Thermodynamics of Transitions between Nonequilibrium States

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Continuously stirred tank reactors can make transitions between stationary states, from stationary to oscillatory states, and *vice versa.* With the aim of characterizing these transitions thermodynamically, we calculate for some specific models the entropy increment due to mixing of the inflow into the reactor contents and the entropy production due to chemical reaction. These thermodynamic quantities are, however, found not always appropriate in describing the transitions. To explore another possibility, we also evaluate the thermodynamic force and flux of chemical reaction. It is shown as a result that spontaneous transitions are invariably accompanied by a decrease in the thermodynamic force or flux or both; i.e., the effects of irreversible processes relax at least in terms of the thermodynamic force or flux for nonequilibrium transitions. The same type of regularity is observed when the residence time is lengthened in stationary states.

I. Introduction

Equilibrium thermodynamics is concerned with changes between equilibrium states. As is well-known, it predicts, for example, that entropy increases for any spontaneous adiabatic change and that the Gibbs free energy decreases in any spontaneous process in which the temperature and pressure are kept constant.

Nonequilibrium thermodynamics should deal with transitions between nonequilibrium states. Such transitions of a spontaneous nature include those from an unstable to a stable state in multiple stationary states and those from an unstable stationary state to a stable oscillatory state, i.e., a stable limit cycle. For certain systems, transitions in multiple stationary states may be characterized by constructing appropriate Liapunov functions.[1−6] It is an open question, on the other hand, whether or not nonequilibrium transitions in general can be represented in terms of familiar thermodynamic functions.[7−11]

In previous work,[9,10] thermodynamic functions such as entropy and the rate of entropy production due to chemical reactions have been calculated for some kinetic schemes in continuously stirred tank reactors (CSTRs) under isothermal and adiabatic operation. It is found for these systems that the entropy increases and/or the entropy production decreases for spontaneous transitions. The same behavior is observed when stable stationary states are continuously shifted by increasing the residence time in the reactor.

The present paper attempts to extend the treatment to a nonadiabatic CSTR system. It is thereby shown that the thermodynamic force and flux of chemical reaction are more useful than the entropy and entropy production in describing nonequilibrium transitions.

II. Thermodynamic Preliminaries

We first give the thermodynamic background necessary to the present problem, reviewing some results of earlier work.[11] The CSTR to be considered contains N species of ideal gases taking part in r chemical reactions. The change in entropy per unit time through the reactor of constant volume V and in a stationary state is given by

$$\hat{S}v - S_0 v_0 = \Phi + \hat{P}V + \frac{Q}{T} \tag{1}$$

with

$$\Phi = v_0 \sum_{i=1}^{N} c_{i0} \left(\int_{T_0}^{T} \frac{c_{Vi}(T)}{T} \, dT - \frac{1}{T} \int_{T_0}^{T} c_{Vi}(T) \, dT \right) +$$
$$Rv_0 \sum_{i=1}^{N} c_{i0} \ln \frac{c_{i0}}{c_i} + R \sum_{i=1}^{N} (c_i v - c_{i0} v_0) + \frac{p_0 v_0 - pv}{T} \tag{2}$$

$$\hat{P} = \sum_{\rho=1}^{r} A_\rho w_\rho / T \tag{3}$$

Here, $\hat{S}_0$ ($\hat{S}$), v_0 (v), T_0 (T), and p_0 (p) are the entropy per unit volume, volumetric rate, absolute temperature, and pressure of the inflow (outflow), respectively; c_{i0} (c_i) is the concentration of species i in the inflow (outflow) (The quantities $\hat{S}$, T, p, and c_i pertain also to the reactor mixture as a result of sufficient stirring.); c_{Vi} is the partial molar heat capacity at constant volume of species i; R is the gas constant; Φ is the entropy of mixing, i.e., the entropy source per unit time due to mixing of the inflow into the reactor contents (for an expression for Φ other than eq 2, see the Appendix.); $\hat{P}$ is the entropy production per unit time and unit volume due to the chemical reactions, with A_ρ and w_ρ the affinity and rate of reaction ρ, respectively; and Q is the heat absorbed per unit time by the reactor from its surroundings.

It is shown that for $p_0 \geq p$, Φ is always nonnegative. The entropy production $\hat{P}$ is also nonnegative if mass action principles are applied to chemical reactions. Equation 1 then gives an illustration of the validity of the second law of thermodynamics:

$$\hat{S}v - S_0 v_0 \geq \frac{Q}{T} \tag{4}$$

In theoretical studies, the rate of the inflow and of the outflow are often set equal when effects of the residence time are

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systematically investigated. Equations 1 and 2 then become

$$\hat{S}v - \hat{S}_0'v = \Phi' + \hat{P}V + \frac{Q}{T} \tag{5}$$

$$\Phi' = v\sum_i c_{i0}'\left(\int_{T_0}^{T}\frac{c_{Vi}(T)}{T}\,dT - \frac{1}{T}\int_{T_0}^{T}c_{Vi}(T)\,dT\right) +$$
$$Rv\sum_i c_{i0}'\ln\frac{c_{i0}'}{c_i} + R\sum_i(c_i - c_{i0}')v + \frac{(p_0'-p)v}{T} \tag{6}$$

where primes have been attached to the quantities referring to the inflow except for its temperature T_0. We call such a CSTR system "fictitious," since it cannot be operated in practice unless $p_0' \geq p$.

This system, however, can always be transformed into a physically realizable one (to be called a "real" system) in the following way without altering the stationary state in the reactor and the conditions in the outflow. We assume that the inflow temperature (T_0) is the same in the fictitious and the corresponding real systems and that the pressure is essentially uniform throughout the real system. Omitting again the primes from the quantities relevant to the inflow in the real system, we then get

$$p_0 = RT_0\sum_i c_{i0} = p = RT\sum_i c_i \tag{7}$$

so that

$$\sum_i c_{i0} = (T/T_0)\sum_i c_i \tag{8}$$

Since the inflow per unit time should contain the same amount of each species in the fictitious and real systems, we have

$$c_{i0}'v = c_{i0}v_0 \quad \text{for} \quad i = 1, ..., N \tag{9}$$

where the inflow rate is again represented by v_0 in the real system. Summation of eq 9 over i gives

$$v_0 = \frac{v\sum_i c_{i0}'}{\sum_i c_{i0}} \tag{10}$$

Substituting eq 8 into eq 10 yields

$$v_0 = \frac{vT_0\sum_i c_{i0}'}{T\sum_i c_i} \tag{11}$$

Equation 11 allows us to determine the inflow rate v_0 in a real system from the given conditions of a fictitious system. It follows from eqs 2, 6, 9, and 11 and the relation

$$p_0' = RT_0\sum_i c_{i0}' \tag{12}$$

that the entropies of mixing Φ' and Φ in a fictitious system and the corresponding real system, respectively, are intercon-

nected by

$$\Phi = \Phi' + Rv\ln\frac{T\sum_i c_i}{T_0\sum_i c_{i0}'}\sum_i c_{i0}' \tag{13}$$

For oscillatory states in which a limit cycle is formed, eqs 5, 1, and 13 are replaced by

$$\langle\hat{S}\rangle v - \hat{S}_0'v = \langle\Phi'\rangle + \langle\hat{P}\rangle V + \left\langle\frac{Q}{T}\right\rangle \tag{14}$$

$$\langle\hat{S}\rangle v - \langle\hat{S}_0 v_0\rangle = \langle\Phi\rangle + \langle\hat{P}\rangle V + \left\langle\frac{Q}{T}\right\rangle \tag{15}$$

$$\langle\Phi\rangle = \langle\Phi'\rangle + Rv\left\langle\ln\frac{v}{v_0}\sum_i c_{i0}'\right\rangle \tag{16}$$

where the angle brackets designate time averages over one period of the limit cycle, v_0 is evaluated as before from v by means of eq 11, and Φ' and Φ are given by eqs 6 and 2, respectively.

While Φ and $\langle\Phi\rangle$ are always nonnegative, Φ' and $\langle\Phi'\rangle$ are not necessarily so. When the entropy of mixing is used later, it will mean Φ or $\langle\Phi\rangle$, not Φ' or $\langle\Phi'\rangle$.

III. Description in Terms of Entropy and Entropy Production

In prior articles,[9,10] we have calculated the entropy and entropy production of reactor contents in isothermal and adiabatic CSTRs with the reaction mechanism

$$A + nB \rightleftharpoons (n + 1)B \tag{17}$$

$$B \rightleftharpoons C \tag{18}$$

where $n = 0, 1,$ or 2. Either the entropy or the entropy production is always found to increase or decrease, respectively, or both behaviors are observed for spontaneous transitions from an unstable stationary state to a stable stationary or oscillatory state when the residence time is kept fixed. The same trend applies when the residence time is lengthened in stable stationary states. In these systems, the entropy is maximized and the entropy production vanishes at equilibrium, i.e., when the residence time becomes infinity.[12] The above findings therefore imply that the effects of irreversible processes relax in light of the entropy or entropy production, or both for spontaneous transitions and when the residence time is increased in stationary states.

This treatment is, however, invalidated for nonadiabatic systems since the entropy does not necessarily have a maximum value at equilibrium.[12] A remedy might be to utilize the entropy of mixing instead of the entropy itself. This is motivated by the fact that a numerical reexamination of the isothermal and adiabatic systems studied previously reveals that the entropy of mixing is maximum at equilibrium and that the statements in the preceding paragraph are still valid even if the entropy is replaced by the entropy of mixing.

To investigate whether or not this argument can be extended to nonadiabatic systems, we now deal with the simplest one in which a first-order reversible reaction

$$A \rightleftharpoons B \tag{19}$$

proceeds. We assume that the reaction conforms to a mass

action law and that heat exchange is described by Newton's law

$$Q = hA(T_a - T) \qquad (20)$$

where h is a heat transfer coefficient, A an effective surface area, and T_a an ambient temperature. (A similar nonadiabatic system with $T_a = T_0$ has been treated earlier in a different context.[12]) Considering a fictitious system as before, we set $v_0 = v$ but, for simplicity, write the inflow concentrations c_{A0} and c_{B0} without primes. The mass and energy balance equations and eqs 3, 6, and 13 then take the forms[12]

$$V\frac{dc_A}{dt} = v(c_{A0} - c_A) - V[k_+(T)c_A - k_-(T)c_B] \qquad (21)$$

$$V\frac{dc_B}{dt} = v(c_{B0} - c_B) + V[k_+(T)c_A - k_-(T)c_B] \qquad (22)$$

$$\hat{C}_{V0}V\frac{dT}{dt} = v\hat{C}_{p0}(T_0 - T) - V\Delta H[k_+(T)c_A - k_-(T)c_B] + $$
$$RTv[(c_{A0} + c_{B0}) - (c_A + c_B)] + hA(T_a - T) \quad (23)$$

$$\hat{P} = R[k_+(T)c_A - k_-(T)c_B] \ln\frac{k_+(T)c_A}{k_-(T)c_B} \qquad (24)$$

$$\Phi = \Phi' + R(c_{A0} + c_{B0})v \ln\frac{T(c_A + c_B)}{T_0(c_{A0} + c_{B0})} \qquad (25)$$

where

$$\Phi' = v\left[\hat{C}_{V0}\ln\frac{T}{T_0} - \frac{\hat{C}_{p0}(T - T_0)}{T} + \right.$$
$$\left. R\left(c_{A0}\ln\frac{c_{A0}}{c_A} + c_{B0}\ln\frac{c_{B0}}{c_B}\right)\right] \quad (26)$$

Here, $\hat{C}_{V0}$ and $\hat{C}_{p0}$ are the heat capacities at constant volume and pressure, respectively, per unit volume of the inflow, and have been regarded as independent of temperature

$$\hat{C}_{V0} = \sum_i c_{i0}c_{Vi}, \quad \hat{C}_{p0} = \sum_i c_{i0}c_{pi} \qquad (27)$$

where c_{pi} is the partial molar heat capacity at constant pressure of species i, $-\Delta H$ is the heat of reaction, and $k_+(T)$ and $k_-(T)$ are the rate constants in the forward and reverse directions, respectively, and are supposed to obey Arrhenius kinetics

$$k_+(T) = A_+ \exp[-E_+/(RT)] \qquad (28)$$

$$k_-(T) = A_- \exp[-E_-/(RT)]$$

where A_+ and A_- are the preexponential factors and E_+ and E_- the activation energies. The rate constants are connected with thermodynamic functions as

$$\frac{k_+(T)}{k_-(T)} = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(\frac{-\Delta H + T\Delta S}{RT}\right) \qquad (29)$$

where ΔG and ΔS are the standard Gibbs free energy and entropy changes, respectively. We take ΔH and ΔS as constants independent of temperature. In eq 23, the heat capacity at constant volume of the reactor mixture has been approximated

by $\hat{C}_{V0}V$. In the derivation of eq 26 from eq 6, use has been made of eqs 7 and 12 and the thermodynamic relation

$$c_{pi} = c_{Vi} + R \qquad (30)$$

With the introduction of the dimensionless variables

$$\tau = k_+(T_0)t, \quad \alpha = \frac{c_A}{c_{A0}}, \quad \beta = \frac{c_B}{c_{A0}}, \quad \theta = \frac{E_+(T - T_0)}{RT_0^2} \qquad (31)$$

and parameters

$$\tau_{res} = k_+(T_0)t_{res}, \quad \beta_0 = \frac{c_{B0}}{c_{A0}}, \quad \theta_a = \frac{E_+(T_a - T_0)}{RT_0^2}, \quad \epsilon = \frac{RT_0}{E_+},$$

$$\eta = -\frac{\Delta H}{RT_0}, \quad \zeta = \frac{\Delta S}{R}, \quad B = -\frac{C_{A0}E_+\Delta H}{\hat{C}_{p0}RT_0^2},$$

$$\lambda = \frac{hA}{\hat{C}_{p0}k_+(T_0)V}, \quad \chi = \frac{\hat{C}_{V0}}{\hat{C}_{p0}} = 1 - \frac{B\epsilon(1 + \beta_0)}{\eta} \qquad (32)$$

where t_{res} is the mean residence time, i.e., $t_{res} = V/v$, eqs 21–26 may be rewritten as

$$\frac{d\alpha}{d\tau} = \frac{1 - \alpha}{\tau_{res}} - \exp\left(\frac{\theta}{1 + \epsilon\theta}\right)\left[\alpha - \beta\exp\left(-\frac{\eta}{1 + \epsilon\theta} - \zeta\right)\right] \qquad (33)$$

$$\frac{d\beta}{d\tau} = \frac{\beta_0 - \beta}{\tau_{res}} + \exp\left(\frac{\theta}{1 + \epsilon\theta}\right)\left[\alpha - \beta\exp\left(-\frac{\eta}{1 + \epsilon\theta} - \zeta\right)\right] \qquad (34)$$

$$\chi\frac{d\theta}{d\tau} = -\frac{\theta}{\tau_{res}} + B\exp\left(\frac{\theta}{1 + \epsilon\theta}\right)\left[\alpha - \beta\exp\left(-\frac{\eta}{1 + \epsilon\theta} - \right.\right.$$
$$\left.\left.\zeta\right)\right] + \frac{B(1 + \epsilon\theta)(1 + \beta_0 - \alpha - \beta)}{\eta\tau_{res}} + \lambda(\theta_a - \theta) \quad (35)$$

$$\sigma = \exp\left(\frac{\theta}{1 + \epsilon\theta}\right)\left[\alpha - \beta\exp\left(-\frac{\eta}{1 + \epsilon\theta} - \zeta\right)\right]\left(\frac{\eta}{1 + \epsilon\theta} + \zeta + \right.$$
$$\left. \ln\frac{\alpha}{\beta}\right) \quad (36)$$

$$\phi = \phi' + (1 + \beta_0)\ln\frac{(1 + \epsilon\theta)(\alpha + \beta)}{1 + \beta_0} \qquad (37)$$

$$\phi' = \frac{\chi\eta}{B\epsilon}\ln(1 + \epsilon\theta) - \frac{\eta\theta}{B(1 + \epsilon\theta)} - \ln\alpha + \beta_0\ln\frac{\beta_0}{\beta} \qquad (38)$$

where σ, ϕ, and ϕ' are a dimensionless entropy production and dimensionless entropies of mixing, respectively, defined by

$$\sigma = \frac{\hat{P}}{Rc_{A0}k_+(T_0)}, \quad \phi = \frac{\Phi}{Rc_{A0}v}, \quad \phi' = \frac{\Phi'}{Rc_{A0}v} \qquad (39)$$

In this paper, we are interested in stationary and sustained oscillatory states, which may be considered to be established after the elapse of ample time. Addition of eqs 33 and 34 then leads to[10]

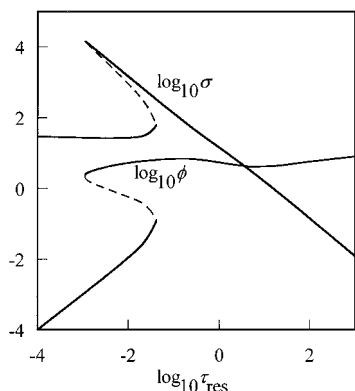$$\alpha + \beta = 1 + \beta_0 \qquad (40)$$

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Figure 1. Dependence of the entropy of mixing ϕ and entropy production σ in stationary states on the residence time τ_{res} for a CSTR in which a first-order reaction A $\rightleftharpoons$ B takes place. Stable and unstable states are represented by solid and dashed lines, respectively. Parameter values are $B = 10$, $\epsilon = 10^{-6}$, $\eta = 10$, $\zeta = 10$, $\lambda = 1$, $\theta_a = 1$, $\beta_0 = 0$.

which may be utilized to eliminate β in eqs 33 and 35:

$$\frac{d\alpha}{d\tau} = \frac{1-\alpha}{\tau_{res}} - \exp\left(\frac{\theta}{1+\epsilon\theta}\right)\left[\alpha - (1+\beta_0-\alpha) \times \right.$$
$$\left. \exp\left(-\frac{\eta}{1+\epsilon\theta} - \zeta\right)\right] \quad (41)$$

$$\chi\frac{d\theta}{d\tau} = -\frac{\theta}{\tau_{res}} + B\exp\left(\frac{\theta}{1+\epsilon\theta}\right)\left[\alpha - (1+\beta_0-\alpha) \times \right.$$
$$\left. \exp\left(-\frac{\eta}{1+\epsilon\theta} - \zeta\right)\right] + \lambda(\theta_a - \theta) \quad (42)$$

For stationary states, adding eq 41 multiplied by B to eq 42, we have

$$\theta = \frac{B(1-\alpha) + \lambda\tau_{res}\theta_a}{1 + \lambda\tau_{res}} \quad (43)$$

Substitution of eq 43 back into eq 41 with $d\alpha/d\tau = 0$ yields

$$\frac{1-\alpha}{\tau_{res}} - \exp\left[\frac{B(1-\alpha) + \lambda\theta_a\tau_{res}}{1 + \lambda\tau_{res} + B\epsilon(1-\alpha) + \lambda\epsilon\theta_a\tau_{res}}\right] \times$$
$$\left\{\alpha - (1+\beta_0-\alpha)\exp\left[-\right.\right.$$
$$\left.\left.\frac{\eta(1+\lambda\tau_{res})}{1 + \lambda\tau_{res} + B\epsilon(1-\alpha) + \lambda\epsilon\theta_a\tau_{res}} - \zeta\right]\right\} = 0 \quad (44)$$

When the values of the parameters B, ϵ, η, ζ, λ, θ_a, β_0, and τ_{res} are given, we obtain the stationary-state values of α, β, and θ by solving eq 44 numerically for α and using eqs 40 and 43. The entropy of mixing ϕ and entropy production σ are then evaluated from eqs 36−38. For oscillatory behavior, the values of $\langle\phi\rangle$ and $\langle\sigma\rangle$ are computed by averaging eqs 36−38 over a period of a limit cycle while solving eqs 41 and 42 numerically by means of a Gear or a Runge−Kutta method.

Such calculations have been made for a wide variety of parameter values. Typical results are shown in Figures 1 and 2, where ϕ, σ, $\langle\phi\rangle$, and $\langle\sigma\rangle$ are depicted as a function of τ_{res}, with solid and dashed lines denoting stable and unstable states (stationary or oscillatory), respectively. Figure 1 indicates that ϕ increases and/or σ decreases with increasing τ_{res} and that, in a range of τ_{res} where multiple (i.e., triple) stationary states exist, the same is true for spontaneous transitions from unstable to stable stationary states. Figure 2 displays representative data for oscillatory behavior. In each figure, the solid circle stands
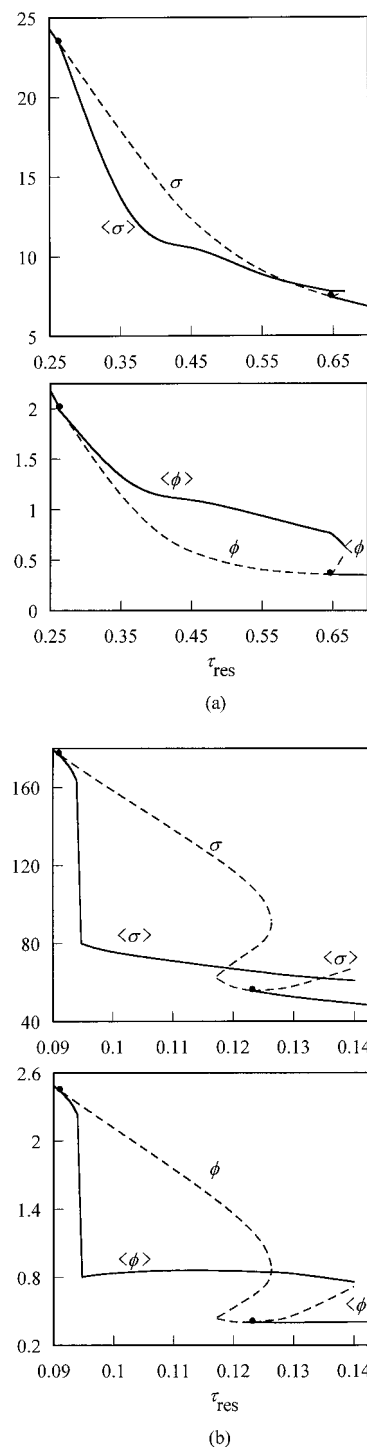

(a)

(b)

Figure 2. Entropy of mixing ϕ ($\langle\phi\rangle$) and entropy production σ ($\langle\sigma\rangle$) in stationary (oscillatory) states as a function of the residence time τ_{res} for a CSTR with a first-order reaction. Stable and unstable states, stationary or oscillatory, are designated by solid and dashed lines, respectively. The solid circles refer to points of Hopf bifurcation. Parameter values: (a) $B = 20$, $\epsilon = 10^{-3}$, $\eta = 10$, $\zeta = 0$, $\lambda = 12$, $\theta_a = -0.7$, $\beta_0 = 1$; (b) $B = 16$, $\epsilon = 10^{-6}$, $\eta = 10$, $\zeta = 10$, $\lambda = 22.8$, $\theta_a = 0$, $\beta_0 = 0$.

for a Hopf bifurcation point at which a limit cycle appears. More precisely, the left and the right bifurcations are a supercritical and a subcritical one at which a stable and an unstable limit cycle emerge, respectively. In these systems, those transitions that are spontaneous for fixed values of τ_{res} are from unstable stationary states to stable oscillatory states and from unstable oscillatory states to stable stationary or oscillatory states. It may be seen that all these transitions are accompanied by either an increase in ϕ or a decrease in σ or both.
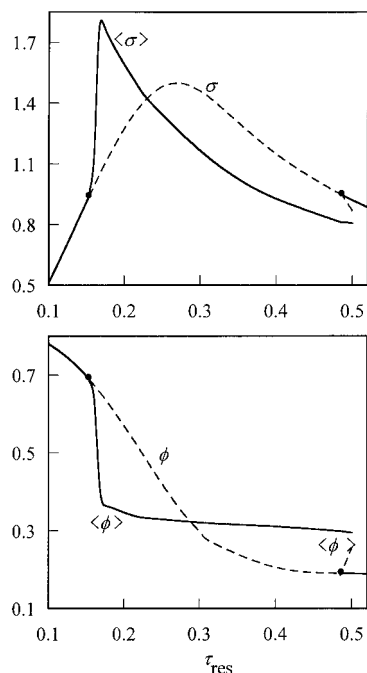
Figure 3. Entropy of mixing ϕ ($\langle\phi\rangle$) and entropy production σ ($\langle\sigma\rangle$) in stationary (oscillatory) states as a function of the residence time τ_{res} for a CSTR with a first-order reaction and with the parameter values $B = 20$, $\epsilon = 10^{-2}$, $\eta = 1$, $\zeta = 1$, $\lambda = 12$, $\theta_a = -0.5$, $\beta_0 = 1$. The graphic notation is the same as in Figure 2.

Nevertheless, the above systematic trends, albeit prevalent in many cases, are violated for some combinations of parameter values. An example is presented in Figure 3, where the solid and dashed lines and solid circles have the same meaning as in Figure 2. It may be observed that ϕ decreases and σ increases as τ_{res} is increased in stationary states below the left bifurcation and that the same behavior applies for spontaneous transitions from unstable stationary states to stable oscillatory states over a certain range of τ_{res}.

IV. Description in Terms of Thermodynamic Forces and Flows

If the notion, as stated in section III, that the effects of irreversible processes diminish in some way for spontaneous transitions and for the lengthening of the residence time in stationary states has any validity, one might expect that this is reflected more directly in the so-called thermodynamic forces and fluxes of chemical reactions, both of which vanish at equilibrium. Specifically, the thermodynamic force of reaction ρ is given by its affinity divided by the temperature of the system, i.e., A_ρ/T, and the corresponding flux is the reaction rate w_ρ itself. It should be remarked that although the thermodynamic flux is proportional to the force in near-equilibrium situations, it is not generally so for far-from-equilibrium regions of main concern here.

For the specific CSTR system examined in section III, the dimensionless thermodynamic force X and flux J of reaction 19 read

$$X = \frac{\eta}{1 + \epsilon\theta} + \zeta + \ln\frac{\alpha}{\beta} \qquad (45)$$

$$J = \exp\left(\frac{\theta}{1 + \epsilon\theta}\right)\left[\alpha - \beta\exp\left(-\frac{\eta}{1 + \epsilon\theta} - \zeta\right)\right] \qquad (46)$$

Note that multiplication of these quantities produces the entropy production σ given by eq 36. The values of X and J at stationary
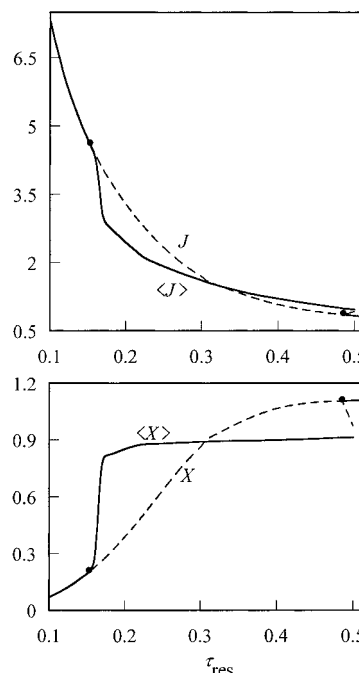

Figure 4. Thermodynamic force X ($\langle X\rangle$) and flux J ($\langle J\rangle$) of chemical reaction in stationary (oscillatory) states as a function of the residence time τ_{res} for the same system as in Figure 3.

states and their averaged values over limit cycles have also been calculated in a way similar to that employed for ϕ and σ. By way of illustration, Figure 4 shows results for the system considered in Figure 3, whose behavior could not be characterized well on the basis of ϕ and σ. Figure 4 reveals that there is always a decrease in X or J or both for spontaneous transitions as well as with increasing τ_{res} in stationary states. Such systematic trends are found to be followed by a large number of systems including those represented by Figures 1 and 2.

Isothermal CSTRs with the two-reaction scheme of 17 and 18 have also been investigated. In this case, the sums of the thermodynamic forces and of the fluxes are taken as measures of irreversibility. Although detailed results are omitted here, all the systems examined, without exception, exhibit the same type of regularity as above.

These findings may be considered to imply that the effects of irreversible processes are reduced with regard to thermodynamic forces and/or fluxes for spontaneous transitions and when the residence time is elongated in stationary states.

V. Concluding Remarks

It has been suggested in the preceding section that the effects of irreversibility lessen at least in light of thermodynamic forces or fluxes for possible nonequilibrium transitions. For the present, the author could not provide an *a priori* basis for such general trends but thinks that it should be confirmed empirically by various examples. In this respect, it may be intriguing to apply the present treatment to chemical systems different from CSTRs and to transitions involving irreversible processes other than chemical reactions. Studies of this nature are now contemplated.

Appendix. Derivation of an Alternative Expression for the Entropy of Mixing

The entropy of mixing Φ in CSTR systems is different from the conventional one for mixtures. To gain further insight into Φ, we express it in another form. For the notation not explained below, see the first paragraph of section II.

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With the use of the partial molar entropy s_i, enthalpy h_i, and Gibbs free energy (i.e., chemical potential) μ_i of species i in the reactor, the change in entropy of the reactor contents (or outflow) relative to the inflow is written as

$$\hat{S}v - \hat{S}_0 v_0 = v\sum_{i=1}^{N} s_i c_i - \hat{S}_0 v_0 = \frac{v}{T}\sum_{i=1}^{N} h_i c_i - \frac{v}{T}\sum_{i=1}^{N} \mu_i c_i - \hat{S}_0 v_0 \tag{A1}$$

As stationary states, conservation of mass for species i and of energy gives

$$c_i v = c_{i0} v_0 + V\sum_{\rho=1}^{r} \nu_{i\rho} w_\rho \tag{A2}$$

$$v\sum_i h_i c_i = v_0 \sum_i h_{i0} c_{i0} + Q \tag{A3}$$

where $\nu_{i\rho}$ is the stoichiometric coefficient of species i in reaction ρ, to be understood as positive or negative according to whether it is a net product or reactant of the reaction, and h_{i0} is the partial molar enthalpy of species i in the inflow. (Equation A3 follows readily from eq 2 of ref 11.) Substituting eqs A2 and A3 into eq A1, we have

$$\hat{S}v - \hat{S}_0 v_0 = -\frac{v_0}{T}\sum_i \mu_i c_{i0} - \hat{S}_0 v_0 + \frac{v_0}{T}\sum_i h_{i0} c_{i0} + \hat{P}V + \frac{Q}{T} \tag{A4}$$

where the definition of the affinity

$$A_\rho = -\sum_i \nu_{i\rho} \mu_i \tag{A5}$$

and eq 3 of the text have been used. Identification of the right-hand sides of eqs A4 and 1 yields the desired result:

$$\Phi = -\frac{v_0}{T}\sum_i \mu_i c_{i0} - \hat{S}_0 v_0 + \frac{v_0}{T}\sum_i h_{i0} c_{i0} \tag{A6}$$

The first two terms on the right of eq A6 as a whole may be regarded as representing the entropy of mixing of the inflow with the reactor mixture at constant internal energy and volume in view of the thermodynamic relation

$$\left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_i'} = -\frac{\mu_i}{T} \tag{A7}$$

where S and U are the entropy and internal energy of the mixture, respectively, n_i is the mole number of species i, and the subscript n_i' indicates that the mole number of every species except i is kept constant. The last term of eq A6 may be interpreted as an entropy change due to the inflow of enthalpy into the reactor.

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