What can be stated by the Glansdorff–Prigogine criterion concerning the stability of mass-action kinetic systems?

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We investigate which general results concerning the local stability of steady states of arbitrary chemical reaction networks can be deduced with the Glansdorff–Prigogine stability criterion. Especially, it is proven that the presence of an autocatalytic reaction is not a necessary condition for a violation of the thermodynamic stability condition. It turns out that every reaction with at least one variable reactant at each side of the reaction equation can potentially destabilize the steady states. An explicit example of a simple reaction system without autocatalytic reactions where the stability of the steady state changes via a supercritical Hopf bifurcation is discussed. Furthermore, in expanding the original concept for proving local stability to global stability analyses, a general way for constructing different Lyapunov functions is given. © 1999 American Institute of Physics.

I. INTRODUCTION

The theory of thermodynamics allows one to derive in the classical deductive manner according to the ideal prototype of Euklid’s “Elements” from few general axioms a multitude of prominent results. However, up to now the theory is valid only at equilibrium and near equilibrium. In the general nonequilibrium case the multifarious dynamical phenomena are not covered in such a general way by the thermodynamic theory.

Near equilibrium, where linear relations between the thermodynamic flows and forces are valid, the celebrated Onsager–Casimir theory is fully satisfactory to understand and describe the observed phenomena. The Brussels group developed their theory with the aim to derive in the thermodynamic framework interesting results also for systems far from equilibrium (cf. Ref. 1). An important field of applications has been, from the very beginning, chemical reaction networks.1–3 Chemical systems have also been used to demonstrate that the Glansdorff–Prigogine stability criterion is not necessary, but only sufficient for the local stability of steady states.4,5 Nevertheless, it could be that for modeling of chemical systems interesting and relevant results follow from this criterion. For example, one could find a subclass of reaction networks with only thermodynamically stable steady states which directly implies kinetic stability (according to the usual mathematical local stability theory).

In this context it is especially interesting to note that it has often been stated that reaction networks with unstable steady states contain autocatalytic reactions. The Brussels group showed that special autocatalytic reactions yield a destabilizing contribution in the framework of the Glansdorff–Prigogine stability theory.1–3 Indeed, all known oscillating reaction systems (e.g., model systems such as the Brusselator,3 the Lotka–Volterra system,6 the Oregonator,7 or the smallest chemical reaction system with Hopf bifurcation8) contain at least one autocatalytic reaction. On the other hand, e.g., the homogeneous Turing system (cf. Ref. 3) with its cross-catalytic property in the absence of a direct autocatalytic reaction always has a locally stable steady state. Thus, the question arises whether an autocatalytic reaction is really necessary for an unstable steady state (e.g., for a Hopf bifurcation) of the whole network. It should be noted that in all known chemical and biochemical reaction systems which show sustained oscillations the stable limit cycle always arises via a supercritical Hopf bifurcation.9

In this work we investigate in a general manner the thermodynamic stability of arbitrary mass-action kinetic reaction networks. In particular, we show that former analyses of single reactions with the result that autocatalytic reactions destabilize the steady state and nonautocatalytic ones do not, has not been carried out in the necessary generality. It is demonstrated that (without knowledge of the steady state concentrations) with the studied criterion the stability of the steady states can be proven only for a very restricted class of reaction networks. Furthermore, we present a simple example of a reaction system with a supercritical Hopf bifurcation, which does not contain an autocatalytic reaction.

In the analysis we confine ourselves to the important case of reaction networks with mass-action kinetics where one reaction can be written as

\[
S + \sum_i k_i \frac{v_i}{k_{i\rightarrow}} X_i = P + \sum_i v_i \frac{v_i}{k_{i\rightarrow}} X_i \quad (v_i^+, v_i^-, k_i, k_i = 0). \quad (1)
\]

The reaction velocity is assumed to be proportional to the concentrations of the involved reactants (in consideration of their molecularity). Here S and P denote the sum of the constant substances and products and \( k_i \) and \( k_{i\rightarrow} \) the rate coefficients of the forward and backward unidirectional reaction, respectively. \( X_i \) is the \( i \)th variable reactant and \( v_i^+ \) and \( v_i^- \) its stoichiometric coefficients. In this case a simple unambiguous definition for an autocatalytic reaction can be given. The considered reaction is autocatalytic, if

\[
v_i^+ \neq 0, \quad v_i^- \neq 0, \quad v_i^+ \neq v_i^- \quad (2)
\]

for at least one reactant \( X_i \).
II. THERMODYNAMIC STABILITY ANALYSIS OF ARBITRARY MASS-ACTION KINETIC REACTION NETWORKS

According to the general theory developed by the Brussels group (cf. Ref. 1), the thermodynamic equilibrium state is locally stable if the excess entropy \( \delta^2 S \), taken at equilibrium, is negative for arbitrary small deviations, i.e.,

\[
(\delta^2 S)_{eq} < 0.
\]

(3)

If the system is thermally and mechanically stable, this condition reduces to the condition for stability with respect to diffusion, i.e.,

\[
\sum_i \delta \mu_i \delta n_i > 0,
\]

(4)

where \( \mu_i, n_i \) denote the chemical potential and the mole number of reactant \( X_i \), respectively.

The thermodynamic theory for local stability of nonequilibrium steady states (ss) is based on the assumption of stable local equilibrium (cf. Ref. 1). In purely mathematical terms, this can be expressed in terms of a negative definite function, which for physical reasons may be termed excess entropy density:

\[
(\delta^2 S)_{ss} < 0.
\]

(5)

In the domain of phase space where this is a negative definite function it serves as an appropriate Lyapunov function which can prove the stability of the steady states.

The analyzed steady state is globally stable in a domain \( D \) of the phase space if the time derivative of the excess entropy density, i.e., the excess entropy production density is positive for all deviations contained in \( D \):

\[
\frac{d(\delta^2 S)_{ss}}{dt} > 0.
\]

(6)

To prove the local stability it is sufficient to analyze the linearized form at the steady state (cf. Appendix B, Ref. 4). It is clear that this criterion is only sufficient for the usual mathematical local stability, because the latter does not require any Lyapunov function. For homogeneous chemical reaction systems (6) simplifies to

\[
\sum_j v_j A_j > 0,
\]

(7)

where \( v_j, A_j \) denote the reaction velocity and the affinity of the \( j \)th reaction, respectively. This expression has the interesting property that it consists of a sum of different terms, each belonging exactly to one reaction. Of course the thermodynamic stability condition (7) can only be violated if at least one term is negative.

We now successively prove the following (1) For systems under constant temperature and pressure the excess entropy density is a negative definite function in the whole phase space \( \delta^2 S = f(c_i) \), where \( c_i \) denotes the concentration of reactant \( X_i \). (2) Already the simple reaction \( X=Y \) (this is the simplest nonautocatalytic reaction with variable substrate and product) always yields a negative term in the excess entropy production density. (3) Reaction networks consisting exclusively of reactions where one side of the reaction equation contains only constant ("outer") reactants always have locally stable steady states.

A. The excess entropy density is a negative definite function in the whole phase space

For systems under constant temperature and pressure condition Eq. (5) reduces to

\[
L = \sum_{i,k} (\partial \mu_i / \partial c_k)_{ss} \delta c_i \delta c_k > 0,
\]

(8)

where \( L \) is proportional to the negative excess entropy density. This quadratic form is positive definite if its form matrix \( F = (\partial \mu_i / \partial c_k)_{ss} / (RT) \) is positive definite (\( R \) and \( T \) denote the gas constant and temperature, respectively). With the chemical potential of the \( i \)th variable reactant given by

\[
\mu_i = \mu_i^0 + RT \ln c_i,
\]

(9)

\( F \) reduces to

\[
F = \text{diag} \left( \frac{1}{c_1}, \ldots, \frac{1}{c_n} \right).
\]

(10)

Because for positive-valued steady states \( \{\bar{c}_i\} \) all eigenvalues of \( F \) are positive, the function \( L \) is positive definite (and thus the excess entropy density negative definite) and therefore well suited to serve as a Lyapunov function.

B. The simplest example

The tendency of an autocatalytic reaction to destabilize the steady state of the whole system has been explained with the help of the Glansdorff–Prigogine stability criterion (e.g., Refs. 1–3). In order to analyze a special reaction for its ability to destabilize the stationary state one must take into account the variation of all involved variable substances. In doing so, one recognizes that already the simplest monomolecular reaction \( X=Y \) with variable substrate and product always yields a negative term in the excess entropy production density.

From the affinity \( A = RT \ln (qx/y) \), where \( q \) is the equilibrium constant and the corresponding reaction velocity \( v = k_+ x - k_- y \), where lower case characters denote the concentration of the reactants, one obtains for the first variation

\[
\delta A = RT \left( \frac{\delta x}{x} - \frac{\delta y}{y} \right), \quad \delta v = k_+ \delta x - k_- \delta y.
\]

(11)

Upon combining one finds the quadratic form

\[
\delta v \delta A = RT \left( k_+ \frac{k_-}{y} (\delta x)^2 + k_- \frac{k_+}{x} (\delta y)^2 - \frac{k_+}{x} + \frac{k_-}{y} \right) \delta x \delta y.
\]

(12)

Note that the excess entropy production density contains the negative \( \delta x \delta y \) term. The whole expression is positive.
semidefinite if and only if \( 2k_+k_-/(\bar{x}\bar{y}) \geq (k_-/\bar{x})^2 + (k_+/(\bar{y}))^2 \), which for \((x,y) \neq (\bar{x},\bar{y})\) never holds. The equality sign is obtained in the equilibrium case.

Generally one studies the definiteness of quadratic forms with \(n\) variables via its form matrices \(F\). A quadratic form is positive definite if all main minors of its matrix are positive. At sufficient distance from equilibrium, however, the one-dimensional case:

\[
F = \begin{pmatrix}
\frac{k_+}{x} & -\frac{1}{2} \left( \frac{k_+}{y} + \frac{k_-}{x} \right) \\
\frac{1}{2} \left( \frac{k_+}{y} + \frac{k_-}{x} \right) & \frac{k_-}{y}
\end{pmatrix}
\]

Both \(1 \times 1\) main minors are always positive, because the unidirectional reaction rates as well as the steady state concentrations are positive, but the determinant \(\det(F)\) is negative semidefinite:

\[
\det(F) = -\frac{1}{4} \left( \frac{k_+}{y} - \frac{k_-}{x} \right)^2.
\]

Note that in the equilibrium case the determinant is zero and the whole quadratic form positive semidefinite \((\bar{y}/(RTk_-)) \partial \nu \partial \Lambda = (q \partial x - \partial y)^2\).

Herewith, we have shown that for this simplest case the excess entropy production density, i.e., in the sum (7), one generally has to analyze an \(n \times n\) form matrix \(F\). The considered reaction always stabilizes the steady state if \(F\) is positive semidefinite, i.e., if \(F\) has only non-negative main minors.

C. The general case

In order to decide whether an arbitrary reaction of the form (1) yields a positive or a negative contribution in the excess entropy production density, i.e., in the sum (7), one generally has to analyze an \(n \times n\) form matrix \(F\). The considered reaction always stabilizes the steady state if \(F\) is positive semidefinite, i.e., if \(F\) has only non-negative main minors. It will be shown that for all drawn conclusions it is sufficient to analyze a general reaction with two variable substances of the form

\[
\begin{align*}
 aX + bY & \to cX + dY, \quad F = \begin{pmatrix} k_+ & k_- \\ k_- & k_+ \end{pmatrix}
\end{align*}
\]

where possible constant reactants are incorporated into the rate constants (which are therefore sometimes termed “apparent” rate constants). The velocity (mass-action kinetics) and affinity (ideal solute systems) of this reaction can be written as

\[
\begin{align*}
 v & = k_+ x^a y^b - k_- x^c y^d, \quad A = RT \ln(q x^a - c y^b - d),
\end{align*}
\]

yielding

\[
\begin{align*}
 \delta v & = (k_+ a \bar{x}^{a-1} y^b - k_- c \bar{x}^{c-1} y^d) \delta x \\
 & \quad + (k_+ b \bar{x}^{a-1} y^{b-1} - k_- d \bar{x}^{c} y^{d-1}) \delta y, \\
 \delta \Lambda & = RT \left( \frac{a-c}{\bar{x}} \delta x + \frac{b-d}{\bar{y}} \delta y \right).
\end{align*}
\]

Therefore, \(\delta v \partial \Lambda/(RT) = F \partial x \partial y\), with the form-matrix explicitly reading

\[
F = \begin{pmatrix}
\frac{a-c}{\bar{x}} m_{11} & \frac{1}{2} \left( \frac{a-c}{\bar{x}} m_{22} + \frac{b-d}{\bar{y}} m_{11} \right) \\
\frac{1}{2} \left( \frac{a-c}{\bar{x}} m_{22} + \frac{b-d}{\bar{y}} m_{11} \right) & \frac{b-d}{\bar{y}} m_{22}
\end{pmatrix}
\]

where \(m_{11} = k_+ a \bar{x}^{a-1} y^b - k_- c \bar{x}^{c-1} y^d, \ m_{22} = k_+ b \bar{x}^{a} y^{b-1} - k_- d \bar{x}^{c} y^{d-1}\).

1. One-dimensional case

For example, for \(b = d, \ a \neq c\) the problem is reduced to the one-dimensional case:

\[
\text{sgn}(F_{1D}) = \text{sgn}((a-c)(aq-c\bar{x}^{-a})).
\]

If one side of the corresponding reaction equation in Eq. (15) is constant, i.e., for \(a = 0\) or \(c = 0\), one recognizes \(F_{1D} > 0\). In all other cases \(\text{sgn}(F_{1D})\) generally depends on the steady state concentration \(\bar{x}\). In the special case where the steady state equals the thermodynamic equilibrium \(\bar{x}^{-a} = q\), \(F_{1D}\) is positive. At sufficient distance from equilibrium, however, one cannot estimate the sign of \(F_{1D}\) without knowledge of \(\bar{x}\). Both \(1 \times 1\) main minors of \(F\) in Eq. (19) are positive if and only if

\[
(a=0 \text{ or } c=0) \text{ and } (b=0 \text{ or } d=0).
\]

2. Two-dimensional case

The \(2 \times 2\) main minor of \(F\) (19) is its determinant

\[
\det(F) = -\frac{1}{4} \left( \frac{a-c}{\bar{x}} m_{22} - \frac{b-d}{\bar{y}} m_{11} \right)^2 \leq 0.
\]

We analyze under what conditions this expression vanishes. In the two-variable case \((a \neq c \text{ and } b \neq d)\) \(\det(F) = 0\) can be rewritten as

\[
(bc-ad)(q \bar{x}^{-a} \bar{y}^{b-d} - 1) = 0.
\]

This expression vanishes at equilibrium \(q = \bar{x}^{-a} \bar{y}^{d-b}\), or if \(ad = bc\).

In the nonequilibrium case it follows from Eqs. (21) and (24) that the only possibility for positive semidefinite \(F\) reads
shows that the coefficients at the steady state

or

\( (c = 0, \quad d = 0). \) (25)

As can be seen already from Eqs. (17) and (18) arbitrary reactions with \( n \) variables and only constant reactants at one side of the reaction equation always stabilize the steady state, thus completing our analysis. Therefore, we have shown that only reactions with constant reactants at one side of the reaction equation tend to stabilize the steady state(s) of the reaction network.

III. A SIMPLE MASS-ACTION KINETIC SYSTEM WITH HOPF BIFURCATION CONSISTING ONLY OF NONAUTOCATALYTIC REACTIONS

We demonstrate that the sample system:

\[ k_0 \]
\[ A \rightarrow X, \]
\[ 2Y \rightleftharpoons Z, \]
\[ k_{-1} \]
\[ k_2 \]
\[ X + Z \rightarrow Y + Z, \]
\[ k_3 \]
\[ Y \rightarrow B, \]

\[ T = -(k_1k_2 + 5k_{-1} + k_{-1}^2)/k_{-1}, \]
\[ K = -(k_1^2 + 5k_{-1} + k_2^2 + k_1^2k_{-1} - 2k_{-1}^2)/(k_1k_{-1}) \] (30)
\[ D = -k_1k_2. \]

For the choice that \( k_1 = 1, \quad k_{-1} = 1 \) one obtains

\[ T = -(6 + k_2), \]
\[ K = 1 - 6k_2, \]
\[ D = -k_2, \] (31)

\[ TK + D = k_2^2 + 17/3k_2 - 1, \]
i.e., the Hopf bifurcation occurs at \( k_2^* = k_2 = (\sqrt{325} - 17)/6 \approx 0.1713 \) (from \( 6k_2^*/k_2^2 > 1 \) it follows that \( K < 0 \)). Numerical integration shows that it is supercritical bifurcation, i.e., a stable limit cycle arises, which becomes unstable if \( k_2 \) is lowered to \( k_2^* \approx 0.1576 \).

IV. DISCUSSION

In this work we systematically have studied the capability of the Glansdorff–Prigogine stability citerion for general statements about the stability of steady states of mass-action kinetic systems. Let us summarize the most important results.

Generally, i.e., without the restriction to mass-action kinetic systems, three points need to be emphasized

1. Originally the concept of local stability proof by use of the excess entropy density has been based on the assumption of local equilibrium. This very concept can be used in a strict mathematical formulation without reference to local equilibrium. An arbitrary function may be used as a Lyapunov function for steady states, because it is a nonoscillatory form at the equilibrium point.

2. The Glansdorff–Prigogine stability citerion is only a sufficient theorem. For example, the corresponding nonequilibrium form of the equilibrium point does not mean in general the definiteness of the corresponding quadratic form at the non-equilibrium steady state point. Without giving here an explicit example, one can imagine systems where the equilibrium quadratic form is negative definite, but the corresponding nonequilibrium form not. By contrast, the function excess entropy density can be ideally suited to serve as a Lyapunov function for steady states, because it is (positive or negative) definite in a surrounding of this point without fulfilling this condition at the equilibrium point.

3. The Glansdorff–Prigogine stability citerion is only a sufficient criterion, but not a necessary condition for local stability of the corresponding steady state. Nevertheless, two decades ago there was an intensive discussion about this point in the...
A steady state is considered if the system is in a state where the rate of change of the state variables is zero. Keizer and Chang were able to construct as an extension of the well-known trimolecular model, whereby one of these systems demonstrated in Ref. 19 to yield as asymptotic limit cases the so termed “stochastic potential” by Graham 14 for Fokker–Planck processes, generalized by Hanggi 15 for Markovian master equations and recently studied in related form e.g., by Ross and co-workers.

The decomposition of the trimolecular reaction according to system (26) is only bimolecular in the forward and backward direction of all reactions. However, the stability analysis, especially the determination of the Hopf bifurcation hyperplane, has not been done in our general way.

Simple systems such as Eq. (27) are well suited for the application of local bifurcation theory (cf., e.g., Ref. 21) to analytically prove that the occurring Hopf bifurcation is indeed supercritical.

One further point is especially interesting with regard to actual studies. The stable limit cycle of the original trimolecular two-variable model becomes unstable (and the system diverges) if the velocity constant of the autocatalytic reaction is sufficiently small. If one simply adds a further intermediate variable as a storage substance, the stable limit cycle exhibits a period doubling cascade into chaos when lowering the autocatalytic reaction rate. 20 If the rate is lowered even further, the stable chaotic attractor becomes unstable and the system diverges again. In contrast, in system (27) we observed the same (two-dimensional) behavior than in the original two-variable model. 20 Of course the period doubling and the chaotic region in the parameter space could be so narrow that we did not find it numerically, but it seems that the trajectories of the whole three-dimensional model are in fact confined to a two-dimensional surface in the long time limit. Thus, system (27) is a good candidate for applying “no-chaos theorems” in similar form as recently presented in Ref. 23.

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APPENDIX A: PROOF OF THE POSITIVE DEFINITENESS OF A FUNCTION CONSTRUCTED USING MOLE NUMBERS INSTEAD OF CONCENTRATIONS

If one uses the chemical potential of reactant X_i as a function of the mole fraction x_i (note that in this appendix x_i is used for the mole fraction of reactant X_i and not for its concentration) instead of the concentration c_i [like in Eq. (9)], one obtains another function for the excess entropy density. This can be used as a Lyapunov function if it fulfills the condition of definiteness. We here prove that this condition is always fulfilled, because the form matrix of the according quadratic form is positive definite. With

$$\mu_i = \mu_i^0 + RT \ln x_i.$$  \hspace{1cm} (A1)

(with the mole fraction $x_i = c_i / (\Sigma_i c_i + c_j)$) one obtains the function

$$L_{mf} = \sum_{i,k} (\partial \mu_i / \partial c_k) \partial c_i \partial c_k > 0.$$ \hspace{1cm} (A2)
Here, $c_c$ denotes the concentration of the constant substances. If $c_c$ is very large, $L_{\text{mf}}$ becomes identical to $L$ of Eq. (8). The form matrix $F$ of this quadratic form can be written as

$$F = \frac{1}{(\Sigma c_i + c_c) \Pi c_i} \tilde{F}$$

with

$$\tilde{F} = \begin{pmatrix}
\Pi \sum c_i^2 + c_i & -\Pi c_i & \cdots & -\Pi c_i \\
-\Pi c_i & \Pi \sum c_i^3 - c_i & \cdots & \cdots \\
\cdots & \cdots & \ddots & \cdots \\
-\Pi c_i & -\Pi c_i & \cdots & \Pi \sum c_i^2 + c_i
\end{pmatrix}$$

This real symmetric matrix is positive definite if—after the triangle decomposition $\tilde{F} = CB$, where without loss of generality we can set $c_{ii} = 1$ for all $i$—all diagonal elements $b_{ii}$ are larger than zero (cf. Ref. 24). One immediately recognizes $b_{11} > 0$.

Applying the Gaussian algorithm to $\tilde{F}$ to generate the upper triangular matrix $B$, after elimination of the first row and the first column the new matrix $\tilde{F}_1$ reads

$$\tilde{F}_1 = \frac{(\Sigma c_i + c_c) c_1}{\sum c_i^2} \tilde{F}_1$$

with

$$\tilde{F}_1 = \begin{pmatrix}
0 & 0 & \cdots & 0 \\
0 & \Pi \sum c_i^3 + c_i & \cdots & -\Pi c_i \\
\cdots & \cdots & \ddots & \cdots \\
0 & -\Pi c_i & \cdots & \Pi \sum c_i^2 + c_i
\end{pmatrix}.$$  

One now recognizes that $b_{ii} > 0$ and that this likewise works for all remaining $n - 2$ steps. In each step, one $c_i$ is eliminated and the new appearing $b_{ii}$ is larger than zero which finishes the proof.

It follows that the function $L_{\text{mf}}$ is, like the function $L$ (8), for the ideal solute systems under consideration always a suited Lyapunov function, because it fulfills the necessary condition of definiteness.

In Ref. 4 we have shown that in the considered sample system the region of the parameter space for which the (local) stability of the steady state can be proven with the help of the Lyapunov function $L_{\text{mf}}$ is generally smaller than the region for which the (local) stability can be proven with $L$.

**APPENDIX B: CONSTRUCTION OF DIFFERENT LYAPUNOV FUNCTIONS ON THE BASIS OF THE GLANSDOFF–PRIGOGINE CRITERION**

We demonstrate a simple procedure for the construction of Lyapunov functions for proving the global stability of steady states in a domain of the parameter space containing the equilibrium point. For the sake of simplicity we confine ourselves to the simple case of thermal and mechanical stable homogeneous systems.

According to the Glansdorff–Prigogine theory the equilibrium of these systems is locally stable if condition (4) is fulfilled. With the assumption of stable local equilibrium these authors derived the inequality (7) being a condition for local stability of the considered steady state. Because this derivation is based on the idea of using the excess entropy density as a Lyapunov function, it is natural to study with this function global stability as well. As we have shown in Sec. II A (and in Appendix A for the more general function $L_{\text{mf}}$), the function

$$L_{\text{eed}} = \sum \frac{(c_i - c_i^0)^2}{c_i^0}$$

is positive definite, and therefore well suited to serve as a Lyapunov function. $L_{\text{eed}}$ is the function $L$ (8) with finite deviations $\Delta c_i$ instead of infinitesimal deviations $\delta c_i$.

Starting from

$$(\delta^2 s)_{ss} \propto \sum (\delta \mu, \delta c_i)_{ss},$$

we show that related Lyapunov functions can be obtained. The function $L_{\text{eed}}$ follows directly from Eq. (B2) if one uses for the variation of the concentrations the finite deviation from the steady state $\Delta c_i$. If, in addition, one uses for the chemical potentials the finite deviation $\Delta \mu_{ss}$, one obtains

$$L_{\mu} = \sum \frac{(c_i - c_i^0) \ln \frac{c_i}{c_i^0}}{c_i^0}.$$  

This function is positive definite (for $c_i \neq c_i^0$) and therefore suited to serve as a Lyapunov function.

A third related function can be obtained from the relation

$$\frac{1}{2} \frac{\partial}{\partial t} \delta^2 s = - \sum \delta \left( \frac{\mu_i}{T} \right) \frac{\partial}{\partial t} \delta c_i \geq 0,$$  

where $s$ is the entropy.
which one obtains in deriving Eq. (7) (cf. Ref. 1). If one uses instead of the first variation for both, the chemical potential and the concentration, the finite deviation $\Delta$, the time derivative of this third function reads: 
\[ dL_{\text{Shear}}/dt = \sum_i c_i \ln(c_i/\bar{c}_i) \bar{c}_i, \]

yielding

\[ L_{\text{Shear}} = \sum_i c_i \ln \frac{c_i}{\bar{c}_i} - c_i + \bar{c}_i, \]  

which is positive definite. This is the well-known Lyapunov function for chemical reaction systems used first by Shear, who deduced the expression from the Boltzmann H-Theorem.

Both functions $L_{\text{fd}}$ and $L_{\text{Shear}}$ prove the local stability of the considered steady state exactly for the same region in the parameter space as the function $L_{\text{eqd}}$, which follows by expansion of the logarithm of these functions. However, in Ref. 4 we have shown that $L_{\text{Shear}}$ is better suited for proving the global stability. Indeed, in Ref. 25 it has been shown that with the help of $L_{\text{Shear}}$ the global stability of the thermodynamical equilibrium point can be proven in the whole phase space for arbitrary generalized mass-action kinetic systems.

Further related Lyapunov functions follow from $L_{\text{fd}}$ and $L_{\text{Shear}}$ if one again takes the chemical potential as a function of the mole fraction as outlined for $L_{\text{eqd}}$. In Appendix A.

This idea for the construction of different Lyapunov functions is interesting also with respect to more general systems than only thermal and mechanical stable homogeneous ones, for which more general expressions of the excess entropy density, e.g., $1/2 \delta^2 s = \delta(1/T) \delta u + \delta(p/T) \delta v - \delta(\mu_i/T) \delta c_i$, exist.

20. This model, being more simple than the ‘Brusselator,’ constitutes the ‘simplest’ two-component reaction system with limit cycle oscillations and is known as (a) Selkov System [E. E. Selkov, Eur. J. Biochem. 4, 70 (1966)], (b) Schnakenberg system [J. Schnakenberg, J. Theor. Biol. 81, 389 (1979)], or (c) Gray–Scott system (cf. K. Alhumaizi and R. Aris, Surveying a Dynamical System: A study of the Gray-Scott Reaction in a Two-phase Reactor (Longmans, New York, 1995)].