



Study of stability Analysis of Chemical reactions

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Abstract-

Different theories of stability including Gibbs-Duhem Theory of Stability, theory of thermodynamic stability of nonequilibrium states, Comprehensive Thermodynamic Theory of Stability of Irreversible Processes (CTTSIP) have been studied in this paper. CTTSIP is developed using Lyapunov's second (direct) method of stability of motion and the second law of thermodynamics. In fact, CTTSIP is compact and similar to the Gibbs-Duhem stability theory of states of equilibrium thermodynamics.

CTTSIP has been applied to chemically oscillating system of Brusselator Model and the results are obtained after systematic computation and simulation of the expressions by Mathematica software.

Keywords- thermodynamic stability, Irreversible Processes, Brusselator Model, computation and simulation, Mathematica,

1. Introduction

Nature and natural phenomena are very mysterious, we know the processes of fluctuation, instability, evolution, self-organization and formation structures in chaos on all level of chemistry and biology to cosmology. Majority of them fall in the fold of irreversible processes. We have so far gain enough understanding through molecular interaction that these phenomena are occurred at far from equilibrium, but it is interesting to know how these forces produce the long range coherence in nonequilibrium situations. The processes, which are impossible to realize at equilibrium, become possible in far from equilibrium situations. Indeed irreversible processes lead the system to certain space-time structures. It is interesting to study how these real processes react to the perturbations: whether the systems or processes remain stable or become unstable under the external disturbances.



2. Gibbs-Duhem Theory of Stability

The laws of thermodynamics establish the thermodynamic variables of equilibrium states. The equilibrium states in spatially uniform closed systems are completely described by only two variables. Using Clausius inequality the general equilibrium conditions for a closed thermodynamic system, capable of performing PV work can be deduced as¹⁻⁷

$$TdS \geq dU + PdV \quad (1)$$

Thus, on incorporating Clausius inequality, the direction of natural transformations is introduced. At constant internal energy ($dU = 0$) and volume ($dV = 0$), eq.(1) gives

$$dS \geq 0 \quad (\text{Const. } U, V) \quad (2)$$

showing that the entropy, S , seeks a maximum at constant U and V . Setting dS and dV equal to zero in equation (1), we obtain

$$dU \leq 0 \quad (\text{Const. } S, V) \quad (3)$$

that is the internal energy “seeks a minimum” under conditions of constant entropy and volume. Under conditions of constant entropy and pressure, equation (3) becomes

$$d(U + PV) = dH \leq 0 \quad (4)$$

Similarly using $A \equiv U - TS$ and $G \equiv U + PV - TS$, we obtain the free-energy minimization principle, namely,

$$dA \leq 0 \quad (5)$$

$$dG \leq 0 \quad (6)$$

Thus, in all natural processes occurring in closed adiabatic systems, the entropy continually increases. Using the principle of maximization of entropy for an adiabatic evolution of a system and minimization of thermodynamic potentials (U , H , A and G), the Gibbs-Duhem theory of stability of equilibrium states, for global level, immediately evolves as¹⁻⁷

$$S = \max., \quad (7)$$

$$\delta S = \sum_i \left(\frac{\partial S}{\partial x_i} \right) \delta x_i = 0, \quad (8)$$

$$\delta^2 S = \sum_{i,j} \left(\frac{\partial^2 S}{\partial x_i \partial x_j} \right) \delta x_i \delta x_j < 0, \quad (9)$$

where δx_i and δx_j are traditionally termed as the virtual displacements from the chosen equilibrium state and equation (9), (< 0) describes the stability of equilibrium state. Thus, the description of non-equilibrium thermodynamics was introduced through the natural outcome of Gibbs-Duhem theory of stability. However, it does not focus on the thermodynamic description of nonequilibrium states. In view of this, the need of formulations of thermodynamic theory for nonequilibrium states felt. These efforts naturally led to the development of stability theory for nonequilibrium states.



In the past several attempts had been made to develop suitable thermodynamic theory of stability for nonequilibrium states using Lyapunov's direct method of stability of motion⁸⁻¹². The well documented thermodynamic theory of stability of nonequilibrium states in so-called local equilibrium assumption (LEA) is developed by Glansdorff and Prigogine⁴⁻⁷. We discuss this theory in the following section.

3. Stability of Nonequilibrium States

Glansdorff and Prigogine have described a theory of thermodynamic stability of nonequilibrium states⁴⁻⁷ which is supposed to confirm with so-called local equilibrium assumption. For such state they have proposed, at the local level description, namely,

$$(\delta^2 s) = \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 s}{\partial y_i \partial y_j} \right) \delta y_i \delta y_j < 0, \quad (10)$$

$$\frac{\partial}{\partial t} (\delta^2 s) \geq 0, \quad (11)$$

where s is the per unit mass entropy, y_i and y_j are the thermodynamic variables for such nonequilibrium states and equation (11) (\geq) describes the asymptotic stability. Note that equations (10) and (11) are the conditions under the constraint of adiabaticity. Under the non-adiabatic conditions no guarantee is given by the second law of thermodynamics that $\delta^2 S$ will be negative quantity. Moreover, the virtual displacements such as δx_i and δx_j of system in equilibrium may cause the generation of a spatial non-uniformity. Thus, if on perturbation a spatial non-uniformity gets generated then there is no *locus standii* of the global level variables x_i 's. Therefore, it is clear that $\delta^2 S$ cannot be taken as a thermodynamic Lyapunov function for all type of perturbations of equilibrium states.

A detailed investigation of Glansdorff and Prigogine's proposals had been undertaken by Landsberg¹³, Keizer and Fox¹⁴ and Lavenda¹⁵. They found that Glansdorff and Prigogine's stability theory suffers from serious drawbacks, namely: Landsberg²⁹ had criticized the maximization of 's' within the domain of local equilibrium state because at the local level each small pocket has the features of the open systems and hence δs cannot be equated to zero because it is not guaranteed so by the second law of thermodynamics. On the other hand, equation (11) according to Landsberg appears to be a new law whose basis remains unknown and termed as a *basic trick*. Keizer and Fox also contested the validity of the proposals of equations (10) and (11) and which they have shown as not having a thermodynamic sanction. Of course, on developing an irreversible thermodynamic framework one would obtain an appropriate set of local level thermodynamic variables x_i 's and x_j 's and for this type of analysis it is first required to establish an entropy function in nonequilibrium state that too based on the law of thermodynamics.



In case nonequilibrium stationary states Prigogine concluded that a NSS corresponds to minimum production of entropy. However, later Lavenda has unambiguously proved that the said principle of minimum production of entropy is an erroneous conclusion. Lavenda clearly asserts that to arrive at the thermodynamic stability of a so-called local equilibrium state there should be a guarantee given by the law of thermodynamics.

Few other proposals on thermodynamic theory of stability and Lyapunov function is the free energy (Gibbs or Helmholtz) of the system were developed¹⁶⁻¹⁹. However, they too are incapable of dealing with all nonequilibrium situations especially those having their origin in the existence of spatial non uniformity and work only in the cases of linear nonequilibrium situations or close to equilibrium.

4. Lyapunov's Direct Method of Stability of Motion

Lyapunov's direct method of stability of motion⁸⁻¹² involves the identification of suitable sign definite Lyapunov function and then determines its total time derivative. The sign and behaviour of this time derivative of the Lyapunov function then tell us whether the dynamic system is stable, asymptotically stable, and stable under constantly acting small disturbances or unstable. The gist this method is described below. Let the given differential equations of the perturbed motion be

$$\frac{dx_i}{dt} = X_i(t, x_1, x_2, \dots, x_n) \quad (i=1, 2, \dots, n) \quad (12)$$

The trivial solution of equation (12) is

$$x_i \equiv 0 \quad (13)$$

Where x_i 's have been defined as,

$$x_i \equiv |z_i - z_i^0|, \quad x_{i0} = |z_{i0} - z_{i0}^0| = \chi = \text{small const.} \quad (14)$$

is then read as where z_i^0 are the coordinates of the real motion and z_i are those for the corresponding perturbed trajectory. The equations of unperturbed motion

$$x_i^0 \equiv 0, \quad x_{i0}^0 = 0 \quad (15)$$

Thus x_i 's are the small perturbation coordinates in the domain

$$t \geq t_0, \quad t_0 \geq 0, \quad x_i \leq H, \quad H > 0 \quad (16)$$

where H is a sufficiently small positive constant and

$$\therefore X_i(t, 0, 0, \dots, 0) = 0 \quad (17)$$

Let $V(t, x_1, x_2, \dots, x_n)$ be a differentiable Lyapunov function such that,

$$V(t, x_1, x_2, \dots, x_n) \leq \varepsilon(x_1, x_2, \dots, x_n) > 0 \quad (18)$$

$$V(t, 0, 0, \dots, 0) = 0, \quad \varepsilon(0, 0, \dots, 0) = 0 \quad (19)$$

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



$$\frac{dV_i}{dt} = \left(\frac{\partial V_i}{\partial t} + \sum_i \frac{\partial V_i}{\partial x_i} X_i \right) < 0 \quad (20)$$

for $t \geq t_0$, the unperturbed motion is stable. Outside an arbitrarily small neighbourhood of the origin if

$$\sum_i x_i^2 \geq \delta^2 > 0, t \geq T_0 \geq t_0 \quad (21)$$

and in addition to eq.(6.20), if we have

$$\frac{dV}{dt} \leq -\beta < 0 \quad (22)$$

where δ^2 and β are the positive constants, then $x_i \equiv 0$ ($i = 1, 2, 3, \dots, n$) is asymptotically stable. Further, if,

$$V > 0, \quad V(t, 0, 0, 0) \equiv 0, \quad \frac{dV}{dt} \leq -\beta < 0 \quad (23)$$

and the derivatives $\partial V / \partial x_i$ are the finite then the unperturbed motion is stable under the constantly acting small disturbances. This is Malkin's theorem⁸⁻¹².

Recently A. A. Bhalekar has developed stability theory using the fabrics of Lyapunov's direct method stability of motion known as Comprehensive Thermodynamic Theory of Stability of Irreversible Processes (CTTSIP)²⁰⁻²³. The proposed CTTSIP is comprehensive as well as generalized one. CTTSIP is applicable to any real processes, as it does not impose any restrictions regarding type and extent of irreversibility. Using the setup of CTTSIP, the stability analysis of several physical and chemical problems have been reported, such as the stability of (i) equilibrium and nonequilibrium states²³, (ii) the rigid body heat conduction²³, (iii) the stress relaxation processes in viscoelastic fluids^{24,25}, (iv) elementary chemical reactions^{26,27}, and (v) enzyme catalysed reactions²⁸. Using CTTSIP the stability of industrial chemical reactions such as ammonia synthesis and oxidation of sulphur dioxide under temperature perturbation has been reported²⁹⁻³¹.

4.1. Stability of Chemical Reactions by Lyapunov Analysis

There are several ways to identify Lyapunov function, L_s for chemically reacting system. We know that the rate of entropy production¹⁻⁷, Σ_s for multi steps chemical reaction at constant temperature, T and pressure, p is given by

$$\Sigma_s = \sum_i \frac{A_i}{T} \frac{d\xi_i}{dt} > 0, \quad (i = 1, 2, 3, \dots) \quad (24)$$

eq.(24) which is function of mole numbers of reacting species, that is

$$\Sigma_s = \Sigma_s(n_1, n_2, \dots, n_i) > 0, \quad (i = 1, 2, 3, \dots) \quad (25)$$

where n_i ($i = 1, 2, 3, \dots$) is the mole numbers of the reacting species (coordinates).

Now, on account of a small perturbation of coordinates from the real (unperturbed) system, there is change in amount of rate of entropy production, is defined by $\delta \Sigma_s$.

In mathematical terms the $\delta \Sigma_s$ is obtained by differentiating Σ_s , that is



$$\delta\Sigma_s = \frac{\partial\Sigma_s}{\partial n_1} \delta n_1 + \frac{\partial\Sigma_s}{\partial n_2} \delta n_2 + \dots + \frac{\partial\Sigma_s}{\partial n_i} \delta n_i \quad (26)$$

where δn_i is the perturbation coordinate, that is small change in mole numbers on perturbation. Notice that

$$\delta\Sigma_s \approx 0 \quad (27)$$

and

$$\delta n_i \approx 0 \quad (28)$$

depend on the behaviour of the process and act of the perturbation. Note that, in our earlier discussions on the theories of stability of motion the small change in entropy, $\delta\Sigma_s$ is identify as Lyapunov function, L_s so in this case as well. Therefore, eq.(26), is further reproduced as

$$L_s = \frac{\partial\Sigma_s}{\partial n_1} \delta n_1 + \frac{\partial\Sigma_s}{\partial n_2} \delta n_2 + \dots + \frac{\partial\Sigma_s}{\partial n_i} \delta n_i. \quad (29)$$

Thus, L_s becomes the function of perturbation coordinate, δn_i and hence, the total time derivative of L_s is obtained from eq.(29) as

$$\frac{dL_s}{dt} = \frac{\partial\Sigma_s}{\partial n_1} \frac{d(\delta n_1)}{dt} + \frac{\partial\Sigma_s}{\partial n_2} \frac{d(\delta n_2)}{dt} + \dots + \frac{\partial\Sigma_s}{\partial n_i} \frac{d(\delta n_i)}{dt}. \quad (30)$$

In equation (30), $\partial\Sigma_s/\partial n_1$, $\partial\Sigma_s/\partial n_2$, $\partial\Sigma_s/\partial n_i$ are identified as gradient of the Lyapunov function, L_s .

Further, the rate equations¹⁻⁷ for any chemical reactions, read as

$$\begin{aligned} \frac{dn_1}{dt} &= f(n_1, n_2, \dots, n_i) \\ \frac{dn_2}{dt} &= g(n_1, n_2, \dots, n_i) \\ &\vdots \\ \frac{dn_i}{dt} &= h(n_1, n_2, \dots, n_i) \end{aligned} \quad (31)$$

The rate equations are also the function of reacting coordinates. Thus, small change in mole numbers, δn_i on effect of perturbation is obtained as

$$\begin{aligned} \frac{d(\delta n_1)}{dt} &= \frac{\partial f}{\partial n_1} \delta n_1 + \frac{\partial f}{\partial n_2} \delta n_2 + \dots + \frac{\partial f}{\partial n_i} \delta n_i \\ \frac{d(\delta n_2)}{dt} &= \frac{\partial g}{\partial n_1} \delta n_1 + \frac{\partial g}{\partial n_2} \delta n_2 + \dots + \frac{\partial g}{\partial n_i} \delta n_i \text{ and so on.} \end{aligned} \quad (32)$$

equation (32) gives how the perturbation coordinates advance with time in perturbation space.

Now with equations.(29) and (30), one can easily establish the stability of the processes using the fabrics of the Lyapunov's direct method of stability of motion. The given process is stable and asymptotically stable if one satisfy:

$$L_s > 0, \quad \frac{dL_s}{dt} \leq \beta < 0 \quad \text{or} \quad L_s < 0, \quad \frac{dL_s}{dt} \geq \beta > 0 \quad (33)$$



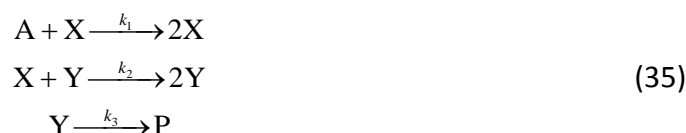
and unstable if

$$L_s > 0, \quad \frac{dL_s}{dt} > 0 \quad \text{or} \quad L_s < 0, \quad \frac{dL_s}{dt} < 0 \quad (34)$$

The finiteness of gradient of Lyapunov function along with condition given in eq.(32), ensures the stability under constantly acting small disturbances, as per Malkin's theorem.

4.2. The Lotka-Volterra Model

The Lotka-Volterra prey-predator model³⁷⁻⁴² consisting of three reactions steps,



where first two reaction steps follow second order kinetics in which two reactants produces a product, while third reaction is the first order kinetics in which single reactant in a single step produces a product. X is the population of rabbits, which reproduce auto catalytically, A is the amount of grass, which assumed to be constant, or at least in great excess compared with its consumption by the rabbits, Y is the population of lynxes (bobcats), and P represents the dead lynxes which again assumed to be constant. k_i ($i=1, 2, 3$) are the forward rate constants. Assuming the reverse rate constants are insignificant, the expression for rate equations for Lotka-Volterra reaction scheme are given by chemical kinetics³⁷⁻⁴², that read as

$$\frac{d\xi_1}{dt} = v_1 = k_1[A][X] \quad (36)$$

$$\frac{d\xi_2}{dt} = v_2 = k_2[X][Y] \quad (37)$$

$$\frac{d\xi_3}{dt} = v_3 = k_3[Y] \quad (38)$$

$$\frac{d[X]}{dt} = k_1[A][X] - k_2[X][Y] = v_1 - v_2 \quad (39)$$

$$\frac{d[Y]}{dt} = k_2[X][Y] - k_3[Y] = v_2 - v_3 \quad (40)$$

where ξ_i ($i=1,2,3$) is the extent of reaction, v_i ($i=1,2,3$) is the rate of reaction.

There is an initial transient behavior during which the intermediates show normal behavior of progression. After this, however, the system begins to move away from the steady state. The concentration of X and Y begins to oscillate and their rate becomes nonzero. The rate of change of concentration of intermediate in this case given by equations.(39) and (40).

For constant concentration of A and P we obtain sustain oscillations and intermediates oscillate in the finite limit of concentrations. However, for closed system that concentration of A and P are no more time independent and oscillations



decay in time. The oscillatory behavior of intermediates X and Y are plotted with time by using commercial software Mathematica-10. For computer programming, following rate constants and concentration of reactants and products were assumed.

Table 1.1

$k_1 = k_2 = 1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, k_3 = 3 \text{ s}^{-1}$
$[X] = 0.1 \text{ mol dm}^{-3}$
$[A] = 3.0 \text{ mol dm}^{-3}$
$[P] = 1 \text{ mol dm}^{-3}$

The observations, obtained through Mathematica programming are shown in Fig.1 and 2. The concentrations of intermediate species vary between the certain maximum and minimum values are shown in Fig 1

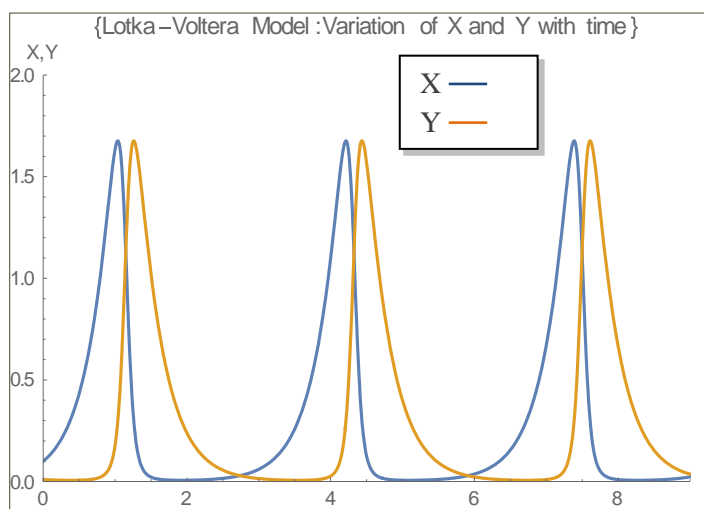


Fig 1: Variation of X and Y with time

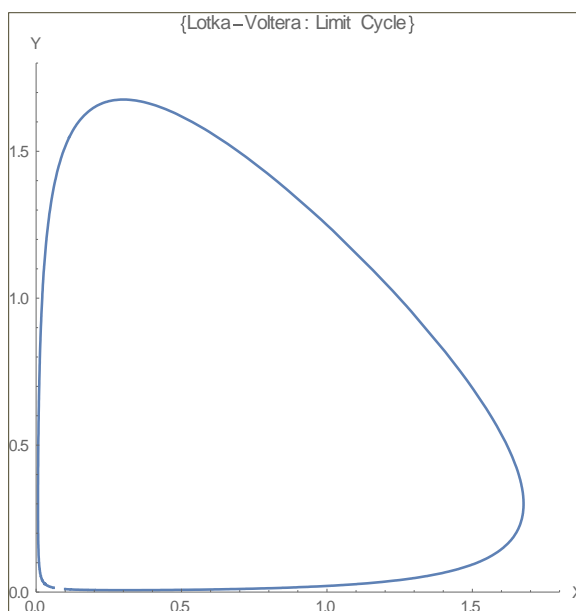


Fig 2: Maximum and minimum values (Limit Cycle) in which X and Y are oscillating

The expressions for chemical affinities⁴⁻⁷ for the reaction scheme of Lotka-Volterra model described in equation (35), read as

$$A_1 = A_1^\phi + RT \ln \left(\frac{[A]}{[X]} \right) \quad (41)$$

$$A_2 = A_2^\phi + RT \ln \left(\frac{[X]}{[Y]} \right) \quad (42)$$

$$A_3 = A_3^\phi + RT \ln \left(\frac{[Y]}{[P]} \right) \quad (43)$$

where A_1^ϕ , A_2^ϕ and A_3^ϕ are the chemical affinities of the standard states and A_1 , A_2 and A_3 are the chemical affinities of the corresponding states and R is the gas constants.

4.2.1 Steady State Analysis

In steady state the concentrations of intermediate species X and Y remain time independent, that is

$$\frac{d[X]^s}{dt} = k_1[A][X]^s - k_2[X]^s[Y]^s = v_1^s - v_2^s = 0 \quad (44)$$

$$\frac{d[Y]^s}{dt} = k_2[X]^s[Y]^s - k_3[Y]^s = v_2^s - v_3^s = 0. \quad (45)$$

where $[X]^s$ and $[Y]^s$ are the concentrations of X and Y in steady state respectively. Notice that the equation.(44) and (45) gave the new identity that is

$$v_1^s = v_2^s = v_3^s = v \quad (46)$$

After solving equation (44) and (45), the steady state concentrations of X and Y are obtained as,

$$[X]^s = \left(\frac{k_3}{k_1[A]} \right) [Y]^s, \quad [X]^s = \frac{k_3}{k_2}, \quad [Y]^s = \frac{k_1}{k_2} [A]. \quad (47)$$

The stability of steady state has been investigated by Jacobian matrix¹⁰⁻¹⁵ and Lyapunov direct method of stability of motion at constant T and p in subsequent sections.

4.2.2. Stability Analysis

In this case, the concentration of intermediate species, X and Y are no more time independent, that is

$$\frac{d[X]}{dt} = k_1[A][X] - k_2[X][Y] \neq 0 \quad (48)$$

$$\frac{d[Y]}{dt} = k_2[X][Y] - k_3[Y] \neq 0. \quad (49)$$

The rate of entropy production in this case is given by

$$\Sigma = \frac{A_1}{T} v_1 + \frac{A_2}{T} v_2 + \frac{A_3}{T} v_3 > 0 \quad (50)$$

where Σ is positive definite as per the dictates of second law of thermodynamics.

Notice that at constant the temperature and pressure, the Σ is the function of and mole numbers of A, X, Y and P. Thus, we have

$$\Sigma = \Sigma(A, X, Y, P) > 0. \quad (51)$$

In the beginning of our analysis we assumed that [A] and [P] are constant and hence equation (51) reduces to

$$\Sigma = \Sigma(X, Y) > 0. \quad (52)$$

Now, the concentration of X and Y are perturbed by sufficiently small amount δX and δY then, we have

$$\delta \Sigma = \frac{\partial \Sigma}{\partial X} \delta X + \frac{\partial \Sigma}{\partial Y} \delta Y \quad (53)$$

where $\delta \Sigma = L_s$, as CTTSIP identifies the excess rate of entropy production as Lyapunov function. Now, from equation (52) and (53), we obtain

$$\begin{aligned} \frac{\partial \Sigma}{\partial X} = & v_1 \frac{\partial(A_1/T)}{\partial X} + \frac{A_1}{T} \frac{\partial v_1}{\partial X} + v_2 \frac{\partial(A_2/T)}{\partial X} + \frac{A_2}{T} \frac{\partial v_2}{\partial X} \\ & + v_3 \frac{\partial(A_3/T)}{\partial X} + \frac{A_3}{T} \frac{\partial v_3}{\partial X} \end{aligned} \quad (54)$$

and



$$\frac{\partial \Sigma}{\partial Y} = v_1 \frac{\partial(A_1/T)}{\partial Y} + \frac{A_1}{T} \frac{\partial v_1}{\partial Y} + v_2 \frac{\partial(A_2/T)}{\partial Y} + \frac{A_2}{T} \frac{\partial v_2}{\partial Y} + v_3 \frac{\partial(A_3/T)}{\partial Y} + \frac{A_3}{T} \frac{\partial v_3}{\partial Y} \quad (55)$$

From the expressions of rate equations and affinities, we further obtain

$$\frac{\partial v_1}{\partial X} = k_1[A], \quad \frac{\partial v_2}{\partial X} = k_2[Y], \quad \frac{\partial v_3}{\partial X} = 0 \quad (56)$$

$$\frac{\partial v_1}{\partial Y} = 0, \quad \frac{\partial v_2}{\partial Y} = k_2[X], \quad \frac{\partial v_3}{\partial Y} = k_3 \quad (57)$$

$$\frac{\partial(A_1/T)}{\partial X} = -\frac{R}{[X]}, \quad \frac{\partial(A_2/T)}{\partial X} = \frac{R}{[X]}, \quad \frac{\partial(A_3/T)}{\partial X} = 0 \quad (58)$$

$$\frac{\partial(A_1/T)}{\partial Y} = 0, \quad \frac{\partial(A_2/T)}{\partial Y} = -\frac{R}{[Y]}, \quad \frac{\partial(A_3/T)}{\partial Y} = \frac{R}{[Y]} \quad (59)$$

Using equation (54) and (55) and on substituting quantities from equations (56)-(59) in equation (53), we have

$$L_s = \delta \Sigma = \left(\frac{A_1}{T} k_1[A] + \frac{A_2}{T} k_2[Y] + R(k_2[Y] - k_1[A]) \right) \delta X + \left(\frac{A_2}{T} k_2[X] + \frac{A_3}{T} k_3 + R(k_3[Y] - k_2[X]) \right) \delta Y \quad (60)$$

which is equivalent to

$$L_s = \left(\frac{A_1}{T} v_1 + \frac{A_2}{T} v_2 + R(v_2 - v_1) \right) \frac{\delta X}{[X]} + \left(\frac{A_2}{T} v_2 + \frac{A_3}{T} v_3 + R(v_3 - v_2) \right) \frac{\delta Y}{[Y]} \quad (61)$$

As per the CTTSP³⁷⁻⁴⁰, we have here identified, $\delta \Sigma = L_s$ the excess rate of entropy production is required Lyapunov function for stability analysis. For steady state, we have

$$v_1 = v_2 = v_3 = v. \quad (62)$$

This identity reduces equation (61) gives

$$L_s = v \left(\frac{A_1}{T} + \frac{A_2}{T} \right) \frac{\delta X}{[X]} + v \left(\frac{A_2}{T} + \frac{A_3}{T} \right) \frac{\delta Y}{[Y]} \quad (63)$$

We now derive the rate equations of perturbation coordinates, δX and δY from equation (48) and (49) by adopting the identical procedure which is applied earlier for obtaining Lyapunov function, thus we have,

$$\frac{d[X]}{dt} = f(X, Y) \quad (64)$$

$$\frac{d[Y]}{dt} = g(X, Y). \quad (65)$$



Thus, for sufficiently small and finite perturbation of mole numbers of X and Y from original state, gives

$$\delta\left(\frac{d[X]}{dt}\right) = \frac{\partial f}{\partial X}\delta X + \frac{\partial f}{\partial Y}\delta Y \quad (66)$$

$$\delta\left(\frac{d[Y]}{dt}\right) = \frac{\partial g}{\partial X}\delta X + \frac{\partial g}{\partial Y}\delta Y \quad (67)$$

where

$$f(X, Y) = k_1[A][X] - k_2[X][Y] \quad \text{and} \quad (68)$$

$$g(X, Y) = k_2[X][Y] - k_3[Y]. \quad (69)$$

From equation (68) and (69), the expressions of rate equations in perturbation space are obtained as,

$$\frac{\partial f}{\partial X} = k_1[A] - k_2[Y], \quad \frac{\partial f}{\partial Y} = -k_2[X] \quad \text{and} \quad (70)$$

$$\frac{\partial g}{\partial X} = k_2[Y], \quad \frac{\partial g}{\partial Y} = k_2[X] - k_3. \quad (71)$$

Thus, using equation (70) and (71) in equation (66) and (67), we obtain the required expressions for perturbation coordinates as

$$\frac{d(\delta X)}{dt} = (k_1[A] - k_2[Y])\delta X - k_2[X]\delta Y \quad \text{and} \quad (72)$$

$$\frac{d(\delta Y)}{dt} = k_2[Y]\delta X + (k_2[X] - k_3)\delta Y, \quad (73)$$

which are equivalent to

$$\frac{d(\delta X)}{dt} = (v_1 - v_2)\frac{\delta X}{[X]} - v_2\frac{\delta Y}{[Y]} \quad \text{and} \quad (74)$$

$$\frac{d(\delta Y)}{dt} = (v_2 - v_3)\frac{\delta Y}{[Y]} + v_2\frac{\delta X}{[X]}. \quad (75)$$

In case of steady state, one has

$$\frac{d(\delta X)}{dt} = -v_2\frac{\delta Y}{[Y]} \quad (76)$$

$$\frac{d(\delta Y)}{dt} = v_2\frac{\delta X}{[X]}. \quad (77)$$

Now, we scrutinize the stability of the process by using the fabrics of the Lyapunov's direct method of stability of motion. For this purpose we must require the total time derivative of Lyapunov function, dL_s/dt which is obtained from equation (63) as

$$\frac{dL_s}{dt} = \frac{\partial \Sigma}{\partial X}\frac{d(\delta X)}{dt} + \frac{\partial \Sigma}{\partial Y}\frac{d(\delta Y)}{dt}. \quad (78)$$

The operative expression of dL_s/dt is obtained from equation (78) by differentiating perturbation coordinates with time, that is



$$\begin{aligned} \frac{dL_s}{dt} = & \left(\frac{A_1}{T} k_1 [A] + \frac{A_2}{T} k_2 [Y] + R(k_2 [Y] - k_1 [A]) \right) \frac{d(\delta X)}{dt} \\ & + \left(\frac{A_2}{T} k_2 [X] + \frac{A_3}{T} k_3 + R(k_3 - k_2 [X]) \right) \frac{d(\delta Y)}{dt} \end{aligned} \quad (79)$$

On substituting the values of $d(\delta X)/dt$ and $d(\delta Y)/dt$ in equation (79), the final expression for dL_s/dt is obtained as,

$$\begin{aligned} \frac{dL_s}{dt} = & \left(\frac{A_1}{T} k_1 [A] + \frac{A_2}{T} k_2 [Y] + R(k_2 [Y] - k_1 [A]) \right) \\ & \times \left((k_1 [A] - k_2 [Y]) \delta X - k_2 [X] \delta Y \right) \\ & + \left(\frac{A_2}{T} k_2 [X] + \frac{A_3}{T} k_3 + R(k_3 - k_2 [X]) \right) \\ & \times \left(k_2 [Y] \delta X + (k_2 [X] - k_3) \delta Y \right) \end{aligned} \quad (80)$$

However, using equation (74) and (75), we have

$$\begin{aligned} \frac{dL_s}{dt} = & \frac{1}{[X]} \left(\frac{A_1}{T} v_1 + \frac{A_2}{T} v_2 + R(v_2 - v_1) \right) \left\{ (v_1 - v_2) \frac{\delta X}{[X]} - v_2 \frac{\delta Y}{[Y]} \right\} \\ & + \frac{1}{[Y]} \left(\frac{A_2}{T} v_2 + \frac{A_3}{T} v_3 + R(v_3 - v_2) \right) \left\{ v_2 \frac{\delta X}{[X]} + (v_2 - v_3) \frac{\delta Y}{[Y]} \right\}. \end{aligned} \quad (81)$$

In case of steady states, equation (81) becomes

$$\frac{dL_s}{dt} = -\frac{v^2}{[X][Y]} \left(\frac{A_1}{T} + \frac{A_2}{T} \right) \delta Y + \frac{v^2}{[X][Y]} \left(\frac{A_2}{T} + \frac{A_3}{T} \right) \delta X \quad (82)$$

which is equivalent to

$$\frac{dL_s}{dt} = -k_2 v \left(\frac{A_1}{T} + \frac{A_2}{T} \right) \delta Y + k_2 v \left(\frac{A_2}{T} + \frac{A_3}{T} \right) \delta X. \quad (83)$$

In this analysis, it shows that the gradient of Lyapunov function is finite and positive definite. Hence, the behaviour of perturbation coordinates, δX and δY with time is important for the identification sign of L_s and dL_s/dt , and then the stability of the state. Using Mathematica software, the graphical presentations of perturbation coordinates, L_s and dL_s/dt with time are shown in following figures.

Case 1: Steady state



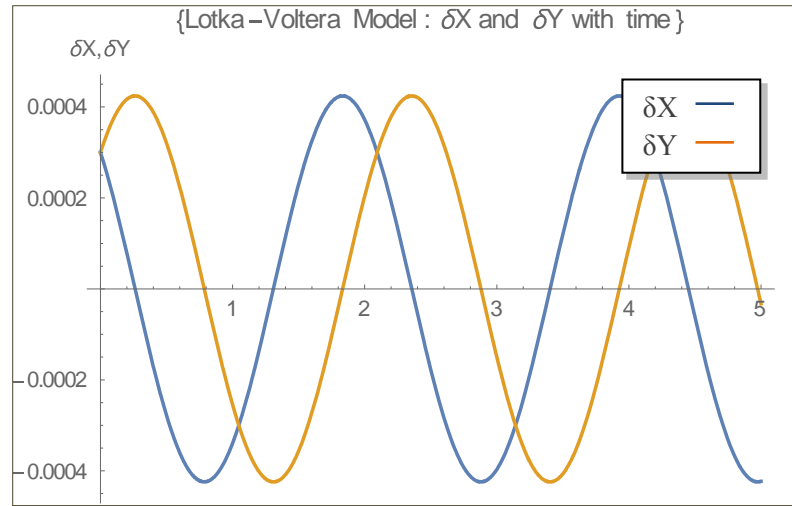


Fig 3: Oscillating behavior of δX and δY with time

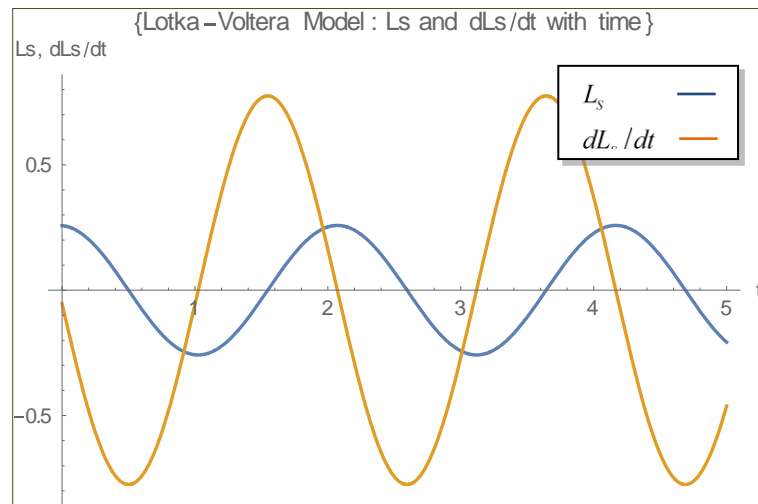
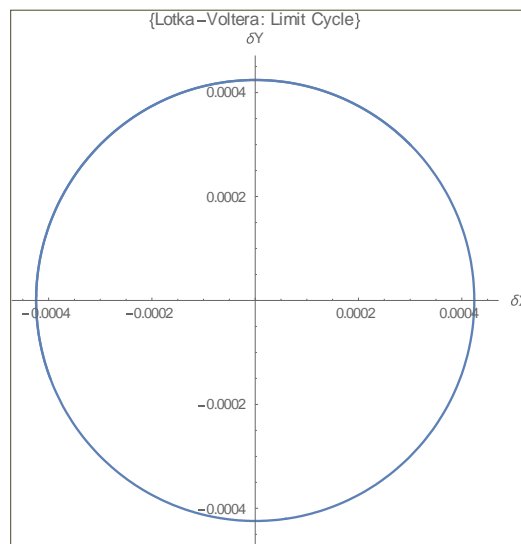


Fig 4: Sustain oscillations of L_s and dL_s/dt with time



From Fig 3-5, it indicates that the steady state is unstable on perturbation. It is clear that small disturbances to intermediates species create inception of sustain oscillation. system parameters are changed on perturbation so that the system passes through the bifurcation limit cycle or periodic orbit develops surrounding the steady state.

Case 2: Chemical oscillations

1. There is domain in periodic oscillations which gives clear instability on perturbation of intermediate coordinates. The behaviour of L_s and dL_s/dt with time, are shown following figures. Note that the graphical presentation of L_s and dL_s/dt shows they have same (positive) signs. This indicates that the perturbation is not decayed rather it grows with time. Hence, small perturbation in this region is unstable and uncontrollable.

2.

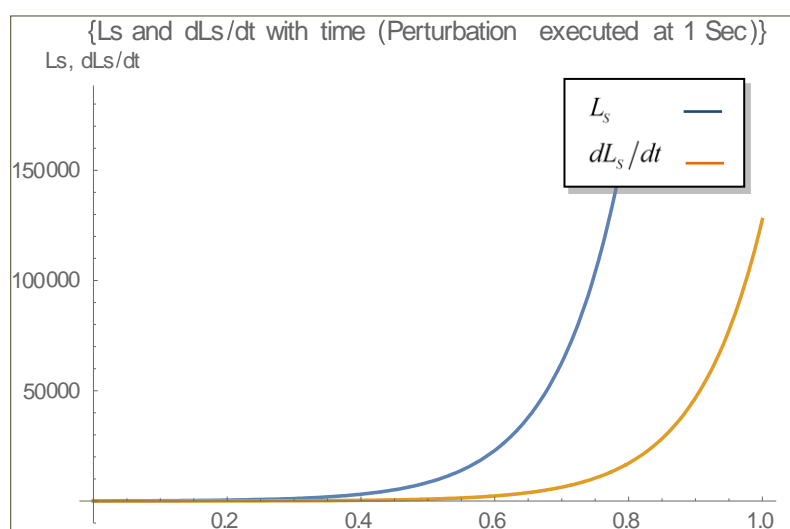


Fig 6: Unstable state as $L_s > 0$ and $dL_s/dt > 0$ have positive (same) signs

3. At certain points of chemical oscillations, perturbation leads to formation of another pattern of oscillations of coordinates. From graphical presentation of Mathematica software shows that these oscillations grow with time beyond the control. This is again the clear case of instability of the process.

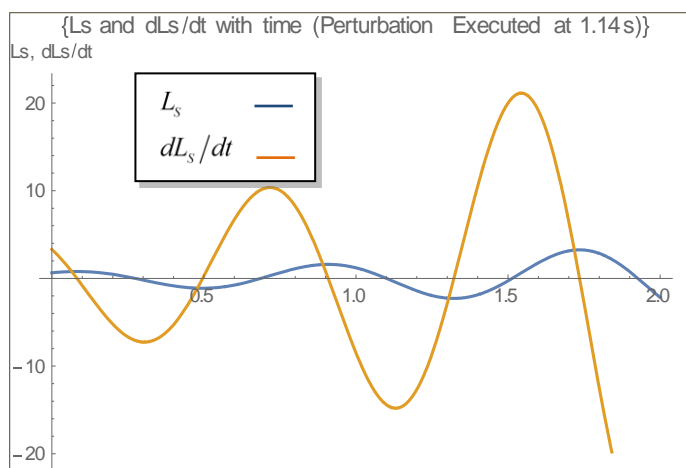


Fig 7: Unstable state as L_s and dL_s/dt are oscillating and growing with time

- There is small domain where the perturbation leads damped oscillations. The oscillations decay with time and tend to diminish on original trajectory. In this case there are small fluctuations in the beginning of onset of perturbation but these fluctuations gradually disappear and trajectory tends to converge on original trajectory. In this event the stability of the process is guaranteed as per the Lyapunov analysis.

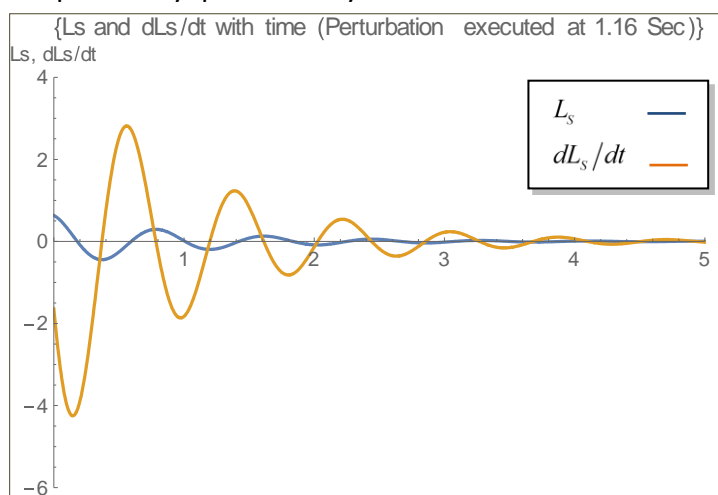


Fig 8: Stable state as L_s and dL_s/dt are oscillating and decaying with time

- There is domain where the stability is clearly visible because L_s and dL_s/dt have definite signs. In this case, $L_s < 0$ and $dL_s/dt > 0$ and tend to vanishes on real trajectory. This shows the stability of the process as per the Lyapunov's

direct method of stability of motion. The domain with this property is very small.

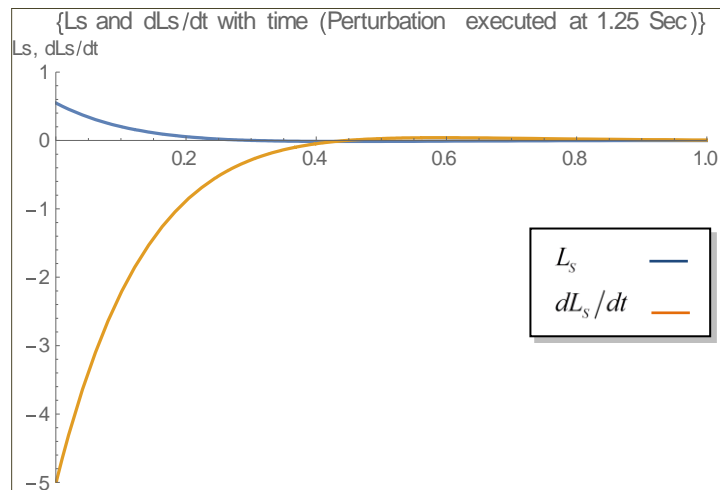


Fig 9: Stable state as $L_s < 0$ and $dL_s/dt > 0$ (opposite signs)

4.3. Brusselator Model

In the previous section we have seen that how the tools of Lyapunov's direct method of stability of motion deal to study the stability analysis of oscillatory behavior of Lotka-Volterra model³²⁻³⁶. Although this model generates sustained oscillatory behavior from the simple chemical reaction with mass action kinetics, but it is not an appropriate description of any actual chemistry of ecological system. It is successful in generating the oscillatory behaviour. The model has an oscillatory solution for any values of the rate constant and food supply, A and initial values of X and Y . The amplitude and period of oscillations are obtained depend on all of these quantities; there is an infinite array of oscillatory solutions. If the system is perturbed, it continues to oscillate, but with a new period and amplitude, until it is perturbed again. In the presence of any significant amount of noise, the behavior would hardly be recognizable as periodic, since it would constantly be jumping from one oscillatory behavior to another. Real chemical system does not behave this way. This oscillates only within a finite range of parameters, and they have a single mode of oscillation, to which they return if the system is perturbed. The first chemically respectable model was proposed by Prigogine (1968)⁵ and dubbed the 'Brusselator' by Tyson (1973)⁴²⁻⁴⁵. In this paper, we shall discuss the thermodynamic stability of the Brusselator model by Lyapunov function analysis.

We consider a Brusselator model reaction³⁷⁻⁴⁰, which exhibits oscillations in finite limits of concentrations at constant temperature and pressure, namely



The net reaction of this scheme is



We assume the concentrations of the reactants A and B are maintained at a desired nonequilibrium value through appropriate flows. The products D and P are removed as they are formed. We also assume the reaction occurs in a solution that is well stirred, hence homogeneous. If we further assume that all the reverse reactions are insignificant, they can be neglected. As per the chemical kinetics⁴⁶⁻⁴⁸, the rate equations for the given model reaction in terms of extent of advancement of chemical reaction, read as,

$$\frac{d\xi_1}{dt} = k_1[A] = v_1 > 0 \tag{86}$$

$$\frac{d\xi_2}{dt} = k_2[B][X] = v_2 > 0 \tag{87}$$

$$\frac{d\xi_3}{dt} = k_3[X]^2[Y] = v_3 > 0 \tag{88}$$

$$\frac{d\xi_4}{dt} = k_4[X] = v_4 > 0 \tag{89}$$

$$\frac{d[X]}{dt} = k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X] = v_1 - v_2 + v_3 - v_4 \tag{90}$$

$$\frac{d[Y]}{dt} = k_2[B][X] - k_3[X]^2[Y] = v_2 - v_3 \tag{91}$$

where [A], [B], [X], [Y], [D] and [E] are molar concentrations of the species A, B, X, Y, D and E respectively, k_i ($i = 1, 2, 3, 4$) is the rate constant, v_i ($i = 1, 2, 3, 4$) is the rate of chemical reaction. There is an initial temporary behavior during which the intermediates show normal behavior of progression. After this, however, the system begins to move away from the steady state. The concentration of X and Y begins to oscillate and their rate becomes nonzero.

For constant concentration of A and B, we obtain sustain oscillations and intermediates oscillate in the finite limit of concentrations. However, for closed system that concentration of A and B are no more time independent and oscillations decay in time.

The oscillatory behaviour of X and Y are drawn by using Mathematica-10 Software (Fig10, 11). For the purpose following typical values of rate constants and concentrations of reactants and products are used for simulation:



Table 1.2

$k_1 = 1 s^{-1}$	$k_2 = 1 dm^6 mol^{-2} s^{-1}$
$k_3 = 1 dm^6 mol^{-2} s^{-1}$	$k_4 = 1 s^{-1}$
$[A] = 1 mol dm^{-3}$	$[B] = 3 mol dm^{-3}$
$[D] = 1 mol dm^{-3}$	$[P] = 1 mol dm^{-3}$
$[X]_s = 1 mol dm^{-3}$	$[Y]_s = 2 \times 10^{-2} mol dm^{-3}$

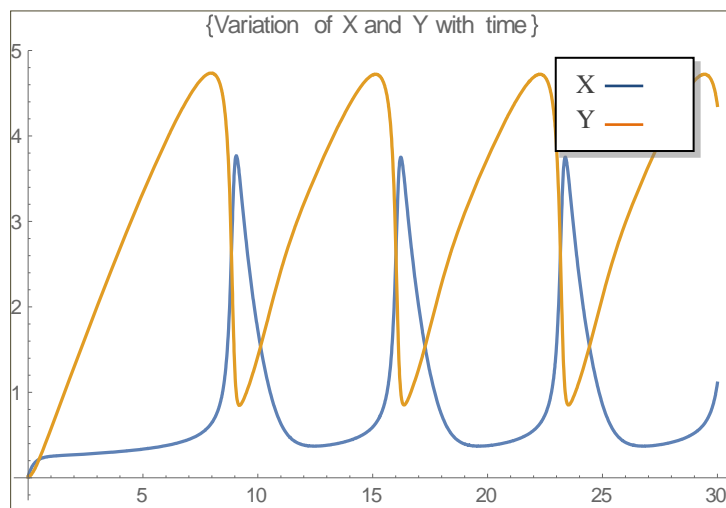


Fig 10: Variation of X and Y with time

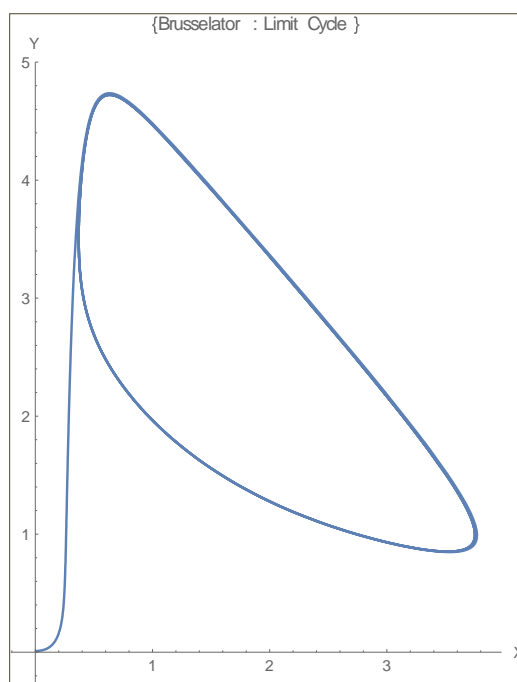


Fig 11: Maximum and minimum values (Limit Cycle) in which X and Y are oscillating



Prior to analysis by Lyapunov function, we take brief survey of relevant aspect of steady state and oscillatory state.

4.3.1 Steady State Analysis

In steady state situation, the concentration of intermediate species, X and Y are the time independent, that is

$$\frac{d[X]^s}{dt} = k_1[A] - k_2[B][X]^s + k_3[X]^s[Y]^s - k_4[X]^s = 0 \quad (92)$$

$$\frac{d[Y]^s}{dt} = k_2[B][X]^s - k_3[X]^s[Y]^s = 0 \quad (93)$$

Solving equations (92) and (93), steady state concentrations of X and Y are obtained as

$$v_1^s = v_4^s = k_1[A], \quad v_2^s = v_3^s = \frac{k_1 k_2}{k_4}[A][B] \quad (94)$$

$$[X]^s = \frac{k_1}{k_4}[A], \quad [Y]^s = \frac{k_4 k_2}{k_3 k_1} \frac{[B]}{[A]} \quad (95)$$

4.3.2 Stability by Lyapunov Analysis

In this case, the concentration of intermediate species, X and Y are no more time independent, that is

$$\frac{d[X]}{dt} = k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X] \neq 0 \quad (96)$$

$$\frac{d[Y]}{dt} = k_2[B][X] - k_3[X]^2[Y] \neq 0 \quad \text{and} \quad (97)$$

$$v_1 - v_4 \neq 0, \quad v_2 - v_3 \neq 0 \quad (98)$$

The rate of entropy production in this case is given by

$$\Sigma = \frac{A_1}{T} v_1 + \frac{A_2}{T} v_2 + \frac{A_3}{T} v_3 + \frac{A_4}{T} v_4 > 0 \quad (99)$$

where Σ is positive definite as per the dictates of second law of thermodynamics. The expression for the chemical affinities for unperturbed system are given by the chemical thermodynamics and in this case they are

$$\frac{A_1}{T} = \frac{A_1^\phi}{T} + R(\ln[A] - \ln[X]) \quad (100)$$

$$\frac{A_2}{T} = \frac{A_2^\phi}{T} + R(\ln[B][X] - \ln[Y][D]) \quad (101)$$

$$\frac{A_3}{T} = \frac{A_3^\phi}{T} + R(\ln[Y] - \ln[X]) \quad (102)$$

$$\frac{A_4}{T} = \frac{A_4^\phi}{T} + R(\ln[X] - \ln[P]) \quad (103)$$



Now, the concentration of X and Y are perturbed by sufficiently small amount, δX and δY by keeping the concentration of A, B, D and P constant, we then have

$$\delta \Sigma = L_s = \frac{\partial \Sigma}{\partial X} \delta X + \frac{\partial \Sigma}{\partial Y} \delta Y \quad (104)$$

Now, from equations (103) and (104), we obtain

$$\begin{aligned} \frac{\partial \Sigma}{\partial X} = & v_1 \frac{\partial(A_1/T)}{\partial X} + \frac{A_1}{T} \frac{\partial v_1}{\partial X} + v_2 \frac{\partial(A_2/T)}{\partial X} + \frac{A_2}{T} \frac{\partial v_2}{\partial X} \\ & + v_3 \frac{\partial(A_3/T)}{\partial X} + \frac{A_3}{T} \frac{\partial v_3}{\partial X} + v_4 \frac{\partial(A_4/T)}{\partial X} + \frac{A_4}{T} \frac{\partial v_4}{\partial X} \end{aligned} \quad (105)$$

and

$$\begin{aligned} \frac{\partial \Sigma}{\partial Y} = & v_1 \frac{\partial(A_1/T)}{\partial Y} + \frac{A_1}{T} \frac{\partial v_1}{\partial Y} + v_2 \frac{\partial(A_2/T)}{\partial Y} + \frac{A_2}{T} \frac{\partial v_2}{\partial Y} \\ & + v_3 \frac{\partial(A_3/T)}{\partial Y} + \frac{A_3}{T} \frac{\partial v_3}{\partial Y} + v_4 \frac{\partial(A_4/T)}{\partial Y} + \frac{A_4}{T} \frac{\partial v_4}{\partial Y} \end{aligned} \quad (106)$$

From the expressions of rate equations (86)-(89) and affinities, eqs.(100)-(103), we obtain

$$\frac{\partial v_1}{\partial X} = 0, \quad \frac{\partial v_2}{\partial X} = k_2 [Y], \quad \frac{\partial v_3}{\partial X} = 2k_3 [X][Y], \quad \frac{\partial v_4}{\partial X} = k_4 \quad (107)$$

$$\frac{\partial v_1}{\partial Y} = 0, \quad \frac{\partial v_2}{\partial Y} = 0, \quad \frac{\partial v_3}{\partial Y} = k_3 [X]^2, \quad \frac{\partial v_4}{\partial Y} = 0 \quad (108)$$

$$\frac{\partial(A_1/T)}{\partial X} = -\frac{R}{[X]}, \quad \frac{\partial(A_2/T)}{\partial X} = \frac{R}{[X]}, \quad (109)$$

$$\frac{\partial(A_3/T)}{\partial X} = -\frac{R}{[X]}, \quad \frac{\partial(A_4/T)}{\partial X} = \frac{R}{[X]}$$

$$\frac{\partial(A_1/T)}{\partial Y} = 0, \quad \frac{\partial(A_2/T)}{\partial Y} = -\frac{R}{[Y]}, \quad (110)$$

$$\frac{\partial(A_3/T)}{\partial Y} = \frac{R}{[Y]}, \quad \frac{\partial(A_4/T)}{\partial Y} = 0$$

On substituting the quantities from equations.(107)-(110) in equation (104), we have

$$\begin{aligned} L_s = \delta \Sigma = & \left(\frac{A_2}{T} k_2 [B] + 2 \frac{A_3}{T} k_3 [X][Y] + \frac{A_4}{T} k_4 \right) \delta X \\ & - \frac{R}{[X]} (v_1 - v_2 + v_3 - v_4) \delta X \\ & + \left(\frac{A_3}{T} k_3 [X]^2 - \frac{R}{[Y]} (v_2 - v_3) \right) \delta Y \end{aligned} \quad (111)$$

In case of steady state equation (111) becomes

$$L_s = \left(\frac{A_2}{T} k_2 [B] + 2 \frac{A_3}{T} k_3 [X][Y] + \frac{A_4}{T} k_4 \right) \delta X + \left(\frac{A_3}{T} k_3 [X]^2 \right) \delta Y \quad (112)$$

We have here identified, $\delta \Sigma = L_s$ the excess rate of entropy production is required Lyapunov function for stability analysis.



We now derive the rate equations of perturbation coordinates, δX and δY from equations (96) and (97). Adopting identical procedure which is applied for obtaining Lyapunov function, we identify,

$$\frac{d[X]}{dt} = f(X, Y) \quad (113)$$

$$\frac{d[Y]}{dt} = g(X, Y). \quad (114)$$

Thus, for sufficiently small and finite perturbation of mole numbers of X and Y from original state, gives

$$\delta \left(\frac{d[X]}{dt} \right) = \frac{\partial f}{\partial X} \delta X + \frac{\partial f}{\partial Y} \delta Y \quad (115)$$

$$\delta \left(\frac{d[Y]}{dt} \right) = \frac{\partial g}{\partial X} \delta X + \frac{\partial g}{\partial Y} \delta Y \quad (116)$$

where

$$f(X, Y) = k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X] \quad \text{and} \quad (117)$$

$$g(X, Y) = k_2[B][X] - k_3[X]^2[Y]. \quad (118)$$

From equations.(13) and (14), the expressions required for calculation of rate equations in perturbation space are obtained as,

$$\frac{\partial f}{\partial X} = -k_2[B] + 2k_3[X][Y] - k_4, \quad \frac{\partial f}{\partial Y} = k_3[X]^2, \quad \text{and} \quad (119)$$

$$\frac{\partial g}{\partial X} = k_2[B] - 2k_3[X][Y], \quad \frac{\partial g}{\partial Y} = -k_3[X]^2. \quad (120)$$

Thus, from equations (119) and (120), the required expressions for perturbation coordinates, are obtained as

$$\frac{d(\delta X)}{dt} = (-k_2[B] + 2k_3[X][Y] - k_4)\delta X + k_3[X]^2 \delta Y \quad (121)$$

$$\frac{d(\delta Y)}{dt} = (k_2[B] - 2k_3[X][Y])\delta X - k_3[X]^2 \delta Y. \quad (122)$$

In steady state situation equations (121) and (122) become

$$\frac{d(\delta X)}{dt} = (k_3[X][Y] - k_4)\delta X + k_3[X]^2 \delta Y = (v_3 - v_4) \frac{\delta X}{[X]} + v_3 \frac{\delta Y}{[Y]} \quad (123)$$

$$\frac{d(\delta Y)}{dt} = -k_3[X][Y]\delta X - k_3[X]^2 \delta Y = -v_3 \left(\frac{\delta X}{[X]} + \frac{\delta Y}{[Y]} \right) \quad (124)$$

Now, we scrutinize the stability of the process by using the fabrics of the Lyapunov's direct method of stability of motion. For this purpose we must require the total time derivative of Lyapunov function, dL_s/dt which is obtained as

$$\frac{dL_s}{dt} = \frac{\partial \Sigma}{\partial X} \frac{d(\delta X)}{dt} + \frac{\partial \Sigma}{\partial Y} \frac{d(\delta Y)}{dt}. \quad (125)$$



The required expression of dL_s/dt is obtained from eq.(111) by differentiating perturbation coordinates with time, that is

$$\begin{aligned} \frac{dL_s}{dt} = & \left(\frac{A_2}{T} k_2 [B] + 2 \frac{A_3}{T} k_3 [X][Y] + \frac{A_4}{T} k_4 \right) \frac{d(\delta X)}{dt} \\ & - \frac{R}{[X]} (v_1 - v_2 + v_3 - v_4) \frac{d(\delta X)}{dt} \\ & + \left(\frac{A_3}{T} k_3 [X]^2 - \frac{R}{[Y]} (v_2 - v_3) \right) \frac{d(\delta Y)}{dt} \end{aligned} \quad (126)$$

On substituting the values of $d(\delta X)/dt$ and $d(\delta Y)/dt$ in equation (126), the final expression for dL_s/dt is obtained as,

$$\begin{aligned} \frac{dL_s}{dt} = & \left(\frac{A_2}{T} k_2 [B] + 2 \frac{A_3}{T} k_3 [X][Y] + \frac{A_4}{T} k_4 \right) \\ & \times \left\{ (-k_2 [B] + 2k_3 [X][Y] - k_4) \delta X + k_3 [X]^2 \delta Y \right\} \\ & - \frac{R}{[X]} (v_1 - v_2 + v_3 - v_4) \times \left\{ (-k_2 [B] + 2k_3 [X][Y] - k_4) \delta X + k_3 [X]^2 \delta Y \right\} \\ & + \left(\frac{A_3}{T} k_3 [X]^2 - \frac{R}{[Y]} (v_2 - v_3) \right) \times \left\{ (k_2 [B] - 2k_3 [X][Y]) \delta X - k_3 [X]^2 \delta Y \right\} \end{aligned} \quad (127)$$

In case of steady state the total time derivative of Lyapunov function reads as,

$$\begin{aligned} \frac{dL_s}{dt} = & \left(\frac{A_2}{T} k_2 [B] + 2 \frac{A_3}{T} k_3 [X][Y] + \frac{A_4}{T} k_4 \right) \left((v_3 - v_4) \frac{\delta X}{[X]} + v_3 \frac{\delta Y}{[Y]} \right) \\ & - \left(\frac{A_3}{T} k_3 [X]^2 \right) v_3 \left(\frac{\delta X}{[X]} + \frac{\delta Y}{[Y]} \right) \end{aligned} \quad (128)$$

From above mathematical expressions of L_s and dL_s/dt , it is difficult to interpret the stability of the process because several undetermined components are involved there.

Results and conclusion

It is easy to predict the results after systematic computation and simulation of these expressions by Mathematica software.

Notice that in expressions of L_s and dL_s/dt are highly nonlinear and involve several complex terms. Due to which it is difficult predicts the stability and instability of the process. However, these complex equations are easily solved by Mathematica-10 commercial software. The results derived from software are given below:

Case 1: Steady state



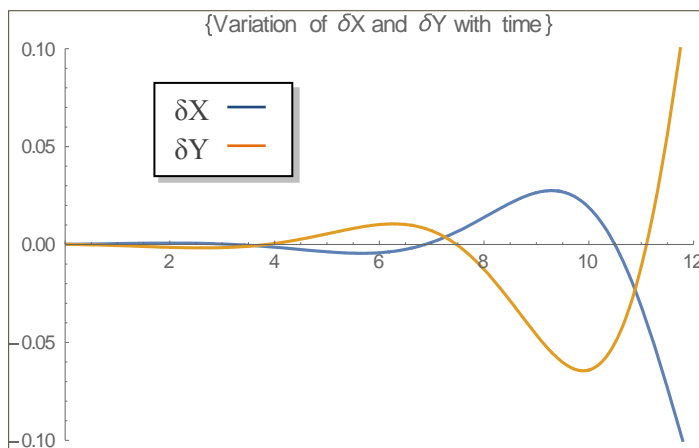


Fig 12: δX and δY oscillate and grow with time

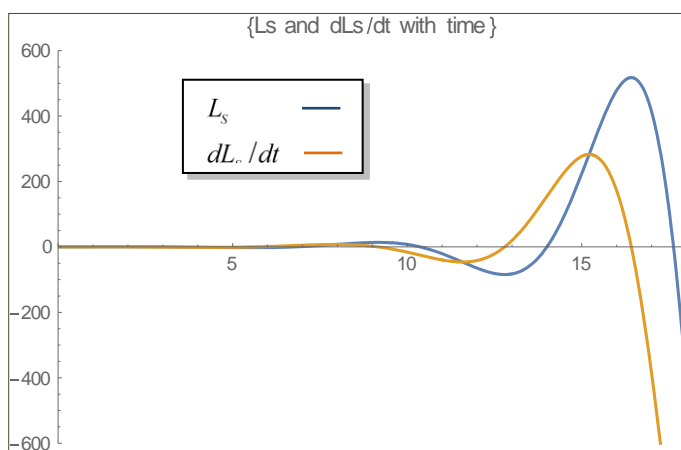


Fig 13: L_s and dL_s/dt oscillate and grow with time

Fig 13 establishes that the steady state of Brusselator model of chemical organization is unstable on perturbation. It is clearly observed that small disturbances to intermediates species lead to onset of oscillations which grow steeply with time. On perturbation system parameters are varied so that the system passes through the bifurcation limit cycle or periodic orbit develops surrounding the steady state.

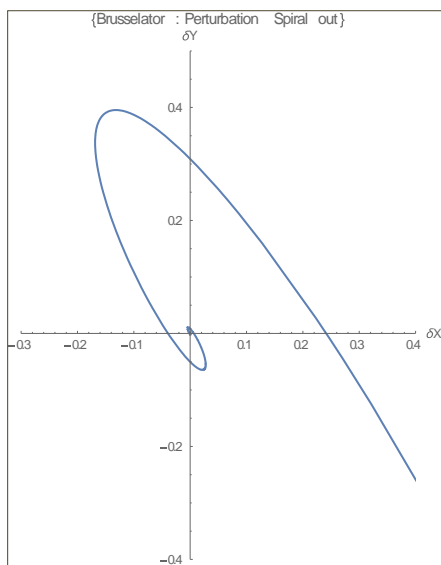


Fig 14: δX and δY spiral out around steady state

Case 2: Chemical Oscillations

1. There is domain where the stability is clearly visible because L_s and dL_s/dt have definite signs. In this case, $L_s > 0$ and $dL_s/dt < 0$ and tend to vanishes on real trajectory. This shows the asymptotic stability of the process as per the Lyapunov's direct method of stability of motion.

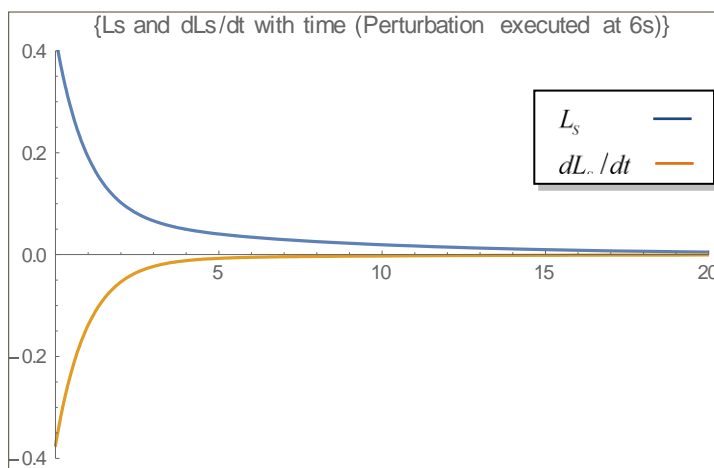


Fig 15: Stable state as $L_s > 0$ and $dL_s/dt < 0$

2. There is small domain where the perturbation leads damped oscillations. The oscillations decay with time and tend to diminishes on original trajectory. In this case there are small fluctuations in the beginning of onset of perturbation but these fluctuations gradually disappear and trajectory tends to converge on original trajectory. In these situations the stability of the process is guaranteed as per the Lyapunov analysis.



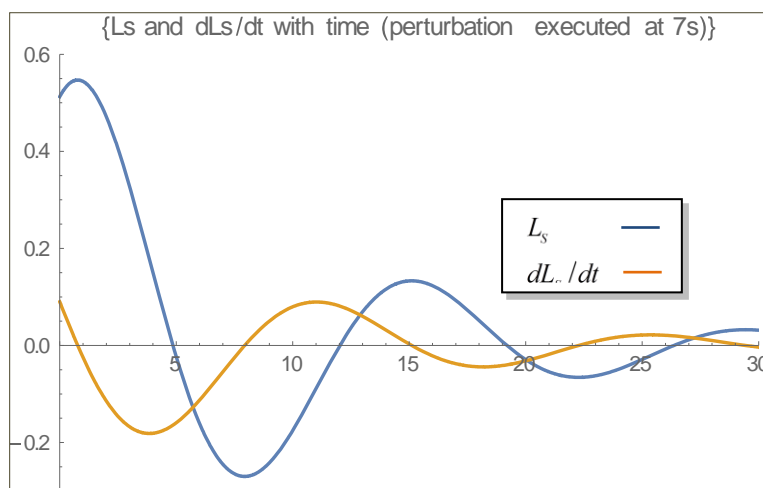


Fig 16: Stable state as L_s and dL_s/dt are oscillating and decaying with time

- At certain points, perturbation leads to formation of another pattern of oscillations of coordinates. From graphical presentation shows that these oscillations grow with time beyond the control. This is again the clear case of instability of the process.

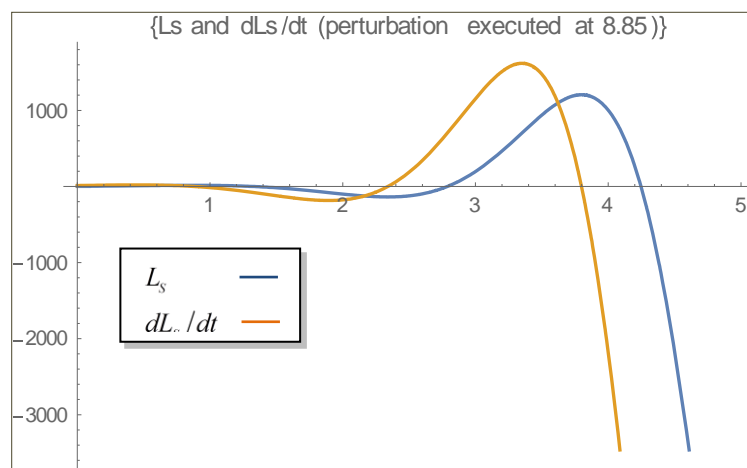


Fig 17: Unstable state as L_s and dL_s/dt oscillate and grow with time

- There is domain in periodic oscillations which gives clear instability on perturbation of intermediate coordinates. For example, when perturbation is executed before the onset of oscillations, the analysis shows that the process is unstable. The behaviour of L_s and dL_s/dt with time, are shown in figures. Note that the graphical presentation of L_s and dL_s/dt shows they have same (positive) signs. This indicates that the perturbation grows with time. Hence, small perturbation in this region is unstable and uncontrollable.

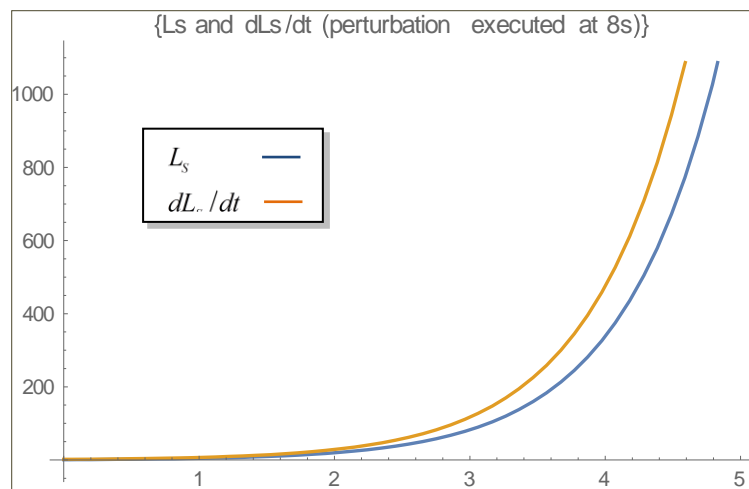


Fig 18: Unstable state as $L_s < 0$ and $dL_s/dt < 0$ have same

Our analysis shows that the chemical oscillations in Brusselator model are very sensitive to small perturbation. There is big domain of chemical oscillations which is susceptible to instability of the process on effect of perturbation. In some domain, perturbation tends to onset of oscillatory behaviour. There is very tiny domain over which the stability on perturbation is guaranteed.

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