Application of Lyapunov's Direct Method of Stability To Autocatalytic Reactions

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Abstract

Lyapunov's direct method is use for finding the stability of motion.It is also known as second method suitably and deals the necessary aspects of stability determination of dynamic systems to analyze the effect of the perturbation on the steady state. This paper investigate the stability of real processes irrespective of the type and extent of irreversibility using the tools of Lyapunov's direct theory stability of motion. It compare the results obtained from above these methods in ambit of the law of thermodynamics. This study helps to investigate the extent of constraints of applicability of Lyapunov analysis to determine the stability of spatially uniform chemical systems as well as the domain of stability and instability by using software like Mathematica.

Keywords: Autocatalytic Reaction, Lyapunov's method, Irreversible Thermodynamics

1. Introduction

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. Thus it would be beneficial if it could be known by thermodynamic considerations what are the constraints under which the given process remains stable or becomes unstable. It indeed would save our time, efforts and inputs that would otherwise may go waste. In this event by thermodynamic controls one may perhaps achieve dynamic stability too by a suitable manipulation of the system variables.

2 Theory of stability

There are several ways to identify Lyapunov function, L_S for chemically reacting system. We know that the rate of entropy production [1], Σ_S for single step chemical reaction at constant temperature, T and pressure, p is given by eq.(1) which is function of mole numbers of reacting species, that is

$$\Sigma_S = \Sigma_S\left(n_1, n_2, ..., n_i\right) > 0, \qquad \left(i = 1,2,3..........\right) \tag{1}$$

where $n_i\left(i = 1,2,3..........\right)$ 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

$$\delta\Sigma_S = \frac{\partial\Sigma_S}{\partial n_1}\delta n_1 + \frac{\partial\Sigma_S}{\partial n_2}\delta n_2 + ...+ \frac{\partial\Sigma_S}{\partial n_i}\delta n_i \qquad (2)$$

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

$$\delta\Sigma_S \text{ ¤ } 0 \qquad (3)$$

and

$$\delta n_i \text{ ¤ } 0 \qquad (4)$$

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 $\delta\Sigma_S$, identify as Lyapunov function, L_S [2] and reads as

$$L_S = \frac{\partial\Sigma_S}{\partial n_1}\delta n_1 + \frac{\partial\Sigma_S}{\partial n_2}\delta n_2 + ...+ \frac{\partial\Sigma_S}{\partial n_i}\delta n_i . \qquad (5)$$

Thus, L_S becomes the function of perturbation coordinate, δn_i and hence, the total time derivative of L_S is obtained from eq.(5) as

$$\frac{dL_S}{dt} = \frac{\partial\Sigma_S}{\partial n_1}\frac{d(\delta n_1)}{dt} + \frac{\partial\Sigma_S}{\partial n_2}\frac{d(\delta n_2)}{dt} + ...+ \frac{\partial\Sigma_S}{\partial n_i}\frac{d(\delta n_i)}{dt}. \qquad (6)$$

Where $\partial\Sigma_S/\partial n_1$, $\partial\Sigma_S/\partial n_2$, $\partial\Sigma_S/\partial n_i$ are identified as gradient of the Lyapunov function, L_S for any chemically reacting system, according to Dalktons'law and De Donderian law[3][4].

Further, the rate equations for any chemical reactions, read as

$$\frac{dn_1}{dt} = f(n_1, n_2, ..., n_i), \frac{dn_2}{dt} = g(n_1, n_2, ..., n_i)...... \frac{dn_i}{dt} = h(n_1, n_2, ..., n_i) \qquad (7)$$

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

$$\frac{d(\delta n_1)}{dt} = \frac{\partial f}{\partial n_1}\delta n_1 + \frac{\partial f}{\partial n_2}\delta n_2 + ...+ \frac{\partial f}{\partial n_i}\delta n_i and \frac{d(\delta n_2)}{dt} = \frac{\partial g}{\partial n_1}\delta n_1 + \frac{\partial g}{\partial n_2}\delta n_2 + ...+ \frac{\partial g}{\partial n_i}\delta n_i \qquad (8)$$

Eq.(8) gives how the perturbation coordinates advance with time in perturbation space. Now with eqs.(5) and (6), one can easily establish the stability of the processes using the fabrics of the Lyapunov's direct method of stability of motion[3]. If any process satisfy the following condition then it is stable and asymptotically stable

$$L_S > 0, \quad \frac{dL_S}{dt} \le \beta < 0 \quad \text{or} \quad L_S < 0, \quad \frac{dL_S}{dt} \ge \beta > 0 \qquad (9)$$

and unstable if

$$L_S > 0, \quad \frac{dL_S}{dt} > 0 \quad \text{or} \quad L_S < 0, \quad \frac{dL_S}{dt} < 0 \qquad (10)$$

The finiteness of gradient of Lyapunov function along with condition given in eq.(9), As per Malkin's theorem it show stability under constantly acting small disturbances.

3. Representative Reaction

For the investigation of thermodynamic stability, an autocatalytic reaction proceeding at finite rate and at constant T and p has been considered. The representative reaction of of this category has been selected for the for the analysis is

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2B, \qquad (11)$$

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.

As per the chemical kinetics [4], the rate equation in terms of extent of advancement, ξ of chemical reaction, reads as

$$-\frac{d[A]}{dt}=\frac{d[B]}{dt}=\frac{d\xi}{dt}=\left(k_1[A]-k_{-1}[B]\right)[B]>0, \quad (12)$$

where $[A]$ and $[B]$ are the mole numbers of reaction species A and B respectively, ξ is the extent of chemical reaction. Notice that in eq.(13) the sum of concentration of reactant species A and B remains constant in reaction mixture for closed system, that is

$$[A]+[B]=\text{constant}. \quad (13)$$

Using commercial software Mathematica-10, published by Wolfram, the variation of A and B with time has been shown in table (1) and figures.

Table 1. Change of conc. of A and X with time for typical value of $k_1=1$ and $k_{-1}=1$

$t(Sec)$	$[A]$	$[B]$	$[A]/[B]$	
35	0.08033	0.02067	3.887	35
36	0.07909	0.02191	3.609	36
37	0.07783	0.02317	3.359	37
38	0.07656	0.02444	3.132	38
39	0.07528	0.02572	2.927	39
40	0.07401	0.02699	2.742	40
41	0.07275	0.02825	2.575	41
42	0.07150	0.02950	2.424	42
43	0.07027	0.03073	2.287	43
44	0.06907	0.03193	2.163	44
45	0.06790	0.03310	2.051	45

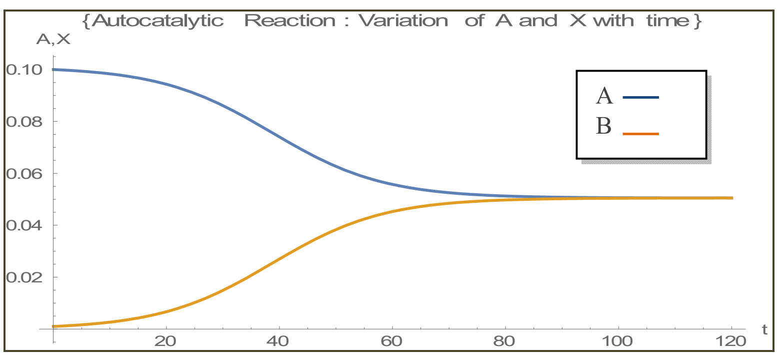

Figure 1. Variation of A and B with time for typical value of $k_1=1$ and $k_{-1}=1$

4. The Stability Analysis

Now, we consider that the mole numbers of A and B, are perturbed by sufficiently small amount, δA and δB respectively. Denoting unperturbed quantities with superscript, '0' and perturbed ones without subscript or superscript, we have a set of equations, namely;

$$-\frac{d[A]}{dt}=\frac{d[B]}{dt}=\frac{d\xi}{dt}=\left(k_1[A]-k_{-1}[B]\right)[B]>0, \quad (14)$$

$$\delta A+\delta B=0, \tag{15}$$

where eqs.(14) is the rate equations on perturbed states of the system, eq.(15) is the perturbation in mole numbers of species A and B. Identity in eq.(16) is obtained from eq.(14) for closed system. Further, eq.(16) in terms of extent of reaction and using reaction stiochiometry is obtained as

$$\delta\xi=\delta B=-\delta A \tag{16}$$

$$\frac{d(\delta\xi)}{dt}=\left[k_1[A]_0-(k_1+2k_{-1})[B]_0\right]\delta\xi \tag{17}$$

Eq.17 is the rate expression in perturbation space .

Thus, the expression for chemical affinity in perturbation space is obtained by chemical thermodynamics.

$$\frac{\delta \mathrm{A}}{T}=R\left(\frac{\delta[A]}{[A]_0}-\frac{\delta[B]}{[B]_0}\right)=-R\left(\frac{1}{[A]_0}+\frac{1}{[B]_0}\right)\delta\xi<0 \tag{18}$$

For chemically reacting spatially uniform closed systems, The rate of entropy production due to the single autocatalytic reaction in absence of mechanical and thermal interactions reads as

$$\Sigma_0^S=\frac{\mathrm{A}_0}{T}\frac{d\xi_0}{dt}>0 \tag{19}$$

where Σ_0^S is the expression of rate of entropy production of unperturbed state.. Simillarly, the rate of entropy production of perturbed state, reads as

$$\Sigma^S=\frac{\mathrm{A}}{T}\frac{d\xi}{dt}>0 \tag{20}$$

Lyapunov function, L_S is the excess rate of entropy production, therefore, in this case it is defined as

$$L_S=\Sigma_S-\Sigma_0^S=\frac{\mathrm{A}}{T}\frac{d\xi}{dt}-\frac{\mathrm{A}_0}{T}\frac{d\xi_0}{dt} \tag{21}$$

After the mathematical manipulation, L_S is obtained as

$$\begin{aligned}L_S=&-R\left(\frac{1}{[A]_0}+\frac{1}{[B]_0}\right)\left(k_1[A]_0-k_{-1}[B]_0\right)[B]_0\,\delta\xi\\&+\frac{\mathrm{A}_0}{T}\left(k_1[A]_0-(k_1+2k_{-1})[B]_0\right)\delta\xi\end{aligned} \tag{22}$$

Notice that in the perturbation space L_S is the function of perturbation coordinate, $\delta\xi$ that is

$$L_S=L_S(\delta\xi) \tag{23}$$

the total derivative of Lyapunov function, L_S is now obtained as,

$$\begin{aligned}\frac{dL_S}{dt}=&\left\{-R\left(\frac{1}{[A]_0}+\frac{1}{[B]_0}\right)\left(k_1[A]_0-k_{-1}[B]_0\right)[B]_0+\right\}\left(k_1[A]_0-(k_1+2k_{-1})[B]_0\right)\delta\xi\\&+\left\{\frac{\mathrm{A}_0}{T}\left(k_1[A]_0-(k_1+2k_{-1})[B]_0\right)\right\}\left(k_1[A]_0-(k_1+2k_{-1})[B]_0\right)\delta\xi\end{aligned} \tag{24}$$

Now, denoting

$$\left(\frac{1}{[A]_0}+\frac{1}{[B]_0}\right)\left(k_1[A]_0-k_{-1}[B]_0\right)[X]_0=P\geq 0 \tag{25}$$

is positive definite quantity and diminises at chemical equilibrium, and

$$\left(k_1[A]_0-(k_1+2k_{-1})[B]_0\right)=Q\gtrless 0 \tag{26}$$

is either positive or negative. On substituting these identities in eqs.(25) and (26), we have

$$L_S = \left[-RP + \frac{A_0}{T} Q \right] \delta\xi \tag{27}$$

and

$$\frac{dL_S}{dt} = \left[-RP + \frac{A_0}{T} Q \right] Q\, \delta\xi . \tag{28}$$

Now we identify the stability of the given system as per the fabrics of Lyapunov's direct method of stability of motion [3] in different physical situations, discussed in following section:

(a) If $Q \ge 0$ and $-RP + \frac{A_0}{T} Q \le 0$ then $L_S \le 0,\ \frac{dL_S}{dt} \le 0.$

In this case both, $L_S \le 0,\ dL_S/dt \le 0$, have same sign and hence the process is unstable.

(b) If $Q \ge 0$ and $-RP + \frac{A_0}{T} Q \ge 0$ then $L_S \ge 0,\ \frac{dL_S}{dt} \ge 0.$

Again this situation leads to instability as both the, L_S and dL_S/dt, have same sign.

(c) If $Q \le 0$ then $L_S \le 0,\ \frac{dL_S}{dt} \ge 0$

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[4].

$$\left(k_1 [A]_0 - \left(k_1 + 2k_{-1} \right) [B]_0 \right) = Q \le 0 \tag{29}$$

Therefore, from eq.(29), the conditions for stability is

$$[A]_0 \le \left(1 + \frac{2k_{-1}}{k_1} \right) [B]_0 . \tag{30}$$

Case 1: For $k_1 \approx k_{-1}$, ,

$$\frac{[A]_0}{[B]_0} \le 3, \tag{31}$$

that is the stability the given process, ensured if the concentration of B is at least one third of the concentration of A[5]. Above observations have been verified by using Mathematica software, depicted in following figures.

From the plot it is clearly indicate that for $k_{-1} \approx k_1$, the condition of stability is $[A]_0/[B]_0 \le 3$. It shows that for all value of $[A]_0/[B]_0 > 3$,

$$\frac{d(\delta\xi)}{dt} > 0,\ L_S < 0 \ \text{and}\ \frac{dL_S}{dt} < 0, \tag{32}$$

$\delta\xi$ is increasing with time and both L_S and dL_S/dt have same sign (negative). This indicates that the given process is unstable as the Lyapunov's direct method of stability of motion. However, for $[A]_0/[B]_0 \le 3$,

$$\frac{d(\delta\xi)}{dt} < 0,\ L_S < 0 \ \text{and}\ \frac{dL_S}{dt} > 0, \tag{33}$$

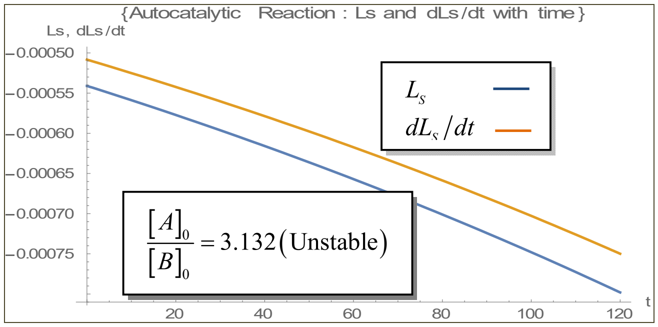

Figure 1. L_S and dL_S/dt **with time for typical value of** $k_1 = 1$ **and** $k_{-1} = 1$

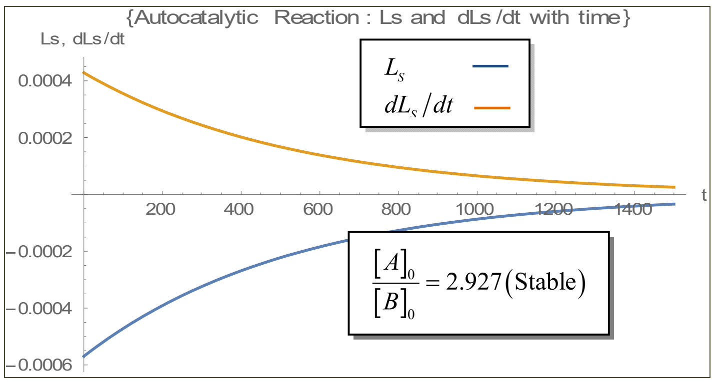

Figure 2. L_S and dL_S/dt **with time for typical value of** $k_1 = 1$ **and** $k_{-1} = 1$

$\delta\xi$ is decreasing with time, L_S is negative and dL_S/dt is positive. Opposite sign of L_S and dL_S/dt proves that the process under investigation is stable[6].

5 Conclusion

The study explored the tools of Lyapunov's direct method of stability of motion (Second method). It is useful to investigate the stability of autocatalytic reactions. It observed the finiteness of Lyapunov's function along with the conditions given for the stability ensured the stability under constantly acting small disturbances as per the m Malkins theorem .

6 References

6.1. Journal Article

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