International Journal of Engineering and Technical Research (IJETR)
ISSN: 2321-0869, Volume-3, Issue-5, May 2015

Comprehensive Thermodynamic Theory of Stability of Irreversible Processes (CTTSIP): The Setup for *Autonomous Systems* and Application

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Abstract— **In the present communication, for the first time a version of Bhalekar's *Comprehensive Thermodynamic Theory of Stability of Irreversible Processes* (CTTSIP) namely CTTSIP for *Autonomous Systems* has been described. The *Autonomous Systems* are defined in terms of the differential equations of motion in which the time variable t does not appear explicitly and hence all functions remain only implicitly time dependent. As in CTTSIP one uses the fabric of Lyapunov theory of stability of motion, there evolve the conditions of thermodynamic stability, thermodynamic asymptotic stability, thermodynamic stability under constantly acting small disturbances and thermodynamic instability. As an example this new version of CTTSIP has been applied to chemically oscillating system of Brusselator Model. The regions of thermodynamic asymptotic stability and stability under constantly acting perturbation emerge.**

Index Terms—**Thermodynamic Stability, Autonomous Systems, Irreversible Thermodynamics, Chemical Oscillations, Brusselator Model.**

I. Introduction

One of the present authors (AAB) has developed a Comprehensive Thermodynamic Theory of Stability of Irreversible Processes (CTTSIP) [1-4]. The basic fabric of CTTSIP is that, it is woven using Lyapunov's second (direct) method of stability of motion [5-8] and the second law of thermodynamics [9-12]. Indeed, CTTSIP is compact and similar to the Gibbs-Duhem stability theory [9-11, 13] of states of equilibrium thermodynamics. Unlike the Glansdorff and Prigogine theory [10] for so-called local equilibrium states, in CTTSIP,

1. one does not require the assumption of local equilibrium, (in fact, it has been demonstrated elsewhere [1-4] that its is a physically non-existent assumption),
2. importantly it has a sound thermodynamics basis [1, 2, 4].

During the last decade, this framework has been well tested and applied to a variety of real irreversible processes from laboratory [1, 4, 14-18] to industry [19, 20]. Now on taking a stock of the status of CTTSIP we realized that the majority of thermodynamic systems fall under the category of *Autonomous Systems* as described by the original stalwarts who propagated Lyapunov's second method of stability of motion (see for example: [5, 21]). Hence, we take an opportunity to describe, in this paper, a version of CTTSIP applicable to *Autonomous Systems* and illustrate its utility by applying it to a representative autonomous system, namely, oscillatory chemical reaction of Brusselator model. In Appendix A we have briefly described Lyapunov's direct method of stability of motion for ready reference and the original setup of generalized CTTSIP has been presented in Appendix B.

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*Financial Support from University Grant Commission (UGC), New Delhi is greatfully Acknowledged.

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II. CTTSIP Setup for *Autonomous Systems*

There are four building blocks of CTTSIP setup, namely

1. the identification of thermodynamic coordinate and corresponding space,
2. defining of thermodynamic perturbation coordinates,
3. construction of thermodynamic constitutive equations in terms of perturbation coordinates and
4. defining of thermodynamic Lyapunov function that we describe in the following subsections.

A. *Thermodynamic Perturbation Coordinates, Space and Constitutive Equations*

Let $x_i^0(t)$'s be the thermodynamic coordinates of the given process on the unperturbed trajectory and $x_i(t)$'s be that on the perturbed one. The *thermodynamic perturbation coordinates*, $\alpha_i(t)$'s then get defined as,

$$\alpha_i(t) = (x_i(t) - x_i^0(t)) \gtrless 0, \quad (i = 1, 2, \cdots, n) \tag{2.1}$$

and hence the equation of *unperturbed trajectory* is obtained as,

$$\alpha_i^0(t) \equiv 0 \qquad (i = 1, 2, \cdots, n). \tag{2.2}$$

where in the above equations the superscript '0' denotes the quantity on the unperturbed trajectory. Further, as per requirement of Lyapunov theory the perturbation coordinates should satisfy the following condition namely,

$$|\alpha_i(0)| = |x_i(0) - x_i^0(0)| \equiv \lambda_i \ (i = 1, 2, \cdots, n), \tag{2.3}$$

Where, λ_i is a sufficiently small number

where for the sake of brevity we have shown by '0' the values of the parameters at $t = t_0$, the time at which the perturbation has been effected.

In this way $\alpha_i(t)$ ŝ are the *sufficiently small perturbation coordinates* in the domain

$$t \geq t_0, \quad t \geq 0, \quad |\alpha_i(t)| \leq \zeta, \quad \zeta > 0, \tag{2.4}$$

where ζ is a sufficiently small positive number.

These perturbation coordinates in turn determine the *thermodynamic perturbation space*.

The *thermodynamic perturbation constitutive equations* of motion within the perturbation space in general, are described as,

$$\frac{d\alpha_i}{dt} = f_i(\alpha_1(t), \alpha_2(t), \alpha_3(t), \cdots, \alpha_n(t)). \tag{2.5}$$

Thus, we see that the trivial solution of equation (2.5) is equation (2.2).

B. The Choice of Thermodynamic Lyapunov Function

For defining *thermodynamic Lyapunov function* we take the help of *Clausius-Duhem inequality* [12, 22-24], namely

$$\rho \frac{ds}{dt} + \nabla \cdot J_s = \sigma_s \geq 0, \tag{2.6}$$

where ρ is the mass density, s is the per unit mass entropy, J_s is the non-convective entropy flux density and σ_s is the entropy source strength.

In CTTSIP[1-4] we use the above described sign definite entropy source strength function and define *thermodynamic Lyapunov function*, $\mathcal{L}_s$, as,

$$\mathcal{L}_s = (\sigma_s(t) - \sigma_s^0(t)) \gtreqless 0, \tag{2.7}$$

where, $\sigma_s(t)$ and $\sigma_s^0(t)$ are the respective entropy source strengths and are positive definite quantities[12, 25, 26] as guaranteed by the second law of thermodynamics appears in the Clausius-Duhem inequality[12, 22-24]. Since we are using the thermodynamic function, namely the entropy source strength in defining the Lyapunov function it automatically gets thermodynamic sanction. Hence, $\mathcal{L}_s$ is the excess rate of entropy production per unit volume.

Thus the *self consistency* of this choice of thermodynamic Lyapunov function gets demonstrated by the fact that when it is the case of thermodynamic stability of an equilibrium state the second law of thermodynamic guarantees $\sigma_s^0 = 0$ and hence the thermodynamic Lyapunov function reads as $\mathcal{L}_s = \sigma_s(t)$, that is the entropy source strength itself takes the role of Lyapunov function in this case. Which is nothing else but the Gibbs-Duhem stability theory of equilibrium states [10, 27].

Recall that, the thermodynamics of irreversible processes provide the following dependence of entropy source strength [12, 25, 26], $\sigma_s(t)$, namely,

$$\sigma_s(t) = \sigma_s(x_1, x_2, x_3, \ldots\ldots, x_n) \tag{2.8}$$

or more elaborately as,

$$\sigma_s(t) = \sigma_s(x_1(t), x_2(t), x_3(t), \ldots\ldots, x_n(t)) \tag{2.9}$$

for autonomous systems.

Therefore, the fundamental dependence of $\mathcal{L}_s$ is obtained as,

$$\mathcal{L}_s(t) = \mathcal{L}_s(\alpha_1(t), \alpha_2(t), \alpha_3(t), \cdots, \alpha_n(t)).$$

or more elaborately as,

$$\begin{aligned} &\mathcal{L}_s(t) = \mathcal{L}_s(\alpha_1(t), \alpha_2(t), \alpha_3(t), \cdots, \alpha_n(t)) \geq \\ &\varepsilon(\alpha_1, \alpha_2, \alpha_3, \cdots) > 0 \quad \mathit{for} \quad t \geq t_0 \end{aligned} \tag{2.11}$$

or

$$\begin{aligned} &\mathcal{L}_s(t) = \mathcal{L}_s(\alpha_1(t), \alpha_2(t), \alpha_3(t), \cdots, \alpha_n(t)) \\ &\leq -\eta(\alpha_1, \alpha_2, \alpha_3, \cdots) < 0 \quad \mathit{for} \quad t \geq t_0, \end{aligned} \tag{2.12}$$

corresponding to the two options of equation (2.7), where $\mathcal{L}_s$ is differentiable function [28] and ε and η are continuous positive numbers. Thus, from equation (2.10) we obtain the following equation of *unperturbed trajectory*, namely:

$$\mathcal{L}_s(t) = \mathcal{L}_s(0, 0, 0, \cdots\cdots, 0) \equiv 0 \quad \mathit{for} \quad t \geq t_0, \tag{2.13}$$

in both the cases of equations (2.11) and (2.12) with

$$\begin{aligned} &\varepsilon(0, 0, 0, \cdots\cdots) = 0 \quad \text{and} \quad \text{also} \\ &\eta(0, 0, 0, \cdots\cdots) = 0. \end{aligned} \tag{2.14}$$

From the above description it gets established that the majority of thermodynamic systems constitute the *Autonomous Systems* as has been defined in Lyapunov theory of stability of motion [6, 8].

The total time derivative of thermodynamic Lyapunov function, $\mathcal{L}_s(t)$, in the case of *Autonomous systems* read as,

$$\frac{d\mathcal{L}_s}{dt} = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i} \right) \frac{d\alpha_i}{dt}. \tag{2.15}$$

C. Thermodynamic Stability of Autonomous Systems

1. For autonomous systems along with the condition of equations (2.11) and (2.13) if, the following condition is followed, namely:

$$\dot{\mathcal{L}}_s(t) = \frac{d\mathcal{L}_s}{dt} = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i} \right) \frac{d\alpha_i}{dt} \leq 0, \tag{2.16}$$

then *unperturbed(real) trajectory under investigation is guaranteed as thermodynamically stable*.

2. Whereas along with the conditions of equations (2.12) and (2.13) if, we have,

$$\dot{\mathcal{L}}_s(t) = \frac{d\mathcal{L}_s}{dt} = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i} \right) \frac{d\alpha_i}{dt} \geq 0, \tag{2.17}$$

then also the *unperturbed(real) trajectory under investigation is guaranteed as thermodynamically stable.*

Recall that the fundamental dependencies of entropy source strength on α_i's read as,

$$\sigma_s = \sigma_s(\alpha_1(t), \alpha_2(t), \alpha_3(t), \cdots\cdots) > 0, \tag{2.18}$$

$$\sigma_s^0 = \sigma_s(0, 0, 0, 0, \cdots\cdots) > 0 \tag{2.19}$$

and the positive definiteness of (2.18) and (2.19) is guaranteed by the second law of thermodynamics [10-12].

D. Thermodynamic Asymptotic Stability

On following the Lyapunov theory we arrive at the following description of *thermodynamic asymptotic stability of a real trajectory* in the said two cases namely;

1. The validity either of equations (2.11) and (2.13) and in addition [21]

$$\sum_i \alpha_i^2 \geq \rho^2 > 0, \quad t \geq T_0 \geq t_0 \tag{2.20}$$

and

$$\dot{\mathcal{L}}_s(t) = \frac{d\mathcal{L}_s}{dt} = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i} \right) \frac{d\alpha_i}{dt} \leq -\beta < 0. \tag{2.21}$$

2. Equations (2.12), (2.13), (2.20) and

$$\dot{\mathcal{L}}_s(t) = \frac{d\mathcal{L}_s}{dt} = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i} \right) \frac{d\alpha_i}{dt} \geq \beta > 0, \tag{2.22}$$

with $d\alpha_i / dt$ given by equation (2.5) in the domain prescribed in equation (2.4) where

$$\beta = \beta(\alpha_1, \alpha_2, \alpha_3, \cdots\cdot, \alpha_n) > 0, \tag{2.23}$$

$$\beta^0 = \beta(0, 0, 0, \cdots\cdot, 0) \equiv 0, \tag{2.24}$$

that is, β is a strictly positive number and vanishes only at the origin or equivalently on the real trajectory. This in terms of $\mathcal{L}_s$ means that $d\mathcal{L}_s / dt$ vanishes only at the origin or equivalently on the real trajectory and outside it is strictly negative (positive) quantity.

E. Thermodynamic Stability Under the Constantly Acting Small Disturbances

In addition to the conditions prescribed in either equations (2.11), (2.13), (2.20), (2.21), (2.23) and (2.24) or equations (2.12), (2.13), (2.20), and (2.22)-(2.24) if the partial derivatives $\partial \mathcal{L}_s / \partial \alpha_i$ remain finite, then *thermodynamic stability guaranteed, is also against the constantly acting small disturbances.* This assertion is based on Malkinôs theorem[6, 8, 21].

III. Theorems of Thermodynamic Stability for Real Trajectories of *Autonomous Systems*

The above presented thermodynamic stability description for *Autonomous Systems* culminates into the following theorems, namely:

Theorem I. *For a system of equation* (2.4) *of the perturbed motion in the thermodynamic perturbation space determined by equations* (2.1) - (2.3) *and restricted by equation* (2.5), *if there exists a differentiable thermodynamic Lyapunov function* $\mathcal{L}_s(t) = \mathcal{L}_s\left(\alpha_1(t), \alpha_2(t), \alpha_3(t), \cdots\cdot\right)$ *defined by equation* (2.7), *which satisfies the following conditions in the neighborhood of the coordinate origin for* $t \geq t_0$*; namely*:

$$\mathcal{L}_s(t) = \mathcal{L}_s\left(\alpha_1(t), \alpha_2(t), \alpha_3(t), \cdots\cdot, \alpha_n(t)\right) \geq \varepsilon\left(\alpha_1, \alpha_2, \alpha_3, \cdots\cdot, \alpha_n\right) > 0, \tag{I-1}$$

with $\mathcal{L}_s^0(t) = \mathcal{L}_s\left(0, 0, 0, \cdots\cdot, 0\right) \equiv 0$ *, where* ε *is a strictly positive continuous function that vanishes only at the origin,* $\varepsilon^0 = \varepsilon\left(0, 0, 0, \cdots\cdot, 0\right) \equiv 0$*, that is,* $\mathcal{L}_s(t)$ *has a strict minimum at the origin*, and *the derivative*

$$\dot{\mathcal{L}}_s(t) = \frac{d\mathcal{L}_s}{dt} = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i} \right) \cdot \frac{d\alpha_i}{dt} \leq 0, \tag{I-2}$$

then the trivial solution of the system of equation (2.4), *namely* $\alpha_i^0 \equiv 0$ *, that is equation* (2.2), *constitutes a stable motion in thermodynamic space.* Similarly, the pair of equations,

$$\mathcal{L}_s(t) = \mathcal{L}_s\left(\alpha_1(t), \alpha_2(t), \alpha_3(t), \cdots\cdot, \alpha_n(t)\right) \leq -\eta\left(\alpha_1, \alpha_2, \alpha_3, \cdots\cdot, \alpha_n\right) < 0$$

and

$$\dot{\mathcal{L}}_s(t) = \frac{d\mathcal{L}_s}{dt} = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i} \right) \cdot \frac{d\alpha_i}{dt} \geq 0,$$

for $t \geq t_0$ *establish that the trivial solution of the system of equation* (2.4), *namely* $\alpha_i^0 \equiv 0$ *, that is equation*(2.2), *constitutes a stable motion in thermodynamic space.*

Theorem II. *For the system of equations* (2.4) *of the perturbed motion in the thermodynamic space defined by equations* (2.1)-(2.3) *in the domain determined by equation* (2.5), *if there exists a differentiable thermodynamic Lyapunov function,*

$\mathcal{L}_s(t) = \mathcal{L}_s\left(\alpha_1(t), \alpha_2(t), \alpha_3(t), \cdots\cdot, \alpha_n(t)\right)$*, defined by equation* (2.7), *which satisfies the following conditions in the neighborhood of the coordinate origin for* $t \geq t_0$*; namely*:

$$\mathcal{L}_s(t) = \mathcal{L}_s\left(\alpha_1, \alpha_2, \alpha_3, \cdots\cdot, \alpha_n\right) \geq \varepsilon\left(\alpha_1, \alpha_2, \alpha_3, \cdots\cdot, \alpha_n\right) > 0, \tag{II-1}$$

with $\mathcal{L}_s^0(t) = \mathcal{L}_s\left(0, 0, 0, \cdots\cdot, 0\right) \equiv 0$ *, where* ε *is a strictly positive continuous function that vanishes only at the origin,* $\varepsilon^0 = \varepsilon\left(0, 0, 0, \cdots\cdot, 0\right) \equiv 0$*, that is,* $\mathcal{L}_s(t)$ *has a strict minimum at the origin*, and *the derivative*

$$\dot{\mathcal{L}}_s(t) = \frac{d\mathcal{L}_s}{dt} = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i} \right) \cdot \frac{d\alpha_i}{dt} \leq -\varepsilon_2 < 0, \tag{II-2}$$

where ε_2 *is strictly positive continuous function that vanishes only at the origin,* $\varepsilon_2^0 = \varepsilon_2(0, 0, 0, \cdots\cdot, 0) \equiv 0$ *, then the trivial solution of the system of equations* (2.4), *namely* $\alpha_i^0 \equiv 0$ *, that is equation* (2.2), *constitutes an asymptotically stable motion in thermodynamic space.*

Similarly the following pair of equations, namely:

$$\mathcal{L}_s(t) = \mathcal{L}_s\left(\alpha_1, \alpha_2, \alpha_3, \cdots\cdot, \alpha_n\right) \leq -\eta\left(\alpha_1, \alpha_2, \alpha_3, \cdots\cdot, \alpha_n\right) < 0,$$

$$\dot{\mathcal{L}}_s(t) = \frac{d\mathcal{L}_s}{dt} = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i} \right) \cdot \frac{d\alpha_i}{dt} \geq \eta_2 > 0,$$

for $t \geq t_0$ *establish that the trivial solution of the system of equation* (2.7), *namely* $\alpha_i^0 \equiv 0$ *, that is equation* (2.2), *constitutes an asymptotically stable motion in thermodynamic space.* (II-3) *in addition if the derivatives* $\partial \mathcal{L}_s / \partial \alpha_i \; (i = 1, 2, 3, \cdots\cdot, n)$ *are finite (bounded in absolute value), then the said trajectory (real) in thermodynamic space is obtained as stable under the constantly acting small disturbances*.

IV. APPLICATION TO CHEMICAL OSCILLATIONS IN BRUSSELATOR MODEL

We exemplify the use of CTTSIP for autonomous systems described in sections 2 and 3 by applying it to the chemical oscillations in Brusselator model. In the mathematical model of Brusselator two intermediate species show oscillating behavior. The schematic representation of it is [29, 30],

$$A \xrightarrow{k_1} X \tag{4.1}$$

$$2X + Y \xrightarrow{k_2} 3X \tag{4.2}$$

$$B + X \xrightarrow{k_3} Y + D \tag{4.3}$$

$$X \xrightarrow{k_4} E \tag{4.4}$$

where A and B are the reactants, X and Y are the intermediates, D and E are the products. The rate equation for such autocatalytic reactions are fundamentally non-linear.

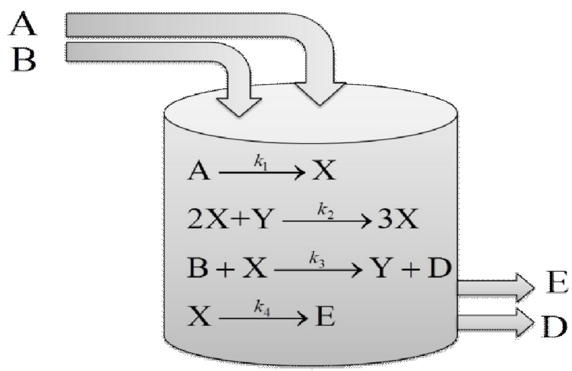

Figure 1: Schematic representation of Brusselator model

In the Brusselator model, it is assumed that the concentration of reactants óAô and óBô are kept constant at a desired feeding rate by means of continuous-flow stirred tank reactor (CSTR) as illustrated in the figure 1 and the concentration of óDô and óEô are removed continuously from the system as they are being produced. k_1, k_2, k_3 and k_4 are rate constants of the respective chemical reactions.

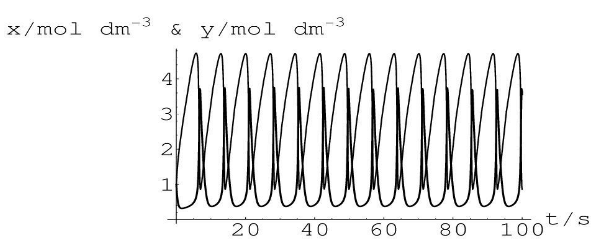

Figure 2: Oscillating behaviour of óXô and óYô with time, where the bold line indicate oscillations in the concentration of intermediateóX ôand other line represent the oscillations in concentration of óYô intermediate.

From chemical kinetics [31], the rates of change of intermediate species on unperturbed trajectory are given by,

$$\frac{dX^0}{dt} = k_1 A^0 + k_2 (X^0)^2 Y^0 - k_3 X^0 B^0 - k_4 X^0, \tag{4.5}$$

$$\frac{dY^0}{dt} = -k_2 (X^0)^2 Y^0 + k_3 X^0 B^0, \tag{4.6}$$

and that on the perturbed trajectory by,

$$\frac{dX}{dt} = k_1 A^0 + k_2 (X)^2 Y - k_3 X B^0 - k_4 X, \tag{4.7}$$

$$\frac{dY}{dt} = -k_2 (X)^2 Y + k_3 X B^0. \tag{4.8}$$

Notice that as the concentrations of A and B are maintained constant in the reactor by the constant rate of feed in, the concentrations of A^0 and B^0 have been used in equations 4.5 to 4.8. Also, notice that for the sake of bravity we have shown the concentrations of chemical species by their chemical symbols itself. The superscript ^{0} on the symbols describe the concentrations on the unperturbed trajectory and without superscript they represent concentrations on the perturbed trajectory. In this case, oscillations [13, 29, 30] sustain as long as reactants are continuously fed into and products are removed from the reactor. The oscillating behavior of intermediates óX ô and óYô are generated graphically by subjecting their rate expressions for numerical computations using *Mathematica Software* and is represented in figure 2.

Let us now consider a case when concentrations of both autocatalytic intermediates that oscillate, namely, X and Y are perturbed simultaneously by sufficiently small amount say óδX ôand óδY , that is,

$$\delta \mathrm{X} = \mathrm{X} - \mathrm{X}^0 \quad \text{and} \quad \delta \mathrm{Y} = \mathrm{Y} - \mathrm{Y}^0. \tag{4.9}$$

The equations of motion within the thermodynamic perturbation space are then obtained as,

$$\frac{d(X - X^0)}{dt} = \frac{d(\delta X)}{dt} \tag{4.10}$$

$$= (k_2 Y^0 (2X - \delta X) - B k_3 - k_4)\delta X$$

and

$$\frac{d(Y - Y^0)}{dt} = \frac{d(\delta Y)}{dt} = -(k_2 (X^0)^2)\delta Y. \tag{4.11}$$

In the present case, the operative expression of thermodynamic Lyapunov function, $\mathcal{L}_s$, would be of the form,

$$\mathcal{L}_s = \left(\frac{\partial \Sigma_s}{\partial(\delta X)} \right)^0 (\delta X) + \left(\frac{\partial \Sigma_s}{\partial(\delta Y)} \right)^0 (\delta Y) \gtrless 0 \tag{4.12}$$

and the operative expression of total time derivative of $\mathcal{L}_s$, would be

$$\frac{d\mathcal{L}_s}{dt} = \left(\frac{\partial \mathcal{L}_s}{\partial(\delta X)} \right) \cdot \frac{d(\delta X)}{dt} + \left(\frac{\partial \mathcal{L}_s}{\partial(\delta Y)} \right) \cdot \frac{d(\delta Y)}{dt}. \tag{4.13}$$

Let us recall the definition of global level rates of entropy production [9, 11, 32-33] on the unperturbed trajectory as,

$$\Sigma_s^0 = \frac{\mathcal{A}_i^0}{T}\cdot\frac{d(\xi)_i^0}{dt}+\frac{\mathcal{A}_{ii}^0}{T}\cdot\frac{d(\xi)_{ii}^0}{dt}+ \frac{\mathcal{A}_{iii}^0}{T}\cdot\frac{d(\xi)_{iii}^0}{dt}+\frac{\mathcal{A}_{iv}^0}{T}\cdot\frac{d(\xi)_{iv}^0}{dt}>0, \quad (4.14)$$

and accordingly on perturbed trajectory it would reads as,

$$\Sigma_s = \frac{\mathcal{A}_i}{T}\cdot\frac{d(\xi)_i}{dt}+\frac{\mathcal{A}_{ii}}{T}\cdot\frac{d(\xi)_{ii}}{dt}+ \frac{\mathcal{A}_{iii}}{T}\cdot\frac{d(\xi)_{iii}}{dt}+\frac{\mathcal{A}_{iv}}{T}\cdot\frac{d(\xi)_{iv}}{dt}>0. \quad (4.15)$$

On substituting the rate expressions and further solving, we get,

$$\Sigma_s = \frac{\mathcal{A}_i}{T}(k_1A^0)+\frac{\mathcal{A}_{ii}}{T}(k_2X^2Y)+ \frac{\mathcal{A}_{iii}}{T}(k_3XB^0)+\frac{\mathcal{A}_{iv}}{T}(k_4X)>0. \quad (4.16)$$

Notice that the positive signs of equations (4.14), (4.15) and (4.16) are dictated by the second law of thermodynamics. Using CTTSIP [4] for *Autonomous Systems*, the thermodynamic Lyapunov function, $\mathcal{L}_s$, is constructed by differentiating equation (4.16) partially with respect to δX first then with respect to δY, we get,

$$\frac{\partial\Sigma_s}{\partial(\delta X)} = -\frac{R}{X}k_1A^0+\left(2\frac{\mathcal{A}_{ii}}{T}-R\right)k_2XY+ \left(\frac{\mathcal{A}_{iii}}{T}+R\right)k_3B^0+\left(\frac{\mathcal{A}_{iv}}{T}+R\right)k_4 \quad (4.17)$$

and

$$\frac{\partial\Sigma_s}{\partial(\delta Y)} = \left(\frac{\mathcal{A}_{ii}}{T}+R\right)k_2X^2-\left(\frac{R}{T}\right)k_3XB^0. \quad (4.18)$$

On imposing the condition of real trajectory, it gives

$$\left(\frac{\partial\Sigma_s}{\partial(\delta X)}\right)^0 = -\frac{R}{X^0}k_1A^0+\left(2\frac{\mathcal{A}_{ii}^0}{T}-R\right)k_2X^0Y^0+ \left(\frac{\mathcal{A}_{iii}^0}{T}+R\right)k_3B^0+\left(\frac{\mathcal{A}_{iv}^0}{T}+R\right)k_4 \quad (4.19)$$

and

$$\left(\frac{\partial\Sigma_s}{\partial(\delta Y)}\right)^0 = \left(\frac{\mathcal{A}_{ii}^0}{T}+R\right)k_2(X^0)^2-\left(\frac{R}{T}\right)k_3X^0B^0. \quad (4.20)$$

Accordingly, the operative expression of thermodynamic Lyapunov function, $\mathcal{L}_s$, would be of the form,

$$\mathcal{L}_s = \left(\frac{\partial\Sigma_s}{\partial(\delta X)}\right)^0(\delta X)+\left(\frac{\partial\Sigma_s}{\partial(\delta Y)}\right)^0(\delta Y)\gtrless 0 \quad (4.21)$$

on substituting equation (4.17) and (4.18) in the equation (4.21), expression of thermodynamic Lyapunov function, $\mathcal{L}_s$, gets simplified as,

$$\mathcal{L}_s = -\left[\frac{R}{X^0}k_1A^0+\left(2\frac{\mathcal{A}_{ii}^0}{T}-R\right)k_2X^0Y^0+ \left(\frac{\mathcal{A}_{iii}^0}{T}+R\right)k_3B^0+\left(\frac{\mathcal{A}_{iv}^0}{T}+R\right)k_4\right](\delta X) +\left[\left(\frac{\mathcal{A}_{ii}^0}{T}+R\right)k_2(X^0)^2-(R)k_3X^0B^0\right](\delta Y)\gtrless 0. \quad (4.22)$$

Now, the operative expression of total time derivative of $\mathcal{L}_s$, would be

$$\frac{d\mathcal{L}_s}{dt} = \left(\frac{\partial\mathcal{L}_s}{\partial(\delta X)}\right)\cdot\frac{d(\delta X)}{dt}+\left(\frac{\partial\mathcal{L}_s}{\partial(\delta Y)}\right)\cdot\frac{d(\delta Y)}{dt}. \quad (4.23)$$

On partial differentiation of (4.22) with respect to the perturbation coordinates δX and δY, we get the expressions of gradient of $\mathcal{L}_s$ as,

$$\frac{\partial\mathcal{L}_s}{\partial(\delta X)} = -\frac{R}{X^0}k_1A^0+\left(2\frac{\mathcal{A}_{ii}^0}{T}-R\right)k_2X^0Y^0+ \left(\frac{\mathcal{A}_{iii}^0}{T}+R\right)k_3B^0+\left(\frac{\mathcal{A}_{iv}^0}{T}+R\right)k_4 \quad \textit{is} \quad \textit{finite} \quad (4.24)$$

and

$$\frac{\partial\mathcal{L}_s}{\partial(\delta Y)} = \left(\frac{\mathcal{A}_{ii}^0}{T}+R\right)k_2(X^0)^2-(R)k_3X^0B^0 \quad \textit{is} \quad \textit{finite.} \quad (4.25)$$

On substituting equations (4.10), (4.11), (4.24) and (4.25), in equation (4.23) we get,

$$\frac{d\mathcal{L}_s}{dt} = \left[-\frac{R}{X^0}k_1A^0+\left(2\frac{\mathcal{A}_{ii}^0}{T}-R\right)k_2X^0Y^0+\left(\frac{\mathcal{A}_{iii}^0}{T}+R\right) k_3B^0+\left(\frac{\mathcal{A}_{iv}^0}{T}+R\right)k_4\right][\left(k_2Y^0(2X-\delta X)-B^0k_3-k_4\right)\delta X] -\left[\left(\frac{\mathcal{A}_{ii}^0}{T}+R\right)k_2(X^0)^2-\left(\frac{R}{T}\right)k_3X^0B^0\right](k_2(X^0)^2)\delta Y. \quad (4.26)$$

A. Thermodynamic Stability Discussion

Because For determining the thermodynamic stability of Brusselator model the final expressions of $\mathcal{L}_s$ and $d\mathcal{L}_s/dt$ given in equations (4.22) and (4.26) are used. Now, in view of the complex nature of both the expressions, they are solved computationally using software *Mathematica 5.0*, developed by *WOLFRAM RESEARCH INC., USA*. The schematic presentations of this model have been generated using this software.

Following numerical constants have been used for computational inputs, namely, k_1 =1mol dm^{-3} s^{-1}; k_2 =1mol dm^{-3} s^{-1}; k_3 =1mol dm^{-3} s^{-1}; k_4 =1mol dm^{-3} s^{-1}; A =1 mol dm^{-3}; B =3 mol dm^{-3}; Y =1 mol dm^{-3} and X = 1 mol dm^{-3}. Results of computations are depicted graphically in figure 3 and figure 4. Figure 3 shows smooth and continuous decrease of positive $\mathcal{L}_s$ while the figure 4 of $d\mathcal{L}_s / dt$ shows its negative values which are not continuous and this may be attributed due to feedback mechanism of autocatalytic species leading to oscillations. This means that, natures of both the graphs favor the thermodynamic stability. Now, as per the description in CTTSIP above in section 2.4, the thermodynamic asymptotic stability of any process is guaranteed if in addition to opposite signs of $\mathcal{L}_s$ and $d\mathcal{L}_s / dt$, the following condition remains satisfied, namely,

$$\sum_i (\delta X)_i^2 \geq \rho_X^2 > 0 \;\; and \;\; \sum_i (\delta Y)_i^2 \geq \rho_Y^2 > 0, \tag{4.27}$$

where, ρ_X, ρ_Y are any arbitrary positive definite constants. Further, to establish that the process is thermodynamic stable under constantly acting small disturbances as per *Malkin's theorem*, we have verified the finiteness of the gradients of $\mathcal{L}_s$ with respect to its perturbation coordinates computationally. Corresponding graphical variation of gradients have been shown in figures 5 and 6. Figure 5 shows that the gradient of thermodynamic Lyapunov function $\mathcal{L}_s$, with respect to perturbation of intermediate ôXô initially, decreases a while and then starts increasing with progress of time, reaches certain maxima and further decreases back to original level. Moreover, during the course of this trend of decrease, increase and again decrease, the gradient remains finite and there is no sign of its deflection towards infinity. Similar behavior is observed in the case of gradient of thermodynamic Lyapunov function $\mathcal{L}_s$, with respect to the perturbation coordinate of intermediate ôYô establishing the *finiteness of the gradients*. Thus, for Brusselator model, the *thermodynamic stability under constantly acting small disturbances is also established* as per *Malkins theorem* [6, 8].

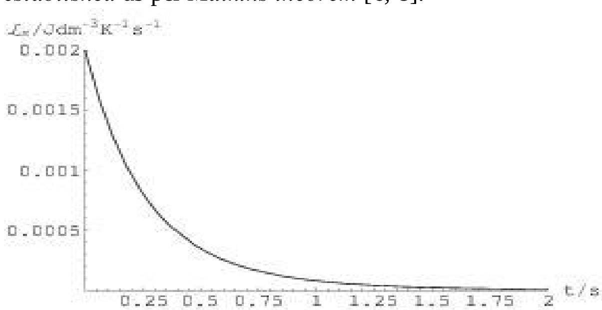

Figure 3: Plot of $\mathcal{L}_s$ with time when the concentrations of intermediates are perturbed.

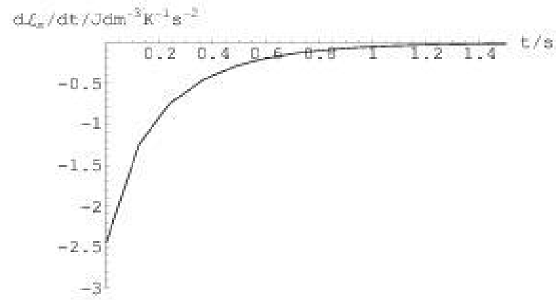

Figure 4: Behavior of $d\mathcal{L}_s / dt$ with time when the concentrations of intermediates are perturbed.

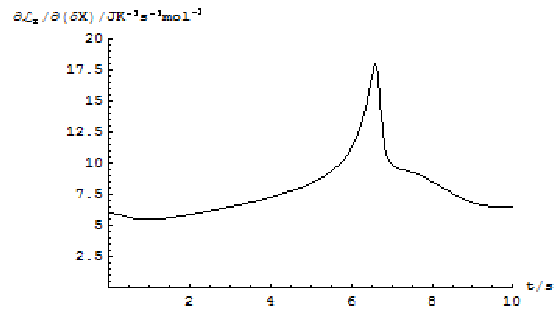

Figure 5: A plot of $\partial\mathcal{L}_s / \partial(\delta X)$ with time showing finiteness of $\mathcal{L}_s$ against the perturbation in X. Therefore, the process is thermodynamic stable under constantly acting small disturbances as per Malkin's theorem [6, 8].

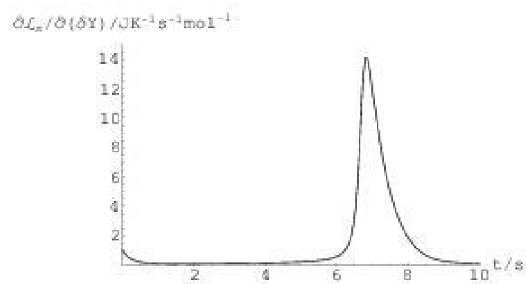

Figure 5: A plot of $\partial\mathcal{L}_s / \partial(\delta \mathrm{Y})$ with time showing finiteness of $\mathcal{L}_s$ against the perturbation in Y. Therefore, the process is thermodynamic stable under constantly acting small disturbances as per Malkin's theorem [6, 8].

V. Conclusion

In the present paper, we have reported for the first time the version of Bhalekarôs Comprehensive Thermodynamic Theory of Stability of Irreversible Processes (CTTSIP) for the *Autonomous Systems*. Since in autonomous systems the explicit time variable does not appear, hence all the functions remain time dependent only implicitly. Therefore, in the CTTSIP for *Autonomous Systems* the local time derivative of thermodynamic Lyapunov function does not appear. Additionally, to guarantee that the process is thermodynamically asymptotically stable one needs to satisfy an additional conditions described in equation 2.20, that is a crucial ingredient of the theory. In the present communication, we have demonstrated the use of the thermodynamic Lyapunov function as defined in CTTSIP also for *Autonomous Systems* in a systematic way to predict the thermodynamic stability aspects of the processes. As a representative example, we have discussed, the thermodynamic stability of Brusselator model which consists of a set of autocatalytic oscillating reactions. Appropriate perturbation coordinates are selected within the thermodynamic space namely, δX and δY . Corresponding thermodynamic Lyapunov function is constructed as per the steps of CTTSIP and the expression of their total time derivative was obtained. Finally, by generating the graphical representations of these expressions using the *Mathematica Software*, the thermodynamic asymptotic stability and stability under constantly acting small disturbances get demonstrated in the present case. This is the reason that the intermediates continue the usual oscillations even after perturbation in its observed natural trajectory. Evidently, from all our earlier studies using generalized CTTSIP and present study using CTTSIP for *Autonomous systems*, it gets lucidly illustrated that there are no restrictions at all on the applications of CTTSIP of *Autonomous Systems*. Thus the comprehensive character of the framework of CTTSIP of *Autonomous Systems* get adequately illustrated in this paper.

APPENDIX

A. Lyapunov's Direct (Second) Method of Stability of Motion

For the convenience of readers herein we describe a gist of Lyapunovôs direct (second) method of stability of motion. The reader is advised to refer the original references on this subject cited in this paper to get its details.

1. Let the given differential equations of the *perturbed motion* be,

$$\frac{dx_i}{dt} = X_i\left(t, x_1, x_2, x_3, \cdots\cdots, x_n\right) \qquad (i = 1, 2, 3, \cdots\cdots, n). \tag{6.1}$$

The trivial solution of equation (6.1) is,

$$x_i = 0 \qquad (i = 1, 2, 3, \cdots\cdots, n), \tag{6.2}$$

where x_i ôs have been defined as,

$$x_i(t) = | y_i(t) - y_i^0(t) |,$$
$$x_i(0) = | y_i(0) - y_i^0(0) | = \lambda_i \tag{6.3}$$

where $y_i^0(t)$ are the coordinates of the real motion under investigation and correspondingly $y_i(t)$ are those for the perturbed trajectory. The equation of unperturbed motion then reads as,

$$x_i^0(t) = 0 \quad and \quad x_i^0(0) = 0. \tag{6.4}$$

Thus x_i ôs are the small *perturbation coordinates* in the domain,

$$t \geq t_0, t_0 \geq 0, x_i \leq H, H > 0, \tag{6.5}$$

where H is a sufficiently small positive constant and

$$X_i\left(t, 0, 0, 0, \cdots\cdots, 0\right) = 0 \qquad (i = 1, 2, 3, \cdots\cdots, n). \tag{6.6}$$

2. Let $V\left(t, x_1, x_2, x_3, \cdots\cdots, x_n\right)$ be a *differentiable Lyapunov function* such that,

(a) $V\left(t, x_1, x_2, x_3, \cdots\cdots, x_n\right) \geq \varepsilon\left(x_1, x_2, x_3, \cdots\cdots, x_n\right) > 0,$

$$\varepsilon\left(0, 0, 0, \cdots\cdots, 0\right) = 0, V\left(t, 0, 0, 0, \cdots\cdots, 0\right) = 0. \tag{6.8}$$

That is V has a *strict minimum* at the origin and ε is a continuous positive number.

(b) Now if

$$V \cdot \frac{dV}{dt} = \left(\frac{\partial V}{\partial t} + \sum_i \frac{\partial V}{\partial x_i} \cdot X_i\right) \leq 0, \tag{6.9}$$

for $t \geq t_0$, then the *unperturbed motion is stable*.

3. Outside an *arbitrarily small neighborhood* of the origin if

$$\sum_i x_i^2 \geq \rho^2 > 0, \quad t \geq T_O \geq t_0 \tag{6.10}$$

and in addition to equations (6.7) and (6.9) if we have

$$\frac{dV}{dt} \leq -\beta < 0, \tag{6.11}$$

where ρ^2 and β are the positive constants, then $x_i \equiv 0\,(i = 1, 2, 3, \cdots, n)$ is *asymptotically stable*.

4. Further, if

$$V > 0, V(t, 0, 0, 0, \cdots, 0) \equiv 0, \frac{dV}{dt} \leq -\beta < 0 \tag{6.12}$$

and the derivatives $\partial V / \partial x_i$ are all finite, then the *unperturbed motion* is *stable under constantly acting small disturbances*. This is Malkinôs Theorem [6, 8, 21].

B. Generalized CTTSIP Setup

The gist of the generalized setup of CTTSIP is described below[1-4].

Let $Y_i^0(t)$ ôs be the thermodynamic coordinates of the given process on the unperturbed trajectory and $Y_i(t)$ ôs be that on the perturbed one. The perturbation coordinates, $\alpha_i(t)$ ôs are defined as,

$$\alpha_i(t) = (Y_i(t) - Y_i^0(t)) \gtrless 0, \quad (i = 1, 2, \cdots, n) \tag{7.1}$$

and hence the equation of unperturbed trajectory is obtained as,

$$\alpha_i^0 \equiv 0. \tag{7.2}$$

Thus on using $\alpha_i(t)$ the thermodynamic perturbation space gets defined. The constitutive equations of motion within the perturbation space in general are described as,

$$\frac{\mathrm{d}\alpha_i}{\mathrm{d}t} = f_i(\alpha_1, \alpha_2, \alpha_3, \cdots; t) \quad (i = 1, 2, \cdots, n). \tag{7.3}$$

The domain of thermodynamic perturbation space is determined by

$$t \geq t_0, \quad t \geq 0, \quad \alpha_i \leq \varepsilon, \quad \varepsilon > 0$$

and the trivial solution of equations (7.3) is (7.2).

In CTTSIP[4] the thermodynamic Lyapunov function, $\mathcal{L}_s$, is defined as,

$$\mathcal{L}_s = (\sigma_s(t) - \sigma_s^0(t)) \gtrless 0, \tag{7.4}$$

where, $\sigma_s(t)$ and $\sigma_s^0(t)$ are the respective entropy source strengths and are positive definite quantities [12, 25, 26] as per the second law of thermodynamics that appears in the Clausius-Duhem inequality [12, 22-24]. Since we are using the thermodynamic function, namely the entropy source strength in defining the Lyapunov function the CTTSIP inherits thermodynamic base. Notice that, $\mathcal{L}_s$ is the excess rate of entropy production per unit volume. Obviously, by definition we have,

$$\mathcal{L}_s = \mathcal{L}_s(\alpha_1, \alpha_2, \alpha_3, \cdots, t) > 0 \tag{7.5}$$

or

$$\mathcal{L}_s = \mathcal{L}_s(\alpha_1, \alpha_2, \alpha_3, \cdots, t) < 0, \tag{7.6}$$

and on the unperturbed trajectory we have,

$$\mathcal{L}_s^0 = \mathcal{L}_s(0, 0, 0, \cdots, t) \equiv 0, \tag{7.7}$$

where $\mathcal{L}_s$ is a differentiable function [28]. As we need to work within the thermodynamic perturbation space let us expand $\sigma_s(t)$ in terms of $\alpha_i(t)$ ȇs that gives,

$$\sigma_s - \sigma_s^0 = \sum_i \left(\frac{\partial \sigma_s}{\partial \alpha_i}\right)^0 \alpha_i + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 \sigma_s}{\partial \alpha_i \partial \alpha_j}\right)^0 \alpha_i \alpha_j + \frac{1}{6}\sum_{i,j,k}\left(\frac{\partial^3 \sigma_s}{\partial \alpha_i \partial \alpha_j \partial \alpha_k}\right)^0 \alpha_i \alpha_j \alpha_k + \cdots\cdots \tag{7.8}$$

Notice that, for the sake of brevity the time dependence of quantities has not been shown. The thermodynamic Lyapunov function, $\mathcal{L}_s$, is then given as (c. f. equation(7.4)),

$$\mathcal{L}_s = \sum_i \left(\frac{\partial \sigma_s}{\partial \alpha_i}\right)^0 \alpha_i + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 \sigma_s}{\partial \alpha_i \partial \alpha_j}\right)^0 \alpha_i \alpha_j + \frac{1}{6}\sum_{i,j,k}\left(\frac{\partial^3 \sigma_s}{\partial \alpha_i \partial \alpha_j \partial \alpha_k}\right)^0 \alpha_i \alpha_j \alpha_k + \cdots\cdots \gtrless 0. \tag{7.9}$$

Alternatively, $\mathcal{L}_s$ can be expanded directly in terms of α_i ȇs as,

$$\mathcal{L}_s = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i}\right)^0 \alpha_i + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 \mathcal{L}_s}{\partial \alpha_i \partial \alpha_j}\right)^0 \alpha_i \alpha_j + \frac{1}{6}\sum_{i,j,k}\left(\frac{\partial^3 \mathcal{L}_s}{\partial \alpha_i \partial \alpha_j \partial \alpha_k}\right)^0 \alpha_i \alpha_j \alpha_k + \cdots\cdots \gtrless 0. \tag{7.10}$$

Moreover,

1. If $(\partial \sigma_s / \partial \alpha_i)^0 \neq 0$ and hence $(\partial \mathcal{L}_s / \partial \alpha_i)^0 \neq 0$, and as per the requirement of Lyapunovȇs theory of stability of motion [5-8, 21] α_i ȇs need to be sufficiently small the higher order terms in the expression of $\sigma_s(t)$ and $\mathcal{L}_s(t)$ can be ignored and hence the expressions for them get restricted to,

$$\sigma_s - \sigma_s^0 \simeq \sum_i \left(\frac{\partial \sigma_s}{\partial \alpha_i}\right)^0 \alpha_i, \tag{7.11}$$

$$\mathcal{L}_s = \sigma_s - \sigma_s^0 \simeq \sum_i \left(\frac{\partial \sigma_s}{\partial \alpha_i}\right)^0 \alpha_i = \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i}\right)^0 \alpha_i \gtrless 0. \tag{7.12}$$

In equation (7.12) each $(\partial \mathcal{L}_s / \partial \alpha_i)^0$ may be either positive or negative. The preceding assertion gets elaborated on differentiating equation (7.12) as follows.

$$\frac{\partial \mathcal{L}_s}{\partial \alpha_j} = \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_j}\right)^0 = \frac{\partial}{\partial \alpha_j}\left(\sum_i \left(\frac{\partial \sigma_s}{\partial \alpha_i}\right)^0 \alpha_i\right) = \left(\frac{\partial \sigma_s}{\partial \alpha_j}\right) \gtrless 0. \tag{7.13}$$

The total time derivative of $\mathcal{L}_s$ then reads as,

$$\frac{d\mathcal{L}_s}{dt} = \frac{\partial \mathcal{L}_s}{\partial t} + \sum_i \left(\frac{\partial \mathcal{L}_s}{\partial \alpha_i}\right)\frac{d\alpha_i}{dt}. \tag{7.14}$$

which transforms to,

$$\frac{d\mathcal{L}_s}{dt} = \sum_i \alpha_i \frac{\partial}{\partial t}\left(\frac{\partial \sigma_s}{\partial \alpha_i}\right)^0 + \sum_i \left(\frac{\partial \sigma_s}{\partial \alpha_i}\right)^0 \frac{d\alpha_i}{dt}. \tag{7.15}$$

2. If $(\partial \sigma_s / \partial \alpha_i)^0 = 0$ and hence $(\partial \mathcal{L}_s / \partial \alpha_i)^0 = 0$, we have to go for the second order terms, namely:

$$\mathcal{L}_s = (\sigma_s - \sigma_s^0) \simeq \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 \sigma_s}{\partial \alpha_i \partial \alpha_j}\right)^0 \alpha_i \alpha_j, = \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 L_s}{\partial \alpha_i \partial \alpha_j}\right)^0 \alpha_i \alpha_j \gtrless 0, \tag{7.16}$$

provided $(\partial^2 \sigma_s / \partial \alpha_i \partial \alpha_j)^0 \neq 0$. The differentiation of $\mathcal{L}_s$ successively with respect to α_k and α_l produces the following two expressions, namely:

$$\frac{\partial \mathcal{L}_s}{\partial \alpha_k} = \sum_i \left(\frac{\partial^2 \mathcal{L}_s}{\partial \alpha_i \partial \alpha_k}\right)^0 \alpha_i = \frac{1}{2}\frac{\partial}{\partial \alpha_k}\left(\sum_{i,j}\left(\frac{\partial^2 \sigma_s}{\partial \alpha_i \partial \alpha_j}\right)^0 \alpha_i \alpha_j\right) = \sum_i \left(\frac{\partial^2 \sigma_s}{\partial \alpha_i \partial \alpha_k}\right)^0 \alpha_i$$

$$\frac{\partial^2 \mathcal{L}_s}{\partial \alpha_l \partial \alpha_k} = \left(\frac{\partial^2 \mathcal{L}_s}{\partial \alpha_l \partial \alpha_k}\right)^0 = \left(\frac{\partial^2 \sigma_s}{\partial \alpha_l \partial \alpha_k}\right) \gtrless 0. \tag{7.18}$$

The total time rate of $\mathcal{L}_s$ then reads as,

$$\frac{d\mathcal{L}_s}{dt} = \frac{1}{2}\sum_{i,j}\alpha_i\alpha_j \frac{\partial}{\partial t}\left(\frac{\partial^2\sigma_s}{\partial\alpha_i\partial\alpha_j}\right)^0 + \sum_j\left(\sum_i \alpha_i\left(\frac{\partial^2\sigma_s}{\partial\alpha_i\partial\alpha_j}\right)^0\right)\frac{d\alpha_j}{dt}. \tag{7.19}$$

3. However, if $(\partial\sigma_s/\partial\alpha_i)^0 = 0$ and $\left(\partial^2\sigma_s/\partial\alpha_i,\partial\alpha_j\right)^0 = 0$,

   we have to go for a third order approximation, namely:

$$\mathcal{L}_s = (\sigma_s - \sigma_s^0) \simeq \frac{1}{6}\sum_{i,j,k}\left(\frac{\partial^3\sigma_s}{\partial\alpha_i\partial\alpha_j\partial\alpha_k}\right)^0 \alpha_i\alpha_j\alpha_k, \tag{7.20}$$

provided $\left(\partial^3\sigma_s/\partial\alpha_i\partial\alpha_j\partial\alpha_k\right)^0 \neq 0$. The total time derivative of $\mathcal{L}_s$ then reads as,

$$\frac{d\mathcal{L}_s}{dt} = \frac{1}{6}\sum_{i,j,k}\alpha_i\alpha_j\alpha_k\frac{\partial}{\partial t}\left(\frac{\partial^3\sigma_s}{\partial\alpha_i\partial\alpha_j\partial\alpha_k}\right)^0 + \frac{1}{2}\sum_k\left(\sum_{i,j}\left(\frac{\partial^3\sigma_s}{\partial\alpha_i\partial\alpha_j\partial\alpha_k}\right)^0\alpha_i\alpha_j\right)\frac{d\alpha_k}{dt}. \tag{7.21}$$

4. In this sequence if up to (n-1)[th] derivatives of σ_s happen to vanish at the origin, one needs to go for the n[th] derivative of σ_s at the origin. That is, if, $(\partial\sigma_s/\partial\alpha_i)^0 = 0$, $\left(\partial^2\sigma_s/\partial\alpha_i\partial\alpha_j\right)^0 = 0$ and so oné $\left((\partial^n\sigma_s/\partial\alpha_i\partial\alpha_j\partial\alpha_k\cdots\partial\alpha_{(n-1)})^0 = 0\right)$, we have to go for n^{th} order derivative, namely:

$$\mathcal{L}_s = (\sigma_s - \sigma_s^0) \simeq \frac{1}{n!}\sum_{i,j,k,\cdots}\left(\frac{\partial^n\sigma_s}{\partial\alpha_i\partial\alpha_j\partial\alpha_k\cdots}\right)^0\alpha_i\alpha_j\alpha_k\cdots, \tag{7.22}$$

provided $\left(\partial^n\sigma_s/\partial\alpha_i\partial\alpha_j\partial\alpha_k\cdots\right)^0 \neq 0$. The total time derivative then read as,

$$\frac{d\mathcal{L}_s}{dt} = \frac{1}{n!}\sum_{i,j,k,\cdots}(\alpha_i\alpha_j\alpha_k\cdots)\frac{\partial}{\partial t}\left(\frac{\partial^n\sigma_s}{\partial\alpha_i\partial\alpha_j\partial\alpha_k\cdots}\right)^0 + \frac{n}{n!}\sum_n\left(\sum_{i,j,k,\cdots}\left(\frac{\partial^n\sigma_s}{\partial\alpha_i\partial\alpha_j\partial\alpha_k\cdots}\right)^0(\alpha_i\alpha_j\alpha_k\cdots)\right)\frac{d\alpha_n}{dt}$$

The conclusions about the thermodynamic stability of a process is then drawn using Lyapunov and Malkinôs theorems [5-8, 21] by establishing the signs of $\mathcal{L}_s$, $d\mathcal{L}_s/dt$ and whether the magnitude of each gradient $(\partial\mathcal{L}_s/\partial\alpha_i)$ is finite or not.

1. The unperturbed trajectory is said to be a thermodynamically stable one when,

$$\mathcal{L}_s \cdot \frac{d\mathcal{L}_s}{dt} < 0. \tag{7.23}$$

2. The thermodynamic asymptotic stability is obtained if, either

$$\mathcal{L}_s > 0, \quad \frac{d\mathcal{L}_s}{dt} \leq -\beta < 0 \tag{7.24}$$

$$\mathcal{L}_s < 0, \quad \frac{d\mathcal{L}_s}{dt} \geq \beta > 0, \tag{7.25}$$

   where β is strictly a positive number that vanishes only at the origin.

3. The thermodynamic stability under constantly acting small disturbances, as per Malkinôs theorem, is obtained if in addition to equation (7.24) or (7.25) each $(\partial\mathcal{L}_s/\partial\alpha_i)$ is finite.

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