



Stability of Autocatalytic Reaction by Lyapunov Function Analysis

Dethe Pragati¹, Burande Chandrakant², Burande Bharati³ and Megha Sawangikar⁴

¹Priyadarshini College of Engineering, Nagpur, INDIA

²Vilasrao Deshmukh College of Engineering and Technology, Mouda, Nagpur, INDIA

³Priyadarshini Indira Gandhi College of Engineering, Nagpur, INDIA

⁴Datta Meghe College of Engineering, Technology and Research, Wardha, INDIA

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Abstract

Thermodynamic stability of autocatalytic reaction by Lyapunov function analysis using the framework of CTTSIP has been investigated in this paper. The stability analysis of autocatalytic reactions is complex in mechanism. The feedback mechanism in autocatalytic reaction plays vital role in some biological and industrial processes. This autocatalytic feedback mechanism also leads to the oscillatory chemical reaction.

Keywords: Irreversible thermodynamics, stability, autocatalytic reaction, Lyapunov analysis.

Introduction

Lyapunov's direct method of stability of motion^{1, 2} also known as second method aptly deals the necessary aspects of stability determination of dynamic systems. It is found that Lyapunov's theory of stability of motion inherits thermodynamic type of generality. The main ingredient of Lyapunov's direct method of stability of motion is the identification of Lyapunov function. The sign of the function and its time derivative then tell us whether the dynamic system is stable or unstable. The gist this method is described below.

Let the given differential equations in the perturbation space be

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

where $\delta x_i = x_i - x_i^0$ is the coordinate in perturbation space, x_i is the perturbation coordinate and x_i^0 is the coordinate of unperturbed motion (real trajectory). On real trajectory, coordinate δx_i vanishes, that is

$$\delta x_i = x_i - x_i^0 \equiv 0. \quad (2)$$

Similarly, on real trajectory

$$X_i(t, 0, 0, \dots, 0) = 0. \quad (3)$$

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

$$V(t, \delta x_1, \delta x_2, \dots, \delta x_n) \geq 0. \quad (4)$$

Note that V is the function of only time, t and coordinate, δx_i .

The function, V has a strict minimum at the origin (on real trajectory), that is

$$V(t, 0, 0, \dots, 0) = 0. \quad (5)$$

The total time derivative of Lyapunov function, V is then written as

$$\dot{V} = \frac{dV_i}{dt} = \left(\frac{\partial V_i}{\partial t} + \sum_i \frac{\partial V_i}{\partial x_i} X_i \right) \quad (6)$$

According to Lyapunov's direct method of stability of motion, the system is stable and asymptotically stable if

$$V(t, \delta x_1, \delta x_2, \dots, \delta x_n) > 0, \quad \dot{V} \leq -\beta < 0 \quad (7)$$

and

$$V(t, \delta x_1, \delta x_2, \dots, \delta x_n) < 0, \quad \dot{V} \geq \beta > 0 \quad (8)$$

where β is positive definite. The system under investigation is unstable if

$$V(t, \delta x_1, \delta x_2, \dots, \delta x_n) > 0, \quad \dot{V} \geq \beta > 0 \quad (9)$$

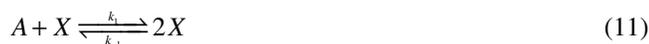
and

$$V(t, \delta x_1, \delta x_2, \dots, \delta x_n) < 0, \quad \dot{V} \leq -\beta < 0. \quad (10)$$

The main feature of Lyapunov's direct method of stability of motion is that it directly assigns the stability of motion without actual finding the solution of the function. Thus, because of its simplicity, this theory finds wider applications in the fields of science and technology.

Representative reaction

In this paper we discussed the thermodynamic stability of autocatalytic reactions using Lyapunov's direct method of stability of motion. We consider the selected autocatalytic reaction proceeding at finite rates, at constant T and p . The representative reaction^{3,4} of this category is given below.



where A and X are the chemical species, k_1 is the rate constants of forward reactions and k_{-1} is that of reverse reaction.

Thermodynamic space

For applying Lyapunov's direct method of stability of motion to a real process one first needs to choose an appropriate thermodynamic space. For chemically reacting spatially uniform closed systems, the traditional Gibbs relation gives an appropriate expression for rate of entropy production^{5, 6}. The traditional Gibbs relation for a spatially uniform closed system undergoing chemical conversions at finite rates read as,

$$\frac{ds}{dt} = \frac{1}{T} \frac{dU}{dt} + \frac{p}{T} \frac{dV}{dt} - \frac{1}{T} \sum_k \mu_k \frac{dn_k}{dt} \quad (12)$$

where S is the entropy, T is the temperature, p is the pressure, U is the internal energy, V is the volume, μ_k is the chemical potential per mole of the component k and n_k 's are the mole numbers. Notice that the first and second terms on the right-hand-side of Equation (12) are generated due to the thermal and mechanical interactions of the system with its surrounding and the last term originates due to the occurrence of a chemical reaction proceeding at finite rate. Further if the irreversibility is only due to a single chemical reaction occurring at a finite rate, then from Dalton's law⁷, we have

$$dn_k = \nu_k d\xi, \quad (13)$$

where ξ is the extent of advancement of the chemical reaction and ν_k 's are the stoichiometric coefficients and by convention are taken positive for the products and negative for the reactants. Further, the standard expression for chemical affinity⁸, \mathcal{A} , is

$$\mathcal{A} = \sum_k \mu_k \nu_k. \quad (14)$$

On substitution of Equation(13) and (14) in Equation(12) gives

$$\frac{ds}{dt} = \frac{1}{T} \frac{dU}{dt} + \frac{p}{T} \frac{dV}{dt} + \frac{\mathcal{A}}{T} \frac{d\xi}{dt} \quad (15)$$

Equation (15) is the De Donderian equation^{9,10}. Thus, in the absence of irreversibility in thermal and mechanical

interactions, the rate of entropy production, Σ_s , due to a single chemical reaction reads as

$$\Sigma_s = \frac{\mathcal{A}}{T} \frac{d\xi}{dt} > 0. \quad (16)$$

Equation(16) conforms the positive definite rate of entropy production for any non-equilibrium processes as per the second law of thermodynamics.

Using the expression for rate of entropy production given in Equation(16), we now discuss the stability of autocatalytic chemical reaction at constant T and p in different physical situations.

In stability analysis our first job is to identify Lyapunov function, L_s . In this case we generate operative L_s in following way:

$$L_s = \delta \Sigma_s = \delta \left(\frac{\mathcal{A}}{T} \frac{d\xi}{dt} \right) = \frac{\mathcal{A}}{T} \frac{d(\delta\xi)}{dt} + \frac{\delta\mathcal{A}}{T} \frac{d\xi}{dt} \quad (17)$$

Perturbation before chemical equilibrium

As per the chemical kinetics^{11, 12}, the rate equation for the chemical reaction, given by Equation(11), in terms of extent of advancement of chemical reaction, reads as

$$-\frac{d[A]}{dt} = \frac{d[X]}{dt} = \frac{d\xi}{dt} = (k_1[A] - k_{-1}[X])[X] > 0, \quad (18)$$

where $[A]$ and $[X]$ are the mole numbers of reaction species A and X respectively, ξ is the extent of chemical reaction. Notice that in Equation(11) the sum of concentration of reactant species A and X remains constant in reaction mixture, that is

$$[A] + [X] = \text{constant} \quad (19)$$

On perturbation in mole numbers of A and X , Equation (19) gives,

$$\delta[A] + \delta[X] = 0, \quad (20)$$

where $\delta[A]$ and $\delta[X]$ are sufficiently small. Equation (20) in terms of extent of reaction express as,

$$-\delta[A] = \delta[X] = \delta\xi \quad (21)$$

Therefore, in perturbation space the relevant expression of rate equations is obtained from Equation(18), that is

$$\frac{d(\delta[A])}{dt} = \frac{d(\delta[X])}{dt} = \frac{d(\delta\xi)}{dt} = (k_1[A] - k_{-1}[X])\delta[X] + (k_1\delta[A] - k_{-1}\delta[X])[X] \quad (22)$$

From Equation(21), the rate expression, Equation(22) in perturbation space is modified as

$$\frac{d(\delta\xi)}{dt} = (k_1A - k_{-1}X)\delta\xi - (k_1 + k_{-1})X\delta\xi = [k_1A - (k_1 + 2k_{-1})X]\delta\xi \quad (23)$$

The expression for the chemical affinity on unperurbed trajectory are given by chemical thermodynamics and in this case that reads as

$$\mathcal{A} = \mathcal{A}^\theta + RT \ln \left(\frac{[A]}{[X]} \right) = RT \ln \left(\frac{k_1[A]}{k_{-1}[X]} \right) > 0, \quad (24)$$

where \mathcal{A}^θ is the chemical affinity of standard state, \mathcal{A} is the chemical affinity of corresponding state and R is the gas constant. In perturbation space the expression for chemical affinity is given by

$$\delta\mathcal{A} = RT \left(\frac{\delta[A]}{[A]} - \frac{\delta[X]}{[X]} \right) = -RT \left(\frac{1}{[A]} + \frac{1}{[X]} \right) \delta\xi < 0 \quad (25)$$

From Equation(17), the required expression for Lyapunov function, L_s is obtained as

$$L_s = \left\{ -R \left(\frac{1}{[A]} + \frac{1}{[X]} \right) (k_1[A] - k_{-1}[X])[X] + \frac{\mathcal{A}}{T} (k_1[A] - (k_1 + 2k_{-1})[X]) \right\} \delta\xi \quad (26)$$

Notice that in the perturbation space, L_s is the function of perturbation coordinate, $\delta\xi$ and time, t , that is

$$L_s = L_s(t, \delta\xi) \quad (27)$$

The total time derivative of L_s from Equation(27), reads as,

$$\frac{dL_s}{dt} = \frac{\partial L_s}{\partial t} + \frac{\partial L_s}{\partial(\delta\xi)} \frac{d(\delta\xi)}{dt}, \quad (28)$$

where $\partial L_s / \partial t$ is the local time derivative and $\partial L_s / \partial(\delta\xi)$ is the gradient of Lyapunov function, L_s . From Equation(26), we easily obtain the local time derivative and gradient of L_s . The local time derivative, $\partial L_s / \partial t = 0$, because the $L_s = L_s(t, \delta\xi)$ is function of $\delta\xi$. However, the gradient of L_s is obtained as,

$$\frac{\partial L_s}{\partial(\delta\xi)} = \left\{ -R \left(\frac{1}{[A]} + \frac{1}{[X]} \right) (k_1[A] - k_{-1}[X])[X] + \frac{\mathcal{A}}{T} (k_1[A] - (k_1 + 2k_{-1})[X]) \right\} \quad (29)$$

Thus from Equation(28) and (29), the total derivative of Lyapunov function, L_s now becomes

$$\frac{dL_s}{dt} = \left\{ -R \left(\frac{1}{[A]} + \frac{1}{[X]} \right) (k_1[A] - k_{-1}[X])[X] + \frac{\mathcal{A}}{T} (k_1[A] - (k_1 + 2k_{-1})[X]) \right\} [k_1A - (k_1 + 2k_{-1})X] \delta\xi \quad (30)$$

On substituting

$$\left(\frac{1}{[A]} + \frac{1}{[X]} \right) (k_1[A] - k_{-1}[X])[X] = P \leq 0 \quad [\text{positive definite}] \quad (31)$$

and

$$(k_1[A] - (k_1 + 2k_{-1})[X]) = Q \quad [\text{either positive or negative}], \quad (32)$$

Equation(26) and (30), respectively recast as,

$$L_s = \left[-RP + \frac{\mathcal{A}}{T} Q \right] \delta\xi \quad (33)$$

and

$$\frac{dL_s}{dt} = \left[-RP + \frac{\mathcal{A}}{T} Q \right] Q \delta\xi. \quad (34)$$

Now we identify the stability of the given reaction as per the fabrics of Lyapunov's direct method of stability of motion.

i. If $Q \geq 0$ and $RP \geq \frac{\mathcal{A}}{T} Q$ then $L_s \leq 0, \frac{dL_s}{dt} \leq 0.$

In this case both, $L_s \leq 0, dL_s/dt \leq 0$, have same sign and hence the process is unstable.

ii. If $Q \geq 0$ and $RP \leq \frac{\mathcal{A}}{T} Q$ then $L_s \geq 0, \frac{dL_s}{dt} \geq 0.$

Again this situation leads to instability to the process as both, L_s and dL_s/dt , have same sign.

iii. If $Q \leq 0$ then $L_s \leq 0, \frac{dL_s}{dt} \geq 0$

In this condition the given process is stable because L_s and dL_s/dt have opposite signs. In first two cases Lyapunov's stability of motion is not guaranteed while in third case stability is ensured provided

$$(k_1[A] - (k_1 + 2k_{-1})[X]) = Q \leq 0 \quad (35)$$

Therefore, from Equation(35), the physical conditions for stability is

$$[A] \leq \left(1 + \frac{2k_{-1}}{k_1} \right) [X]. \quad (36)$$

For $k_{-1} \approx k_1, [X] \geq [A]/3$, that is the stability the given process, ensured if the concentration of X is at least one third of the concentration of A .

For $k_{-1} \ll k_1, [X] \geq [A]$, in this case the stability is guaranteed if and only the concentration of X is greater that the concentration of A .

Stability when the concentration of A is higher than X

The concentration of A is kept constant and higher than X by continuous supplying it from outside. In this case small fluctuation in concentration of A is insignificant as compare to X. Then, only perturbation in X is significant. In this situation the rate equation in perturbation space is obtained as,

$$\frac{d(\delta\xi)}{dt} = [k_1[A] - 2k_{-1}[X]]\delta\xi. \quad (37)$$

Similarly, the expression for chemical affinity in perturbation space is obtained as,

$$\delta A = -\frac{RT}{[A]}\delta\xi < 0. \quad (38)$$

From Equation(37) and (38), the required expression for Lyapunov function, L_s is obtained as,

$$L_s = \left\{ -R(k_1[A] - k_{-1}[X])[X] + \frac{A}{T}(k_1[A] - 2k_{-1}[X]) \right\} \delta\xi. \quad (39)$$

Thus, the total time derivative of L_s from Equation(28) and (39) is obtained as,

$$\frac{dL_s}{dt} = \left\{ -R(k_1[A] - k_{-1}[X]) + \frac{A}{T}(k_1[A] - 2k_{-1}[X]) \right\} (k_1[A] - 2k_{-1}[X]) \delta\xi. \quad (40)$$

On substituting

$$\begin{aligned} (k_1[A] - k_{-1}[X]) &= M \leq 0 \quad [\text{positive definite}] \quad \text{and} \quad (41) \\ (k_1[A] - 2k_{-1}[X]) &= N \quad [\text{either positive or negative}], \end{aligned} \quad (42)$$

in Equation(39) and (40), we obtain

$$L_s = \left[-RM + \frac{A}{T}N \right] \delta\xi \quad \text{and} \quad (43)$$

$$\frac{dL_s}{dt} = \left[-RM + \frac{A}{T}N \right] N \delta\xi. \quad (44)$$

Now, we consider Equation(43) and (44) for the stability analysis in different physical conditions.

$$\text{i. If } N \geq 0, \quad L_s \leq 0, \quad \frac{dL_s}{dt} \leq 0.$$

Then process is unstable because both, $L_s \leq 0$, $dL_s/dt \leq 0$ have same sign.

$$\text{ii. If } N \leq 0 \quad \text{then} \quad L_s \leq 0, \quad \frac{dL_s}{dt} \geq 0.$$

In this case the process is stable as per the fabrics of Lyapunov's direct method of stability of motion. Thus the stability of motion is guaranteed for all values of A and X if one satisfy the condition, $(k_1[A] - 2k_{-1}[X]) = N \leq 0$.

Therefore, the physical conditions for stability is

$$(k_1[A] - 2k_{-1}[X]) \leq 0 \Rightarrow [A] \leq \frac{2k_{-1}}{k_1}[X]. \quad (45)$$

For $k_{-1} \approx k_1$, $[X] \geq [A]/2$, that is the stability ensured if the concentration of X is at least half the concentration of A.

For $k_{-1} \ll k_1$, $[X] \geq [A]$, in this case the stability is guaranteed if and only the concentration of X is greater than the concentration of A.

Conclusion

In this paper we have explored the tools of Lyapunov's direct method of stability of motion (direct method) to investigate the stability of autocatalytic reactions. We have discussed almost all possibilities of perturbations of reactants away from chemical equilibrium. The domain of stability and instability is clearly revealed in our exercise. Autocatalytic reactions in equilibrium state show stability. It is found that away from equilibrium, the stability is guaranteed under certain constrains. The constraints are mostly the relative concentration of reactants and the ratio of forward rate to reverse rate at the time of perturbation.

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