

# Steady state thermodynamics for homogeneous chemical systems

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We contribute to the development of steady state thermodynamics for isothermal and homogeneous chemical systems, through a generalized Einstein fluctuation relation, by utilizing a local steady state interpretation of static concentration fluctuations of reaction intermediates. For systems of constrained total chemical affinity the “next-particle ratio” of the probability density,  $q = P(N+1)/P(N)$ , derived from a usual chemical master equation is employed for the construction of chemical potential steady state laws. This analysis is based on the identification of the exponent of the distribution, as a generalized availability of local fluctuations. Further, pressure steady state laws are derived through a generalized Gibbs–Duhem equation, restricted to constant “disequilibrium variables.” Such variables are introduced as state variables, in addition to the classic ones, for the characterization of steady states. They relate to externally controlled generalized forces or affinities, which induce the flows of mass through the system. Within the local steady state approach, the state laws enable the construction of the generalized availability, as state function for quasisteady state processes beginning from a reference state. This quantity is found to provide a Liapounov function for the deterministic evolution of the system towards stationary states in analogy to a previously developed local equilibrium theory. The analysis is applied to two-variable chemical systems of high stoichiometry change, but should be capable of extension to general hydrodynamic systems. © 1994 American Institute of Physics.

## I. INTRODUCTION

Nonlinear chemical systems, when constrained far from equilibrium, exhibit rich dynamic behavior by developing single or multiple steady states, oscillatory and chaotic behavior.<sup>1–3</sup> From all these, only the stationary steady states resemble equilibrium, since, in this case, the macroscopic properties are maintained in time, despite the flow of mass, momentum or energy through the body of the chemical system. Such flows are necessary to maintain the state of the system far from equilibrium.

Similarly, in the microscopic level, the state variables that characterize a steady state are distributed uniquely around their mean values, as in the case of equilibrium, though the forms of the distributions can change drastically as the state of the system is removed far from equilibrium. The relevant concentration fluctuations of isothermal reacting systems have been described by markovian birth–death chemical master equations,<sup>4</sup> which in addition, reproduce the phenomenological chemical kinetic laws in the macroscopic limit.

The stochastic description of fluctuations further, has been utilized in the development of a macroscopic steady state thermodynamic theory<sup>2,5,6</sup> in analogy to classic thermodynamics, through a generalized Einstein fluctuation relation,

$$P(\delta Z) \propto e^{-\delta\Phi}, \quad (1)$$

where  $P$  is the probability distribution for change of intermediate species,  $\delta Z$ , and  $\delta\Phi$  is the accompanying change of a scalar potential compatible to the constraints imposed on the system. Consequently, with temperature retaining physi-

cal meaning at steady state conditions, macroscopic energy potentials,  $\Pi$ , and generalized entropy,  $\Sigma$ , have been introduced by relating  $kT\Phi$  to  $\Pi$  or  $T\Sigma$ .

However, the lack of global solutions of the chemical master equations which provide the probability density, led to the employment of static correlations,  $\sigma_{ij}$ , as a source of analytic information for the theory,<sup>5,6</sup>

$$\sigma_{ij}^{-1} = \partial^2 \Phi / \partial Z_i \partial Z_j. \quad (2)$$

The static correlations are more easily accessible and have been used for the construction of state laws through integration of Eq. (2) along steady states, though not always with complete success. This is so, because additional state variables to those of equilibrium, termed “disequilibrium variables,”<sup>7</sup> are needed for the description of steady states, and information about their effect on nonequilibrium chemical systems is currently lacking.

In the approach followed by Keizer,<sup>2</sup> steady state thermodynamics has been developed, by utilizing the entropic representation through,

$$\partial^2 \Sigma / \partial Z_i \partial Z_j = k \sigma_{ij}^{-1}. \quad (3)$$

Here, the fluctuations of macroscopic variables at stationary noncritical steady states are considered Gaussian and determined from a generalized “fluctuation-dissipation” theorem. This formulation is compatible to the master equation approach, because the Gaussian distributions, although approximate, are asymptotic solutions of the master equation, at least to dominant order in  $1/V$ , where  $V$  is the volume of the system.<sup>8</sup> In this theory, the fluxes that keep the system far from equilibrium, together with the variables that characterize the baths that affect them, are treated as disequilibrium variables. Although this description of steady states is in

principle complete, the disequilibrium variables are not related to the formalism and thus their effect on the system has remained undetermined. This deficiency, however, does not restrict the applicability of the theory for states of the same disequilibrium variables and many relevant examples have been presented in the literature.<sup>9</sup>

Based on the results of steady state thermodynamic analysis, we have proceeded in the construction of chemical potential and pressure state laws,<sup>7</sup> by exploiting the analytic results of stochastic theory for isothermal one-intermediate chemical models. The crucial step was the identification of a disequilibrium parameter, which relates to variables that appear in the master equation and characterizes the steady states. This parameter is related exponentially to the total chemical affinity, which, in turn, has been identified as the disequilibrium variable of the system. This consideration is in accordance to Keizer's introduction of fluxes as state variables, since, at least close to equilibrium, the chemical affinity relates monotonically to the flux of mass through the system. Other similar such variables have been identified for the characterization of stationary states in the past through computer simulations<sup>10</sup> and experiments with general hydrodynamic systems.<sup>11</sup>

The purpose of this paper is to proceed further in the development of steady state thermodynamics of homogeneous and isothermal chemical systems, while working within the master equation approach, by first extending the construction of steady state laws for generalized intensive classic variables that retain meaning at steady states, such as the chemical potential and pressure, to many-intermediate systems, and then by introducing generalized potentials which can provide evolution criteria for the deterministic motion of chemical macroscopic variables around steady states. This is accomplished by treating the relaxing system in a local steady state approach, in analogy to the local equilibrium considerations of similar systems. Such a procedure has been followed by Ross and co-workers,<sup>12</sup> (RHH), by utilizing a local equilibrium approach for the description of fluctuations around stationary steady states. The central quantity introduced is the "excess work,"  $\varphi$ , which is required to reverse a fluctuation of concentrations relative to the work available at a similar imposed change of state variables. This function identified from a fluctuation relation has been found to provide a Liapunov function for the deterministic evolution of chemical systems toward stable steady states.

The current procedure is to start with a generalized Einstein fluctuation relation and find, first, a relation between the chemical potential and the probability density. Further, due to the lack of general solution for a usual chemical master equation, a relation of the chemical potential to yet another quantity which determines the probability density, the "next-particle ratio,"  $q = P(Z+1)/P(Z)$ ,<sup>13</sup> is derived. For this quantity, an equation is obtained from the master equation, that can be solved more easily at stationary conditions to order  $1/V$ .

A basic quantity in our analysis is the generalized energy potential,  $\Pi$ , which is characteristic of the steady states of a chemical system and fulfills Eq. (1),  $P(\delta Z) \propto \exp(-\delta\Pi/kT)$ ,

in the case of local steady state fluctuations. In addition, our potential is defined as first order homogeneous function of the relevant classic extensive variables,  $Z$ , in resemblance to previously developed thermodynamic theories.<sup>5,7</sup> A similar consideration for the extensive disequilibrium variables, as not necessary to the current analysis, is not introduced here, though it has been endorsed by Keizer<sup>2</sup> and has been found to comply with computer simulation results on hydrodynamic systems.<sup>10</sup> Here, we will consider as intensive such variables only chemical affinities which are controlled through coupling of the system to chemical baths via species selective membranes.

Further, generalized intensive classic variables are defined through

$$z = (\partial\Pi/\partial Z)_R, \quad (4)$$

where  $z$  is  $T$ ,  $-P$ ,  $\mu$  when  $Z$  is  $S$  (generalized entropy),  $V$ ,  $N$ , respectively, and  $R$  represents remaining extensive variables and disequilibrium variables. Likewise, extensive and intensive disequilibrium variables,  $\Psi$  and  $A$ , are related through

$$A = (\partial\Pi/\partial\Psi)_R. \quad (5)$$

The above considerations enable the definition of other potentials,  $\Pi'$ , through Legendre transforms over some of the classic variables (at least),

$$\Pi' = \Pi - \sum_i z_i Z_i. \quad (6)$$

We can, also, write a differential form for the potential expanded in terms of all variables,

$$d\Pi = \sum_i z_i dZ_i + \sum_i \Psi_i dA_i. \quad (7)$$

Through this equation and  $\Pi = \sum_i z_i Z_i$  we obtain a generalized Gibbs–Duhem equation for states of the same  $A$ -variables,

$$\sum_i Z_i dz_i = 0. \quad (8)$$

The connection of thermodynamics to the probability density of a master equation has been implemented through a generalized Einstein fluctuation relation of the form

$$P(\mathbf{Z}^s, \boldsymbol{\eta}^s; \mathbf{Z}^r, \boldsymbol{\eta}^r) \propto \exp[-[\Pi(\mathbf{Z}^s, \boldsymbol{\eta}^s) - \Pi(\mathbf{Z}^r, \boldsymbol{\eta}^r)]/kT], \quad (9)$$

where superscripts  $s$  and  $r$  refer to final (local) states and reference states, respectively, and bold letters represent collectively all relevant variables as vectors. The  $\boldsymbol{\eta}$  parameters are convenient state determining (disequilibrium-) parameters, precursors of the disequilibrium variables to which they relate monotonically. However, the probability density on the left-hand side (LHS) of this relation, as determined from a usual chemical master equation, does not depend on disequilibrium parameters of the final state,  $\boldsymbol{\eta}^r$ , and thus additional considerations about these parameters are required. The freedom to choose these parameters has been restricted in the past, by requiring the chemical potential differences determined through such a relation and  $\mu \approx \partial \ln \Pi / \partial Z$  to be additive.<sup>7</sup> It was found in the case of one-variable systems, and will be generalized below for many-variable nonlinear

systems, that this is fulfilled whenever  $\eta^s = \eta^r$ . With this interpretation, chemical potential and pressure state laws have been constructed, the latter through the generalized Gibbs–Duhem equation, Eq. (8).

In the following we first present a general method for the construction of state laws, through the determination of next-particle ratios of the probability distribution. In Sec. III we develop evolution criteria for systems amenable to local steady state analysis, by studying the performance of thermodynamic potentials of complex systems as Liapounov functions of the corresponding kinetic equations. Finally, in the discussion we summarize our results and comment on the possibility of determining the dependence of steady state thermodynamics on disequilibrium variables.

## II. THERMODYNAMIC STEADY STATE LAWS

A system amenable to analysis through the master equation approach, consists of a reaction chamber of constant volume, coupled to a thermal bath and two chemical baths which control the temperature and the chemical potential of reactants and products,  $A$  and  $B$ , of a chain reaction of the form



In order to isolate the kinetic processes from other transport phenomena, as required in the current approach, we assume fast relaxation of concentration, momentum and thermal gradients compared to chemical rates throughout the system. For such a system, the nonequilibrium effects become evident through the modifications that are induced on the ideal local equilibrium state laws of the chemical potential and pressure of the intermediate species.

To derive a state law for the chemical potentials, we have interpreted the difference of potentials at the exponent of Eq. (9) as a generalized availability,<sup>7</sup> which for a quasi-steady state process that varies  $X$  and  $Y$  (represented collectively by  $Z$ ) is given by

$$\Delta\Pi = \int_r^s \sum_i (\mu_i^s - \mu_i^r) dZ_i, \quad (11)$$

where the summation runs over all intermediate chemical species. For a final state ( $s$ ) close to an initial (reference) state ( $r$ ), we can now connect the chemical potentials to the probability density, by relating Eqs. (9) and (11), and obtain

$$\mu_i^s - \mu_i^r = -kT \ln P/dZ_i. \quad (12)$$

Since it is not possible to determine global solutions for the probability densities of the birth–death master equations, to proceed further, we derive an equation for the next-particle ratio of the probability,  $q_i(\{Z_{j \neq i}\}, t) = P(Z_i + 1, \{Z_{j \neq i}\}, t) / P(Z_i, \{Z_{j \neq i}\}, t)$ , which allows the determination of the chemical potentials in the macroscopic limit through

$$\mu_i^s - \mu_i^r = -kT(q_i - 1) \approx -kT \ln q_i, \quad (13)$$

where Eq. (12) has been used in the first equality. Although the second equality appears approximate for states far from each other, since it holds for  $q_i \approx 1$ , the final result should be general without any limitation on the distance between states. This is so, because the differences of the chemical potential between consecutive states will turn out to be additive, as they should be. Finally, to derive an equation for the  $q$ 's we start from the master equation, which for a general chain chemical reaction model

$$\sum_i \nu_{i\alpha}^- Z_i \stackrel{j_\alpha^+}{=} \sum_i \nu_{i\alpha}^+ Z_i, \quad (14)$$

involving ( $\alpha$ ) reversible reactions of reactants  $Z_i$ , takes the following compact form:<sup>4,14</sup>

$$\begin{aligned} \partial P(\mathbf{Z}, t) / \partial t &= -P(\mathbf{Z} + \mathbf{n}_\alpha, t) \sum_\alpha [j_\alpha^+(\mathbf{Z} + \mathbf{n}_\alpha, \mathbf{Z}) + j_\alpha^-(\mathbf{Z} - \mathbf{n}_\alpha, \mathbf{Z})] \\ &\quad + \sum_\alpha P(\mathbf{Z} - \mathbf{n}_\alpha) j_\alpha^+(\mathbf{Z} - \mathbf{n}_\alpha, \mathbf{Z}) \\ &\quad + \sum_\alpha P(\mathbf{Z} + \mathbf{n}_\alpha) j_\alpha^-(\mathbf{Z} + \mathbf{n}_\alpha, \mathbf{Z}), \end{aligned} \quad (15)$$

where the vectors  $\mathbf{Z}$  and  $\mathbf{n}$  represent the number of intermediate species  $\{Z_i\}$  only and their changes at every reaction step,  $\{n_{i\alpha}\}$ , with  $n_{i\alpha} = \nu_{i\alpha}^+ - \nu_{i\alpha}^-$ . The transition probabilities,  $j$ , for large  $Z$  are given by

$$j_\alpha^\pm = k_\alpha^\pm \prod_i Z_i^{\nu_{i\alpha}}, \quad (16)$$

where, in order for the extensivity property of the transition probabilities to be insured, the constants  $k_\alpha^\pm$  relate to the usual reaction rates,  $\hat{k}_\alpha^\pm$ , through

$$k_\alpha^\pm = \hat{k}_\alpha^\pm (V^{-\sum \nu_{i\alpha}^\pm}). \quad (17)$$

The corresponding kinetic equations have the form  $\dot{z}_i = \sum_\alpha n_{i\alpha} (t_\alpha^+ - t_\alpha^-)$ , where  $z_i = Z_i/V$  and the rates of the mass action law,  $t_\alpha^\pm$ , relate to the transition probabilities through  $V t_\alpha^\pm = j_\alpha^\pm$ .

Since in the macroscopic limit  $j(\mathbf{Z} \pm \mathbf{n}_\alpha) \approx j(\mathbf{Z})$  and  $q_i(\{Z_j + n_j\}, t) \approx q_i(\{Z_j\}, t)$ , to order  $1/V$ , (for relatively small  $n_i$ ), by dividing Eq. (15) with  $P(\mathbf{Z}, t)$  we obtain an equation for  $q_i$ ,

$$\sum_\alpha j_\alpha^+ (\prod_i q_i^{\nu_{i\alpha}^+})^{-1} + \sum_\alpha j_\alpha^- (\prod_i q_i^{\nu_{i\alpha}^-}) - \sum_\alpha (j_\alpha^+ + j_\alpha^-) = 0. \quad (18)$$

The solution of this equation requires approximate techniques in the case of complex reaction mechanisms, as it is discussed in the appendix for a model of high stoichiometry change, but for the system adopted above, with  $m=1$  and  $n=1$ , this equation acquires a simple form that allows an analytic result to be derived,

$$\begin{aligned} q_y(1 - q_x)[j_1^+ - (j_1^- + j_2^+)q_x + j_2^-q_y] \\ + q_x(1 - q_y)[j_3^- (j_2^- + j_3^+)q_y + j_2^+q_x] = 0. \end{aligned} \quad (19)$$

For one-variable systems we recover previously derived results, by fixing the  $Y$  variable, through the identification  $Y \equiv B$ , and setting  $q_y = 1$  in the above equation. The equation obtained,

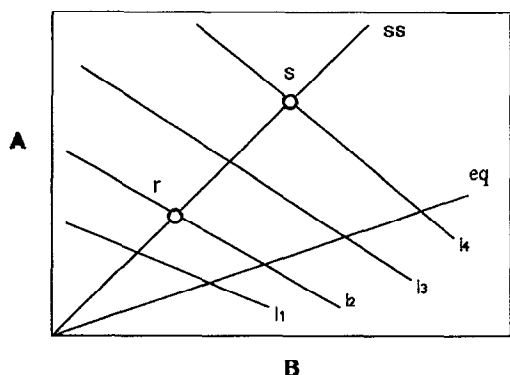


FIG. 1. Schematic representation of stable steady states in the space of  $A$  and  $B$  variables. The states of the same  $\eta$ -parameter arrange themselves along straight lines, ( $ss$ ), one of which represents the equilibrium states, ( $eq$ ). Chemical potential scales are defined along such lines with respect to reference states, ( $r$ ). The inclined lines ( $li$ ) represent steady states of the same  $X$  variable.

$$(1 - q_x)[j_1^+ + j_2^- - (j_1^- + j_2^+)q_x] = 0, \tag{20}$$

has two solutions, one of which is trivial,  $q_x = 1$ , since it corresponds to comparison of states at the peak of the distribution, and the other one,  $q_x = (j_1^+ + j_2^-)/(j_1^- + j_2^+)$ , reproduces the chemical potential steady state law derived from an analytic solution of the master equation,<sup>7</sup>

$$\mu^s - \mu^r = kT \ln[(j_1^- + j_2^+)/(j_1^+ + j_2^-)]. \tag{21}$$

Here, the  $X$  variable in the transition probabilities,  $j$ , refers to a state ( $s$ ) and the  $A$  and  $B$  appearing in  $j_1^+$  and  $j_2^-$  refer to a reference state in relation to which the chemical potential scale is defined. This result is compatible to Keizer's theory, since the covariance matrix determined through  $kT\sigma^{-1} = \partial\mu/\partial X$  fulfills his fluctuation-dissipation relation. In addition, Eq. (21) is identical to the result of RHH,<sup>12(a)</sup> though the chemical potential difference has been interpreted differently as species specific chemical affinity within a local equilibrium approach.

We have found before, that in order for the above chemical potential difference to be additive, or otherwise in order for relation

$$\mu^s - \mu^r = (\mu^s - \mu^l) + (\mu^l - \mu^r) \tag{22}$$

to be an identity for chemical potential differences substituted from Eq. (21), the three states ( $s$ ), ( $l$ ), and ( $r$ ), (and thus any state connected by this equation), must be characterized by the same disequilibrium  $\eta$ -parameter,

$$\eta^s = \eta^l = \eta^r, \tag{23}$$

defined by  $\eta = A/B$ .<sup>7</sup> In the space of  $A$  and  $B$  variables (Fig. 1), such states lie on a straight line that passes through the origin of the axes. In the figure, the  $\eta$ -parameter determines the slope of line ( $ss$ ), and for  $\eta = K^{-1}$ , where  $K$  is the equilibrium constant, it identifies the equilibrium states ( $eq$ ). This parameter provides a measure of the deviation of steady states from equilibrium, and is related to other physically meaningful quantities, such as the flux of mass through the

system and the total chemical affinity which here is externally constrained. The latter quantity, which relates monotonically to  $\eta$ ,

$$A \propto \ln \eta, \tag{24}$$

has been selected as disequilibrium variable, and together with  $X$  provide the chemical state variables of the system, the remaining ones being  $V$  and  $T$ .

To extend this analysis to two-variable systems, we first investigate if the known chemical potential laws of equilibrium fulfill Eq. (19). It is easily verified that, in the cases of general systems at equilibrium and linear systems at steady states, the ideal chemical potential laws [ $\mu_i^s - \mu_i^r = kT \ln(Z_i^s/Z_i^r) = -kT \ln q_i$ ] are compatible with this equation. Specifically, the two long brackets upon setting  $q_X = X^r/X^s$  and  $q_Y = Y^r/Y^s$ , that is,

$$(j_1^- + j_2^+)q_X - j_2^- q_Y = j_1^+, \tag{25}$$

$$-j_2^+ q_X + (j_2^- + j_3^+)q_Y = j_3^-.$$

As in the previous case, the  $X$  and  $Y$  variables in these equations refer to any state ( $s$ ) and the  $A$  and  $B$ , that appear in  $j_1^+$  and  $j_3^-$ , to a reference state ( $r$ ).

Since the set of these equations is not restricted to apply only at equilibrium, it can be used to supply chemical potential laws for general nonequilibrium steady states. Such an analysis requires the identification of a disequilibrium variable that is needed for the full characterization of steady states, in addition to  $X$  or  $Y$ . As in the previous case, it suffices to consider that the  $q$ 's relate states, ( $s$ ) and ( $r$ ), such that  $\eta^s = A^s/B^s = A^r/B^r = \eta^r$ . Assuming  $\gamma$  to be a common scaling factor for the  $A$ 's and  $B$ 's, ( $A^s = A^r/\gamma$  and  $B^s = B^r/\gamma$ ), we infer that  $q_X = q_Y = 1/\gamma$  fulfill Eq. (25). This is so because the  $q$ 's and the variables  $A$  and  $B$ , which appear in  $j_1^+$  and  $j_3^-$ , relate linearly. We thus infer that the additivity property for the chemical potentials is insured provided the compared states are characterized by the same  $\eta$ -parameter. This is a more general conclusion than the one derived for one-variable systems in the past and can be further extended to many-step stochastic processes, though the  $\eta$ -parameter should be defined differently. An example for a two-step process is given in the Appendix.

Since the  $\eta$ -parameter relates monotonically to the externally controlled total chemical affinity, Eq. (24), assuming ideal laws for the species that interact through the chemical baths, the chemical affinity can be identified, again, as the disequilibrium variable of the system. The remaining state variables are the  $X$  (or  $Y$ ) variable, the volume and the temperature of the system.

The chemical potential for states of the same total chemical affinity can now be defined through

$$\mu_X^s = \mu_X^r - kT \ln q_X$$

and

$$\mu_Y^s = \mu_Y^r - kT \ln q_Y, \tag{26}$$

where  $\mu^r$  represent chemical potentials of a reference state. Even better, by utilizing the scaling property of the  $q$ 's we obtain a general expression for the chemical potentials of  $X$

and  $Y$ ,  $\mu^s = \mu^r + kT \ln \gamma$ , and by defining  $\mu_X^r = \mu_Y^r$ , the form of the chemical potentials allows us to obtain  $\mu_X^s = \mu_Y^s$  for all states of the same total chemical affinity. This "convention" generalizes the equality of the chemical potentials of intermediate species at equilibrium, for general steady states.

In the above expressions,  $\gamma$  actually represents relative activities related to number densities through activity coefficients,  $\alpha$ , by  $\gamma_X = \alpha_X X/X^r$  and  $\gamma_Y = \alpha_Y Y/Y^r$ . Analytic expressions for the activities, in terms of  $X$  and  $Y$  variables, are obtained from  $\gamma = 1/q_X$  (or  $\gamma = 1/q_Y$ ) and analytic solutions of Eqs. (25) for the  $q$ 's,

$$q_X = [j_1^+ (j_2^- + j_3^-) + j_2^- j_3^-] / D$$

or

$$q_Y = [j_3^- (j_1^- + j_2^+) + j_1^- j_2^+] / D, \quad (27)$$

with  $D = (j_1^- + j_2^+) (j_2^- + j_3^-) - j_2^+ j_2^-$ . For linear systems, or nonlinear systems at equilibrium, the activity coefficient becomes equal to unity implying ideality for the system.

To proceed further in the construction of pressure steady state laws, we have to look beyond the master equation approach and work with a generalized Gibbs–Duhem equation at constant  $V$ ,  $T$ , and  $\mathcal{L}$ ,

$$\int_r V dP = \int_r X d\mu_X + Y d\mu_Y$$

or

$$(P - P^r) V = \int_r (X + Y) d\mu, \quad (28)$$

where we have made use of the convention  $\mu_X = \mu_Y = \mu$ . The integration of this expression is straightforward but leads to a lengthy expression. Instead, we follow here an approximate but simpler iterative solution of the Gibbs–Duhem equation in differential form,

$$V d(P_X + P_Y) = X d\mu_X + Y d\mu_Y = (X + Y) d\mu. \quad (29)$$

The method is to substitute the  $X$  and  $Y$  variables in the above equation through the ideal state laws,  $X = P_X V / kT$ ,  $Y = P_Y V / kT$ , and  $P = P_X + P_Y$ , and deduce new approximate steady state laws. These laws can be further iterated, to obtain more accurate limiting laws. A single substitution produces the following approximate steady state laws,

$$\begin{aligned} P_X V / XRT &= 1 - (P_X / X) [X(k_2^- + k_3^+) / J_X \\ &\quad + Y k_2^+ / J_Y] \Delta J / J, \\ P_Y V / YRT &= 1, \end{aligned} \quad (30)$$

with

$$\begin{aligned} J_X &= k_1^+ A^r X (k_2^- + k_3^+) + k_2^- k_3^- B^r, \\ J_Y &= k_3^- B^r (k_1^- X + k_2^+) + k_1^+ k_2^+ A^r X, \\ J &= k_1^- X (k_2^- + k_3^+) + k_2^+ k_3^+, \end{aligned}$$

and

$$\Delta J = k_1^+ k_2^+ k_3^+ A^r - k_1^- k_2^- k_3^- B^r,$$

where  $X$  and  $Y$  refer to any state, ( $s$ ). This result has been obtained with the use of Eq. (16) to express the relevant transition probabilities. We observe that the state law for the  $Y$  intermediate remains ideal at this level of approximation, due to the fact that it reacts only through linear steps in the considered model. In addition, it is easily checked that at equilibrium the law for  $X$  reduces also to the ideal state law, since in this case  $\Delta J = 0$ .

The nonidealities observed at nonequilibrium conditions are due to non-Poissonian deformations of concentration distributions,<sup>14</sup> which depend on the asymmetry of the stoichiometry of the forward and backward reaction steps of the nonlinear models.

### III. KINETIC STABILITY CRITERIA

Chemical systems evolve towards stable stationary states according to phenomenological kinetic laws, in the same way they approach equilibrium. In addition, a macroscopic thermodynamic description has been developed based on the introduction of nonclassic disequilibrium variables, in analogy to thermodynamics. It is thus expected that around steady states, kinetic stability criteria would hold, as in the case of equilibrating systems or general nonequilibrium systems that are amenable to local equilibrium description.<sup>12</sup> Indeed, we observe that for the models considered below the generalized availability, Eq. (11), is a Liapounov function in the domain of attraction of stable stationary states. We have to mention here that, despite the similarity in appearance of this availability with the excess work  $\varphi$  of RHH, the two quantities differ, since in the former the chemical potentials depend on a disequilibrium variable, not introduced in any equivalent way in the local equilibrium approach.

In addition, since our approach is compatible to Keizer's steady state thermodynamics our generalized availability,  $\Delta\Pi$ , has a counterpart in the latter theory. The corresponding quantity of this theory which has been developed in an entropic representation is the second differential of the generalized entropy,  $\delta^2\Delta\Sigma$ , also identified as Liapounov function.<sup>2</sup> More precisely,  $2\Delta\Pi$  or even better the second variation  $\delta^2\Delta\Pi$  corresponds to  $-T\delta^2\Delta\Sigma$ . However, despite the similarity of the two quantities, differences exist in the construction and in the interpretation of stochastic results concerning the identification of disequilibrium variables as presented in the introduction. The former difference is of order  $1/V$  and thus Keizer's theory approaches the results from the master equation at the macroscopic level, but the latter difference can be alleviated only close to equilibrium where linear laws prevail and thus our disequilibrium variable, that is the chemical affinity, relates linearly to Keizer's mass flux.

In the current approach the integration of  $d\Pi$  along any path in the  $X, Y$  variable space requires the knowledge of dependence of the chemical potential on the  $A$ -variable. Since such information is currently lacking, in order to derive stability criteria we have to rely on a local steady state approach, according to which, states along an  $X, Y$  path should be represented by steady states of independent  $X$  and  $Y$  components with  $A$ -variables equal to  $A^r$ . This assumption eliminates the  $A$ -variable dependence from the availability, but introduces complexity into the analysis, especially for

nonlinear many-variable systems. However, general results can be derived for one-variable nonlinear and two variable linear models, which we present in the following.

### A. One-intermediate nonlinear chemical systems

In the case of the one-variable model considered above, with chemical potential given by Eq. (21), the availability along a deterministic path (traced in reverse direction) from a reference state ( $r$ ) to a state characterized by  $X$  is calculated from

$$\Delta\Pi = kT \int_r \ln[(j_1^- + j_2^+) / (j_1^+ + j_2^-)] dX. \quad (31)$$

The proof that  $\Delta\Pi$  is a Liapunov function for the relaxing macroscopic motion of the chemical system starting from an initial state close to a (reference) stable steady state, is obtained by analyzing the sign of  $\Delta\Pi$  in relation to the sign of  $d\Delta\Pi/dt$  along the relevant deterministic path.<sup>15</sup> Specifically, the sign of the two quantities should be different and  $\Delta\Pi$  should vanish only at the (reference) steady state. Since  $\Delta\Pi=0$  only at  $X=X^r$  and

$$\begin{aligned} d\Delta\Pi/dt &= kT \ln[(j_1^- + j_2^+) / (j_1^+ + j_2^-)] (dX/dt) \\ &= kT \ln[(j_1^- + j_2^+) / (j_1^+ + j_2^-)] (j_1^- + j_2^+ - j_1^+ - j_2^-), \end{aligned} \quad (32)$$

is a negative definite quantity, we are left to consider whether  $\Delta\Pi$  is a positive definite quantity around stable steady states. It is verified, that for stable states this is indeed the case, by expanding the integrand of Eq. (31) around the reference state and then performing the integration

$$\begin{aligned} \Delta\Pi &= kT [(j_1^- + j_2^+ - j_1^+ - j_2^-)' / (j_1^- + j_2^+ + j_1^+ + j_2^-)]_r \\ &\quad \times (X - X_r)^2 + O[(X - X_r)^3], \end{aligned} \quad (33)$$

where the prime indicates differentiation with respect to  $X$  and the subscript  $r$  indicates quantities evaluated at the reference state. The numerator of the dominant contribution of this expression, which determines the sign of  $\Delta\Pi$ , determines also the stability of the deterministic motion, as can be inferred from the linear stability analysis of the relevant kinetic equation

$$d\delta x/dt = (j_1^- + j_2^+ - j_1^+ - j_2^-)'_r \delta x, \quad (34)$$

with  $\delta x = (X - X^r)/V$ . For stable states, the quantity in the brackets should be negative definite and consistently  $\Delta\Pi \leq 0$ . In conclusion, we find that the sign of  $\Delta\Pi$  provides a necessary and sufficient condition for the kinetic stability of steady states of the chemical system.

### B. Two-intermediate linear chemical systems

In the case of a two-intermediate model with  $m=0$  and  $n=1$ , the predicted chemical potential laws are ideal, thereby allowing a simple expansion around steady states to be derived for  $\Delta\Pi$ . To dominant order in  $\delta x$  and  $\delta y$  we obtain

$$\Delta\Pi = kT [(X - X_r)^2 / 2X^r + (Y - Y_r)^2 / 2Y^r] \geq 0 \quad (35)$$

and

$$\begin{aligned} d\Delta\Pi/dt &= kT [\ln(X/X^r) dX/dt + \ln(Y/Y^r) dY/dt] \\ &\approx kT \mathbf{V}^t \mathbf{M} \mathbf{V}, \end{aligned} \quad (36)$$

where  $\mathbf{V}^t$  is the transpose of vector  $\mathbf{V}$  with components  $\delta X$  and  $\delta Y$ , and  $\mathbf{M}$  is a matrix

$$\mathbf{M} = \begin{bmatrix} j_X^x/X^r & j_X^y/X^r \\ j_Y^x/Y^r & j_Y^y/Y^r \end{bmatrix}, \quad (37)$$

with

$$\begin{aligned} j_X &= j_1^+ + j_2^- - j_1^- - j_2^+, \\ j_Y &= j_2^+ + j_3^- - j_2^- - j_3^+, \end{aligned}$$

and where the superscripts,  $x$  and  $y$ , indicate partial differentiation with respect to the denoted variables.

Since  $\Delta\Pi$  is positive definite, we should require  $d\Delta\Pi/dt \leq 0$  for stable states, or otherwise that the eigenvalues ( $\epsilon_1, \epsilon_2$ ) of the matrix of the quadratic form,  $\mathbf{M}$ , be both negative,

$$\begin{aligned} \epsilon_1 + \epsilon_2 &= j_X^x/X^r + j_Y^y/Y^r < 0 \\ \epsilon_1 \epsilon_2 &= (j_X^x j_Y^y - j_X^y j_Y^x) / X^r Y^r > 0. \end{aligned} \quad (38)$$

These inequalities can be proved with the help of linear stability analysis of the kinetic equations, which produces a stability matrix,  $\mathbf{L}$ , of negative eigenvalues, ( $\varrho_1, \varrho_2$ ), in the case of stable steady states,

$$d\delta\mathbf{V}/dt = \mathbf{L}\delta\mathbf{V}, \quad (39)$$

where  $\delta\mathbf{V} = (\delta X, \delta Y)$  and

$$\mathbf{L} = \begin{bmatrix} j_X^x & j_X^y \\ j_Y^x & j_Y^y \end{bmatrix}. \quad (40)$$

Thus, in the case of stable states we obtain

$$\begin{aligned} \varrho_1 + \varrho_2 &= j_X^x + j_Y^y < 0, \\ \varrho_1 \varrho_2 &= (j_X^x j_Y^y - j_X^y j_Y^x) > 0. \end{aligned} \quad (41)$$

Even more, by inspection we deduce that for the models considered above, Eq. (10),  $j_X^x$  and  $j_Y^y$  are separately negative. These conditions ensure inequalities (38) and thus again we deduce that  $\Delta\Pi$  provides a necessary and sufficient condition for the stability of linear systems.

## IV. DISCUSSION

The main result of this work is that steady state laws for many-intermediate homogeneous and isothermal chemical systems have been derived from the results of stochastic analysis, by the use of a generalized Einstein fluctuation relation applied at steady state conditions. Such a relation provides a connection between thermodynamics and probability distribution of fluctuations, which in the current approach are derived from a usual birth–death chemical master equation. The exponent of the distribution is identified as a generalized availability which characterizes the deviation of a steady state from a reference one in a local steady state manner. This allows the connection of the chemical potential to the next-particle ratio of the probability distribution,  $P(Z+1)/P(Z)$ , for which, in turn, an equation is derived from the

master equation. The systematic solution of this equation provides chemical potential steady state laws for a large class of chemical models in contrast to previous heuristic approaches.

Although the chemical potential steady state laws are derived directly from stochastic analysis, pressure state laws are derived indirectly by the use of a generalized Gibbs–Duhem equation. The nonequilibrium effects become evident in both state laws through introduction of corrections to the ideal laws of equilibrium.

The crucial step in the interpretation of stochastic results is the identification of the chemical affinity as disequilibrium variable for the characterization of the steady states. However, it has been realized that information about this variable is not contained in the probability distribution of a usual chemical master equation and thus other methods have to be employed for this purpose. Experiment, computer simulation, and generalized master equations that can take account of the effect of externally controlled chemical affinities can provide some means along this line. In addition, we have proved here, in the case of one-variable nonlinear and two-variables linear models, that the generalized availability defined in a local steady state approach is a Liapounov function for the deterministic macroscopic motion of the system towards stationary steady states. We can thus formulate necessary and sufficient kinetic stability criteria for certain reaction models by examining the definiteness of this function and its rate of change along a kinetic path, in analogy to the previously developed local equilibrium theory of John Ross and coworkers. Although the results depend on the models considered, similar analysis should be applicable to other more complex chemical systems, as well as to general hydrodynamic systems.

## APPENDIX

We consider a one-variable two-step chemical model, consistent with the general system introduced above, Eq. (10),



The relevant equation for  $q$ , Eq. (18), is a third order equation forbidding a simple analytic solution,

$$j_1^- q^3 + (j_1^- + j_2^+) q^2 - (\hat{j}_1^+ + \hat{j}_2^-) q - \hat{j}_1^+ = 0, \quad (\text{A2})$$

where the hats indicate that the  $A$  and  $B$  variables involved in the corresponding  $j$ 's refer to a reference state. Despite this, simple results can be derived for some special cases. First, for equilibrium states,  $j_1^+ = j_1^-$  and  $j_2^+ = j_2^-$ , this equation becomes

$$(q+1)(j_1^+ q^2 - \hat{j}_1^+) + q(j_2^- q - \hat{j}_2^-) = 0. \quad (\text{A3})$$

By inspection we find that for  $q=1/\gamma$  the two square brackets vanish upon setting  $A^s/A^r = \gamma^2$  and  $B^s/B^r = \gamma$ . This implies that the equality  $A^s/A^r = (B^s/B^r)^2$  should hold, or otherwise that the ratio  $\eta_e = A/B^2$ , should be the same for the compared states. Obviously this is fulfilled, since the inverse of the ratio is equal to the equilibrium constant. Again, as in the models discussed in Sec. III, the value of the inverse of the equilibrium constant is the value which the disequilibrium  $\eta$ -parameter acquires at equilibrium. This parameter relates monotonically to the total chemical affinity since  $\ln \eta_e \propto \mu_A - 2\mu_B = \mathcal{A}$ .

Another simple result is derived by setting  $j_1^- = 0$  in Eq. (A2),

$$(2j_1^+ + j_2^-) q^2 - (\hat{j}_1^+ + \hat{j}_2^-) q - \hat{j}_1^+ = 0, \quad (\text{A4})$$

where we have made use of the steady state condition  $j_2^+ = 2j_1^+ + j_2^-$ . By setting  $q=1/\gamma$  and  $B^s/B^r = \gamma$  in this equation, we deduce that  $A^s/A^r = \gamma(\gamma+1)/2$ , or otherwise that

$$2A^s/A^r = (B^s/B^r)(1 + B^s/B^r). \quad (\text{A5})$$

In the space of the chemical  $A$  and  $B$  variables, this relation restricts the compared states to a line, along which chemical and pressure scales can be defined.

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