

Part V

Order Through Fluctuations

18

Nonlinear Thermodynamics

18.1 Far-from-Equilibrium Systems

Systems that are subject to a flow of energy and matter can be driven far from thermodynamic equilibrium, into the ‘nonlinear’ regime. In the nonlinear regime, the thermodynamic flows J_α are no longer linear functions of thermodynamic forces F_α . In the case of chemical reactions, we have seen that a system is in the linear regime if the affinities A_k are small compared to RT , i.e. $|A_k/RT| \ll 1$. The value of RT at $T = 300$ K is about 2.5 kJ mol⁻¹. Since the affinities of chemical reactions can easily reach the range 10 – 100 kJ mol⁻¹, the nonlinear regime is easily reached for chemical processes (Exercise 18.1). It is more difficult to reach the nonlinear regime for transport processes such as heat conduction and diffusion.

In Nature, far-from-equilibrium systems are ubiquitous. The Earth as a whole is an open system subject to the constant flow of energy from the Sun. This influx of solar energy sustains the biosphere, and is ultimately responsible for maintaining an atmosphere out of thermodynamic equilibrium (Exercise 18.2). Every living cell lives through the flow of matter and energy.

As we shall see in the following sections, far-from-equilibrium states can lose their stability and evolve to one of the many states available to the system. Irreversible processes and the boundary conditions do not uniquely specify the nonequilibrium state to which the system will evolve; driven by internal fluctuations or other small external influences, the system leaves the unstable state and evolves to one of the many possible new states. These new states can be highly organized and are called **dissipative structures**.

Dissipative structures behave in an unpredictable way. Small external influences play a significant role; causes that determine the behavior of the system are no longer within the system. It becomes extremely difficult, if not impossible, to approximate such systems as isolated or closed systems. As for the certainty of Newtonian and Laplacian planetary motion and the uniqueness of equilibrium states, both begin to fade; we see instead a probabilistic Nature that generates new organized structures, a Nature that can create living organisms.

18.2 General Properties of Entropy Production

In the linear regime we saw that the stationary states are those in which the total entropy production $P = \int_V \sigma \, dV$ reaches a minimum. This criterion also assured the stability of the stationary state. In the

far-from-equilibrium nonlinear regime, there is no such general principle for determining the state of the system. Far-from-equilibrium states can become unstable and evolve to new organized states and we will identify the thermodynamic conditions under which this may happen.

We begin by noting some general properties of the total entropy production P . These are statements regarding the time evolution of change δP due to small changes in the forces δF_k and the flows δJ_k . Let P be the entropy production in a nonequilibrium stationary state. Since $P = \int_V \sigma \, dV = \int_V \sum_k F_k J_k \, dV$, the rate of change in P can be written as

$$\begin{aligned} \frac{dP}{dt} &= \int_V \left(\frac{d\sigma}{dt} \right) dV = \int_V \left(\sum_k \frac{dF_k}{dt} J_k \right) dV + \int_V \left(\sum_k F_k \frac{dJ_k}{dt} \right) dV \\ &\equiv \frac{d_F P}{dt} + \frac{d_J P}{dt} \end{aligned} \quad (18.2.1)$$

in which $d_F P/dt$ is the change due to the changes in F_k and $d_J P/dt$ is the change due to the changes in J_k . Two general properties can now be stated [1–3]:

a. In the linear regime:

$$\boxed{\frac{d_F P}{dt} = \frac{d_J P}{dt}} \quad (18.2.2)$$

b. For time-independent boundary conditions, even outside the linear regime:

$$\boxed{\frac{d_F P}{dt} \leq 0} \quad (18.2.3)$$

($d_F P/dt = 0$ at the stationary state).

In contrast to the variation dG in the Gibbs free energy G , $d_F P$ is not a differential of a state function. Hence the fact that $d_F P$ can only decrease does not tell us how the state will evolve.

The first of the above relations follows from the linear relations $J_k = \sum_i L_{ki} F_i$ and the Onsager reciprocal relations $L_{ki} = L_{ik}$. First we note that

$$\sum_k dF_k J_k = \sum_{ki} dF_k L_{ki} F_i = \sum_{ki} (dF_k L_{ik}) F_i = \sum_i dJ_i F_i \quad (18.2.4)$$

Using this result in the definitions of $d_F P$ and $d_J P$ in Equation (18.2.1), we immediately see that

$$\frac{d_F P}{dt} = \int_V \left(\sum_k \frac{dF_k}{dt} J_k \right) dV = \int_V \left(\sum_k F_k \frac{dJ_k}{dt} \right) dV = \frac{d_J P}{dt} = \frac{1}{2} \frac{dP}{dt} \quad (18.2.5)$$

The general property (18.2.3) when applied to Equation (18.2.5) gives us the result we have seen in the previous chapter:

$$\frac{dP}{dt} = 2 \frac{d_F P}{dt} < 0 \quad \text{in the linear regime} \quad (18.2.6)$$

This shows, once again, that a perturbation in the total entropy production P from its stationary state value will monotonically decrease to its stationary state value, in accordance with the principle of minimum entropy production. A simple proof of Equation (18.2.3) is given in Appendix 18.1.

We see that we now have two inequalities, $P \geq 0$ and $d_{\text{F}}P \leq 0$. The second inequality is an important evolution criterion. Let us indicate briefly two consequences for a homogeneous system of unit volume. If only one concentration, say X , is involved in the evolution, $d_{\text{F}}P = v(X) (\partial A / \partial X) dX \equiv dW$. The variable W , thus defined, is then a ‘kinetic potential’. However, this is rather an exceptional case. The interesting consequence is that time-independent constraints may lead to states that are not stationary, states that oscillate in time. We shall see examples of such systems in Chapter 19, but let us consider here a simple example of a far-from-equilibrium chemical system where the dependence of velocities on affinities are antisymmetric, i.e. $v_1 = lA_2$, $v_2 = -lA_1$ (Onsager’s relations are not valid for systems far from equilibrium). The derivative $d_{\text{F}}P/dt$ in this case becomes

$$\frac{1}{V} \frac{d_{\text{F}}P}{dt} = v_1 \frac{dA_1}{dt} + v_2 \frac{dA_2}{dt} = lA_2 \frac{dA_1}{dt} - lA_1 \frac{dA_2}{dt} \leq 0 \quad (18.2.7)$$

By introducing the polar coordinates $A_1 = r \cos \theta$ and $A_2 = r \sin \theta$, it is easy to see that this equation can be written as

$$\frac{1}{V} \frac{d_{\text{F}}P}{dt} = -lr^2 \frac{d\theta}{dt} \leq 0 \quad (18.2.8)$$

The system rotates irreversibly in a direction determined by the sign of l . An example of such a system is the well-known Lotka–Volterra ‘prey–predator’ interaction given as an exercise (Exercise 18.9). We can also apply this inequality to derive a *sufficient condition* for the stability of a steady state. If all fluctuations $\delta_{\text{F}}P > 0$ then the steady state is stable. However, here it is more expedient to use the Lyapunov theory of stability to which we turn now.

18.3 Stability of Nonequilibrium Stationary States

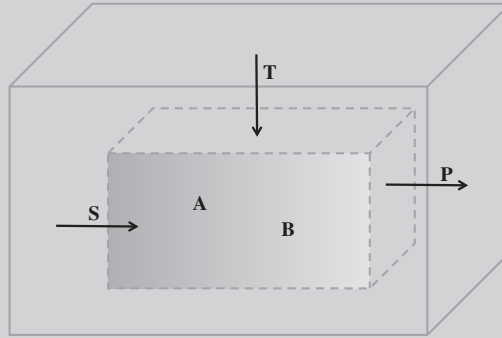
A very general criterion for stability of a state was formulated by Lyapunov [4]. We shall obtain the conditions for the stability of a nonequilibrium state using Lyapunov’s theory.

18.3.1 Lyapunov’s Theory of Stability

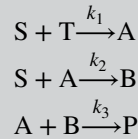
Lyapunov’s formulation gives conditions for stability in precise mathematical terms (with clear intuitive meaning). Let X_s be a stationary state of a physical system. In general, X may be an r -dimensional vector with components X_k , $k = 1, 2, \dots, r$. We shall denote the components of X_s by X_{sk} . Let the time evolution of X be described by an equation

$$\frac{dX_k}{dt} = Z_k(X_1, X_2, \dots, X_r; \lambda_j) \quad (18.3.1)$$

in which the λ_j are parameters that may or may not be independent of time. A simple example of such an equation is given in Box 18.1. In general, if the X_k are functions not only of time t but also of positions \mathbf{x} , then Equation (18.3.1) will be a partial differential equation in which Z_k will be a partial differential operator.

Box 18.1 Kinetic equations and Lyapunov stability theory: an example

Consider the open chemical system shown above with the following chemical reactions:



For simplicity, we assume that the reverse reactions can be ignored. If the system is subject to an inflow of S and T and an outflow of P such that the concentrations of these species are maintained constant, we have the following kinetic equations for the concentrations of A and B:

$$\begin{aligned} X_1 &\equiv [A], & X_2 &\equiv [B] \\ \frac{dX_1}{dt} &= k_1[S][T] - k_2[S]X_1 - k_3X_1X_2 \equiv Z_1(X_j, [S], [T]) \\ \frac{dX_2}{dt} &= k_2[S]X_1 - k_3X_1X_2 \equiv Z_2(X_j, [S], [T]) \end{aligned}$$

In this system, [S] and [T] correspond to the parameters λ_j in Equation (18.3.1). For a given value of these parameters, the stationary states X_{s1} and X_{s2} are easily found by setting $dX_1/dt = dX_2/dt = 0$:

$$X_{s1} = \frac{k_1[T]}{2k_2}, \quad X_{s2} = \frac{k_2[S]}{k_3}$$

The stability of this stationary state is determined by examining the evolution of the perturbations δX_1 and δX_2 from this stationary state. A possible Lyapunov function L , for example, is

$$L(\delta X_1, \delta X_2) = [(\delta X_1)^2 + (\delta X_2)^2] > 0$$

If it can be shown that $dL(\delta X_1, \delta X_2)/dt < 0$, then the stationary state (X_{s1}, X_{s2}) is stable.

The stationary state X_{sk} is the solution to the set of coupled equations

$$\frac{dX_k}{dt} = Z_k(X_{s1}, X_{s2}, \dots, X_{sr}; \lambda_j) = 0 \quad (k = 1, 2, \dots, r) \quad (18.3.2)$$

The stability of the stationary state can be understood by looking at the behavior of a small perturbation δX_k . To establish the stability of a state, first a *positive function* $L(\delta X)$ of δX , which may be called a ‘distance’, is defined in the space spanned by X_k . If this ‘distance’ between X_{sk} and the perturbed state ($X_{sk} + \delta X_k$) steadily decreases in time, the stationary state is stable. Thus state X_{sk} is stable if

$$\boxed{L(\delta X_k) > 0 \quad \frac{dL(\delta X_k)}{dt} < 0} \quad (18.3.3)$$

A function L that satisfies Equation (18.3.3) is called a **Lyapunov function**. If the variables X_k are functions of position (as concentrations n_k in a nonequilibrium system can be), L is called a **Lyapunov functional** – a ‘functional’ is a mapping of a set of functions to a number, real or complex. The notion of stability is not restricted to stationary states; it can also be extended to periodic states [4]. However, since we are interested in the stability of nonequilibrium stationary states, we shall not deal with the stability of periodic states at this point.

18.3.2 Second Variation of Entropy – $\delta^2 S$ as a Lyapunov Functional

We have already seen that the second variation of entropy is a function that has a definite sign for any thermodynamic system in local equilibrium. By considering the entropy density $s(\mathbf{x})$ as a function of the energy density $u(\mathbf{x})$ and the concentrations $n_k(\mathbf{x})$, we can write ΔS , the change in entropy from the stationary value, in the form

$$\begin{aligned} \Delta S &= \int \left[\left(\frac{\partial s}{\partial u} \right)_{n_k} \delta u + \sum_k \left(\frac{\partial s}{\partial n_k} \right)_u \delta n_k \right] dV \\ &+ \frac{1}{2} \int \left[\left(\frac{\partial^2 s}{\partial u^2} \right) (\delta u)^2 + 2 \sum_k \left(\frac{\partial^2 s}{\partial u \partial n_k} \right) \delta u \delta n_k + \sum_{ij} \left(\frac{\partial^2 s}{\partial n_i \partial n_j} \right) \delta n_i \delta n_j \right] dV \\ &= \delta S + \frac{1}{2} \delta^2 S \end{aligned} \quad (18.3.4)$$

Since we are considering a nonequilibrium stationary state, the thermodynamic forces and the corresponding flows of energy, \mathbf{J}_u , and matter, \mathbf{J}_k , do not vanish. Hence the first variation $\delta S \neq 0$. The second variation, $\delta^2 S$, has a definite sign because the integrand, which is the second variation of entropy of elemental volume that is locally in equilibrium, is negative (Equation (12.4.10)):

$$\frac{1}{2} \delta^2 S < 0 \quad (18.3.5)$$

Appendix 18.2 contains the derivation of the following general result:

$$\boxed{\frac{d}{dt} \frac{\delta^2 S}{2} = \int_V \sum_k \delta F_k \delta J_k dV} \quad (18.3.6)$$

In Chapter 14 (Equation (14.1.16)) we obtained the same equation for perturbations from the equilibrium state. Equation (18.3.6) shows that the time derivative of $\delta^2 S$ has the same form even under nonequilibrium conditions. The difference is that near equilibrium $\sum_k \delta F_k \delta J_k = \sum_k F_k J_k > 0$; but it is not necessarily so far from equilibrium. We shall refer to this quantity as **excess entropy production**, but, strictly speaking, it is the increase in entropy production only near the equilibrium state; for a perturbation from a nonequilibrium state, the increase in entropy production is equal to $\delta P = \delta_F P + \delta_J P$.

Expressions (18.3.5) and (18.3.6) would define a Lyapunov functional, $L = -\delta^2 S/2$ if the stationary state were such that $\sum_k \delta F_k \delta J_k > 0$. Thus, a nonequilibrium stationary state is stable if

$$\frac{d}{dt} \frac{\delta^2 S}{2} = \int_V \sum_k \delta F_k \delta J_k dV > 0 \quad (18.3.7)$$

If this inequality is violated, it only means that the system *may* be unstable; i.e. $\sum_k \delta F_k \delta J_k < 0$ is a necessary but not a sufficient condition for instability.

18.3.3 Using the Stability Criterion

Since $\delta^2 S < 0$ under both equilibrium and nonequilibrium conditions, the stability of a stationary state is assured if

$$\frac{d}{dt} \frac{\delta^2 S}{2} = \int_V \sum_k \delta F_k \delta J_k dV > 0 \quad (18.3.8)$$

Let us apply this condition to simple chemical systems to understand when a nonequilibrium system may become unstable.

First, let us consider the following reaction:



Assuming these reactions are elementary steps, we write the forward and reverse rates as

$$R_f = k_f[A][B] \quad \text{and} \quad R_r = k_r[C][D] \quad (18.3.10)$$

We assume this system is maintained out of equilibrium by suitable flows. As we have seen in Section 9.5, for a chemical reaction the affinity A and the velocity of reaction v are given by $A = RT \ln(R_f/R_r)$ and $v = (R_f - R_r)$. The time derivative of $\delta^2 S$, the ‘excess entropy production’ (18.3.8), can be written in terms of $\delta F = \delta A/T$ and $\delta J = \delta v$. For a perturbation $\delta[B]$ from the stationary state, it is easy to show that (Exercise 18.4)

$$\frac{1}{2} \frac{d\delta^2 S}{dt} = \int_V \sum_\alpha \delta J_\alpha \delta F_\alpha dV = \int_V \sum_\alpha \frac{\delta A}{T} \delta v dV = Rk_f \int_V \frac{[A]_s}{[B]_s} (\delta[B])^2 dV > 0 \quad (18.3.11)$$

in which the subscript s indicates the nonequilibrium stationary state values of the concentrations. Since $d\delta^2 S/dt$ is positive, the stationary state is stable.

The situation is different, however, for an *autocatalytic* reaction such as



which appears in a reaction scheme called the ‘Brusselator’, which we will consider in the next chapter. For this reaction, we can consider a nonequilibrium stationary state in which the concentrations are $[X]_s$ and $[Y]_s$ and a perturbation δX . Using the forward and reverse rates $R_f = k_f[X]^2[Y]$ and $R_r = k_r[X]^3$ in the expressions $A = RT \ln(R_f/R_r)$ and $v = (R_f - R_r)$, we can once again calculate the excess entropy production to obtain

$$\frac{1}{2} \frac{d\delta^2 S}{dt} = \int_V \frac{\delta A}{T} \delta v dV = -R \int_V (2k_f[X]_s[Y]_s - 3k_r[X]_s^2) \frac{(\delta X)^2}{[X]_s} dV \quad (18.3.13)$$

The excess entropy production can now become negative, particularly if $k_f \gg k_r$. Hence the stability is no longer assured and the stationary state *may* become unstable.

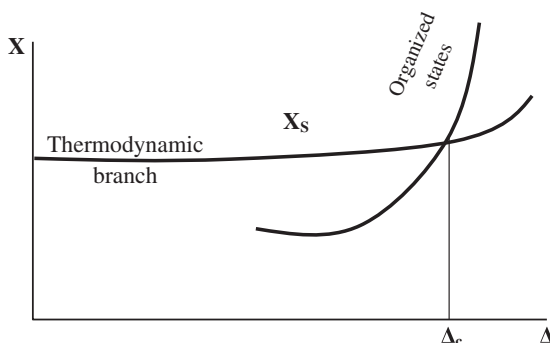


Figure 18.1 Each value of X represents a state of the system. The distance from equilibrium is represented by the parameter Δ . When $\Delta = 0$ the system is in a state of thermodynamic equilibrium. When Δ is small, the system is in a near-equilibrium state, which is an extrapolation of the equilibrium state; this family of states is called the thermodynamic branch. In some systems, such as those with autocatalysis, when Δ reaches a critical value Δ_c , the states belonging to the thermodynamic branch become unstable. When this happens, the system makes a transition to a new branch, which may correspond to organized states.

The above discussion can be summarized through a stability diagram, as shown in Figure 18.1. The value of the parameter Δ is a measure of the distance from equilibrium. For each value of Δ the system will relax to a stationary state, denoted by X_s . The equilibrium state corresponds to $\Delta = 0$; X_s is a continuous extension of the equilibrium state and is called the **thermodynamic branch**. As long as condition (18.3.8) is satisfied, the thermodynamic branch is stable; if it is violated, the thermodynamic branch *may* become unstable. If it does become unstable, the system makes a transition to a new branch, which is generally an organized structure.

If the kinetic equations of the systems are known, there is a well-defined mathematical method to determine at what point the stationary state will become unstable. This is the linear stability analysis we will discuss in the following section. Nonequilibrium instabilities give rise to a great variety of structures, which we will discuss in the next chapter.

18.4 Linear Stability Analysis

In general, the rate equations of a homogeneous chemical system take the general form:

$$\frac{dX_k}{dt} = Z_k(X_1, \dots, X_n; \lambda_j) \quad (18.4.1)$$

where the X_k correspond to concentrations, such as $[X]$ and $[Y]$ in Equation (18.3.12), and λ_j corresponds to concentrations that are maintained at a constant nonequilibrium value. We begin by assuming that a stationary solution X_k^0 of Equation (18.4.1) is known. This means

$$Z_k(X_1^0, \dots, X_n^0, \lambda_j) = 0 \quad (18.4.2)$$

We would like to know if this stationary solution will be stable to small perturbations x_j . Linear stability analysis provides the answer in the following way. Consider a small perturbation x_k :

$$X_k = X_k^0 + x_k(t) \quad (18.4.3)$$

Now the Taylor expansion of $Z_k(X_i)$ gives

$$Z_k(X_i^0 + x_i) = Z_k(X_i^0) + \sum_j \left(\frac{\partial Z_k}{\partial X_j} \right)_0 x_j + \dots \quad (18.4.4)$$

in which the subscript 0 indicates that the derivative is evaluated at the stationary state X_i^0 . In linear stability analysis, only the linear terms in x_j are retained; the higher-order terms are neglected by assuming the x_j are small. Substituting Equation (18.4.4) into Equation (18.4.1), since X_i^0 is a stationary state, we obtain for $x_k(t)$ the linear equation

$$\frac{dx_k}{dt} = \sum_j \Lambda_{kj}(\lambda) x_j \quad (18.4.5)$$

in which $\Lambda_{kj}(\lambda) = (\partial Z_k / \partial X_j)_0$ is a function of the parameter λ . In matrix notation, Equation (18.4.5) can be written as

$$\frac{d\mathbf{x}}{dt} = \Lambda \mathbf{x} \quad (18.4.6)$$

in which the vector $\mathbf{x} = (x_1, x_2, x_3, \dots, x_n)$ and Λ_{kj} are the elements of the matrix Λ . The matrix Λ is sometimes referred to as the **Jacobian matrix**.

The general solution of Equation (18.4.6) can be written if the eigenvalues and the eigenvectors of the matrix Λ are known. Let ω_k be the eigenvalues and $\boldsymbol{\psi}_k$ the corresponding eigenvectors:

$$\Lambda \boldsymbol{\psi}_k = \omega_k \boldsymbol{\psi}_k \quad (18.4.7)$$

In general, for an n -dimensional matrix there are n eigenvalues and n eigenvectors. (Note that $\boldsymbol{\psi}_k$ is a vector and the subscript k indicates different vectors.) If the eigenvalues ω_k and the eigenvectors $\boldsymbol{\psi}_k$ are known, it is easy to see that, corresponding to each eigenvector and its eigenvalue, we have the following solution to Equation (18.4.6):

$$\mathbf{x} = e^{\omega_k t} \boldsymbol{\psi}_k \quad (18.4.8)$$

This can be easily seen by substituting Equation (18.4.8) into Equation (18.4.6). Since a linear combination of solutions of a linear equation is also a solution, the general solution to Equation (18.4.6) can be written as

$$\mathbf{x} = \sum_k c_k e^{\omega_k t} \boldsymbol{\psi}_k \quad (18.4.9)$$

in which the coefficients c_k are determined by \mathbf{x} at $t = 0$. Now the question of stability depends on whether the perturbation \mathbf{x} will grow or decay with time. Clearly, this depends on the eigenvalues ω_k : if one or more of the eigenvalues have a positive real part, the associated solutions (18.4.8) will grow exponentially. The corresponding eigenvectors are called **unstable modes**. Since a random perturbation will be of the form (18.4.9), which includes the unstable modes, the existence of a single eigenvalue with a positive real part is sufficient to make the perturbation grow with time. If all the eigenvalues have negative real parts, any small perturbation \mathbf{x} in the vicinity of the stationary solution will exponentially decay or regress to zero. (This need not be true for large perturbations \mathbf{x} for which the approximation (18.4.5) is not valid.)

Thus, a necessary and sufficient condition for the stability of a stationary state is that all eigenvalues of the associated Jacobian matrix, Λ , have negative real parts. An eigenvalue with a positive real part implies instability.

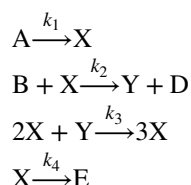
The example given below illustrates the application of the linear stability theory to a chemical system. As we have seen in the previous section, thermodynamic considerations lead us to the conclusion that instability

can arise only when the system is far from thermodynamic equilibrium and, generally, when autocatalysis is present.

The exponential growth of the perturbation does not continue indefinitely; the growth eventually stops due to the nonlinear terms. Through this process, the system makes a transition from an unstable state to a stable state. Thus, driven by instability, the system makes a transition to a new state. This new state is often an organized state, a state with lower entropy. These organized states can be maintained indefinitely as long as the flows are maintained.

18.4.1 An Example

We shall illustrate the use of linear stability theory with the following reaction scheme:



in which we assume A and B are maintained at a constant value while D and E are removed so that all four concentrations are maintained at a constant value. Furthermore, we completely ignore the reverse reactions because we assume their rates to be extremely small. This leads to the following set of kinetic equations that we will study in more detail in the following chapter.

Instead of using X_1 and X_2 , we shall use concentrations $[X]$ and $[Y]$ for the system variables:

$$\frac{d[X]}{dt} = k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X] = Z_1 \quad (18.4.10)$$

$$\frac{d[Y]}{dt} = k_2[B][X] - k_3[X]^2[Y] = Z_2 \quad (18.4.11)$$

Here $[A]$ and $[B]$ are the parameters (concentrations that are maintained at fixed values) corresponding to λ (Equation (18.4.1)). One can easily obtain the stationary solutions to this equation (Example 18.6):

$$[X]_s = \frac{k_1}{k_4}[A], \quad [Y]_s = \frac{k_4 k_2}{k_3 k_1} \frac{[B]}{[A]} \quad (18.4.12)$$

The Jacobian matrix evaluated at the stationary state is

$$\begin{bmatrix} \frac{\partial Z_1}{\partial [X]} & \frac{\partial Z_1}{\partial [Y]} \\ \frac{\partial Z_2}{\partial [X]} & \frac{\partial Z_2}{\partial [Y]} \end{bmatrix} = \begin{bmatrix} -k_2[B] + 2k_3[X]_s[Y]_s - k_4 & k_3[X]_s^2 \\ k_2[B] - 2k_3[X]_s[Y]_s & -k_3[X]_s^2 \end{bmatrix} = \Lambda$$

The product $[X]_s [Y]_s$ in the above matrix can be simplified using Equations (18.4.12) and the resulting matrix has the form:

$$\begin{bmatrix} k_2[B] - k_4 & k_3[X]_s^2 \\ -k_2[B] & -k_3[X]_s^2 \end{bmatrix} = \Lambda \quad (18.4.13)$$

The stationary state (18.4.12) becomes unstable when the real parts of the eigenvalues of (18.4.13) become positive. The **eigenvalue equation** or the **characteristic equation** of a matrix Λ , whose solutions are the eigenvalues, is

$$\text{Det}[\Lambda - \lambda I] = 0 \quad (18.4.14)$$

in which ‘Det’ stands for the determinant. For a 2×2 matrix such as (18.4.13) it is easy to see that the characteristic equation is

$$\lambda^2 - (\Lambda_{11} + \Lambda_{22})\lambda + (\Lambda_{11}\Lambda_{22} - \Lambda_{21}\Lambda_{12}) = 0 \quad (18.4.15)$$

in which Λ_{ij} are the elements of the matrix Λ . If all the matrix elements Λ_{ij} are real, as is the case for chemical systems, the solutions of the characteristic equation must be complex conjugate pairs because coefficients in the equation are real. For the matrix (18.4.13) we shall consider the case of a complex conjugate pair. We shall look at these solutions as functions of the concentration $[B]$ and investigate whether their real parts, which are initially negative, can become positive due to an appropriate change in $[B]$. The point at which the real parts reach zero will be the point of transition from stability to instability.

For Equation (18.4.15), since the coefficient of the linear term is the negative of the sum of the roots (Exercise 18.7), if λ_{\pm} are the two roots, we have

$$\lambda_+ + \lambda_- = (\Lambda_{11} + \Lambda_{22}) = k_2[B] - k_4 - k_3[X]_s^2 \quad (18.4.16)$$

If the real parts of this complex conjugate pair, λ_{\pm} , are negative then $k_2[B] - k_4 - k_3[X]_s^2 < 0$; if they are positive then $k_2[B] - k_4 - k_3[X]_s^2 > 0$.¹ Thus the condition that requires positive real parts for the onset of instability leads to

$$[B] > \frac{k_4}{k_2} + \frac{k_3}{k_2} [X]_s^2$$

or

$$[B] > \frac{k_4}{k_2} + \frac{k_3 k_1^2}{k_2 k_4^2} [A]^2 \quad (18.4.17)$$

where we have used Equation (18.4.12) for $[X]_s$. Thus, for a fixed value of $[A]$, as the value of $[B]$ increases, when condition (18.4.17) is satisfied, the stationary state (18.4.12) becomes unstable. In the next chapter we will see that this instability leads to oscillations.

Linear stability analysis does not provide a means of determining how the system will evolve when a state becomes unstable. To understand the system’s behavior fully, the full nonlinear equation has to be considered. Often we encounter nonlinear equations for which solutions cannot be obtained analytically. However, with the availability of powerful desktop computers and software, numerical solutions can be obtained without much difficulty. To obtain numerical solutions to nonlinear equations considered in the following chapter, *Mathematica* codes are provided at the end of Chapter 19.

¹If λ_{\pm} are real roots, $\lambda_+ + \lambda_- > 0$ implies that at least one of the roots is positive.

Appendix 18.1 A General Property of $d_{\text{F}}P/dt$

In this appendix we show that, regardless of the distance from equilibrium,

$$\frac{d_{\text{F}}P}{dt} \leq 0 \quad (\text{A18.1.1})$$

The validity of (A18.1.1) depends on the validity of the local equilibrium. In Chapter 12 we have seen that the second-order variation of entropy $\delta^2 S$ is negative because quantities such as the molar heat capacity C_V , isothermal compressibility κ_T and $-\sum_{i,j}(\partial A_i/\partial \xi_j)\delta \xi_i \delta \xi_j$ are positive. This condition remains valid for an elemental volume δV , which is in local equilibrium. We can see the relation between the derivative $d_{\text{F}}P/dt$ and quantities such as $-\sum_{i,j}(\partial A_i/\partial \xi_j)\delta \xi_i \delta \xi_j$, which have a definite sign, as follows.

A18.1.1 Chemical Reactions

Consider a closed homogeneous nonequilibrium system undergoing a chemical reaction at uniform constant temperature. The affinities A_k are functions of the extents of reaction ξ_j and

$$\frac{\partial A_k}{\partial t} = \sum_j \left(\frac{\partial A_k}{\partial \xi_j} \right) \left(\frac{\partial \xi_j}{\partial t} \right) = \sum_j \left(\frac{\partial A_k}{\partial \xi_j} \right) v_j \quad (\text{A18.1.2})$$

Therefore:

$$\frac{d_{\text{F}}P}{dt} = \frac{1}{T} \sum_{k,j} \left(\frac{\partial A_k}{\partial \xi_j} \right) v_j v_k \leq 0 \quad (\text{A18.1.3})$$

which follows from the general relation $-\sum_{i,j}(\partial A_i/\partial \xi_j)\delta \xi_i \delta \xi_j \geq 0$ valid for a system in local equilibrium (12.4.5). This proof can be extended to open systems following along the lines of the proof for isothermal diffusion given below.

A18.1.2 Isothermal Diffusion

In this case we begin with

$$\frac{d_{\text{F}}P}{dt} = - \int \sum_k \mathbf{J}_k \cdot \frac{\partial}{\partial t} \nabla \left(\frac{\mu_k}{T} \right) dV = - \int \frac{1}{T} \sum_k \mathbf{J}_k \cdot \nabla \left(\frac{\partial \mu_k}{\partial t} \right) dV \quad (\text{A18.1.4})$$

Using the identity $\nabla \cdot (f\mathbf{J}) = f\nabla \cdot \mathbf{J} + \mathbf{J} \cdot \nabla f$, the right-hand side can be written as

$$- \int \frac{1}{T} \mathbf{J}_k \cdot \nabla \left(\frac{\partial \mu_k}{\partial t} \right) dV = - \int \frac{1}{T} \nabla \cdot \left[\mathbf{J}_k \left(\frac{\partial \mu_k}{\partial t} \right) \right] dV + \int \frac{1}{T} \left(\frac{\partial \mu_k}{\partial t} \right) \nabla \cdot \mathbf{J}_k dV \quad (\text{A18.1.5})$$

Using Gauss's theorem, the first term on the right-hand side can be converted into a surface integral. Since we assume that the value of μ_k is time independent at the boundary, i.e. the boundary conditions are time independent, this surface integral vanishes. Using the relations

$$\frac{\partial \mu_k}{\partial t} = \sum_j \frac{\partial \mu_k}{\partial n_j} \frac{\partial n_j}{\partial t} \quad \text{and} \quad \frac{\partial n_k}{\partial t} = -\nabla \cdot \mathbf{J}_k \quad (\text{A18.1.6})$$

the second term can be written as

$$\int \frac{1}{T} \left(\frac{\partial \mu_k}{\partial t} \right) \nabla \cdot \mathbf{J}_k dV = \frac{-1}{T} \int \sum_j \frac{\partial \mu_k}{\partial n_j} \left(\frac{\partial n_j}{\partial t} \right) \left(\frac{\partial n_k}{\partial t} \right) dV \quad (\text{A18.1.7})$$

Combining Equations (A18.1.7), (A18.1.5) and (A18.1.4), we arrive at

$$\frac{d_F P}{dt} = \frac{-1}{T} \int \sum_{jk} \frac{\partial \mu_k}{\partial n_j} \left(\frac{\partial n_j}{\partial t} \right) \left(\frac{\partial n_k}{\partial t} \right) dV \leq 0$$

The right-hand side of this expression is negative because

$$- \sum_{jk} \frac{\partial \mu_k}{\partial n_j} \left(\frac{\partial n_j}{\partial t} \right) \left(\frac{\partial n_k}{\partial t} \right) \leq 0$$

is valid for systems in local equilibrium (Equation (12.4.9)). The general validity of Equation (18.2.3) is proved in the literature [1].

Appendix 18.2 General Expression for the Time Derivative of $\delta^2 S$

The relation

$$\frac{d}{dt} \frac{\delta^2 S}{2} = \int_V \sum_k \delta F_k \delta J_k dV \quad (\text{A18.2.1})$$

can be obtained as follows. We begin by taking the time derivative of $\delta^2 S/2$ as defined in Equation (18.3.4). For notational simplicity, we shall denote the time derivatives of a quantity x by $\dot{x} \equiv \partial x / \partial t$. The time derivative of $\delta^2 S$ can be written as

$$\begin{aligned} \delta^2 \dot{S} = \int & \left[\left(\frac{\partial^2 s}{\partial u^2} \right) 2\delta u (\delta \dot{u}) + 2 \sum_k \left(\frac{\partial^2 s}{\partial u \partial n_k} \right) (u \delta n_k + \delta u \delta \dot{n}_k) \right. \\ & \left. + 2 \sum_k \left(\frac{\partial^2 s}{\partial n_i \partial n_k} \right) \delta \dot{n}_i \delta n_k \right] dV \end{aligned} \quad (\text{A18.2.2})$$

in which the factor 2 appears in the last term because we used the relation

$$\frac{\partial^2 s}{\partial n_i \partial n_k} = \frac{\partial^2 s}{\partial n_k \partial n_i}$$

Next, noting that $(\partial s / \partial u)_{n_k} = 1/T$ and $(\partial s / \partial n_k)_u = -\mu_k/T$, we can write Equation (A18.2.2) as

$$\begin{aligned} \delta^2 \dot{S} = \int & 2 \left[\left(\frac{\partial}{\partial u} \frac{1}{T} \right) \delta u (\delta \dot{u}) + \sum_k \left(\frac{\partial}{\partial n_k} \frac{1}{T} \right) \delta \dot{u} \delta n_k \right] dV \\ & + \int 2 \left[\sum_k \frac{\partial}{\partial u} \left(\frac{-\mu_k}{T} \right) \delta u \delta \dot{n}_k + \sum_{ik} \frac{\partial}{\partial n_i} \left(\frac{-\mu_k}{T} \right) \delta n_i \delta \dot{n}_k \right] dV \end{aligned} \quad (\text{A18.2.3})$$

We now observe that, since u and n_k are independent variables, we can write

$$\delta \left(\frac{1}{T} \right) = \sum_k \left(\frac{\partial}{\partial n_k} \frac{1}{T} \right) \delta n_k + \left(\frac{\partial}{\partial u} \frac{1}{T} \right) \delta u \quad (\text{A18.2.4})$$

$$\delta \left(\frac{\mu_i}{T} \right) = \sum_k \left(\frac{\partial}{\partial n_k} \frac{\mu_i}{T} \right) \delta n_k + \left(\frac{\partial}{\partial u} \frac{\mu_i}{T} \right) \delta u \quad (\text{A18.2.5})$$

Equations (A18.2.4) and (A18.2.5) enable us to reduce (A18.2.3) to the simple form

$$\delta^2\dot{S} = 2 \int \left[\delta \left(\frac{1}{T} \right) \delta\dot{u} + \sum_k \delta \left(\frac{-\mu_k}{T} \right) \delta\dot{n}_k \right] dV \quad (\text{A18.2.6})$$

This relation can be written in terms of the changes in thermodynamic forces $\delta\nabla(1/T)$ and $\delta\nabla(-\mu_k/T)$ and the corresponding flows $\delta\mathbf{J}_u$ and $\delta\mathbf{J}_k$, using the balance equations for energy density u and the concentrations n_k :

$$\frac{\partial u}{\partial t} = \dot{u} = -\nabla \cdot \mathbf{J}_u \quad (\text{A18.2.7})$$

$$\frac{\partial n_k}{\partial t} = \dot{n}_k = -\nabla \cdot \mathbf{J}_k + \sum_i v_{ki} v_i \quad (\text{A18.2.8})$$

in which v_{ki} is the stoichiometric coefficient of reactant k in reaction i and v_i is the velocity of reaction i . If we denote the stationary state densities and flows by u_s , n_{ks} , \mathbf{J}_{us} , \mathbf{J}_{ks} and v_{is} , we have $\dot{u}_s = -\nabla \cdot \mathbf{J}_{us} = 0$ and $\dot{n}_s = -\nabla \cdot \mathbf{J}_{ks} + \sum_i v_{ki} v_{is} = 0$. Consequently, for a perturbation $u = u_s + \delta u$, $\mathbf{J}_u = \mathbf{J}_{us} + \delta\mathbf{J}_u$, etc., from the stationary state, we have

$$\delta\dot{u} = -\nabla \cdot \delta\mathbf{J}_u \quad (\text{A18.2.9})$$

$$\delta\dot{n}_k = -\nabla \cdot \delta\mathbf{J}_k + \sum_i v_{ki} \delta v_i \quad (\text{A18.2.10})$$

We substitute these expressions for $\delta\dot{u}$ and $\delta\dot{n}_k$ into (A18.2.6) and use the identity

$$\nabla \cdot (f\mathbf{J}) = f\nabla \cdot \mathbf{J} + \mathbf{J} \cdot \nabla f \quad (\text{A18.2.11})$$

in which f is a scalar function and \mathbf{J} is a vector field, and we use Gauss's theorem

$$\int_V (\nabla \cdot \mathbf{J}) dV = \int_\Sigma \mathbf{J} \cdot d\mathbf{a} \quad (\text{A18.2.12})$$

in which Σ is the surface enclosing the volume V and $d\mathbf{a}$ is the element of surface area. All this allows Equation (A18.2.6) to be written as follows:

$$\begin{aligned} \frac{1}{2}\delta^2\dot{S} &= - \int_\Sigma \delta \left(\frac{1}{T} \right) \delta\mathbf{J}_u \cdot d\mathbf{a} + \int_V \delta\nabla \left(\frac{1}{T} \right) \delta\mathbf{J}_u dV \\ &+ \int_\Sigma \sum_k \delta \left(\frac{\mu_k}{T} \right) \delta\mathbf{J}_k \cdot d\mathbf{a} - \int_V \sum_k \delta\nabla \left(\frac{\mu_k}{T} \right) \delta\mathbf{J}_k dV \\ &+ \int_V \left[\sum_i \delta \left(\frac{A_i}{T} \right) \delta v_i \right] dV \end{aligned} \quad (\text{A18.2.13})$$

In obtaining this equation, we have used the relation $\sum_k v_{ki} \delta(\mu_k/T) = -\delta(A_i/T)$. The flows at the surface are fixed by the boundary conditions and are not subject to fluctuations, so the surface terms vanish. This leads us to the required result:

$$\begin{aligned} \frac{1}{2}\delta^2\dot{S} &= \int_V \delta\nabla \left(\frac{1}{T} \right) \delta\mathbf{J}_u dV - \int_V \sum_k \delta\nabla \left(\frac{\mu_k}{T} \right) \delta\mathbf{J}_k dV + \int_V \left[\sum_i \delta \left(\frac{A_i}{T} \right) \delta v_i \right] dV \\ &= \int_V \sum_\alpha \delta F_\alpha \delta J_\alpha dV \end{aligned} \quad (\text{A18.2.14})$$

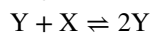
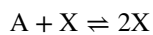
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Exercises

- 18.1** Calculate the affinities of the following reaction systems for a range of concentrations (or partial pressures) of the reactants and the products and compare them with RT at $T = 298$ K. Determine the ranges in which the system is thermodynamically in the linear regime using appropriate data from tables.
- (a) Racemization reaction $L \rightleftharpoons D$ (L and D are enantiomers).
 - (b) Reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (with partial pressures $P_{N_2O_4}$ and P_{NO_2}).
- 18.2**
- (a) What factors would you identify to conclude that the Earth's atmosphere is not in thermodynamic equilibrium?
 - (b) Through an appropriate literature search, determine whether the atmospheres of Mars and Venus are in chemical equilibrium.
- 18.3** For the chemical reaction $A \rightleftharpoons B$, verify the general property $d_F P \leq 0$.
- 18.4**
- (a) Obtain inequality (18.3.11) for a perturbation $\delta[B]$ from the stationary states of reaction (18.3.9).
 - (b) Obtain the 'excess entropy production' (18.3.13) for a perturbation $\delta[X]$ from the stationary states of reaction (18.3.12).
- 18.5** Obtain the excess entropy production and analyze the stability of the stationary states for the following reaction schemes:
- (a) $W \rightleftharpoons X \rightleftharpoons Z$, in which the concentrations of W and Z are maintained fixed at a nonequilibrium value.
 - (b) $W + X \rightleftharpoons 2X$, $X \rightleftharpoons Z$, in which the concentrations of W and Z are maintained fixed at a nonequilibrium value.
- 18.6** Show that the stationary states of Equations (18.4.10) and (18.4.11) are Equations (18.4.12).
- 18.7** For a polynomial equation of the type $\omega^n + A_1\omega^{n-1} + A_2\omega^{n-2} + \dots + A_n = 0$ show that coefficient $A_1 = -(\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n)$ and coefficient $A_n = (-1)^n (\lambda_1 \lambda_2 \lambda_3 \dots \lambda_n)$, where λ_k are roots.
- 18.8** For the following equations, obtain the stationary states and analyze their stability as a function of the parameter λ assuming A, B and C are positive:
- (a) $\frac{dx}{dt} = -Ax^3 + C\lambda x$
 - (b) $\frac{dx}{dt} = -Ax^3 + Bx^2 + C\lambda x$
 - (c) $\frac{dx}{dt} = \lambda x - 2xy$, $\frac{dy}{dt} = -y + xy$
 - (d) $\frac{dx}{dt} = -5x + 6y + x^2 - 3xy + 2y^2$, $\frac{dy}{dt} = -\lambda x - 14y + 2x^2 - 5xy + 4y^2$

18.9 Consider the reaction scheme:



Far from equilibrium, we only keep the forward reactions and we assume A and E are fixed. Using the linear stability theory, show that the perturbations around the nonequilibrium steady state lead to oscillations in [X] and [Y], as was discussed in Section 18.2. This model was used by Lotka and Volterra to describe the ‘struggle of life’ (see V. Volterra, *Theorie Mathématique de la Lutte pour la Vie*, 1931, Gauthier Villars: Paris). Here X is the prey (lamb) and Y is the predator (wolf). This model of the prey–predator interaction shows that the populations X and Y will exhibit oscillations.