the degrees of freedom related to the variables that specify the chemical species of each molecule, which we call microscopic chemical state. The microscopic chemical state is defined as follows. In a reaction, we may say that a molecule at position $i$ is transformed into a molecule of distinct type that remains in the same position $i$. To describe this situation we attach a stochastic variable $\eta_i$ at position $i$ that takes values according to the type of molecule present at position $i$. We adopt the convention that $\eta_i$ takes the values $1, 2, \ldots, q$, according to whether the position $i$ is occupied by a molecule of types $1, 2, \ldots, q$, respectively. If position $i$ is not occupied by any molecule, then $\eta_i$ takes the value zero.

The microscopic chemical state $\eta$ of the whole system is understood as a vector with components $\eta_i$. We assume that the allowed positions, or sites, are finite in number and form a space structure, that is, a lattice of allowed sites. The total number of sites $N$ of the lattice is proportional to the volume $V$ of the recipient and the mean volume $v_i = V/N$ of a cell around a site is of the order of the volume of a molecule. In the
study of chemical kinetics it is usual to deal with quantities that are densities per unit volume. In the present theory, one naturally deals with densities per site. To get the former density, it suffices to divide that latter density by \( v \).

A more complete microscopic description should take into account other degrees of freedom such as those related to the motion of the molecules in which case the position \( i \) of a molecule should be understood as a dynamical variable. However, as usually done in the study of chemical kinetics \cite{12}, we assume that microscopic chemical degrees of freedom are decoupled from the mechanical degrees of freedom, or that the coupling between these two types of degrees of freedom is small. However, the coupling cannot be entirely avoided because the energy released or consumed in a chemical reaction is exchanged in processes involving the mechanical degrees of freedom such as the kinetic and potential energies of the molecules.

A chemical reaction described by expression \( 11 \) can be understood as the annihilation of a group of particles and the creation of another group of particles, which allows to identify the reaction as a transformation of the state \( \eta \) into another state \( \eta' \). We denote by \( R^j_\eta (\eta', \eta) \) and by \( R^j_\eta (\eta', \eta) \) the transition rates from \( \eta \) to \( \eta' \) corresponding to the \( j \)-th forward and backward reaction \( 11 \), respectively. To set up these transition rates, we proceed as follows. We let the system be in contact with a heat reservoir at a temperature \( T \) and assume that the system reaches the thermodynamic equilibrium. This amounts to say that detailed balance is fulfilled, that is,

\[
R^j_\eta (\eta', \eta) P^e(\eta') = R^j_\eta (\eta', \eta) P^e(\eta),
\]

for any pair of states \((\eta, \eta')\) where \( P^e(\eta) \) is the equilibrium Gibbs probability distribution,

\[
P^e(\eta) = \frac{1}{Z} e^{-\beta E(\eta)},
\]

where \( E(\eta) \) is the energy of state \( \eta \) and \( \beta = 1/k_B T \). Therefore, the transition rates of the forward and backward reactions are connected by the relation

\[
\frac{R^j_\eta (\eta', \eta)}{R^j_\eta (\eta', \eta')} = e^{-\beta [E(\eta') - E(\eta)]}.
\]

It should be noted that the right-hand side of this equation can be regarded as a microscopic Arrhenius factor \cite{13, 14}, the difference \( E(\eta') - E(\eta) \) being the activated energy for the transition \( \eta \to \eta' \). The transition rates we shall consider are partially defined by this equation, that is, if the forward transition rate is given then the backward transition rate is defined by equation \( 14 \), and vice-versa.

Next we wish to consider the system in contact with particle reservoirs, one for each type of molecule. In this new situation, we assume that the transition rates \( R^\sigma_\eta (\eta', \eta) \), \( \sigma = \pm 1 \), remains unmodified. That is, the contact with the particle reservoirs, do not modify its form, and equation \( 13 \) should be understood as an equation that defines, or partially defines, the reaction transition rates. Notice that, equation \( 13 \) should not be understood as a detailed balance condition because the equilibrium probability is no longer given by \( 13 \).

In addition to the transition rates related to the chemical reactions, we should consider the transitions that describe the contact with the reservoirs. To find the corresponding transition rates we consider again the situation in which the system is found in thermodynamic equilibrium, described by the following Gibbs probability distribution

\[
P^e(\eta) = \frac{1}{Z} e^{-\beta E(\eta)} + \beta \sum \bar{\eta}, n(\eta),
\]

where \( n(\eta) \) is the number of molecules of type \( i \) in state \( \eta \) and \( \mu_i \) is the chemical potential associated to reservoir \( i \). Denoting by \( C^{\sigma}_i (\eta', \eta) \) and \( C^{\sigma}_i (\eta', \eta) \) the transition rates corresponding to the addition and removal of one particle of type \( i \), respectively, then these rates obey the relation

\[
\frac{C^{\sigma}_i (\eta', \eta)}{C^{\sigma}_i (\eta, \eta')} = e^{-\beta [E(\eta') - E(\eta) + \beta \mu_i (n(\eta') - n(\eta))]},
\]

We are considering that just one molecule is added to or removed from the system so that in this equation, \( n(\eta') - n(\eta) = \pm 1 \). Equation \( 16 \) is assumed to be an equation that defines, or partially defines, the transition rates associated to the contact with the reservoirs. The motivation for this definition is the following. If the system has no reaction, that is, if the only transition rates are \( C^{\sigma}_i (\eta, \eta') \), \( \sigma = \pm 1 \), then in the steady state the system will be found in equilibrium with the distribution \( 15 \) because \( 16 \) is identified, in this case, with detailed balance with respect to \( 15 \).

The stochastic approach to equilibrium and nonequilibrium thermodynamics of chemical reactions that we are considering here is founded on the master equation \( 11 \) with transition rates \( W(\eta, \eta') \) given by

\[
W(\eta, \eta') = \sum_{j=1}^r \sum_{\sigma = \pm 1} R^\sigma_j (\eta, \eta') + \sum_{i=1}^q \sum_{\sigma = \pm 1} C^{\sigma}_i (\eta, \eta').
\]

We remark that the matrices \( R^\sigma_j \) and \( C^{\sigma}_i \) are disjoint, that is, if the entry \((\eta, \eta')\) of one of them is nonzero, then the same entry of any other vanishes. In other words, depending on the states \( \eta \) and \( \eta' \), the transition rate \( W(\eta, \eta') \) is either one of the reaction transition rates \( R^\sigma_j (\eta, \eta') \) or one of the contact transition rates \( C^{\sigma}_i (\eta, \eta') \), which obey equations \( 14 \) and \( 16 \), respectively.

Given these rates we may ask whether they obey detailed balance with respect to the equilibrium probability distribution \( 15 \). By construction, the rates \( C^{\sigma}_i \) indeed obey it. But in general the rates \( R^\sigma_j \) do not. The detailed balance condition for \( R^\sigma_j \) with respect to the equilibrium distribution \( 15 \), is

\[
\frac{R^\sigma_j (\eta', \eta)}{R^\sigma_j (\eta, \eta')} = e^{-\beta [E(\eta') - E(\eta)] + \beta \sum \mu_i (n(\eta') - n(\eta))}.
\]
But the left hand side should be given by equation \(14\). A comparison between equations \(15\) and \(14\) leads us to conclude that \(R_j^\sigma\) does not obey detailed balance unless the summation on the exponent on the right-hand side of equation \(18\) vanish. Taking into account that \(n_i(\eta') - n_i(\eta) = \nu_{ij}\), the summation on the exponent vanishes if

\[\sum_i \mu_i \nu_{ij} = 0, \tag{19}\]

which is the well known equilibrium condition for a system consisting of chemical reactions \(14, 15\). If the chemical potentials \(\mu_i\) fulfill equation \(19\) for each reaction \(j = 1, \ldots, r\), then, when the system reaches the stationary state, it will be found in equilibrium and described by the Gibbs probability distribution \(15\). Otherwise, the system will not reach equilibrium and will be found in a nonequilibrium stationary state.

**IV. NONEQUILIBRIUM REGIME**

When the chemical potentials do not obey condition \(19\), the system will reach a nonequilibrium stationary state because detailed balance condition is not fulfilled, and the system cannot be in equilibrium. At least one reaction is shifted either to the right or to the left, that is, either the products are being created and the reactants being annihilated (backward reaction) or the reactants are being created and the products being annihilated (forward reaction). In the stationary nonequilibrium state, entropy is continuously being produced and the rate of entropy production equals the flux of entropy. Some type of particles are being created and others annihilated, given rise to fluxes of particles either to the system or from the system. The set of reactions may be exothermic, in which case the chemical work is transformed into heat that leaves the system, or endothermic, in which case the heat from the outside is transformed into chemical work.

A nonequilibrium situation is characterized by the existence of fluxes of distinct types such as the energy flux, the particle flux and the entropy flux. If a certain quantity is a conserved quantity then its time variation should be equal to the input flux. This is the case of energy. If we denote by \(\Phi_u\) the flux of energy, that is, the energy per unit time, received by the system from the reservoir then

\[\frac{dT}{dt} = \Phi_u. \tag{20}\]

Comparing this equation with \(43\), we find the following expression for the energy flux

\[\Phi_u = \sum_{\eta, \eta'} W(\eta, \eta')P(\eta')[E(\eta) - E(\eta')]. \tag{21}\]

In addition to the flux of heat, the system may also be subject to the flux of particles. Taking into account that the flux of particles is a consequence of the contact with the particle reservoirs, which are described by the transition rates \(C_i^\sigma(\eta, \eta')\), it follows that the flux of particles \(\Phi_i\) of type \(i\) is expressed by

\[\Phi_i = \sum_{\eta, \eta'} \sum_{\sigma = \pm 1} C_i^\sigma(\eta, \eta')P(\eta')[n_i(\eta) - n_i(\eta')], \tag{22}\]

which can be written as

\[\Phi_i = \sum_{\eta, \eta'} [C_i^+(\eta, \eta') - C_i^-(\eta, \eta')]P(\eta'). \tag{23}\]

In chemical reactions, particles can be created or annihilated. In this sense the number of particles of a certain species may not be a conserved quantity and as a consequence its time variation may not be equal to flux of particle of this species. Accordingly, we write \(32, 33\)

\[\frac{dN_i}{dt} = \Gamma_i + \Phi_i, \tag{24}\]

where \(\Gamma_i\) is interpreted as the rate in which particles of type \(i\) are being created \((\Gamma_i > 0)\) or annihilated \((\Gamma_i < 0)\) inside the system. Comparing this equation with \(15\) and taking into account equation \(22\), we see that

\[\Gamma_i = \sum_{\eta, \eta'} \sum_{j=1}^r \sum_{\sigma = \pm 1} R_j^\sigma(\eta, \eta')P(\eta')[n_i(\eta) - n_i(\eta')]. \tag{25}\]

Bearing in mind that in the \(j\)-th forward reaction, the number of particles of type \(i\) varies by \(\nu_{ij}\) and in the backward by \(-\nu_{ij}\), this equation can be written as

\[\Gamma_i = \sum_{j=1}^r \nu_{ij} X_j, \tag{26}\]

where

\[X_j = \sum_{\eta, \eta'} [R_j^+(\eta, \eta') - R_j^-(\eta, \eta')]P(\eta') \tag{27}\]

is the flux of \(j\)-th reaction. If \(X_j > 0\), the \(j\)-th reaction is shifted to the right, toward the products. If \(X_j < 0\), it is shifted to the left, toward the reactants.

As we have seen, the time variation of the entropy of the system is

\[\frac{dS}{dt} = \Pi + \Phi, \tag{28}\]

which means to say that entropy is also a nonconserved quantity, but differently from the number of particles, it cannot decrease because \(\Pi \geq 0\), which is the expression of the second law of thermodynamics. The replacement of \(17\) into equation \(110\), furnishes an expression for the entropy flux \(\Phi\) in terms of the reaction transition rates \(R_j^\sigma\) and contact transition rates \(C_i^\sigma\). When the resulting expression is compared with the right-hand sides of
From this expression we may conclude that the flux of entropy \( \Phi \) is related to the energy flux \( \Phi_u \) and particle fluxes \( \Phi_i \) by

\[
\Phi = \frac{1}{T} (\Phi_u - \sum_{i=1}^{q} \mu_i \Phi_i).
\]

(29)

The flux of heat from the thermal reservoir is defined as the flux of energy plus the rate of chemical work performed by the system, that is,

\[
\Phi_q = \Phi_u - \sum_{i=1}^{q} \mu_i \Phi_i.
\]

(30)

From this expression we may conclude that

\[
\Phi = \frac{1}{T} \Phi_q,
\]

(31)

that is, the flux of entropy equals the heat flux divided by the temperature, in accordance with Clausius [40].

Let us consider the nonequilibrium stationary state. In this regime \( dU/dt = 0 \), implying \( \Phi_u = 0 \) so that equation (29) reduces to

\[
\Phi = -\frac{1}{T} \sum_{i=1}^{q} \mu_i \Phi_i = \frac{1}{T} \sum_{i=1}^{q} \mu_i \Gamma_i,
\]

(32)

where we have used the result \( \Phi_i = -\Gamma_i \) because \( dN_i/dt = 0 \). But in the stationary state \( dS/dt = 0 \), implying \( \Pi = -\Phi \) and as a consequence

\[
\Pi = -\frac{1}{T} \sum_{i=1}^{q} \mu_i \Gamma_i.
\]

(33)

Taking into account the result (26) and defining the affinity \( A_j^D \) by [32–37]

\[
A_j^D = -\sum_{i=1}^{q} \mu_i \nu_{ij},
\]

(34)

then the rate of entropy production can be written in the bilinear form [32, 36]

\[
\Pi = \frac{1}{T} \sum_{j=1}^{r} A_j^D \dot{X}_j.
\]

(35)

The concept of affinity was introduced by De Donder [38, 39] whereas the bilinear form for the production of entropy was advanced by Prigogine [32, 34]. Here we find it more convenient to defined the affinity as the expression [34] divided by the temperature,

\[
A_j = -\frac{1}{T} \sum_{i=1}^{q} \mu_i \nu_{ij},
\]

(36)

so that

\[
\Pi = \sum_{j=1}^{r} A_j \dot{X}_j.
\]

(37)

Notice that, in equilibrium, not only \( A_j = 0 \) but also \( X_j = 0 \).

V. NUMBER OF PARTICLES REPRESENTATION

Let us apply the present approach to the case in which the energy \( E(\eta) \) depends on \( \eta \) only through the number of particle \( n_i(\eta) \) of each species. We use the notation \( E(n) \) where \( n \) is a vector with components \( n_i, i = 1, 2, \ldots, q \). It is then possible to assume that the reaction transition rates \( R^\tau(\eta, \eta') \) and the contact transition rates \( C_i(\eta, \eta') \) depend on \( \eta \) and \( \eta' \) only through the numbers of particle of each species. The description of the system can thus be made in terms of the stochastic variables \( n_1, n_2, \ldots, n_q \). Assuming that \( P(\eta) \) depends on \( \eta \) only through \( n_i(\eta) \) then the probability \( P(n) \) of \( n \) must be related to \( P(\eta) \) by \( \tilde{P}(n) = A(n)P(\eta) \) where

\[
A(n) = \frac{N!}{n_0!n_1! \cdots n_q!},
\]

(38)

and \( n_0 = N - (n_1 + \cdots + n_q) \) is the number of empty sites. The equilibrium probability distribution in the new representation is thus

\[
\tilde{P}(n) = \frac{A(n)}{\Xi} e^{-\beta E(n)} e^{\beta \sum_i \mu_i n_i}.
\]

(39)

Analogously, the transition rate \( \tilde{W}(n, n') \) from \( n' \) to \( n \) is related to the transition rate \( W(\eta, \eta') \) of the original representation by \( \tilde{W}(n, n') = A(n)W(\eta, \eta') \). In the new representation, the master equation (11) becomes

\[
\frac{d}{dt} \tilde{P}(n) = \sum_{n'} \{ \tilde{W}(n, n') \tilde{P}(n') - \tilde{W}(n', n) \tilde{P}(n) \}.
\]

(40)

Let us write the entropy, given by (6), in the new representation,

\[
S = -k_B \sum_n \ln \frac{\tilde{P}(n)}{A(n)}.
\]

(41)

The expression for the production of entropy (11) and entropy flux (10) in the new representation are

\[
\Pi = k_B \sum_{n,n'} \tilde{W}(n, n') \tilde{P}(n') \ln \frac{\tilde{W}(n, n') \tilde{P}(n')}{\tilde{W}(n', n) \tilde{P}(n)},
\]

(42)

\[
\Phi = -k_B \sum_{n,n'} \tilde{W}(n, n') \tilde{P}(n') \ln \frac{\tilde{W}(n, n') A(n')}{\tilde{W}(n', n) A(n)}.
\]

(43)

It should be noted that the production of entropy in the new representation has the same form of the original representation \( R^\tau(\eta, \eta') \) although that is not true for the entropy and flux of entropy.

The transition rate \( \tilde{W}(n', n) \) is either the transition rate related to one of the reactions (11) or the transition rate related to contact with a particle reservoir. We denote the former by \( R^\tau_f(n) \) and the latter by \( C^\tau_i(n) \).
More precisely, \( R^+_{ij}(n) \) is the transition rate from \( n \) to \( n' \), where \( n' \) the state obtained from \( n \) by the action of the forward reaction \( j \), which amounts to say that
\[
n_i' - n_i = \nu_{ij}^+ - \nu_{ij}^- = \nu_{ij},
\]
whereas \( C^+(n) \) is the transition rate from \( n \) to \( n' \), where \( n' \) stands for the state \( n \) with one more particle of type \( i \) so that \( n_i' - n_i = 1 \). The transition rates \( R^-_{ij}(n) \) and \( C^-_i(n) \) are defined similarly. These transition rates obey the equations
\[
\frac{R^+_{ij}(n)}{A(n)} = \frac{A(n')}{A(n)} e^{-\beta[E(n') - E(n)]},
\]
and
\[
\frac{C^+_i(n)}{C^-_i(n')} = \frac{A(n')}{A(n')} e^{-\beta[E(n') - E(n)] + \beta \mu_i},
\]
which come from equations (13) and (10), respectively.

The expression for the flux of particle becomes
\[
\Phi_1 = \sum_n (C^+_i(n) - C^-_i(n)) \bar{P}(n) = \langle C^+_i \rangle - \langle C^-_i \rangle,
\]
whereas the expression for the flux of the reaction \( X_j \) is
\[
X_j = \sum_n (R^+_j(n) - R^-_j(n)) \bar{P}(n) = \langle R^+_j \rangle - \langle R^-_j \rangle.
\]

VI. RATES OF THE CHEMICAL KINETICS

To proceed further on we need to know how \( E(n) \) depends on \( n \). Here we consider the simplest case in which the energy depends linearly on the number of particles, that is,
\[
E(n) = \sum_{i=1}^q \varepsilon_i n_i,
\]
where \( \varepsilon_i \) is the energy associated to a particle of type \( i \). The variation in energy associated to the \( j \) forward reaction is thus
\[
E(n') - E(n) = \sum_{i=1}^q \varepsilon_i \nu_{ij}.
\]

The knowledge of the dependence of \( E(n) \) on \( n \) is not sufficient to determine the transition rates \( R^+_j \) and \( C^-_i \) since only their ratios are known in terms of \( E(n) \), as follows from equations (45) and (46). There is thus a great deal of freedom in the establishment of the transition rates. As we will see below, we will set up transitions rates that are in accordance with those used in the area of chemical kinetics, also known as transitions rates coming from the laws of mass action.

Instead of the expression (45) for \( A(n) \), we use the following expression
\[
A(n) = \frac{N^{n_1+n_2+...+n_q}}{n_1!n_2!...n_q!},
\]
which is obtained from (13) by assuming that the number of empty sites \( n_0 \) is great enough. Using expression (51) for \( A(n) \) and (19) for \( E(n) \), then equation (45) is written as
\[
\frac{R^+_{ij}(n)}{R^-_{ij}(n')} = \frac{A(n')}{A(n')} \prod_{i=1}^q e^{-\beta \varepsilon_i \nu_{ij}} = \prod_{i=1}^q \frac{n_i!}{n_i'}! (Ne^{-\beta \varepsilon_i})^{\nu_{ij}}.
\]
A solution, which is in agreement with the laws of mass action, is
\[
R^+_{ij}(n) = k_j^+ N \prod_{i=1}^q \frac{n_i!}{(n_i - \nu_{ij})! N^{\nu_{ij}}},
\]
\[
R^-_{ij}(n) = k_j^- N \prod_{i=1}^q \frac{n_i!}{(n_i - \nu_{ij})! N^{\nu_{ij}}},
\]
where the constants of reaction \( k_j^+ \) and \( k_j^- \) must obey relation
\[
\frac{k_j^+}{k_j^-} = \prod_{i=1}^q e^{-\beta \varepsilon_i \nu_{ij}}.
\]
Since \( n_i \) is much larger than the stoichiometric coefficients, we may write
\[
R^+_{ij}(n) = k_j^+ N \prod_{i=1}^q \left( \frac{n_i}{N} \right)^{\nu_{ij}},
\]
\[
R^-_{ij}(n) = k_j^- N \prod_{i=1}^q \left( \frac{n_i}{N} \right)^{\nu_{ij}},
\]
which are in accordance with the law of mass action.22

Similarly, using expression (51) for \( A(n) \) and the result (49) for \( E(n) \), then equation (46) is written as
\[
\frac{C^+_i(n)}{C^-_i(n')} = \frac{N}{n_i + 1} e^{-\beta \varepsilon_i + \beta \mu_i}.
\]
A solution is
\[
C^+_i(n) = c_i^+ N,
\]
\[
C^-_i(n) = c_i^- n_i,
\]
where \( c_i^+ \) and \( c_i^- \) should obey relation
\[
\frac{c_i^+}{c_i^-} = e^{-\beta \varepsilon_i + \beta \mu_i}.
\]
For convenience we define \( x_i = N_i / N \) and the functions
\[
w_j^+ (x) = k_j^+ \prod_{i=1}^{q} x_i^{v_{ij}}, \quad w_j^- (x) = k_j^- \prod_{i=1}^{q} x_i^{v_{ij}},
\]
and
\[
v_i^+ (x) = c_i^+, \quad v_i^- (x) = c_i^- x_i.
\]
In terms of these functions, the transition rates are \( R_j^f = N w_j^f \) and \( C_i^f = N v_i^f \).

VII. STEADY STATE AND ENTROPY PRODUCTION

A solution of the master equation (10) with the transition rates (55), (56), (58), and (60) can easily be obtained in the regime of large \( N \). In this regime, the distribution \( \rho (x) = N P (n) \) of the variables \( x_i = n_i / N \) will be peaked around the averages \( \bar{x}_i = \langle x_i \rangle \). In fact the distribution will be a multivariate Gaussian distribution with variances proportional to \( N \). Therefore, in the limit \( N \to \infty \), the average \( \langle f (x) \rangle \) of a function of \( x \) may be replaced by \( f (\bar{x}) \). Using this result in equation (11), we see that the flux of particles \( \phi_i = \Phi_i / N \) per site is
\[
\phi_i = v_i^+ (\bar{x}) - v_i^- (\bar{x}).
\]
Using the same result in equation (48), the flux of reaction per site \( \chi_j = X_j / N \) is written as
\[
\chi_j = w_j^+ (\bar{x}) - w_j^- (\bar{x}).
\]
Equation (24), that gives the time evolution of \( \langle n_i \rangle \), is thus written as
\[
d\bar{x}_i = \gamma_i + \phi_i,
\]
where
\[
\gamma_i = \sum_{j=1}^{r} v_{ij} \chi_j.
\]
The equation (66) constitute a set of closed equations for \( \bar{x} \).

In the stationary state we may solve for \( \bar{x} \), and obtain the rate of entropy production per site \( P = \Pi / N \), given by
\[
P = \sum_{j=1}^{r} A_j \chi_j.
\]
It is worth writing the affinities in terms of the constants of reaction,
\[
A_j = k_B \left( \ln \frac{k_j^+}{k_j^-} - \sum_{i=1}^{q} v_{ij} \ln \frac{c_i^+}{c_i^-} \right),
\]
obtained from its definition (56) and from the relations (55) and (61). Therefore, we may write the production of entropy as
\[
P = k_B \sum_{j=1}^{r} \left( \ln \frac{k_j^+}{k_j^-} - \sum_{i=1}^{q} v_{ij} \ln \frac{c_i^+}{c_i^-} \right) (w_j^+ - w_j^-).
\]
A simplification on the approach just presented can be obtained by considering that the rate constants \( c_i^+ \) and \( c_i^- \) related to the contact with the reservoirs are large enough. Strictly speaking we will take the limit \( c_i^+ \to \infty \) and \( c_i^- \to \infty \) with the ratio
\[
\frac{c_i^+}{c_i^-} = \zeta_i
\]
finite. According to equation (61) this ratio is \( \zeta_i = e^{-\beta \epsilon_i + \beta \mu_i} \), which we call the activity related to particle of type \( i \), a concept introduced by Lewis [49].

In the present approach it is not necessary that the system exchanges particles of all types. We thus suppose that the system is closed to particles of type \( i = 1, \ldots, q' \) and that it is in contact with reservoirs corresponding to particles of type \( k = q' + 1, \ldots, q \), so that \( q - q' \) is the number of particle reservoirs. Thus for particles of type \( i = 1, \ldots, q' \), the flux \( \phi_i \) vanishes identically. Thus equation (66) is split into two types of equations
\[
\frac{d\bar{x}_i}{dt} = \sum_{j=1}^{r} v_{ij} \chi_j, \quad i = 1, 2, \ldots, q'
\]
\[
\frac{d\bar{x}_k}{dt} = \sum_{j=1}^{r} v_{kj} \chi_j + \phi_k, \quad k = q' + 1, \ldots, q.
\]
Now, for the second set of species the flux of particles is
\[
\phi_k = c_k^+ - c_k^- \bar{x}_k = c_k^- (\zeta_k - \bar{x}_k).
\]
If \( \bar{x}_k \) is large enough, equation (66) will be dominated by this term so that \( \bar{x}_k \) reaches very rapidly the value \( \zeta_k \). Therefore, for the second set of species we may set
\[
\bar{x}_k = \zeta_k \quad k = q' + 1, \ldots, q,
\]
and plug it in the right-hand side of equation (72). This equation is then solved for \( \bar{x}_i, i = 1, \ldots, q' \).

In the stationary state, the entropy production will be given by
\[
P = \sum_{j=1}^{r} A_j (w_j^+ - w_j^-) = \sum_{j=1}^{r} A_j \chi_j,
\]
with the affinity given by
\[
A_j = k_B \left( \ln \frac{k_j^+}{k_j^-} - \sum_{k=q'+1}^{q} v_{kj} \ln \zeta_k \right).
\]
An alternative form to calculate the rate of entropy production is

$$P = \sum_{j=1}^{r} A_j \chi_j - k_B \sum_{i=1}^{q'} \gamma_i \ln \bar{x}_i, \quad (78)$$

which follows from the result that, in this equation, $\gamma_i = 0$ in the stationary state, so that equation (78) becomes identical to equation (76). Using the definition (67) for $\gamma_i$, we get

$$P = \sum_{j=1}^{r} A_j - k_B \sum_{i=1}^{q'} \nu_{ij} \ln \bar{x}_i. \quad (79)$$

Now, from (82) and (77), we find

$$A_j = k_B \left( \ln \frac{w^+_j}{w^-_j} + \sum_{i=1}^{q'} \nu_{ij} \ln \bar{x}_i \right). \quad (80)$$

Replacing this result into (92), we reach the alternative but equivalent form for the rate of entropy production (77)

$$P = k_B \sum_{j=1}^{r} (w^+_j - w^-_j) \ln \frac{w^+_j}{w^-_j}. \quad (81)$$

Although both equations (79) and (81) give the entropy at the stationary state, they are conceptually distinct. Expression (79) is a sum of terms, each one being a product of a flux and a thermodynamic force, or in the present case, a flux of reaction, $\chi_j$, and an affinity, $A_j$. It should be remarked that the first is a thermodynamic density and the second, a thermodynamic field, usually called intensive variable. In addition, expression (79) is suited for an Onsager coefficients [51], which is obtained by expanding $\chi_j$ in terms of $A_j$.

If necessary, the fluxes of particles $\phi_k$ can be computed from the fluxes of reactions $\chi_j$, in the stationary state, by

$$\phi_k = - \sum_{j=1}^{r} \nu_{kj} \chi_j, \quad k = q' + 1, \ldots, q. \quad (82)$$

**VIII. APPLICATIONS**

In the following we apply the present approach to known models of reactive systems. The models are defined by $r$ reactions of type (11) involving $q$ types of particles. The system is close to particles of type $i = 1, \ldots, q'$, and open to particles of type $k = q' + 1, \ldots, q$, and the system is contact only with reservoirs $q - q'$ reservoirs, only. According to the formalism that we have just developed in the second part of the previous section, we may set

$$x_k = \zeta_k, \quad k = q' + 1, \ldots, q. \quad (83)$$

The evolution equation for the $q'$ densities that may vary is given by (72), that is,

$$\frac{dx_i}{dt} = \sum_{j=1}^{r} \nu_{ij} \chi_j, \quad i = 1, 2, \ldots, q', \quad (84)$$

where $\chi_j = w^+_j - w^-_j$, and $w^+_j$ are the transition rates per site, given by (62), with $\zeta_k$ replacing $x_k$. Here we are dropping the bar over $x$.

In each case we consider as parameters of the model the rate constants $k^+_j$ and $k^-_j$ and the activities $\zeta_k$. From these quantities we determine the affinities $A_j$ by the use of equation (77), that is,

$$A_j = \ln \frac{k^+_j}{k^-_j} - \sum_{k=q'+1}^{q} \nu_{kj} \ln \zeta_k, \quad (85)$$

where we have set $k_B = 1$. Equation (84) is solved and the densities $x_i$ are determined at the stationary state, which amounts to solve the equation

$$\sum_{j=1}^{r} \nu_{ij} \chi_j = 0, \quad i = 1, 2, \ldots, q'. \quad (86)$$

From $x_i$ we may determine the fluxes of reactions $\chi_j$, the fluxes of particles $\phi_k$, and the rate of entropy production $P$ by equation (70), that is,

$$P = \sum_{j=1}^{r} A_j \chi_j. \quad (87)$$

In the following we apply the approach we have developed to the case of the first and second Schögl models [51]. The production of entropy of the second model has been determined by several authors [52, 53] by means of formula (81).

**A. First Schögl model**

We start with the case of a chemical system with two reactions and three types of particles, known as the first Schögl model. The reactions are

$$X + A \rightleftharpoons 2X, \quad X \rightleftharpoons B, \quad (88)$$

and the system is in contact with reservoirs of particle of type $A$ and $B$ only. We denote by $x$, $y$, and $z$ the densities of $X$, $A$, and $B$, respectively, and by $a$ and $b$ the activities of $A$ and $B$, respectively. Then

$$y = a, \quad z = b, \quad (89)$$

and

$$\chi_1 = k^+_1 ax - k^-_1 x^2, \quad \chi_2 = k^+_2 x - k^-_2 b. \quad (90)$$
Equation (84), which gives the time evolution of \( x \), becomes
\[
\frac{dx}{dt} = \chi_1 - \chi_2.
\] (91)

In the stationary state
\[
\chi_1 - \chi_2 = 0.
\] (92)

Solving this equation for \( x \) we find
\[
x = \frac{1}{2k_1} \left\{ k_1^+ a - k_2^+ + \left[ (k_1^+ a - k_2^+)^2 + 4k_1^- k_2^+ b \right]^{1/2} \right\}.
\] (93)

The affinities are
\[
A_1 = \ln \frac{k_1^+}{k_1^-} + \ln a,
\] (94)
\[
A_2 = \ln \frac{k_2^+}{k_2^-} - \ln b,
\] (95)

and in the stationary state the rate of entropy production is
\[
P = A_1 \chi_1 + A_2 \chi_2.
\] (96)

From the solution for \( x \) we obtain \( \chi_1 \) and \( \chi_2 \) and \( \Pi \). The fluxes of particle B and C will be \( \phi_2 = \chi_1 \) and \( \phi_3 = -\chi_1 \).

**B. Second Schlögl model**

The reactions of the second Schlögl model are
\[
2X + A \rightleftharpoons 3X, \quad X \rightleftharpoons B,
\] (97)

and again the system is in contact with reservoirs of particle of type A and B, only. Again, we denote by \( x, y, \) and \( z \) the densities of \( X, A, \) and \( B \), respectively, and by \( a \) and \( b \) the activities of \( A \) and \( B \), respectively. Then
\[
y = a, \quad z = b,
\] (98)

and
\[
\chi_1 = k_1^+ a x^2 - k_1^- x^3, \quad \chi_2 = k_2^+ x - k_2^- b.
\] (99)

Equation (84), which gives the time evolution of \( x \), becomes
\[
\frac{dx}{dt} = \chi_1 - \chi_2.
\] (100)

In the stationary state
\[
\chi_1 - \chi_2 = 0,
\] (101)

which is equivalent to
\[
k_1^- x^3 - k_1^+ a x^2 + k_2^+ x - k_2^- b = 0,
\] (102)

and the density \( x \) of particles of type \( X \) is the root of this equation.

The affinities \( A_1 \) and \( A_2 \) have the same form as those of the first model, given by equations (94 and 95), and the rate of entropy production is
\[
P = A_1 \chi_1 + A_2 \chi_2.
\] (103)

Taking into account that \( \chi_1 = \chi_2 \) we may write
\[
P = A \chi,
\] (104)

where \( A = A_1 + A_2 \) and \( \chi = \chi_1 = \chi_2 \).

Solving equation (100), for a given initial condition, and taking the limit \( t \to \infty \), the final value of \( x(t) \) will be a solution of (102). For a given set of the parameters, equation (102) may present a single solution. In this
case, the final value of \( x(t) \) will be this single solution no matter what the initial condition is. For another set of the parameters, equation (102) may have three solutions and the final value of \( x(t) \) will depend on the initial condition. In this case, we have arbitrarily chosen as the initial condition the value of \( x \) at the inflexion point when the solutions of (102) is plotted as a function of \( b \). Under this condition, final value of \( x(t) \) will be unique and \( x \) as function of \( b \) will be single-valued with a jump, indicating a discontinuous phase transition, as shown in figure 1. In principle, the discontinuous transition could be attained from the stationary probability distribution. Then, after taking the limit \( t \to \infty \) followed by \( N \to \infty \), a single-valued with a jump could be obtained \[56\]. However, since we do not have an explicit form of the probability distribution, we used the alternative method just explained.

Figures 1, 2, 3, and 4 show, respectively, the density \( x \), the rate of entropy production \( P \), the affinity \( A \), and the flux of reaction \( \chi \) versus the activity \( b \) for several values of \( a \), and for a set of the values of the rate constants. For \( a < a_c \), there is a discontinuous phase transition, indicated by a jump in \( x \). The rate of entropy production \( P \) and the flux of reaction \( \chi \) also display a jump as shown in figure 2 and 3. Notice that, the activity \( A \) is continuous, in agreement with the fact that it is a thermodynamic field. At \( a = a_c \), the jump in \( x \) shrinks to zero inducing the appearance of a critical point. At this point, the rate of entropy production and the flux of reaction also become continuous.

**IX. CONCLUSION**

We have analyzed reactive systems consisting of several chemical reactions by the use of the stochastic thermodynamics. This approach is based on a stochastic description of the time evolution of the system, here described by a master equation, and founded on two assumptions concerning the entropy. The first being the definition of entropy according to Gibbs and the other is the definition of entropy production based on Schnakenberg expression, which is related to the ratio of the probabilities of the forward and reverse trajectories in the space of microscopic states. We have shown that this approach is fully connected to the energetics, being consistent with thermodynamics.

The stochastic trajectory occurs within a space constituted by the microscopic states, which we choose to be the chemical state of each particle. Under some circumstances, it is possible to reduce to a description in terms of the number of particles of each chemical species. In this case, the master equation is reduced to the chemical master equation. By assuming that the equilibrium is attained when the system is closed to particles, being in contact with a heat reservoir only, we have obtained relations that are obeyed by the transition rates of each reaction. These relations partially defines the rates and are used when the system is in contact with particle reservoirs.

The reactive system is studied by placing it in contact with particle reservoirs, in addition to be in contact with the heat reservoir. When the equilibrium condition given by equation (19) is not obeyed, the system will reach a nonequilibrium stationary state. In this case, there will be fluxes of several types including fluxes of particles and a flux of entropy which equals the entropy production. This last quantity is written as a bilinear form in the affinities and fluxes of particles, that is, a sum of terms, each one being a product of the affinity of a reaction \( A_j \) and the flux of reaction \( \chi_j \). It should be remarked that this form was possible due to the specific form of transition rates we have used here.

We have focus mainly on the production of entropy and applied our approach to the first and second Schlögl models. The second model displays a discontinuous phase
transitions and critical points. The density, the particle flux and the production of entropy show a jump at the transition being continuous at the critical point. We remark that the affinities is continuous, which is consistent with the fact that it is a thermodynamic field, usually called intensive variable.

We have shown that the bilinear form of entropy, given by equation (76), can also be written in the form (81).

Usually, this is the expression used to determine the entropy production within the chemical kinetic approach. Although both these formulas give the same result for the entropy, they are conceptually distinct due to the presence of the affinity, which is a thermodynamic field, in the bilinear form (76). This form is the one appropriate to get for instance the Onsager coefficients.

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