

Thermodynamics Far from Equilibrium: Linear and Nonlinear One-Variable Systems

2.1 Linear One-Variable Systems

We begin as simply as possible, with a linear system, (1.5), repeated here



with rate coefficients k_1 and k_2 for the rate coefficients in the forward and reverse reaction of the first reaction, and similarly k_3 and k_4 for the second reaction. The deterministic rate equation is (1.10), rewritten here in a slightly different form,

$$\frac{dp_X}{dt} = (k_1 p_A + k_4 p_B) - (k_2 + k_3) p_X \quad (2.2)$$

for isothermal ideal gases; the pressures of A and B are held constant in an apparatus as in Fig. 1.1 of Chap. 1. We denote the first term on the rhs of (2.2) by t_X^+ and the second term by t_X^- [1]. The pressure of p_X at the stationary state, with the rhs of (2.2) set to zero, is

$$\frac{p_X^s}{p_X} = \frac{t_X^+}{t_X^-} = \frac{t_X^{+s}}{t_X^-}. \quad (2.3)$$

since t_X^+ is a constant.

Now we need an important hypothesis, that of *local equilibrium*. It is assumed that at each time there exists a temperature, a pressure, and a chemical potential for each chemical species. These quantities are established on time scales short compared with changes in pressure, or concentration, of chemical species due to chemical reaction. Although collisions leading to chemical reactions may perturb, for example, the equilibrium distribution of molecular velocities, that perturbation is generally small and decays in 10–30 ns, a time scale short compared with ranges of reaction rates of micro seconds and longer. There are many examples that fit this hypothesis well [2]. (A phenomenological approach beyond local equilibrium is given in the field of extended

irreversible thermodynamics [3, 4], which we do not discuss here.) We thus write for the chemical potential

$$\mu_X = \mu_X^0 + RT \ln p_X \quad (2.4)$$

where μ_X^0 is the chemical potential in the standard state. Hence we have

$$\mu_X - \mu_X^s = -RT \ln \frac{t_X^+}{t_X^-}. \quad (2.5)$$

We define a thermodynamic state function ϕ [1]

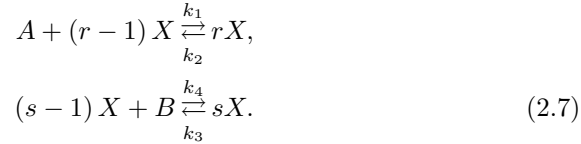
$$\phi(p_X) = V_{II} \int (\mu_X - \mu_X^s) dp_X \quad (2.6)$$

where V_{II} is a volume shown in Fig. 1.1 of Chap. 1. This function has many important properties. At the stationary state of this system ϕ is zero. If we start at the stationary state and increase p_X then $dp_X \geq 0$ and the integrand is larger than zero. Hence ϕ is positive. Similarly, if we start at the stationary state and decrease p_X then dp_X and the integrand are both negative and ϕ is positive. Hence ϕ is an extremum at the stable stationary state, a minimum.

Before discussing further properties of this state function, we can proceed to nonlinear one-variable systems, which also have only one intermediate.

2.2 Nonlinear One-Variable Systems

We write a model stoichiometric equation



and imagine this reaction occurring in the apparatus, Fig. 1.1 of Chap. 1. Since this isothermal system has chambers I and III at constant pressure and chamber II at constant volume the proper thermodynamic function for the entire system is a linear sum of Gibbs free energies for I and III and the Helmholtz free energy for II. If in (2.7) $s = 1$ and $r = 1$ then we have the linear model (2.1). If we set $r = 3$ and $s = 1$ then we have the Schlögl model, (1.12, 1.13). We shall use the results obtained above for the linear model to develop results for the Schlögl model. The deterministic kinetic equation for the Schlögl model was given in (1.14) and is repeated here

$$\frac{dp_X}{dt} = k_1 p_A p_X^2 + k_4 p_B - (k_2 p_X^3 + k_3 p_X). \quad (2.8)$$

The first two positive terms on the rhs of (2.8) are again given the symbol t_X^+ and the two negative terms the symbol t_X^- ; their ratio is

$$\frac{t_X^+}{t_X^-} = \frac{k_1 p_A p_X^2 + k_4 p_B}{k_2 p_X^3 + k_3 p_X}, \quad (2.9)$$

which we use to define the quantity p_X^*

$$\frac{t_X^+}{t_X^-} = \frac{p_X^*}{p_X}. \quad (2.10)$$

Hence p_X^* is

$$p_X^* = \frac{k_1 p_A p_X^2 + k_4 p_B}{k_2 p_X^2 + k_3}. \quad (2.11)$$

The quantity p_X^* is the pressure in a reference state for which (2.10) holds.

If we compare (2.3) with (2.10) we see the similarity obtained by defining p_X^* . We gain some insight by comparing the linear model with the Schlögl model in the following way: assign the same value of p_A to each, the same value of p_B to each, and similarly for T, V_I, V_{II}, V_{III} , the equilibrium constant for the $A \rightleftharpoons X$ reaction and that for the $B \rightleftharpoons X$ reaction. Then the two model systems are ‘instantaneously thermodynamically equivalent.’ If furthermore t_X^+ has the same value in the two systems at each point in time, and the same for t_X^- , the two systems are ‘instantaneously kinetically indistinguishable.’ Hence following (2.5 and 2.6) we may write

$$\mu_X - \mu_X^* = RT \ln \frac{p_X}{p_X^*} = -RT \ln \frac{t_X^+}{t_X^-} \quad (2.12)$$

and for our chosen thermodynamic function

$$\phi^*(p_X) = \int (\mu_X - \mu_X^*) dp_X. \quad (2.13)$$

In the instantaneously indistinguishable linear system p_X^* denotes the pressure of X in the stationary state. The function in (2.13) is an *excess work*, the work of moving the system from a stable stationary state to an arbitrary value p_X compared with the work of moving the system from the stationary state of the instantaneous indistinguishable linear system to p_X .

The integrand in (2.13) is a species-specific activity, which plays a fundamental role, as we now show.

The integrand in (2.13) is a state function and so is ϕ^* ; as before, ϕ^* is an extremum at the stable stationary state, a minimum. We come to that from

$$\begin{aligned} (d(\mu_x - \mu_x^*)/dp_x)|_{ss} &= -RT \left[(dt_x^+/dp_x)_{ss} - (dt_x^-/dp_x)_{ss} \right] / (t_x^+|_{ss}) \\ &= -V_{II} (t_x^+|_{ss})^{-1} [d(dp_x/dt)/dp_x]|_{ss} \end{aligned} \quad (2.14)$$

and (1.24), so that we have the following necessary and sufficient conditions for the species-specific activity (the driving force for species X)

$$\begin{aligned} \mu_x - \mu_x^* &= 0 && \text{at each steady-state,} \\ d(\mu_x - \mu_x^*)/dp_x &> 0 && \text{at each stable steady-state,} \\ d(\mu_x - \mu_x^*)/dp_x &< 0 && \text{at each unstable steady-state, and} \\ d(\mu_x - \mu_x^*)/dp_x &= 0 && \text{at each marginally stable steady-state.} \end{aligned} \quad (2.15)$$

In addition we have

$$d(\mu_x - \mu_x^*)/dp_x = d^2(\mu_x - \mu_x^*)/dp_x^2 = 0 \quad \text{at each critically stable steady-state.} \quad (2.16)$$

It is useful to restate these results in terms necessary and sufficient conditions for the state function $\phi^*(p_X)$, (2.13):

$$\frac{d\phi^*}{dp_X} = 0 \quad \text{at each stationary state} \quad (2.17)$$

$$\begin{aligned} \frac{d^2\phi^*}{dp_X^2} &\geq 0 && \text{at each stable stationary state with the equality sign} \\ &&& \text{holding at marginal stability} \end{aligned} \quad (2.18)$$

$$\begin{aligned} \frac{d^2\phi^*}{dp_X^2} &\leq 0 && \text{at each unstable stationary state with the equality sign} \\ &&& \text{holding at marginal stability} \end{aligned} \quad (2.19)$$

Hence (2.17, 2.18) are necessary and sufficient conditions for the existence and stability of nonequilibrium stationary states.

There are more conditions to be added after developing the connection of the thermodynamic theory to the stochastic theory.

It may seem strange that in (2.12) the chemical potential difference on the lhs is related to the logarithm of a ratio of fluxes and each flux consists of two additive terms. We can find an interpretation by comparison with a single reaction, that of $A + B = C + D$. We can write the flux in the forward direction

$$t^+ = k_f V [A] [B] = V [A] [B] \bar{v}_{AB} \bar{\sigma}_{AB}, \quad (2.20)$$

where the brackets indicate concentrations of species, V is the reaction volume, \bar{v}_{AB} is the average relative speed of A and B, and $\bar{\sigma}_{AB}$ is the reaction cross section, averaged with a weighting of the relative speed. Hence the term $k_f V [A][B]$ is the flux of A and B to form C and D, and $k_f [C][D]$ is the flux of products to form reactants. The chemical potential difference between the products and reactants is the driving force toward equilibrium and is proportional to the logarithm of the ratio of the fluxes in the forward and reverse direction, see (1.20). For the reaction mechanism (2.7), the flux of reactants to form X comes from two sources: the reaction A with X and the reaction B to form X. The total flux is the sum of fluxes from these two sources. Similarly,

the flux of removing X has two sources. In all cases these fluxes are indications of the respective escaping tendencies and hence the relation to the chemical potentials. Thus (2.12) connects the lhs, the chemical driving force toward a stable stationary state, to the ratio of sums of fluxes of X , the rhs.

If A and B are chosen such that the ratio of their pressures equals the equilibrium constant then ϕ^* equals ΔG and $p_X^* = p^s$.

2.3 Dissipation

For a spontaneously occurring chemical reaction at constant pressure, p , and temperature, T , the Gibbs free energy change gives the maximum work, other than pV work, that can be obtained from the reaction. For systems at constant V, T it is the Helmholtz free energy change that yields that measure. If no work is done by the reaction then the respective free energy changes are dissipated, lost. For reactions of ideal gases run in the apparatus in Fig. 1.1 in Chap. 1, we can define a hybrid free energy, M ,

$$M = \mu_A (n_A^I + n_A^{II}) + \mu_B (n_B^{II} + n_B^{III}) + \mu_x n_x^{II} - RT (n_A^{II} + n_B^{II} + n_x^{II}). \quad (2.21)$$

The time rate of change of M is

$$dM/dt = \mu_A dn_A^I/dt + \mu_B dn_B^{III}/dt + \mu_x dn_x^{II}/dt \quad (2.22)$$

if there is no depletion of the reservoirs I and III. According to conservation of mass we have

$$0 = \mu_x^* dn_A^I/dt + \mu_x^* dn_B^{III}/dt + \mu_x^* dn_x^{II}/dt, \quad (2.23)$$

and therefore we may write

$$dM/dt = (\mu_A - \mu_x^*) dn_A^I/dt + (\mu_B - \mu_x^*) dn_B^{III}/dt + (\mu_x - \mu_x^*) dn_x^{II}/dt. \quad (2.24)$$

Hence we write for the dissipation D

$$D = -dM/dt = -dM_{\text{res}}/dt - dM_x/dt \quad (2.25)$$

where the first term on the rhs is the dissipation due to the conversion of A to X at the pressure p_X^* and at the rate $-\frac{dn_A^I}{dt}$ and the conversion of X to B at the same pressure of X and the rate $\frac{dn_B^{III}}{dt}$. The second term on the rhs of (2.25) is

$$\begin{aligned} -dM_x/dt &= -(\mu_x - \mu_x^*) dn_x^{II}/dt \\ &= RT (t_x^+ - t_x^-) \ln (t_x^+/t_x^-) \\ &\equiv D_x. \end{aligned} \quad (2.26)$$

From this last equation it is clear that we have for D_X

$$D_x = -dM_x/dt \geq 0 \quad \text{for all } p_x, \quad (2.27)$$

regardless of the reaction mechanism; the equality holds only at the stationary state.

As we shall discuss later, the total dissipation D is not an extremum at stationary states in general, but there may be exceptions. D_X is such an extremum and the integral

$$\phi^* = \int (\mu_X - \mu_X^*) dn_X \quad (2.28)$$

is a Lyapunov function in the domain of attraction of each stable stationary state.

The dissipation in a reaction can range from zero, for a reversible reaction, to its maximum of ΔG when no work is done in the surroundings. Hence the dissipation can be taken to be a measure of the efficiency of a reaction in regard to doing work. There is more on this subject in Chap. 12.

2.4 Connection of the Thermodynamic Theory with Stochastic Theory

The deterministic theory of chemical kinetics is formulated in terms of pressures, for gases, or concentrations of species for gases and solutions. These quantities are macroscopic variables and fluctuations of these variables are neglected in this approach. But fluctuations do occur and one way of treating them is by stochastic theory. This kind of analysis is also called mesoscopic in that it is intermediate between the deterministic theory and that of statistical mechanics. In stochastic theory, one assumes that fluctuations do occur, say in the number of particles of a given species X , that there is a probability distribution $P(X, t)$ for that number of particles at a given time, and that changes in this distribution occur due to chemical reactions. The transition probabilities of such changes are assumed to be given by macroscopic kinetics. We shall show that the nonequilibrium thermodynamic functions ϕ for linear systems, ϕ^* (for nonlinear systems), the excess work, determines the stationary, time-independent, probability distribution, which leads to a physical interpretation of the connection of the thermodynamic and stochastic theory. At equilibrium, the probability distribution of fluctuations is determined by the Gibbs free energy change at constant T, p , which is the work other than pV work.

We restrict the analysis at first to reaction mechanisms for which the number of molecules of species X changes by ± 1 in each elementary step.

We take the probability distribution to obey the master equation which has been used extensively. For the cubic Schlögl model ((2.7) with $r = 3$, $s = 1$) the master equation is [1, 5]

$$\begin{aligned} \partial P(X, t) / \partial t = & t^+(X-1) P(X-1, t) + t^-(X+1) P(X+1, t) \\ & - [t^+(X) + t^-(X)] P(X, t). \end{aligned} \quad (2.29)$$

The first two terms on the rhs yield an increase in X , the last two terms a decrease in X .

The fluxes in this equation are

$$\begin{aligned} t^+(X) &= c_1 A X (X-1) / 2! + c_4 B, \\ t^-(X) &= c_2 X (X-1) (X-2) / 3! + c_3 X, \end{aligned} \quad (2.30)$$

with the parameters c_i related to the rate coefficients k_i by

$$k_i = V^{m_i-1} (c_i / n_i!) \quad \text{for } 1 \leq i \leq 4, \quad (2.31)$$

where m_i is the molecularity of the i th step and n_i the molecularity in X .

From the master equation, we can derive the result that the average concentration, the average number of X in a volume V , obeys the deterministic rate equation in the limit of large numbers of molecules.

The time-independent solution of the master equation is

$$P_s(X) = P_s(0) \prod_{i=1}^X \frac{t^+(i-1)}{t^-(i)}, \quad (2.32)$$

which by retention of only the leading term in the Euler-MacLaurin summation formula reduces to

$$P_s(X) = N \exp \left[\int_1^X \ln \frac{t^+(y)}{t^-(y)} dy \right] \quad (2.33)$$

and N is a normalization constant. The connection between the thermodynamic and stochastic theory is established with the use of (2.12) to give

$$P_s(X) = N \exp \left[-\frac{1}{RT} \int^X (\mu_x - \mu_x^*) dX \right], \quad (2.34)$$

The Lyapunov function Φ^* , (2.13), is both the thermodynamic driving force toward a stable stationary state and determines the stationary probability distribution of the master equation. The stationary distributions (2.33, 2.34) are nonequilibrium analogs of the Einstein relations at equilibrium, which give fluctuations around equilibrium.

There is another interesting connection [1]. We define $P(X_1, t_1; X_0, t_0)$ to be the probability density of observing X_1 molecules in V at time t_1 given that there are X_0 molecules at t_0 . This function is the solution of the master equation (2.29) for the initial condition

$$P(X, t = t_0) = \delta(X - X_0). \quad (2.35)$$

The probability density can be factored into two terms, [1],

$$P(X_1, t_1; X_0, t_0) = F_1(X_0 \rightarrow X_1) F_2(X_1, X_0, t_1 - t_0), \quad (2.36)$$

in which the first term on the rhs is independent of the path from X_0 to X_1 and independent of the time interval $(t_1 - t_0)$. To the same approximation with which we obtained (2.33) we can reduce the first term to

$$F_1(X_0 \rightarrow X_1) = \exp \left[\left(\frac{1}{2} \right) \int_{x_0}^{x_1} (\ln t^+ / t^-) dX \right], \quad (2.37)$$

and find it to be of the same form as the probability distribution (2.33). It contains the irreversible part of the probability density (2.36).

2.5 Relative Stability of Multiple Stationary Stable States

For systems with multiple stable stationary states there arises the issue of relative stability of such states. As in the previous section we treat systems with a single intermediate and stoichiometric changes in X are limited to ± 1 .

In regions of multistability the stationary probability distribution is bimodal and is shown in Fig. 2.1 for the cubic Schlögl model.

Stable stationary states are located at maxima, labeled 1 and 3, and unstable stationary states at minima, labeled 2.

Consider now the ratio of the probability density (2.36), for a given transition from X_1 to X_2 to that of the reverse transition

$$\frac{P(X_2, t_2; X_1, t_1)}{P(X_1, t_2; X_2, t_1)} = \exp \left[\int_1^2 \ln \frac{t_x^+}{t_x^-} dX \right] \quad (2.38)$$

We obtain this equation with the use of (2.36, 2.37), once for the numerator and once for the denominator on the lhs of (2.38), canceling the F_2 terms, and moving the remaining term in the denominator to the numerator. Equistability of two stable stationary states, labeled now 1 and 3 to correspond to Fig. 2.1, is defined by

$$\frac{P(X_3, t; X_1, 0)}{P(X_1, t; X_3, 0)} = 1, \quad (2.39)$$

which with the use of the second and third line of (2.26) we may also express as

$$\int_2^3 D_x dt = \int_2^1 D_x dt. \quad (2.40)$$

The integral of the species-specific dissipation from the unstable stationary state 2 to the stable stationary state 3 equals, at equistability, to the integral

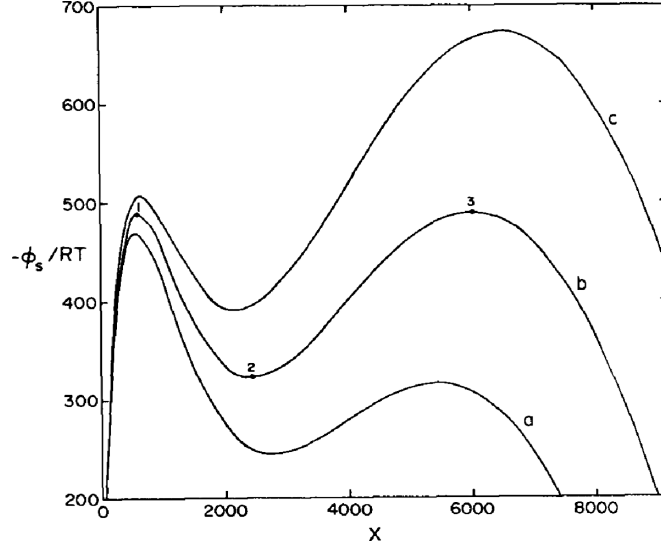


Fig. 2.1. Plot of the integral in (2.34), marked ϕ_s vs. X for the Schlögl model, (1.12, 1.13), with parameters: $c_1 = 3.10^{-10} \text{ s}^{-1}$; $c_2 = 1.10^{-7} \text{ s}^{-1}$; $c^3 = 0.33 \text{ s}^{-1}$; $c_4 = 1.5.10^{-4} \text{ s}^{-1}$; and $A = B$. For curve (a) $B = 9.8.10^6$; for curve (b) $B = 1.01.10^6$; curve (c) $B = 1.04.10^6$. Curve (b) lies close to the equistability of the stable stationary states 1 and 3; 2 marks the unstable stationary state

of the dissipation from the unstable stationary state 2 to the stable stationary state 1, whereas the integral of the total dissipation for the limits in (2.40) goes to infinity and that of the species-specific dissipation is finite. We can restate (2.40) in terms of the excess work (see the first and third equation of (2.26))

$$\int_2^3 (\mu_X - \mu_X^*) dn_X^{\Pi} = \int_2^1 (\mu_X - \mu_X^*) dn_X^{\Pi}; \quad (2.41)$$

at equistability the integral of the excess work from 2 to 3 equals the integral of the excess work from 2 to 1. Equations (2.39–2.41) provide necessary and sufficient conditions of equistability of stable stationary states.

The master equation has been investigated for a sequence of unimolecular (nonautocatalytic) reactions based on moment generating functions [6]; these yield Poissonian stationary distribution for single intermediate systems in terms of the number of particles X of species X , with X^{ss} that number in the stationary state

$$P_s(X) = \left[(X^{ss})^X / X! \right] \exp(-X^{ss}). \quad (2.42)$$

Our results are consistent with (2.41) as can be seen from the use of (2.13) and (2.34), a change of variables to particle numbers X , and the use of Stirling's approximation

$$\begin{aligned}
P_s(X) &= \wp \exp \left[- (k_B T)^{-1} \times \int^{n_x} (\mu_x - \mu_x^{ss}) dn'_x \right] \\
&= \wp \exp (X \ln X^{ss} - X \ln X + X) \\
&= \wp [(X^{ss})^X / X!].
\end{aligned} \tag{2.43}$$

Here p is the normalization constant $\exp(-X^{ss})$. The formulation given in this chapter has the advantage of the physical interpretation in terms of species-specific thermodynamic driving forces and in terms of Liapunov functions; further our formulation is generalizable to autocatalytic systems and many variable systems.

2.6 Reactions with Different Stoichiometries

We analyze systems with stoichiometric changes in X other than ± 1 . We begin by defining the flux

$$t_X^\pm = \sum_j |\nu_{jX}| t_j^\pm \tag{2.44}$$

and again choose p_X^* for any given p_X so that we have

$$\mu_X - \mu_X^* = RT \ln (t_X^- / t_X^+). \tag{2.45}$$

Let the reactions occur in the apparatus Fig. 1.1 of Chap. 1; then the rate of change of the mixed free energy M is

$$dM/dt = \mu_A dn_A^I/dt + \mu_B dn_B^{III}/dt + \mu_X dn_X^{II}/dt, \tag{2.46}$$

and we need to consider conservation of mass. For example, for the reaction mechanism



mass conservation requires

$$0 = \mu_X^* dn_A^I/dt + 2\mu_X^* dn_B^{III}/dt + \mu_X^* dn_X^{II}/dt, \tag{2.47}$$

so that we have

$$\begin{aligned}
\frac{dM}{dt} &= (\mu_A - \mu_X^*) dn_A^I/dt + (\mu_B - 2\mu_X^*) dn_B^{III}/dt \\
&\quad + (\mu_X - \mu_X^*) dn_X^{II}/dt,
\end{aligned} \tag{2.48}$$

The species-specific term in this equation is

$$\begin{aligned}
-dM_X/dt &= -(\mu_X - \mu_X^*) dn_X^{II}/dt \\
&= RT (t_X^+ - t_X^-) \ln (t_X^+ / t_X^-) = D_X
\end{aligned} \tag{2.49}$$

and $D_X \geq 0$ for all p_X .

The relation to the stochastic theory does not generalize here for cases without detailed balance except for the approach to equilibrium, [1].

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