Nonlinear Entropy Production in a Reversible Oregonator Model

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The entropy production in a non-equilibrium state based on the reversible Oregonator model of the Belousov-Zhabotinskii (BZ) reaction system has been studied. The reaction affinity and the reaction rate for the individual steps have been calculated by varying the concentrations of key variables in the system. The result shows a linear relationship between the reaction affinity and the reaction rate in the given concentration range. However, the overall entropy calculated on the basic assumption that the entropy in a reaction system corresponds to the summation of a product of reaction affinity and reaction rate of individual steps shows a nonlinearity of the reaction system. The results well agrees with the fact that the entropy production is not linear or complicated function in a non-linear reaction system.

Key Words : Affinity, Entropy, Fluctuation, Oregonetor, Reaction rate

Introduction

The energy dispersion in mature ecosystems has been basically fixed in plants by photosynthesis using low energy molecules such as water and carbon dioxide in the presence of sunlight. This process enables the plants to use the energy for the regulation and organization in the form of complex mechanism for a complex structure which later follows a similar process to distribute the energy completely, which leads to the conservation of energy in a universe. The conservation of energy in the universe is possible by the large biomasses and the diversification of the energy into the living system.[1] Photosynthesis is therefore a paving process for the evolution of a complex system by capturing a solar energy and by decreasing the entropy of the surrounds including the planet. Thus it is very important to recognize the biological activity with the planetary property, and in the point of continuous interactions of various types occurring in plants, animals, microorganisms, molecules, electrons, energies, and matter, all part of a global whole. Therefore, the analysis of the entropy production in such complex systems has become an important issue in recent years for understanding the various nonlinear systems which can be easily observed around us.[2]

Prigogine *et al.*[3] found a theory regarding on the entropy production in complex systems and introduced a new concept to describe both the reversible and irreversible changes in a chemical reaction system. The main issue derived from the theory is that the evolution and maintenance of the complex open systems are explained by thermodynamic processes far from equilibrium. This is essentially built on the local equilibrium hypothesis with respect to temperature even at nonequilibrium situations. The study of entropy change in a complicated chemical reaction system is very important since the self-organizing chemical systems offer an idea to study new systems which can help for understanding the evolution of biology. Recently, the pattern formation in the chemical system is studied in deep by its implications in biological systems, which means that a chemical system can be used to explicate the behaviors in cellular and tissue development by a relatively simple model. The BZ reaction is a famous system for displaying the chemical oscillations in space and time, which are observed by a periodic color change of the reaction medium. The reaction system is explained by a mechanism developed by R. J. Field, E. Körös, and R. M. Noyes, which is known as FKN mechanism, and it was simplified as Oregonator model on the basis of chemical considerations and by application of the approximation techniques using chemical kinetics.[3] The rate of entropy production in the BZ system is an interesting quantity for a thermodynamic analysis of an irreversible process and the rate of chemical entropy production in such a system is associated with the generalized flux and thermodynamic force. It is positive for all such processes and zero at equilibrium.

In this report the reaction affinity (the tendency of an atom or compound to combine by chemical reaction) and the reaction rate of the individual steps and the overall steps are calculated by varying the concentrations of key variables in the Oregonator model. The overall entropy of the system was calculated by considering the relation that the entropy of a reaction system is the summation of a product of the reaction affinity and the reaction rate of individual steps in the reaction system. The obtained result in this study shows that the overall entropy is nonlinear and also multiple function of the rate of entropy production for the three reaction processes in the BZ system.

Kinetic Model and Method of Calculation

The BZ reaction gives a good model for the cellular automaton that produces spiral waves. Similar spiral waves have also been observed in various biological systems.[3] The BZ reaction is a redox reaction that periodically oscillates between an oxidized and a reduced state, and has been demonstrated by various substitutions. According to the FKN mechanism, the BZ reaction is explained by the composition of complex reaction steps including 18 elementary reactions and 21 chemical species. However, the understanding for the oscillation of the BZ reaction in terms of the FKN mechanism is possible by dividing the overall reaction into three main processes:

$BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O$ (process A)

$BrO_3^- + 4Ce(III) + 5\,H^+ \rightarrow$
$4Ce(IV) + HOBr + 2\,H_2O$ (process B)

$2Ce(IV) + BrMA + MA \rightarrow$
$2Ce(III) + Br^-$ + Other products (process C)

where Br^- is consumed in the process of A, and the process B corresponds to the process of autocatalytic production $HBrO_2$, and the Br^- is produced again in the process C. The elementary reactions for the system have been elucidated by many researchers. A model which is a simplified set composed by only 5 elementary steps isolated from the FKN mechanism, which we call the Oregonator, is very useful to describe various complex behaviors in nonlinear systems. This is the most frequently used model to simulate the dynamic behavior of the BZ system and has been successfully employed for modeling a broad variety of temporal and spatiotemporal phenomena and is as follows:[4-9]

$$\begin{aligned}
&A + Y \rightleftharpoons X + P\\
&X + Y \rightleftharpoons 2P\\
&A + X \rightleftharpoons 2X + Z\\
&2X \rightleftharpoons A + P\\
&Z \rightleftharpoons fY
\end{aligned}\tag{1}$$

where A = $[BrO_3^-]$, P = [HOBr], X = $[HBrO_2]$, Y = $[Br^-]$, Z = 2Ce(IV), and f is a stoichiometric factor which is taken as constant and is 0.5 for the present calculations. Well-stirred reaction system is adopted in this study and the concentrations of A and P are supplied to the reactor cell in the condition that the chemical potential of A in the system equals the chemical potential of P. After introducing the reaction constants, rate equations can be stated by the ordinary differential equations which are deduced for the change in time of each of the three intermediates of the reaction. Then, the differential equation for this model with three variables is written as followings:

$$\begin{aligned}
dX/dt &= k_1AY - k_{-1}XP - k_2XY + k_{-2}P^2 + k_3AX - k_{-3}X^2Z\\
&\quad - 2k_4X^2 + 2k_{-4}AP\\
dY/dt &= k_1AY - k_{-1}XP - k_2XY + k_{-2}P^2 + fk_5Z - fk_{-5}Y\\
dZ/dt &= k_3AX - k_{-3}X^2Z - k_5Z + k_{-5}Y
\end{aligned}\tag{2}$$

where k_i and k_{-i} represents the forward and reverse rate constants of the reactions of the present model and we adopted the values of rate constants which are introduced by Scott et al. being most generally used.[1,2] The differential equations can be scaled as followings:

$$\begin{aligned}
T_x(dx/d\tau) &= \alpha_0 + \alpha_1x + \alpha_2y - \alpha_3xy - \alpha_4x^2 - \alpha_5x^2\\
T_y(dy/d\tau) &= \beta_0 + \beta_1x + \beta_2y - \beta_3xy - \beta_4x^2 - \beta_5x^2\\
T_z(dz/d\tau) &= \gamma_0 + \gamma_1x + \gamma_2y - \gamma_3xy - \gamma_4x^2 - \gamma_5x^2
\end{aligned}\tag{3}$$

where $x = X/X_0$, $y = Y/Y_0$, $z = Z/Z_0$, $X_0 = k_1A/k_2$, $Y_0 = k_5/k_4$, $Z_0 = k_3A/k_2$, $t_0 = (k_1k_3A^2)^{½}$, $\tau = t/t_0$, and $T_x = k_1(k_1k_3A^2)^{½}/k_4$, $T_y = k_5(k_1k_3)^{½}/k_4$, $T_z = k_3(k_1k_3)^{½}/k_2$, $\alpha_0 = (k_{-2}P^2 + 2k_{-4}AP)/A$, $\alpha_1 = k_1(k_3A^2 + k_{-1}P)/k_2$, $\alpha_2 = \alpha_3 = k_1k_5/k_4$, $\alpha_4 = (k_{-3}k_3{k_1}^2)/{k_2}^3$, $\alpha_5 = 2Ak_4{k_1}^2/{k_2}^2$, $\alpha_0 = k_{-2}P^2/A$, $\beta_1 = k_{-1}k_1P/k_2$, $\beta_2 = (k_{-1}k_5/k_5) + (fk_5k_{-5}/Ak_4)$, $\alpha_3 = \alpha_3$, $\beta_4 = fk_3k_5/k_4$, $\gamma_0 = Ak_1k_5/k_2$, $\gamma_1 = \alpha_4$, $\beta_2 = k_3k_5/k_2$, and $\gamma_3 = k_{-5}k_5/Ak_4$.

In the case, the entropy production per unit volume ($d_iS/d\tau$) due to non-equilibrium steady state is given by

$$\left(\frac{d_is}{d\tau}\right) = \left(\frac{1}{T}\right)\sum_i J_i A_i \geq 0 \tag{4}$$

where J_i and A_i are the reaction rate and reaction affinity of the i^{th} reaction, respectively. In the case of Oregonator the thermodynamic description of the rate for the reaction steps in the equation (1) are obtained as $J_1 = k_1AY - k_{-1}XP$, $J_2 = k_2XY - k_{-2}P^2$, $J_3 = k_3AX - k_{-3}X^2Z$, $J_4 = 2k_4X^2 - 2k_{-4}AP$, $J_5 = k_5Z - k_{-5}Y$ and the affinities of the same reaction steps are given as $A_1 = RT\ln(k_1AY/k_{-1}XP)$, $A_2 = RT\ln(k_2XY/k_{-2}P^2)$, $A_3 = RT\ln(k_3A/k_{-3}XZ)$, $A_4 = RT\ln(k_4X^2/k_{-4}AP)$, $A_5 = RT\ln(k_5Z/k_{-5}Y)$. Thus the overall entropy production is the sum of the product of rate and affinity of the individual reactions with the inverse of temperature. The resulting system of equations was solved numerically by Fourth order Runge-Kutta method.[10]

Results and Discussion

Figure 1 shows the affinities of individual reaction steps and average affinity of all the steps in (3) as a function of concentration of scaled parameters x, y and z in the Oregonator model.[2,3] For the lower concentrations there is a gradual increase in affinity as indicated by the curves a, b, and c in the figure. After a certain range there is a sudden rise in the value and remains constant on further increasing in the value of above parameters. If we compare the affinity

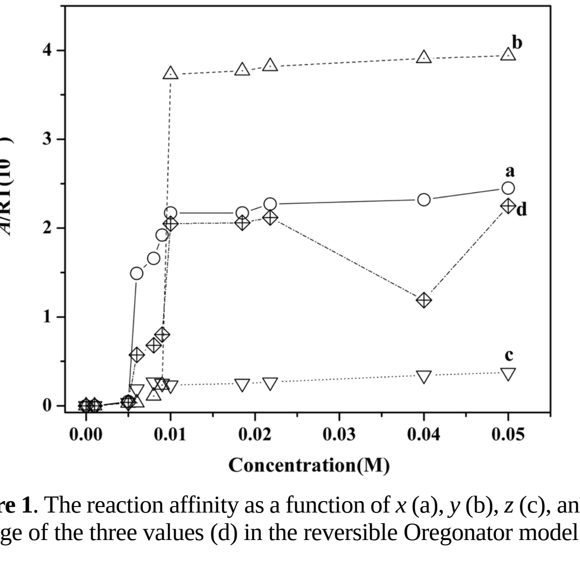

Figure 1. The reaction affinity as a function of x (a), y (b), z (c), and average of the three values (d) in the reversible Oregonator model.

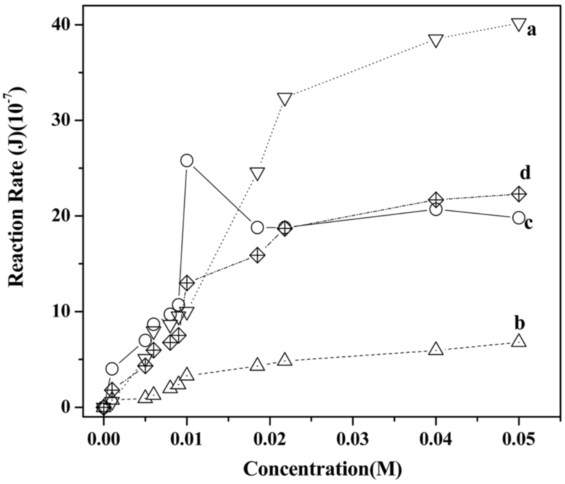

Figure 2. The reaction rate (J) as a function of x (a), y (b), z (c), and average of the three values (d) in the reversible Oregonator model.

curves as in a, b, and c in the figure there is a difference in the magnitudes of affinity value in x, y, and z. The affinity value in y is in the middle range when compared to x, and z has the lowest among them. The average affinities curve for the overall reaction shows an exponential increase with the increase of these concentrations. This clearly indicates that these parameters are the measures of the distance from the state of thermodynamic equilibrium.

Figure 2 shows the reaction rate (J) of individual reaction steps and average rate of all the steps as a function of concentration of scaled parameters x, y, and z in the Oregonator model. For lower concentrations there is a gradual increase in the reaction rate as indicated by the curves a and b in the figure. But there is a sudden jump in the values of c in a slightly higher value of z, after then there is a gradual decrease in the values and further it follows a similar trend as those of a and b which corresponds to x and y, respectively. If we compare reaction rate for the x, y, and z, x possesses higher values than y and z and y possesses lowest values, z is an intermediate of the two values. The curve for the average value for these three follows a similar trend of z.

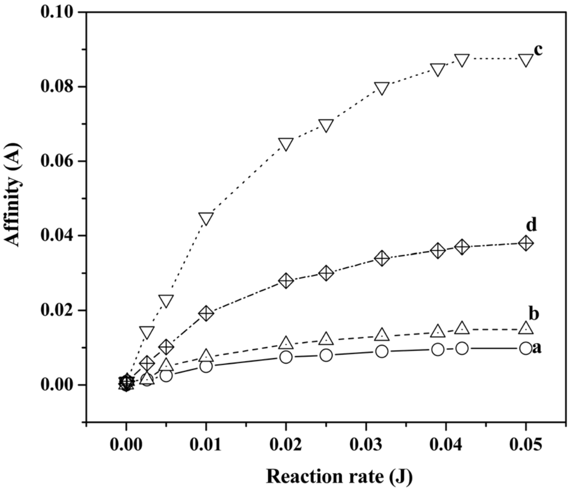

Figure 3. The plot of reaction affinity *vs.* reaction rates as a function of x (a), y (b), z (c), and average of the three values (d) in the reversible Oregonator model.

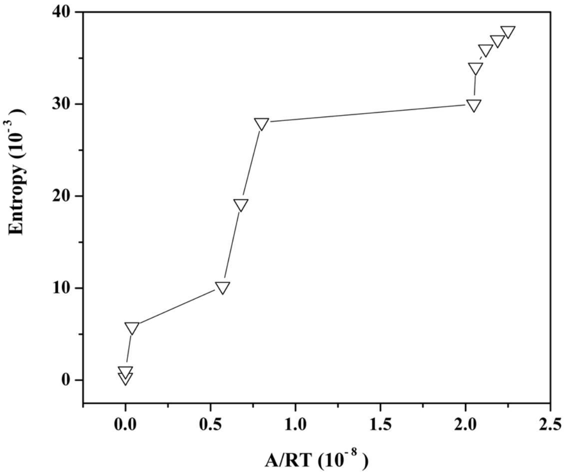

Figure 4. The overall entropy production as a function of overall affinity in the reversible Oregonator model. The entropy increases with a pattern of zig-zag.

Figure 3 is the variation of reaction rates (J_i) of the three individual steps of the model with their corresponding affinities (A_i). The affinities of the first and third reaction rates in the FKN mechanism increase exponentially with the increase of the reaction rate of the corresponding processes. Whereas for the autocatalytic process the reaction rate remains very low until the corresponding affinity overcomes a barrier of $2.95RT$. Beyond which the rate of second process increases exponentially accompanied with a decrease of its affinity. Interestingly, the J_i *vs* A_i plot in Figure 3 displays an interesting allosteric regulatory mechanism of the autocatalytic process. The total reaction rate (J) increases exponentially with the total affinity of A with a similar pattern reported in the previous studies.[13]

Figure 4 shows the overall entropy production as a function of the overall affinities of the reaction process in the reversible Oregonator model. The obtained curve is like a zigzag nature which follows an oscillatory manner as the system progresses with an increase in the affinities of the reaction. As we indicated in our earlier discussion that the study of entropy in a typical systems such as self-organization and pattern formation is quite complicated. This figure well agrees with the fact that the entropy production is not linear in a non-linear reaction system and is a multiple or complicated function of the entropies of individual reactions in a reaction system.[14] Based on the above results as in Figure 4, we consider that the similarity is an emergent property of self-organized complex nonlinear systems obtained generally. This approach may be easily extended to describe other complex pattern-formation systems and this is one of the advantages of the BZ system in particular. It is thus important to conduct the empirical studies whether supports the above conjecture in assessing its validity.

One of the aims of thermodynamics is to provide a characterization of the states of macroscopic systems in terms of state functionals depending on a limited number of observable. It is well-known that at equilibrium entropy provides an elegant description of this sort, largely independent of the details of the processes going on at the microscopic level. Here we have calculated a thermodynamic analog to information entropy production, namely, the thermodynamic entropy production generated by the fluctuations averaged over the invariant distribution of the phase space variables. In the most general case the entropy production of fluctuations contains more detailed, system dependent information on the underlying dynamics. It would also be desirable to analyze more closely the structure of the main expressions in the presence of low-dimensional and spatiotemporal chaos, where the existence of a smooth invariant distribution over the expanding directions allows one to work at the outset in the noiseless limit in so far as the dynamics on the attractor is concerned.

Conclusion

We have studied the entropy production with the concentration of the intermediates during the unstable steady states in the fascinating oscillatory kinetic model of a simple BZ reaction system. For the purpose, the reaction rate and entropy production as a function of reaction affinity are calculated. The obtained values increase with an increase in the values of concentrations, which induces also the increase of the overall entropy. However, the overall entropy which was calculated on the basic assumption that the entropy in a reaction system corresponds to the summation of a product of reaction affinity and reaction rate of individual steps shows a nonlinearity of the reaction system.

The role of individual components is essential for the maintenance of any particular system which plays a leading role of dynamical interactions that take place in a complicated biological system. Thus we can conclude that the overall increase in rate of entropy production is a multiple function of rate of entropy production of the reaction steps in a BZ system.

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