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## Review Stability of Transport and Rate Processes

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### Abstract

About fifty years ago, the Turing instability demonstrated that even simple reaction-diffusion systems might lead to spatial order and differentiation, while the Rayleigh-Bénard instability showed that the maintenance of nonequilibrium might be the source of order in fluids subjected to a thermodynamic force above a critical value. Therefore, distance from global equilibrium in the form of magnitude of a thermodynamic force emerges as another constraint of stability; some systems may enhance perturbations, and evolve to highly organized states called the dissipative structures after a critical distance on the thermodynamic branch. Although the kinetics and transport coefficients represent short-range interactions, chemical instabilities may lead to long-range order and coherent time behavior, such as a chemical clock, known as Hopf bifurcation. Stability analyses of linear and nonlinear modes for stationary homogeneous systems are useful in understanding the formation of organized structures. This review presents the stability of equilibrium and nonequilibrium systems of transport and rate processes with some case studies. It underlines the relationships between complex behavior and stability of systems using the classical and nonequilibrium thermodynamics approaches.

*Keywords: Transport and rate processes, Gibbs stability theory, fluctuation theory, entropy production, dissipative structures, Lyapunov functions*

### 1. Introduction

Since Turing (1952) published 'the chemical basis for morphogenesis,' instability of reaction-diffusion (RD) systems attracted considerable research effort. Mainly, because Turing demonstrated that, even simple RD systems could lead to spatial differentiation due to instability of the homogeneous equilibrium depending on the activator-inhibitor interactions and boundary conditions (Izüs et al, 1995). Later, the classical text by Denn (1975) presented the formulations of many stability problems. With the growing interests in describing complex behavior of biological, chemical, and physical systems, scientists from diverse disciplines are searching answers to question of how a process becomes unstable and sometimes evolves to oscillating and organized structures.

Stability of equilibrium and nonequilibrium systems is continuously tested by internal fluctuations and external perturbations, therefore temperature, concentration, and partial molar volume fluctuate. Hydrodynamic instabilities develop mainly by at least two competing

mechanisms of destabilizing and stabilizing effects, such as (i) kinematic nonlinearity working against viscosity, or (ii) gravity competing with a temperature gradient (Glansdorff and Prigogine, 1963). Light scattering experiments (Dorfman et al., 1994; Ortiz de Zarata et al, 2001; Li et al, 2000, Sagre et al., 1992) have confirmed that a temperature gradient causes nonequilibrium fluctuations in liquid mixtures and polymer solutions due to coupling between the temperature and viscous fluctuations as well as between the concentration and viscous fluctuations through the induced Soret effect. Fluids in nonequilibrium states are capable of exhibiting long-range fluctuations, which are studied by linearized Boussinesq approximations (Sagre et al, 1992) and Monte Carlo simulations (Doering, et al., 1994).

The classical Gibbs stability theory considers the stability of isolated systems in which energy is totally randomized, and entropy reaches its maximum value acting as Lyapunov function (Tarbell, 1977). Gibbs free energy is also Lyapunov function for specified boundary conditions. On the other hand, an equilibrium

state characterized by a thermodynamic potential is a global attractor and asymptotically stable for near nonequilibrium states. At near global equilibrium, irreversible processes reduce perturbations, and drive system back to equilibrium by producing entropy (Edelen, 1973; 1975). However, at far from global equilibrium, perturbations do not tend to decay, and system evolves to metastable or stable coherent behavior stabilized through exchange of energy and matter with the environment. Such states might be highly organized and called dissipative structures created and controlled by hydrodynamic and

illations (Nicolis and Prigogine, 1977; 1989; Scott, 1994; Gray and Scott, 1990; Goldbeater, 1996).

Long evolutionary non-equilibrium processes with critical regulatory steps increase organization and lead to more complex structures, such as biochemical cycles involving oscillatory enzymes. (Barkai and Leibler, 1997; Klein 1998; Klein and Seeling, 1995). This shows that not only hydrodynamic and kinetic parameters also robust regulatory processes and thermodynamic buffering may play important role in the stability of organized structures (Katchalsky and Curran, 1967; Caplan and Essig, 1983; Demirel and Sandler, 2002; Barkai and Leibler, 1997). More interestingly, some external periodic events may affect the evolution of biochemical oscillations (Tsuchiya and Ross, 2003). However, the relationships between the self-organization and the second law of thermodynamics are disputed within the context of biological evolution and origin of life (Yates, 1987), which is outside the scope of this review. A dissipative structure results from a symmetry breaking process at far from global equilibrium due to instability.

In physics, irreversibility and dissipation are interpreted as destruction of available energy, while biological evolution is associated with increased complexity and organization in time and space. Therefore, relationship between the randomness and the entropy is clear only for ideal and noninteracting systems or for systems at global equilibrium. However, the organization associated with the occurrence of dissipative structures under nonequilibrium conditions may not be related to the decrease of entropy in a straightforward manner. We observe the destruction of structure at global equilibrium, while creation of structures at far from global equilibrium. Therefore, distance from global equilibrium appears as a new organizing factor, like lowering of temperature, which can induce long-range correlations leading to phase transitions or self-organization phenomena. As nonequilibrium thermodynamics (NET) theory considers implications of the distance from global equilibrium in its formulation (De Groot,

kinetic parameters (Prigogine, 1947; Nicolis and Prigogine, 1977; 1989; Kondepudi and Prigogine, 1999). The thermodynamic forces (gradients) imposed on a system measure the distance from global equilibrium, which initiates the choice between multiple solutions appearing at a bifurcation point. Complex behavior in transport phenomena is usually associated with spatial instabilities, while chemical systems may sustain temporal instabilities by enhancing or repressing the effect of slight perturbations, such as Belousov-Zhabotinski (BZ) reaction, which is one of the early examples of chemical oscillations (Prigogine, 1952; Katchalsky and Curran, 1967; Wisniewski et al., 1976; Bernstein et al., 1993; Dot, 1999; Kondepudi and Prigogine, 1999; Demirel and Sandler, 2004, Demirel, 2002), it may have a critical role in understanding stability of nonequilibrium systems.

Thermodynamics plays important role towards the stability analysis of transport and rate processes, and the NET approach may enhance and broaden this role. This study reviews the stability analysis based on the conventional Gibbs approach and the NET theory. It considers the stability of equilibrium, near equilibrium, and far from equilibrium states with some case studies.

## 2. The Gibbs Stability Theory

Fluctuations in thermodynamic properties determine the entropy change, which can be expanded in certain fluctuations (Kondepudi and Prigogine, 1999). For an isolated system, the power series expansion of entropy in terms of fluctuation  $x$ , such as extent of reaction, is given by

$$\begin{aligned} \Delta S = S - S_{\text{eq}} &= \left( \frac{\partial S}{\partial x} \right) dx + \frac{1}{2} \left( \frac{\partial^2 S}{\partial x^2} \right) (dx)^2 + \dots \\ &= \delta S + \frac{1}{2} \delta^2 S + \dots < 0 \end{aligned} \quad (1)$$

The change in entropy is due to the second-order term as the first order term vanishes since the entropy reaches its maximum value at equilibrium. Therefore, the system at equilibrium will be stable to perturbations when the entropy decreases and the change is negative. However, the characteristics of perturbations plays important role towards stability. Decaying perturbations lead to stable equilibrium; otherwise instability occurs. More interestingly, when the magnitude of perturbations is very large, system may move to nonlinear region, which is far from global equilibrium on the thermodynamic branch (Nicolis and Prigogine, 1977) where the instability may cause a system to evolve to organized structure.

## 2.1 Thermal stability

For a system with parts 1 and 2, consider a flow of energy  $dU$  from part 1 causing a small fluctuation in temperature  $\delta T$ . Expansion of the total entropy of the parts  $S$  using equation (1), in terms of  $U_1$  and  $U_2$  yields

$$\delta S = \left( \frac{T_2 - T_1}{T_1 T_2} \right) (\delta U) = 0, \text{ and} \quad (2)$$

$$\delta^2 S = -\frac{C_v (\delta T)^2}{T^2} < 0$$

where  $dU_1 = -dU_2 = dU$ , and  $(\partial S / \partial U)_{V,N} = 1/T$ ,  $\delta U = C_v \delta T$ , at equilibrium ( $T = T_1 = T_2$ ). Therefore, fluctuations can only decrease the entropy, and an entropy-generating irreversible process derives the system back to the original state. equation (2) shows that the state at equilibrium is stable to thermal fluctuations because the heat capacity  $C_v$  is positive.

## 2.2 Mechanical stability

For a similar system described above, the second order terms of the entropy due to fluctuations in the volume of a subsystem are expressed by the isothermal compressibility  $\kappa_T$

$$\kappa_T = -\left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial P} \right)_T, \text{ and } \left( \frac{\partial S}{\partial V} \right)_{U,N} = \frac{P}{T} \quad (3)$$

We have  $\delta S = 0$ , as  $P_1/T_1 = P_2/T_2 = P/T$  at equilibrium, and the second derivative becomes

$$\delta^2 S = -\frac{(\delta V)^2}{T \kappa_T V} < 0 \quad (4)$$

Equation (4) shows that the state of equilibrium is stable to fluctuation in volume because the isothermal compressibility is positive.

## 2.3 Chemical stability

Chemical reactions cause fluctuations in mole numbers of various components of a system. equation (1) provides the expansion in terms of affinity  $A$  defined as  $A = -\sum v_i \mu_i$ , where  $v_i$  is the stoichiometric coefficient, and  $\mu_i$  is the chemical potential of species  $i$ ; for example for reaction  $B \rightarrow 2D + E$ , the affinity becomes  $A = \mu_B - 2\mu_D - \mu_E$ . At equilibrium  $\delta S = 0$  and  $A = 0$ . So that the condition for the stability of equilibrium state against the fluctuations in mole numbers is expressed in terms of the extent of reaction  $\xi$

$$\delta^2 S = \frac{1}{T} \left( \frac{\partial A}{\partial \xi} \right)_{\text{eq}} (\delta \xi)^2 < 0 \quad (5)$$

## 2.4 Stability in diffusion

When the fluctuations are due to exchange of matter between the parts, equation (1) becomes

$$\delta^2 S = -\sum_{i,k} \left( \frac{\partial \left( \frac{\mu_{1i}}{T} \right)}{\partial N_k} + \frac{\partial \left( \frac{\mu_{2i}}{T} \right)}{\partial N_k} \right) (\delta N_i \delta N_k) < 0 \quad (6)$$

With  $(\partial S / \partial N_k) = -\mu_k / T$ , and  $\delta N_{1k} = -\delta N_{2k} = \delta N_k$ , and  $\delta S = 0$  as the chemical potentials of the two parts are equal, and equation (6) becomes

$$\delta^2 S = -\sum_{i,k} \left( \frac{\partial}{\partial N_k} \frac{\mu_{1i}}{T} \right) (\delta N_i \delta N_k) < 0 \quad (7)$$

Equation (7) is the stability condition of an equilibrium state when mole numbers fluctuate. For an isothermal binary mixture, equation (7) becomes

$$\frac{\partial \mu_1}{\partial N_1} (\delta N_1)^2 + \frac{\partial \mu_2}{\partial N_2} (\delta N_2)^2 + \frac{\partial \mu_2}{\partial N_1} (\delta N_1) (\delta N_2) + \frac{\partial \mu_1}{\partial N_2} (\delta N_1) (\delta N_2) > 0 \quad (8)$$

where

$$\frac{\partial \mu_1}{\partial N_2} = \frac{\partial}{\partial N_2} \frac{\partial G}{\partial N_1} = \frac{\partial \mu_2}{\partial N_1}$$

By relating the fluctuations into the reaction coordinate  $v_i d\xi = \delta N_i$ , equations (7) and (5) imply that if a system is stable to fluctuations in diffusion, it is also stable to fluctuations in chemical reactions, which is called the Duhem-Jougeut theorem (Kondepudi and Prigogine, 1999). However, a nonequilibrium steady state involving chemical reactions may be unstable even if the system is stable with respect to diffusion.

## 2.5 General stability condition

General condition for the stability of equilibrium state to thermal, volume, and mole number fluctuations is obtained by combining equations (2), (4) and (7)

$$\delta^2 S = -\frac{C_v (\delta T)^2}{T^2} - \frac{(\delta V)^2}{T \kappa_T V} - \sum_{i,j} \left( \frac{\partial}{\partial N_j} \frac{\mu_i}{T} \right) \delta N_i \delta N_j < 0 \quad (9)$$

Equation (9) shows that the second order differential of entropy assumes a quadratic form, and the stability conditions are directly related to

the behavior and signs of the coefficients. It is interesting to see that equation (9) resembles the Gibbs equation  $T\delta S = \delta U + P\delta V - \sum \mu_i \delta N_i$  in the form

$$T\delta^2 S = -\delta T\delta S + \delta P\delta V - \sum_i \delta \mu_i \delta N_i \quad (10)$$

where  $\delta S = \delta Q/T = C_v \delta T/T$ ,  $\delta P = -\delta V/(\kappa_T V)$ , and  $\delta \mu_i = \sum (\partial \mu_i / \partial N_j) dN_j$ .

For a closed system at uniform temperature and pressure, we have

$$T d_i S = T \delta s - dU - p dV \geq 0 \quad (11)$$

Equation (11) results from  $d_i S = dS - d_e S \geq 0$ ,  $d_e S = dQ/T$ ,  $dQ = dU + PdV$ , and leads to a stability criterion for thermodynamic equilibrium. External perturbations or molecular fluctuations must satisfy inequality in equation (11) for equilibrium state to be stable. For a small and arbitrary increment  $\delta$ , equation (11) provides the stability criterion  $\delta U + P\delta V - T\delta S \geq 0$ . At constant  $S$  and  $V$ , stability condition becomes  $\delta U \geq 0$ , indicating that the internal energy assumes a minimum for stable equilibrium- $(\delta U)_{eq} = 0$ . Stability for a finite amplitude perturbation is  $(\Delta U)_{eq} > 0$ , or for an infinitesimal perturbation is  $(\delta^2 U)_{eq} > 0$ . TABLE I shows the equilibrium and stability criteria for various boundary conditions. The last column in TABLE I is not always satisfied for metastable systems, although we often describe both stable and metastable systems as stable.

TABLE I. NECESSARY AND SUFFICIENT CONDITIONS FOR THE STABILITY OF EQUILIBRIUM STATE. FROM GIBBS THEORY

Boundary conditions: Constant properties	Equilibrium criterion	Stability criterion	
		Infinitesimal perturbations	Finite amplitude perturbations
S, V	$(\delta U)_{eq} = 0$	$\delta U \geq 0$	$(\Delta U)_{eq} > 0$ $(\delta^2 U)_{eq} > 0$
U, V	$(\delta S)_{eq} = 0$	$\delta S \leq 0$	$(\Delta S)_{eq} < 0$ $(\delta^2 S)_{eq} < 0$
S, P	$(\delta H)_{eq} = 0$	$\delta H \geq 0$	$(\Delta H)_{eq} > 0$ $(\delta^2 H)_{eq} > 0$
T, V	$(\delta A)_{eq} = 0$	$\delta A \geq 0$	$(\Delta A)_{eq} > 0$ $(\delta^2 A)_{eq} > 0$
T, P	$(\delta G)_{eq} = 0$	$\delta G \geq 0$	$(\Delta G)_{eq} > 0$ $(\delta^2 G)_{eq} > 0$

### 3. Configurational Heat Capacity

Heat absorbed by a system

$$dQ = -VdP + dH = (h_{T,\xi} - V)dP + C_{p,\xi}dT + h_{T,P}d\xi \quad (12)$$

where

$$h_{T,\xi} = \left( \frac{\partial H}{\partial P} \right)_{T,\xi}, C_{p,\xi} = \left( \frac{\partial H}{\partial T} \right)_{P,\xi}, h_{T,P} = \left( \frac{\partial H}{\partial \xi} \right)_{T,P}$$

which may exist in two isomeric forms, changes the temperature, pressure, and extent of transformation between isomers. In equation (12), the term  $C_{p,\xi}$  is the heat capacity at constant composition at very slow relaxation of the transformation. Heat capacity at constant pressure is

$$C_P = \left( \frac{\partial H}{\partial T} \right)_{P,\xi} + \left( \frac{\partial H}{\partial \xi} \right)_{T,P} \left( \frac{d\xi}{dT} \right)_P \quad (13)$$

Second term on the right of equation (13) is called the configurational heat capacity  $C_{PC} = (\partial H / \partial \xi)_{T,P} (d\xi / dT)_P$  due to the relaxation of system to the equilibrium configuration (Kondepudi and Prigogine, 1999). For transformation in equilibrium ( $A=0$ ), we have

$$\left( \frac{\partial H}{\partial \xi} \right)_{T,P} = -T \left( \frac{\partial A}{\partial \xi} \right)_{T,P} \left( \frac{\partial \xi}{\partial T} \right)_{P,A=0} \quad (14)$$

The configurational heat capacity for a transformation at equilibrium and constant pressure is expressed by combining equations (13) and (14)

$$C_{PC,A=0} = -T \left( \frac{\partial A}{\partial \xi} \right)_{T,P} \left( \frac{\partial \xi}{\partial T} \right)_{P,A=0}^2 \quad (15)$$

Since the stability condition for a chemical reaction is  $(\partial A / \partial \xi) < 0$ , the heat capacity at constant composition is always less than heat capacity of a system that remains in equilibrium as it receives heat. Certain fluid molecules, such as supercooled liquid glycerin, can vibrate but not rotate freely, which is called libration. As the temperature increases more molecules rotate, and the variable  $\xi$  becomes the extent of libration-rotation transformation. If the transformation equilibrium is reached rather slowly, the equilibrium is not maintained under heating rapidly, and the heat capacity  $C_{p,\xi}$  will be lower than the heat capacity measured in slow heating (Kondepudi and Prigogine, 1999).

#### 3.1 Phase stability

Phase splitting due to thermodynamic instability and hence symmetry breaking in

equilibrium of a feed mixture affects simulation and design problems of distillation and extraction. To know the exact number of phases contributes considerably towards the success of phase equilibria predictions (Demirel and McDermott, 1984, 1987). For ternary mixtures, feed points located within the binodal curve only split into two liquid phases, and hence the exact number of phases can be estimated (McDermott and Demirel, 1989). Generally, however, the stability analysis based on tangent plane distance with respect to the Gibbs energy of mixing surface predicts the phase stability (Michelsen, 1982; Hua et al., 1996). When the distance  $D$  for a composition  $x$  is negative, a phase with feed mole fractions  $z$  is unstable, and the molar Gibbs energy of mixing surface  $G_m = \Delta G_{mix}/RT$  falls below a plane tangent to the surface at  $z$ . The distance  $D$  is obtained from

$$D(x) = G_m(x) - G_m(z) - \sum_{i=1}^n \left( \frac{\partial G_m}{\partial x_i} \right)_z (x_i - z_i) \quad (16)$$

The subscript  $z$  indicates evaluation of partial differentials at  $x=z$ , and  $n$  is the number of components. The Gibbs energy of mixing, and the reduced Gibbs energy of mixing  $g^E$  is given by

$$G_m(x) = \sum_{i=1}^n x_i \ln x_i + g^E(x) \quad (17)$$

$$g^E = \frac{G^E}{RT} \quad (18)$$

The tangent plane distance analysis minimizes the  $D$  subject to the mole fractions by solving of following system of nonlinear equations, which provide the stationary points

$$\left[ \left( \frac{\partial G_m}{\partial x_i} \right) - \left( \frac{\partial G_m}{\partial x_n} \right) \right] - \left[ \left( \frac{\partial G_m}{\partial x_i} \right) - \left( \frac{\partial G_m}{\partial x_n} \right) \right]_z = 0 \quad i = 1, \dots, n-1 \quad (19)$$

$$\sum_{i=1}^n x_i = 1 \quad (20)$$

#### 4. Stability and Entropy Production

The Gibbs stability theory provides necessary and sufficient conditions to investigate the stability problems with well-defined boundary conditions in equilibrium state

$$dA = -Td_iS \leq 0 \quad (T, V = \text{constant}) \quad (21)$$

$$dG = -Td_iS \leq 0 \quad (T, P = \text{constant}) \quad (22)$$

$$dH = -Td_iS \leq 0 \quad (S, P = \text{constant}) \quad (23)$$

This condition is restrictive for nonequilibrium systems of transport and rate processes. For example, differential form of Fourier's law together with the boundary conditions describe the evolution of heat conduction, and the stability theory at equilibrium refers to the asymptotic state reached after a sufficiently long time; in such cases there exists no thermodynamic potential with a minimum at steady state. Therefore, a stability theory based on the entropy production is more general as it can describe the stability of nonequilibrium states too. The change of total entropy is  $dS = d_eS + d_iS$ . The term  $d_eS$  is the entropy exchange through the boundary that can be positive, zero, or negative, while the term  $d_iS$  is the rate of entropy production, which is always positive for irreversible processes and zero for reversible ones. In NET, the rate of entropy production  $\Phi$  is the product of flux  $J$  and force  $X$  operating in irreversible processes  $\Phi = (d_iS/dt) = \sum J_k X_k$ .

A near equilibrium system is stable to fluctuations if the change of entropy production is negative  $\Delta_iS < 0$ . For isolated systems,  $dS/dt \geq 0$  shows the tendency to increase disorder as  $d_eS/dt = 0$ , and  $dS = d_iS \geq 0$ . For nonisolated systems,  $d_iS/dt > 0$  shows irreversible processes, such as chemical reactions, heat conduction, diffusion, or viscous dissipation. For states near global equilibrium, which are amenable to local description,  $d_iS$  is a bilinear form of fluxes and forces that are related in linear form. However, certain states far from global equilibrium can still be characterized by linear phenomena because of the presence of various regulatory processes, especially in biological systems (Caplan and Essig, 1983). For nonisolated systems, emergence of organized structures needs not be related simply to decrease of entropy, as kinetics, transport coefficients, and fluctuations are interrelated in a complex manner.

The second law for isolated systems shows that the excess entropy,  $\Delta S = S - S_{eq} \leq 0$ , increases monotonically in time,  $d(\Delta S)/dt \geq 0$ . Therefore it plays the role of Lyapunov function, and expresses of global stability (Tarbell, 1977; Bernstein et al., 1993; Ablonczy et al., 2003); equilibrium state is a global attractor, so that an isolated system is globally stable. Deviations from stationary state lead to decrease in entropy production. So that  $d_iS/dt$  is a Lyapunov function that guaranties the global stability of stationary states that are close to global equilibrium.

For nonequilibrium systems far from global equilibrium, the second law does not impose the sign of entropy variation due to the terms  $d_eS$  and  $d_iS$ . Therefore, there is no universal Lyapunov function, which creates ambiguity and also

motivation for many researchers towards derivation of general or approximate formulations of the stability of such systems (Ross and Vlad, 1999; Kondepudi and Prigogine, 1999). For a multicomponent fluid system with  $n$  components, dissipation function in terms of conjugate forces  $X_i$  and fluxes  $J_i$  for  $l$  number of chemical reactions (excluding electrical and magnetic effects) is (Wisniewski et al., 1976)

$$\Phi = \sum_i J_i X_i = \left\{ \mathbf{J}_u \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} \sum_{i=1}^n \mathbf{J}_i \cdot \left[ T \nabla \left( \frac{\mu_i}{T} \right) - \mathbf{F}_i \right] + \frac{1}{T} \tau : (\nabla \mathbf{v}) - \frac{1}{T} \sum_{j=1}^l A_j J_{r,j} \right\} \geq 0 \quad (24)$$

where  $\mathbf{F}_i$  is the force per unit mass of component  $i$ . Here the rate entropy production is the sum of contributions due to heat, mass, momentum transfer, and chemical reactions. equation (24) identifies a set of the conjugate fluxes and forces to be used in the phenomenological equations with the coefficients satisfying the Onsager reciprocal rules in the linear regime (Prigogine, 1947; De Groot, 1952, Wisniewski et al, 1976).

For a chemical reaction entropy production is

$$\frac{d_i S}{dt} = \frac{A}{T} \frac{d\xi}{dt} \quad (25)$$

Approximation of  $A$  due to a small fluctuation of the extent of reaction  $\xi$ ,  $\alpha = (\xi - \xi_{eq})$ , is expressed by  $A = (\partial A / \partial \xi)(\xi - \xi_{eq})$ , and used in (25) to obtain the following stability condition

$$\Delta_i S = \frac{1}{T} \int_0^{\delta \xi} A d\xi = \int_0^{\delta \xi} \left( \frac{\partial A}{\partial \xi} \right)_{eq} \alpha d\alpha = \left( \frac{\partial A}{\partial \xi} \right)_{eq} \frac{(\delta \xi)^2}{2T} < 0 \quad (26)$$

where  $d\xi = d\alpha$ . For  $l$  number of chemical reactions, equation (26) becomes

$$\Delta_i S = \sum_{i,j} \frac{1}{2T} \left( \frac{\partial A_i}{\partial \xi_j} \right)_{eq} \delta \xi_i \delta \xi_j < 0 \quad (27)$$

Equations (26) and (27) do not depend on the boundary conditions imposed on the system.

For a thermal fluctuation of  $T_{eq} + \beta$ , we have

$$d_i S = \left( \frac{1}{T_{eq} + \beta} - \frac{1}{T_{eq}} \right) dQ = -\frac{\beta}{T_{eq}^2} dQ \quad (28)$$

Using  $dQ = C_v d\beta$ , the condition for thermal stability becomes

$$\Delta_i S = \int_0^{\delta T} -\frac{C_v}{T_e^2} \beta d\beta = -\frac{C_v}{T_e^2} \frac{(\delta T)^2}{2} < 0 \quad (29)$$

As before, a general thermodynamic theory of stability formulation is quadratic in the perturbations  $\delta T$ ,  $\delta V$ , and  $\delta N_k$ , because the forces and fluxes vanish at equilibrium

$$\Delta_i S = -\frac{1}{2T} \left[ \frac{C_v (\delta T)^2}{T} + \frac{(\delta V)^2}{\kappa_T V} + \sum_{i,j} \left( \frac{\partial \mu_i}{\partial N_j} \right) \delta N_i \delta N_j \right] < 0 \quad (30)$$

Equation (30) is identical with equation (9), and shows that the contributions to the entropy change due to fluctuations in the equilibrium state is of second order expressed explicitly by  $\delta^2 S / 2$

$$\delta^2 S < 0 \quad (31)$$

$$\frac{1}{2} \frac{d\delta^2 S}{dt} = \sum_k \delta J_k \delta X_k > 0 \quad (32)$$

Equations (31) and (32) describe the stability of equilibrium and nonequilibrium stationary states. The term  $\delta^2 S$  is a Lyapunov functional for a stationary state.

#### 4.1 Thermodynamic fluctuations

Equation (24) does not describe the dynamics of thermodynamic fluctuations, although the NET theory and the thermodynamic fluctuations are connected in deriving the Onsager rules (Mazur, 1998). However, introduction of the notion of internal degrees of freedom into NET, firstly, has resulted Fokker-Planck type differential equations, which extends the applicability of NET, and secondly, thermodynamic fluctuation are implicitly accounted within the NET. Still, this type of extension is limited to mesoscopic domain subject to fluctuations and for very slow processes compared to molecular or microscopic time scale (Mazur, 1998).

Einstein related thermodynamic entropy to the probability of a fluctuation  $\phi$  by

$$\phi = Z e^{\Delta S / k_B} \quad (33)$$

where  $\Delta S$  is the entropy change due to fluctuations from the state of equilibrium,  $Z$  is the normalization constant ensuring that the sum of all probabilities equal to one, and  $k_B = 1.3810^{-23}$  J/K is the Boltzmann constant.

Using in equation (30), the probability  $\varphi$  of fluctuations in  $T$ ,  $V$  and  $N$  is expressed by

$$\varphi(\delta T, \delta V, \delta N) = Z \exp \left\{ -\frac{1}{2} \left[ \frac{C_v(\delta T)^2}{k_B T^2} + \frac{(\delta V)^2}{T k_B k_T V} + \sum_i \left( \frac{\partial \mu_i}{\partial N_j} \right) \delta N_i \delta N_j \right] \right\} \quad (34)$$

In a more general form, the probability is expressed in terms of the products of pairs of variables (Kondepudi and Prigogine, 1999)

$$\varphi = Z \exp \left( \frac{\delta^2 S}{2 k_B} \right) = Z \exp \left[ \frac{-1}{2 k_B T} \left( \delta T \delta S - \delta P \delta V + \sum_k \delta \mu_k \delta N_k \right) \right] \quad (35)$$

If we define a fluctuation in a property  $Y$  as  $(Y_k - Y_{k,eq}) = \alpha_k$ , and using  $\delta^2 S/2 = -1/2 \sum_{ij} g_{ij} \alpha_i \alpha_j$ , where the elements  $g_{ij}$  are appropriate coefficients of matrix  $[g]$ , then the probability is given by

$$\varphi(\alpha_1, \alpha_2, \dots, \alpha_m) = \frac{\sqrt{\det[g]}}{\sqrt{(2\pi k_B)^m}} \exp \left( \frac{-1}{2 k_B} \sum_{i,j=1}^m g_{ij} \alpha_i \alpha_j \right) \quad (36)$$

where  $\det[g]$  is the determinant. For a single variable of  $\alpha$ , we have (Kondepudi and Prigogine, 1999)

$$\varphi(\alpha) = \sqrt{\frac{g}{2\pi k_B}} \exp \left( -\frac{g\alpha^2}{2k_B} \right) \quad (37)$$

### 5. Stability of Stationary States

For chemical reactions, the change of entropy production with time  $P$  is

$$P = \frac{d_i S}{dt} = \sum_k \frac{A_k}{T} \frac{d\xi_k}{dt} = \sum_k \frac{A_k}{T} J_{r,k} \quad (38)$$

The affinity and the reaction velocity are expressed by  $A=A(P, T, \xi)$ ; and  $J_{r,k} = \sum_{ki} L_{ki}(A_i/T)$ . At constant pressure and temperature, we have

$$\frac{dP}{dt} = \frac{2}{T} \sum_{ij} \left( \frac{\partial A_i}{\partial \xi_j} \right)_{P,T} J_{ri} J_{rj} \quad (39)$$

Equations (27) and (39) show that the stability of the nonequilibrium stationary states to fluctuations  $\delta \xi_i$  in the linear regime requires  $P > 0$  and  $dP/dt < 0$ , which are a Lyapunov

conditions (Tarbel, 1977; Kondepudi and Prigogine, 1999) as the matrix  $(\partial A_i / \partial \xi_j)$  is negative definite in near equilibrium.

Dissipative structures can sustain long-range correlations. How the boundary conditions or irreversible processes specify such structures are topics of intensive research (Izüs et al., 1995; Kondepudi and Prigogine, 1999). Ross and Vlad (1999) have presented a review for reaction systems far from global equilibrium and stochastic theory of relative stability, and eikonal solutions for stationary systems and their relations to Lyapunov functions. Temperature and chemical potential are well-defined with the assumption of local equilibrium, and the stationary probability distribution is obtained in the eikonal approximation; so that, fluctuation-dissipation relation for a chemical system with one variable is (Ross and Vlad, 1999)

$$J_r(x) = 2D(x) \tanh \left( -\frac{A(x)}{2k_B T} \right) = 2D(x) \tanh \left( -\frac{1}{2k_B T} \frac{\partial \psi(x)}{\partial x} \right) \quad (40)$$

where  $J_r(x)$  is the net reaction rate representing the flux,  $D(x)$  is a probability diffusion coefficient, and shows the strength of chemical fluctuations,  $A(x)$  is a species-specific affinity representing the thermodynamic force, and  $\psi(x)$  is the stochastic potential. Equation (40) shows a nonlinear relationship between the flux and force, and due to hyperbolic tangent, the reaction rate approaches toward a constant value for large values of the specific affinity.

An evolution criterion (Glansdorff and Prigogine, 1971; Kondepudi and Prigogine, 1999) can be obtained from the rate of change of volumetric entropy production

$$P = \int \sum J X dV > 0$$

$$\frac{dP}{dt} = \int_V \left( \sum_k J_k \frac{dX_k}{dt} \right) dV + \int_V \left( \sum_k X_k \frac{dJ_k}{dt} \right) dV = \frac{d_X P}{dt} + \frac{d_J P}{dt} \quad (41)$$

This equation is independent of type of the phenomenological relations between fluxes and forces. On the other hand, linear phenomenological equations and the Onsager reciprocal relations yield

$$\sum J_k dX_k = \sum L_{jk} X_j dX_k = \sum X_j d(L_{jk} X_k) = \sum X_j dJ_k \quad (42)$$

So that in the linear region, we have



$$\frac{d_X P}{dt} = \frac{d_J P}{dt} = \frac{1}{2} \frac{dP}{dt} \quad (43)$$

For time-independent boundary conditions, we have the general conditions for the stability of a state

$$\frac{dP}{dt} = 2 \frac{d_X P}{dt} \leq 0 \quad (44)$$

Here the equality sign is for stationary states. Unfortunately, equation (44) does not indicate how a state evolves. The relations  $P > 0$ , and  $d_X P < 0$  are called the Lyapunov conditions (Kondepudi and Prigogine, 1999).

Following elementary and autocatalytic reaction examples from Kondepudi and Prigogine (1999) demonstrates clearly how the stability is controlled by the kinetics. For a perturbation  $\delta c_B$  from stationary state of the following elementary reaction  $H + B \rightleftharpoons C + D$  time derivative of excess entropy production is expressed by

$$\begin{aligned} \frac{1}{2} \frac{d\delta^2 S}{dt} &= \sum_i \delta J_{r_i} \delta X_i = \frac{\delta A}{T} \delta J_r \\ &= R k_f \frac{c_{Hs}}{c_{Bs}} (\delta c_B)^2 > 0 \end{aligned} \quad (45)$$

where  $R_f = k_f c_H c_B$  and  $R_b = k_b c_C c_D$ .

The affinity and the reaction velocity are defined by

$$A = RT \ln(R_f / R_b) \quad \text{and} \quad J_r = (R_f - R_b) \quad (46)$$

Since the excessive entropy production is positive, the stationary state is stable.

For the following autocatalytic reaction  $2X + Y = 3X$  with non-equilibrium stationary-state concentrations  $c_X$  and  $c_Y$  and perturbation  $\delta X$ , the following excess entropy production is negative if  $k_f \gg k_b$ , and hence the stationary state becomes unstable

$$\frac{1}{2} \frac{d\delta^2 S}{dt} = -2R k_f c_{Xs} c_{Ys} + 3R k_b c_{Xs}^2 \frac{(\delta c_X)^2}{c_{Xs}} \quad (47)$$

The fundamental quantity, which determines the stability, is the sign of excess volumetric entropy production

$$P(\delta S) = \int \sum \delta J \delta X dV \geq 0 \quad (48)$$

where  $(\delta S)$  is the perturbation in entropy, and together with reaction velocities define the stability condition for chemical reactions (Glansdorff and Prigogine, 1971)

$$P(\delta S) = \frac{\sum_i \delta J_{r,i} \delta A_i}{T} \geq 0 \quad (49)$$

## 6. Evolution Equations

Hamiltonian dynamics show that classical mechanics is invariant to  $(-t)$  and  $(t)$ . In a macroscopic description of dissipative systems, we use collective variables of temperature, pressure, concentration, and convection velocity to define an instantaneous state. The evolution equations of the collective variables are not invariant under time reversal

Chemical reaction:

$$\frac{dc_A}{dt} = -k c_A c_B, \quad A + B \rightarrow D \quad (50)$$

Heat conduction:

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T \quad \alpha > 0 \quad (51)$$

Diffusion:

$$\frac{\partial c}{\partial t} = D \nabla^2 c \quad D > 0 \quad (52)$$

Here  $T$  and  $c$  are called the even variables whose signs do not change upon time reversal, while convection velocity, and momentum of a particle are called the odd variables whose signs change with time reversal.

General form of a dissipative system with macroscopic variables  $X_1, \dots, X_n$ , space  $r$ , and time  $t$ , is expressed by

$$\frac{\partial X_i}{\partial t} = f_i(X_1, \dots, X_n, r, t, \mu) \quad (53)$$

Evolution is influenced by the variation of some control parameters  $\mu$  that can be modified by the environment (Demirel and Sandler, 2002; Tsuchiya and Ross, 2003). The function  $f_i$  has the following properties

at equilibrium:

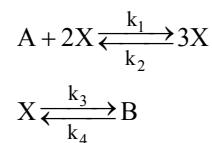
$$f_i([X_{i,eq}], \mu_{eq}) = 0 \quad (54)$$

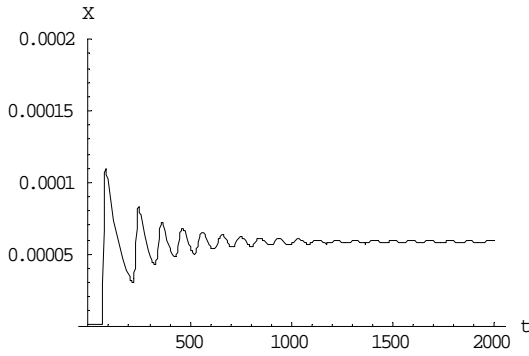
at non-equilibrium steady state:

$$f_i([X_{i,s1}], \mu_s) = 0 \quad (55)$$

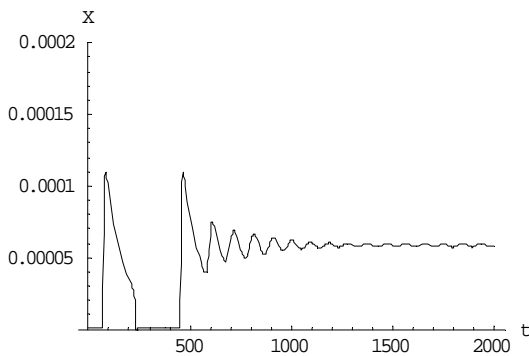
These relation are associated with certain restrictions, such as  $T > 0$ ,  $c > 0$ , and physical systems are highly nongeneric (Nicolis and Prigogine, 1989).

Consider the evolution of following set of reactions

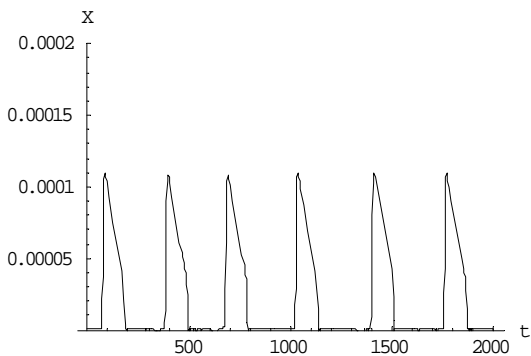




(a)



(b)



(c)

Figure 1. Change of composition  $X$  with time,  $k_1=1.28$ ;  $k_2=8.0$ ;  $k_3=8 \cdot 10^{-5}$ ;  $k_4=2 \cdot 10^3$ ;  $k_5=1.0$ ;  $H=0.06$ ;  $B=0.02$ ; a:  $\mu=0.51319711709999$ , b:  $\mu=0.51319711709999$ , c:  $\mu=0.52$

At fixed concentrations of A and B,  $X$  is the only variable. At equilibrium, detailed balance yields

$$k_1AX^2 = k_2X^3, \text{ and } k_3X = k_4B \quad (56)$$

and imposes a condition on A and B

$$\left(\frac{B}{A}\right)_{\text{eq}} = \frac{k_1k_3}{k_2k_4} \quad (57)$$

At non-equilibrium stationary state, however, we have

$$\frac{dX}{dt} = -k_2X_s^3 + k_1AX_s^2 - k_3X_s + k_4B = 0 \quad (58)$$

Equation (58) has three stationary solutions  $X_s$ . So that nonequilibrium state can reveal the true properties that are disguised at equilibrium and near equilibrium; nonlinearity combined with nonequilibrium constraints may allow the diversification of the behavior of a system.

Macroscopic systems are composed of large number of interacting particles, and the state variables represent either average of instantaneous states over a long time interval, or the most probable states. Most systems communicate with the environment through slight quantities of matter, momentum, or energy, which are treated as 'experimental error' and confidence level. So that the instantaneous state of a system is not stationary state  $X_s$  but rather nearby state  $X$  related to  $X_s$  through the perturbation  $x(t)$

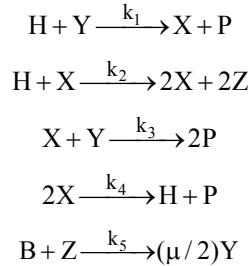
$$X(t) = X_s + x(t) \quad (59)$$

A perturbation may be due to the interference of the environment with the intrinsic dynamics of system or intrinsic internal deviations called the fluctuations that the system generates spontaneously. The property of stability refers to several responses of system to various types of perturbations (Nicolis and Prigogine, 1989):

- i. Perturbations remain smaller than a critical value for all times, and the state  $X_s$  is stable in the sense of Lyapunov. Then we can define the notion of orbital stability as the distance between the reference and perturbed trajectories as whole sequence of possible states.
- ii. Perturbations decay in time, and  $X_s$  is asymptotically stable, which implies irreversibility.
- iii. State  $X(t)$  does not remain in the vicinity of  $X_s$ , and  $x(t)$  cannot remain less than a critical value for all times. Then the reference state  $X_s$  is unstable; system experiences rapid growth of perturbation leading to orbital instability.
- iv. State  $X(t)$  remains in some vicinity of the  $X_s$  for  $x(t) \leq \text{critical}$ , and moves away from  $X_s$  for  $x(t) \geq \text{critical}$ . This represents a locally stable but globally unstable state  $X_s$ .

Sometimes, even spatially homogeneous chemical systems can cause bistability and show complex behavior in time. For example, autocatalysis may occur due to the particular molecular structure and reactivity of certain constituents, and reactions may evolve to new states by amplifying or repressing the effect of a

slight concentration perturbation. BZ reaction system is one example leading to such chemical oscillations. One of the interesting phenomena is the effect of very narrow range of controlling parameter  $\mu$  on the stability of BZ reaction system given by



The evolution equations for the BZ system are

$$\frac{dX}{dt} = k_1HY + k_2HX - k_3XY - 2k_4X^2 \quad (60)$$

$$\frac{dY}{dt} = -k_1HY + k_3XY + (\mu/2)k_5BZ \quad (61)$$

$$\frac{dZ}{dt} = 2k_2HX - k_5BZ \quad (62)$$

Figure 1 shows the effect of the kinetic and controlling parameter  $\mu$  on the evolution of concentration of X estimated from equations (60) to (62).

## 7. Linear Stability Analysis

Consider the state variables  $X_1, \dots, X_i$ , which are continuously subjected to either internal fluctuations or external perturbations, and are represented by a column vector  $\mathbf{X}$ , for which the evolution is expressed by

$$\frac{\partial \mathbf{X}}{\partial t} = f(\mathbf{X}, \mu) \quad (63)$$

Here  $f$  is mainly a nonlinear space operator, and  $\mu$  denotes a set of controlling parameters affecting the evolution, such as thermal conductivity, or chemical rate constants, or concentrations of reactants and products (Nicolis and Prigogine, 1989; Szili and Toth, 1995). The components  $\{X_{is}\}$  represent the stationary and spatially uniform solution, since the reference state  $\mathbf{X}_s$  is a particular solution of equation (63). Stability analysis checks if the stationary solutions will be remain stable to small perturbations of  $\mathbf{x}$

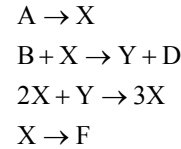
$$\mathbf{X} = \mathbf{X}_s + \mathbf{x}(t) \quad (64)$$

Using equation (64) in equation (63), and by retaining the linear terms only in the Taylor expansion of  $f$ , we obtain

$$\frac{\partial \mathbf{x}}{\partial t} = f([\mathbf{X}_s + \mathbf{x}], \mu) - f(\mathbf{X}_s, \mu) = [\mathbf{a}]\mathbf{x} \quad (65)$$

where  $[\mathbf{a}]$  is the Jacobian matrix with the elements of  $(\partial f_i / \partial X_j)_s$  calculated at stationary state.

A well-known case study is the Brusselator system representing a trimolecular model given by



In the limit of irreversible reactions with the rate constants are unity in a well-stirred reactor, the evolution equations for X and Y become

$$\frac{dX}{dt} = f_1[X, Y, \mu(A, B)] = A - BX + X^2Y - X \quad (66)$$

$$\frac{dY}{dt} = f_2[X, Y, \mu(A, B)] = BX - X^2Y \quad (67)$$

Here the concentrations A and B are specified. Equations (66) and (67) have the stationary solutions of  $X_s = A$ , and  $Y_s = B/A$ . Equation (65) is expressed by

$$\frac{\partial}{\partial t} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{bmatrix} (B-1)x + A^2y + z(x, y) \\ -Bx - A^2y - z(x, y) \end{bmatrix} \quad (68)$$

where  $z(x, y, \lambda) = B/A x^2 + 2Axy + x^2y$  that has quadratic perturbations, and may be neglected. However, when the medium is unstirred and mass transfer is by diffusion only, we have

$$\begin{aligned} \begin{pmatrix} \delta f \\ \delta \mathbf{X} \end{pmatrix}_s &= \begin{pmatrix} B-1 + D_X \nabla^2 & A^2 \\ -B & -A^2 + D_Y \nabla^2 \end{pmatrix} \\ &= \begin{pmatrix} \frac{\partial f_1}{\partial X} & \frac{\partial f_1}{\partial Y} \\ \frac{\partial f_2}{\partial X} & \frac{\partial f_2}{\partial Y} \end{pmatrix} \end{aligned} \quad (69)$$

The Brusselator system that models RD system solved in terms of time and space using the grids of  $N$  and the grid length parameter  $\Delta X$  is shown in Figure 2.

Stability of the stationary states depends on whether the perturbation  $\mathbf{x}$  grows or decays with time. This depends on the eigenvalues of the Jacobian matrix. equation (65) admits solution of the form:

$$\mathbf{x} = \mathbf{u}e^{\lambda t} \quad (70)$$

Here  $\lambda_s$  is the eigenvalue of the Jacobian matrix, usually a complex-valued quantity, and  $\mathbf{u}$  is the

eigenvector. Regardless of whether the eigenvalues are real or complex, the steady state is stable to small perturbations if the two conditions  $\text{tr}[\alpha] < 0$  and  $\text{Det}[\alpha] > 0$  are satisfied simultaneously. If the conditions reach equality then bifurcation with both deterministic and probabilistic elements occurs; fluctuations in the vicinity of the bifurcation points may determine the branch, while only an appropriate nonlinear differential model can describe the evolution of system (Nicolis and Prigogine, 1989, Kondepudi and Prigogine, 1999).

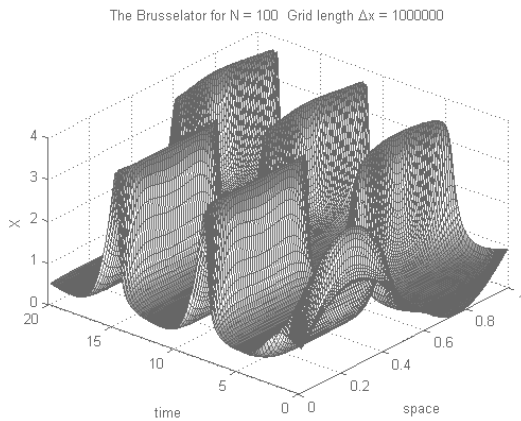


Figure 2. Order in space and time in the Brusselator system

Substitution of equation (70) into (65) yields

$$\alpha(\mu) \cdot \mathbf{u} = \lambda \mathbf{u} \quad (71)$$

This relation, with appropriate boundary conditions, defines an eigenvalue problem; with  $N$  eigenvalues and  $N$  eigenvectors, and the solution would be

$$\mathbf{x} = \sum_i^N c_i \mathbf{u} \exp(\lambda_i t) \quad (72)$$

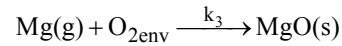
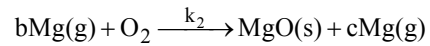
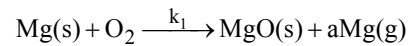
where the constants  $c_i$  can be obtained from the initial conditions. If one or more eigenvalues have a positive real part, then the perturbations grow exponentially, and the corresponding eigenvectors are called unstable modes. If all the eigenvalues, on the other hand, were negative real parts, the perturbations would decay and provide the stability in the vicinity of the stationary solution.

## 8. Case Studies

### 8.1 Reaction diffusion model

The linear stability analysis (Zhu and Li, 2002) may be used to investigate the evolution of a reaction-diffusion model of solid-phase combustion (Feng et al., 1996). The diffusion coefficients of the oxygen and magnesium(g) are

the two controlling parameters beside the kinetics



The flows of Mg and O<sub>2</sub> are:  $\text{Mg(g)} \xrightarrow{k_4} \text{MgO(g)}_{\text{env}}$  and  $\text{O}_2 \xleftarrow{k_5} \text{O}_{2\text{env}}$ ; by assuming that X denotes O<sub>2</sub>, and Y denotes Mg(g), mass-action law yields

$$\frac{dX}{dt} = -k_1 X - k_2 X Y^b + k_5 (X_0 - X) \quad (73)$$

$$\frac{dY}{dt} = a k_1 X + (c-b) k_2 X Y^b - k_3 Y + k_4 (Y_0 - Y) \quad (74)$$

For the combustion equation (65) becomes

$$\frac{dx}{d\tau} = -w x - x y^b + \frac{1-x}{t_0} \quad (75)$$

$$\frac{dy}{d\tau} = a w x + (c-b) x y^b - u y + \frac{y_0 - y}{t_1} \quad (76)$$

where

$$x = \frac{X}{X_0}; y = \frac{Y}{X_0}; \tau = k_2 X_0^b t; w = -\frac{k_1}{k_2 X_0^b};$$

$$v = \frac{k_3}{k_2 X_0^b}; t_0 = \frac{k_2 X_0^b}{k_5}; t_1 = \frac{k_2 X_0^b}{k_4}$$

With the following numerical values:  $a = 1$ ,  $b = 2$ ,  $c = 3$ ,  $w = 1/650$ ,  $v = 1/20$ , and  $y_0 = 0.006$  [Feng et al., 1996], equations (75) and (76) become

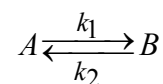
$$\frac{dx}{d\tau} = -\left(\frac{1}{650}\right)x - x y^2 + \frac{1-x}{t_0} \quad (77)$$

$$\frac{dy}{d\tau} = \left(\frac{1}{650}\right)x + x y^2 - \left(\frac{1}{20}\right)y + \frac{0.006 - y}{t_1} \quad (78)$$

The characteristic equation in terms of two controlling parameters  $t_0$  and  $t_1$  is obtained from the eigenvalue problem of equations (77) and (78). As the parameters  $t_0$  and  $t_1$  contain kinetics and transport coefficients, they represent a combined effect, and make the study more interesting and complex.

### 8.2. Adiabatic stirred flow reactor

Consider the following reaction (Dimmers, and Tells, 1974)



The reaction occurs in an adiabatic stirred flow reactor with feed flow rate  $F$ , transient compositions  $c_A, c_B$  and reaction rate  $J_r$ , and total mass of reacting mixtures  $M$ . For small perturbations around the stationary state (s), the following expansions are used

$$\begin{aligned} c_A(t) &= c_{As} + \delta c_A(t) \\ c_B(t) &= c_{Bs} + \delta c_B(t) \\ T(t) &= T_s + \delta T(t) \end{aligned} \quad (79)$$

$$J_r(c_A, c_B, T) = J_{rs}(c_{As}, c_{Bs}, T_s) + \delta J_r(c_A, c_B, T) \quad (80)$$

to find the differential model equations of heat and mass balances

$$\frac{d(\delta c_A)}{dt} = -\frac{F}{M} \delta c_A - \delta J_r \quad (81)$$

$$\frac{d(\delta c_B)}{dt} = -\frac{F}{M} \delta c_B + \delta J_r \quad (82)$$

$$\frac{d(\delta T)}{dt} = -\frac{F}{M} \delta T + \frac{Q}{C_p} \delta J_r \quad (83)$$

In stable systems such disturbances vanish in time and the stationary values are restored. For very small perturbations, the reaction rate disturbance may be expanded with negligible second order and higher terms as follows

$$\begin{aligned} \delta J_r &= \left( \frac{\partial J_r}{\partial c_A} \right)_s \delta c_A + \\ &\quad \left( \frac{\partial J_r}{\partial c_B} \right)_s \delta c_B + \left( \frac{\partial J_r}{\partial T} \right)_s \delta T \end{aligned} \quad (84)$$

This expansion may lead to linearization of differential equations (81) to (83).

In the NET theory, the stability of stationary states is associated with Prigogine's principle of minimum entropy production; applicability of the Prigogine's principle is restricted to stationary states close to global thermodynamic equilibrium where the entropy production serves a Lyapunov function (Bernstein et al., 1993). The principle is not applicable to the stability of continuous reaction systems involving stable and unstable steady states far from global equilibrium. The rate of entropy production is

$$P = \left( \frac{d_i S}{dt} \right) = \frac{1}{T} \frac{dq}{dt} - \sum_i \frac{\mu_i}{T} \frac{dc_i}{dt} \quad (85)$$

and

$$d_x P = \sum_k J_k dX_k = \frac{dq}{dt} d\left(\frac{1}{T}\right) - \sum_i \frac{dc_i}{dt} d\left(\frac{\mu_i}{T}\right) \quad (86)$$

with the differentials defined approximately (Dammers and Tels, 1974) as

$$\begin{aligned} \frac{dq}{dt} &= \frac{d}{dt} (h_A \delta c_A + h_B \delta c_B + C_p \delta T); \\ d\left(\frac{\mu_i}{T}\right) &= R \left( \frac{d(\delta c_i)}{c_{is}} - \frac{h_i}{RT_s} \frac{d(\delta T)}{T_s} \right); \\ d\left(\frac{1}{T}\right) &= -\left( \frac{d(\delta T)}{T_s^2} \right) \end{aligned}$$

Equation (86) becomes

$$d_x P = -R \left( \frac{d(\delta c_A)}{dt} \frac{d(\delta c_A)}{c_{As}} + \frac{d(\delta c_B)}{dt} \frac{d(\delta c_B)}{c_{Bs}} + \frac{C_p}{RT_s} \frac{d(\delta T)}{dt} \frac{d(T)}{T_s} \right) \quad (87)$$

Equation (87) can be used in equation (43) or equation (44) for stability analysis in near global equilibrium.

Tarbel (1977) used the thermodynamic Lyapunov function, which resembles the thermodynamic entropy production function and the asymptotic stability principle. If the eigenvalues of the coefficient matrix of the quadratic form of the entropy production are very large, then the convergence to equilibrium state will be rapid (Edelen, 1975).

### 8.3. Flow in porous medium: diffusion & adsorption controlled flow

The stability of boundary-layer fluxes with diffusion and interfacial coupling is governed by an eigenvalue problem (Halatchev and Denier, 2003). In porous medium, instability may be related with the temperature dependence of the viscosity, thus with the pressure drop for Darcy flow in the porous combustor. A linear stability analysis with perturbation equations with respect to steady state can be used for the thermal instability mechanism (Capitained, 2003; Albers, 2003; Sureskumar, 2001; Lombardo and Mulone, 2002). One example is the stress-induced migration for dilute polymer solutions in the Taylor-Couette device, consisting concentric cylinders rotating at constant velocities (Apostolakis et al., 2002). The Lyapunov functional is used for nonlinear stability of nonlinear diffusion (Flavin and Rionero, 1999).

## 9. Order in Space and Time

Spatiotemporal organizations and the stability and robustness of chemical and biological systems keep attracting growing number of scientists (Othmer and Scriven 1971; Izus et al., 1995; Maini, 1996; Collier et al.,

1996; Maini et al., 1997; Klein and Seelig, 1995; Szili and Toth, 1995; Klein and Mayer, 1997; Klein, 1998; Plahte, 2001). Mainly the Turing instability leads to steady pattern and the Hopf instability leads to oscillation. However, another two examples of Turing instabilities in coupled systems deserve attention. One of them occurs in inhomogeneous arrays of diffusively coupled reactors (Horsthemke and Moore, 2004), and the other results with two coupled layers; one of them supports oscillatory Turing patterns, while the other the stationary Turing structure (Yang and Epstein, 2003). Therefore, the coupling phenomena may add complexity to order in space through temporal patterns.

Biological cells do not exchange species only but signals in highly nonlinear manner (Collier et al., 1996). Continuous models are only applicable to systems where the cell-cell interaction is well approximated by diffusion. For diffusion driven models, the stationary states are stable as long as the number of cells is small, and destabilizes when the number of cells in the lattice increases beyond a certain bifurcation value. Different phase space perturbations from the homogeneous state lead the system to completely different patterned states. The pattern of the final state is influenced by the initial perturbation along an unstable lattice vector (Barkai and Leibler, 1997; Plahte, 2001). For signal driven models the homogeneous state is mainly unstable and independent of the number of cells in the lattice (Allaerts and Roelants, 1995).

Linear Turing analysis may predict patterns, while nonlinear analysis can be useful in explaining them (Murray, 1993). In discrete cellular systems, the eigenvector and eigenvalue analysis of the homogeneous state shows that the set of lattice vectors provides a natural basis for describing the final spatial patterns for each species. Linear analysis gives at best a prediction of the final pattern, and the effects of boundary and initial conditions on the stability of patterns need more research (Izüs et al., 1995). In many cases there is no obvious resemblance between the final, unsteady state and the pattern of the unstable mode, or the mode corresponding to the initial perturbation in case for multiple unstable modes. Turing mechanism can only predict a qualitative resemblance of the final state to the lattice vector resulting from the linear analysis. However, linearization of evolution equations using very small perturbations for biological and chemical systems has limitations due to large experimental errors, and the 'response approaches' that avoid linearization developed

by Vlad et al. (2004) may be promising in that respect.

To solve highly nonlinear differential equations for systems far from global equilibrium the method of cellular automata may be used (Ross and Vlad, 1999). For example, for nonlinear chemical reactions, the reaction space is divided into discrete cells where the time is measured, and local and state variables are attached to these cells. By introducing a set of interaction rules consistent with the macroscopic law of diffusion and with the mass action law, semimicroscopic to macroscopic rate processes or reaction-diffusion systems can be described.

## 10. Conclusions

Thermodynamics play important role in stability of equilibrium and nonequilibrium systems of transport and rate processes. Entropy production approach for nonequilibrium systems appear to be more general in stability analysis. One major implication of the NET theory is the introduction of distance from global equilibrium as another constraint for organized states and hence the instability of nonequilibrium systems.

## Nomenclature

A	affinity (J mol <sup>-1</sup> )
c	concentration (mol m <sup>-3</sup> ),
D	diffusion coefficient (m <sup>2</sup> s <sup>-1</sup> )
F	force per unit mass (kg m s <sup>-2</sup> kg <sup>-1</sup> )
G	Gibbs' free energy (J)
$\bar{h}$	partial specific enthalpy (J mol <sup>-1</sup> )
h	enthalpy (J)
H <sub>r</sub>	heat of reaction (J mol <sup>-1</sup> )
J <sub>q</sub>	heat flux (J m <sup>-2</sup> s <sup>-1</sup> )
J <sub>i</sub>	mass flux for component i (kg m <sup>-2</sup> s <sup>-1</sup> )
J <sub>r</sub>	reaction velocity (flux)
k	thermal conductivity (J m <sup>-1</sup> s <sup>-1</sup> K), reaction rate constant (s <sup>-1</sup> ),
L <sub>ij</sub>	phenomenological coefficient (conductance form)
M	molar mass
n	number of components
N <sub>k</sub>	number of moles
P	pressure (Pa)
r	reaction rate (mol s <sup>-1</sup> )
R	universal gas constant (J mol <sup>-1</sup> K <sup>-1</sup> )
s	entropy density (J K <sup>-1</sup> m <sup>-3</sup> )
S	entropy (J mol <sup>-1</sup> K <sup>-1</sup> )
t	time (s)
T	temperature (K)
u	energy density (J m <sup>-3</sup> )
U	internal energy (J)
v	velocity (m s <sup>-1</sup> )
V	volume (m <sup>3</sup> )
w	mass fraction
X	thermodynamic driving force

## Greek Letters

$\Phi$	entropy production rate ( $\text{J K}^{-1} \text{s}^{-1}$ )
$\mu$	chemical potential ( $\text{J mol}^{-1}$ )
$\nu$	stoichiometric coefficients
$\rho$	density ( $\text{kg m}^{-3}$ )
$\tau$	shear stress ( $\text{kg m}^{-1} \text{s}^{-2}$ )
$\Psi$	dissipation function ( $\text{J s}^{-1}$ )

## Subscripts

b,f	backward and forward respectively
eq	equilibrium
i,j,k	components
s	stationary state

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