Entropy Production in Oscillating Chemical Systems

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The entropy production in oscillating homogenous chemical systems is investigated by analyzing the difference between the average entropy production rate in a stable periodic oscillatory mode and in the corresponding unstable stationary state. A general analytical expression for this difference in the neighborhood of a Hopf bifurcation is derived. The entropy production in two typical models of chemical systems with unstable stationary states and stable periodic oscillations is investigated, using fixed concentrations as control parameters. The models exemplify both positive and negative entropy production rate differences. One of the investigated models has four free concentrations, the other three. The rate expressions are given by second order mass action kinetics with reverse reactions taken into account. The flows of reactants and products are controlled so that only the free concentrations vary, and the entropy of mixing associated with these flows is discussed.

I. Introduction

Systems that exhibit structure in space and/or time (e.g. stationary geometrical patterns, travelling waves, or periodical oscillations) if they are forced away from the thermostatic equilibrium state [1] have begun to yield some of their hitherto unknown properties in recent years. Systems with such structures produce entropy, they are dissipative. This can be viewed as a cost for the environment, and thus raises questions as to why such structures are so common in nature and what factors contribute to their high survival ability. In other words, which evolutionary principles govern the behavior of open systems? If the entropy production is a cost, may not minimization of it be favorable for the system? The present paper is a contribution to the study of questions such as these for dynamical structures, i.e. structures in time.

Dissipative structures typically involve parts of the state space so far from the thermostatic equilibrium that the macroscopic dynamical equations cannot be linearized in terms of quantities which describe deviations from this equilibrium. If the dynamics nevertheless can be satisfactorily (in some sense) described by thermal variables we speak of "nonlinear thermodynamics". Nonlinear thermodynamics is considerably less developed than the older fields of thermostatics and linear thermodynamics, but some general statements valid for large classes of systems have been formulated [1–3].

The entropy production in a class of homogenous and isothermal chemical systems is investigated using mathematical models representative of the class. The models are constructed as compromises between closeness to physical realism and computational tractability. A basic assumption is that the local equilibrium approximation is valid. Furthermore all concentrations are kept homogenous by assuming that the diffusion processes or the effects of the stirring device are very fast compared to effects of the chemical reactions. The reaction rates are assumed to follow the simplest form of the law of mass action in ideal gas mixtures (or dilute solutions), and since true three-body collision-reactions are extremely improbable only second order reactions are used. All reactions are reversible. (The one-way reactions of e.g. the "Brusselator" [1] are thus excluded, as well as the third order reaction.) The basic reason for this approach is that calculation of the entropy production using the thermostatic expression for the chemical potential becomes possible. All fugacity (activity) coefficients are set equal to one.

The entropy production associated with the introduction and extraction of substances is also analyzed. Such flows are intrinsic features of the model since the concentrations of some of the substances are assumed to be kept constant. Variations in the reaction rates show up as variations in these flows and the associated production of entropy of mixing.

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The entropy production in the stirring and temperature control devices is not considered here, nor the entropy production in the devices controlling the flows of reactants and products.

II. Entropy Production Rate Difference

Let the state of a general system be given by a vector $\boldsymbol{x}(t)$, and let the equations of motion be

$$\dot{\boldsymbol{x}} = \boldsymbol{f}(q; \boldsymbol{x}) , \tag{1}$$

where q is a scalar control parameter [4] characterizing f. Denote the stationary state $\boldsymbol{x}^*$ and the entropy production rate $\sigma(\boldsymbol{x}(t))$. For values of q where closed trajectories solve (1) define

$$\Delta(q) = \bar{\sigma}(q) - \sigma^{\text{stat}}(q) , \tag{2}$$

where σ^{stat} is the entropy production rate in chemical reactions in the stationary state, $\sigma(\boldsymbol{x}^*)$, and

$$\bar{\sigma} = \frac{1}{T} \int_C \sigma \, \mathrm{d}t , \tag{3}$$

i.e. the average entropy production rate on a closed trajectory C with period T.

In the neighborhood of a Hopf bifurcation [5] there are two complex conjugate eigenvalues to the jacobian matrix (evaluated at $\boldsymbol{x}^*$), which can be written

$$\lambda_1 = \varepsilon(q) + i\,\omega(q) \quad \text{and} \quad \lambda_2 = \varepsilon(q) - i\,\omega(q) , \tag{4}$$

where $\varepsilon(q^*) = 0$, q^* being the Hopf bifurcation parameter value. (The stationary state is unstable and thus oscillations possible if $\varepsilon(q) > 0$.) Except in pathological cases there exist two corresponding mutually orthogonal eigenvectors which are also orthogonal to all other eigenvectors. These two vectors define a plane in the state space, and using them two orthogonal unit vectors, say $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$, lying in this plane, can be defined so that for sufficiently small positive $\varepsilon(q)$ (i.e. q close to q^*) the closed trajectory is given by the circle

$$\boldsymbol{x}(t) = \boldsymbol{x}^* + r(q)\,(\boldsymbol{e}_1 \cos\omega(q)\,t + \boldsymbol{e}_2 \sin\omega(q)\,t) , \tag{5}$$

where $r(q^*) = 0$.

Expansion of the entropy production rate difference around the stationary state yields

$$\Delta = \frac{1}{T} \int_0^T \{\sigma(\boldsymbol{x}(t)) - \sigma(\boldsymbol{x}^*)\} \, \mathrm{d}t$$

$$= \frac{1}{T} \int_0^T \left\{ (\boldsymbol{x}(t) - (\boldsymbol{x}^*)) \cdot \left(\frac{\partial \sigma}{\partial \boldsymbol{x}} (\boldsymbol{x}^*) \right) + \frac{1}{2} (\boldsymbol{x}(t) - (\boldsymbol{x}^*))\, M\, (\boldsymbol{x}(t) - (\boldsymbol{x}^*)) + \ldots \right\} \mathrm{d}t , \tag{6}$$

where the matrix M is the Hessian matrix evaluated at $\boldsymbol{x}^*$,

$$M = \boldsymbol{\nabla\nabla}\sigma(\boldsymbol{x})\,|_{x=x^*} . \tag{7}$$

The integral over the first term in (6) vanishes when the expression (5) is inserted. To second order

$$\Delta = (\boldsymbol{e}_1 M \boldsymbol{e}_1 + \boldsymbol{e}_2 M \boldsymbol{e}_2)\, r^2/4 . \tag{8}$$

Thus the sign of Δ in the immediate neighborhood of q^* is determined by this sum of quadratic forms. If M is positive or negative definite for q close to q^* then this obviously determines the sign of Δ in this neighborhood. There is no guarantee that it will be always positive or always negative. The two models presented below exemplify both positive and negative values. The derivation above is only valid in an immediate neighborhood of q^*, for parameter values further away $\Delta(q)$ may for instance change sign several times.

III. The Models

The models are simple variations of one of a class of two-dimensional models with exactly soluble elliptical limit cycles, thoroughly analyzed by Escher [6–11]. A common feature of these two-dimensional models is the autocatalytic reaction

$$A + 2X \rightarrow 3X . \tag{9}$$

This reaction is replaced in each model here by a set of mono- and bimolecular, reversible reactions. One set contains two new freely varying substances, Z and W, which makes the model four-dimensional. The reason for the increased dimensionality is that Hopf bifurcations cannot occur in two-dimensional systems with second order rate expressions [12]. The other set contains one extra substance and therefore gives a three-dimensional model. Although oscillations can in principle occur in second order two-dimensional systems where the stationary state is a saddle point, it is much simpler to create oscillating second order systems in three or more dimensions.

The letters A, B, C, and D denote the substances whose concentrations are kept constant (reactants/products) and X, Y, Z, and W the substances whose concentrations are allowed to vary freely. The corresponding small letters are used to denote concentrations. The flows of A, B, C, and D pass through perfect semi-permeable membranes or other devices through which X, Y, Z, and W cannot pass.

The four-dimensional model is given by the reaction scheme

$$A + X \rightleftharpoons Z\,, \qquad (10\,\mathrm{a})$$

$$Z + X \rightleftharpoons W + X\,, \qquad (10\,\mathrm{b})$$

$$W \rightleftharpoons 2X\,, \qquad (10\,\mathrm{c})$$

$$X + Y \rightleftharpoons B\,, \qquad (10\,\mathrm{d})$$

$$2X \rightleftharpoons Y + C\,, \qquad (10\,\mathrm{e})$$

$$Y \rightleftharpoons D\,. \qquad (10\,\mathrm{f})$$

The reactions (10a–c) add up to reaction (9). To get elliptical limit cycles in the X-Y-plane one must exclude the reverse reaction in (9) and (10e) and choose A-B-C-D-concentrations and rate constants appropriately.

The individual reaction rates J_i are given in Table 1, with forward and reverse reaction rate constants denoted by k_i and k_{-i} $(i = 1, \ldots, 6)$, respectively. The rate expressions are

$$\dot{x} = -J_1 + 2J_3 - J_4 - 2J_5\,, \qquad (11\,\mathrm{a})$$

$$\dot{y} = -J_4 + J_5 - J_6\,, \qquad (11\,\mathrm{b})$$

$$\dot{z} = J_1 - J_2\,, \qquad (11\,\mathrm{c})$$

$$\dot{w} = J_2 - J_3\,. \qquad (11\,\mathrm{d})$$

With X, Y, and Z as the free substances the three-dimensional model is given by replacing the reactions (10a–c) by

$$A + Z \rightleftharpoons X + Z\,, \qquad (12\,\mathrm{a})$$

$$Z \rightleftharpoons 2X\,. \qquad (12\,\mathrm{b})$$

Table 1. Reaction rates J_i and affinities A_i.

i	J_i	$\exp(A_i/RT)$	Reaction
1	$k_1 a x - k_{-1} z$	$k_1 a x/(k_{-1} z)$	(10a)
2	$k_2 z x - k_{-2} w x$	$k_2 z/(k_{-2} w)$	(10b)
3	$k_3 w - k_{-3} x^2$	$k_3 w/(k_{-3} x^2)$	(10c)
4	$k_4 x y - k_{-4} b$	$k_4 x y/(k_{-4} b)$	(10d)
5	$k_5 x^2 - k_{-5} c y$	$k_5 x^2/(k_{-5} c y)$	(10e)
6	$k_6 y - k_{-6} d$	$k_6 y/(k_{-6} d)$	(10f)
7	$k_7 a z - k_{-7} x z$	$k_7 a/(k_{-7} x)$	(12a)
8	$k_8 z - k_{-8} x^2$	$k_8 z/(k_{-8} x^2)$	(12b)

The rate expressions are

$$\dot{x} = J_7 + 2J_8 - J_4 - 2J_5\,, \qquad (13\,\mathrm{a})$$

$$\dot{y} = -J_4 + J_5 - J_6\,, \qquad (13\,\mathrm{b})$$

$$\dot{z} = -J_8\,, \qquad (13\,\mathrm{c})$$

where the indices 7 and 8 corresponds to reaction (12a) and (12b), respectively.

IV. Entropy Production in the Models

There are two kinds of contributions to the entropy production in the described models, one due to mixing and one due to chemical reactions. The rate of entropy production due to the reactions is given by

$$\sigma = T^{-1} \sum_i J_i A_i\,, \qquad (14)$$

where T is the temperature and A_i is the affinity of reaction i, defined by

$$A_i = -\sum_j v_{ij}\,\mu_j\,, \qquad (15)$$

where v_{ij} is the stoichiometric coefficient of j $(j = x, y, z, w)$ in reaction i, and μ_j is the chemical potential of j, here assumed to obey the ideal gas/solution relation

$$\mu_j = \mu_j^0 + RT \ln x_j\,, \qquad (16)$$

where μ_j^0 is the standard state chemical potential at the actual temperature and pressure, and x_j denotes the molar fraction. Since the affinities and the reaction rates are zero in the thermostatic equilibrium state, the affinities are as given in Table 1 (setting here and in the following the gas constant $R = 1$ for simplicity). Obviously all terms in the sum in (14) are non-negative, and they are zero only if the reaction rates are zero.

The entropy of mixing when one mole of j is introduced into a system is generally

$$S_{\mathrm{mix}} = -\ln x_j\,. \qquad (17)$$

Since it is assumed that a, b, c, and d are kept constant there are necessarily rates of entropy production due to entropy of mixing in the in- and outflows of A, B, C, and D. These rates are

$$\begin{aligned}\sigma_{\mathrm{mix}} = {} & + J_1 \ln(a/N) - J_4 \ln(b/N) \\ & - J_5 \ln(c/N) - J_6 \ln(d/N)\end{aligned} \qquad (18)$$

in the four-dimensional model and

$$\sigma_{\text{mix}} = + J_7 \ln (a/N) - J_4 \ln (b/N) - J_5 \ln (c/N) - J_6 \ln (d/N) \tag{19}$$

in the three-dimensional one. N is the total molar concentration.

It is simple to change the reaction schemes so that an integral over the in- and outflows on any entire closed trajectory is zero. Since the fixed concentrations can be set equal without changing the dynamical behaviour if the rate constants are changed appropriately (keeping the products constant), it is always possible to make the integral of σ_{mix} over an entire period vanishing for any closed trajectory. As a special case it is then also zero in the stationary state. In fact the sign and magnitude of σ_{mix} is arbitrary for entire classes of models with identical dynamical behavior. Thus it is pointless to make a thorough investigation of the entropy of mixing in models of the kind studied here. In real chemical systems, however, where reactions and rate constants are given by nature, this is not so.

The sum of the two contributions to the entropy production is

$$\sigma_{\text{sum}} = \sigma + \sigma_{\text{mix}} . \tag{20}$$

The total molar concentration N can be much greater than the sum of the concentrations of the reacting molecules, indicating the presence of large amounts of a nonreacting solvent. By an appropriate choice of parameters it is possible to make the sum either greater or smaller than zero on an entire limit cycle. For the four-dimensional model with the reference parameter values given below this can only happen for N larger than approximately 10^{40}, a number that would make the solution very dilute indeed! For reasonable values of N, say $10^4 - 10^5$, the sum is positive in this model.

V. Stability Analysis

To find the interesting regions of the parameter space where a system oscillates the stability of the stationary state(s) is investigated. The stationary states of the dynamical system (11) are given by

$$\bar{y} = (k_{-4} b + k_5 \bar{x}^2 + k_{-6} d)/N_2 , \tag{21}$$

$$\bar{z} = (k_1 a (1 + \beta \bar{x}) + \beta k_{-3} \bar{x}^2)\, \bar{x}/(k_{-1} N_1) , \tag{22}$$

$$\bar{w} = (k_{-3} + k_1 a \alpha + \alpha k_{-3} \bar{x})\, \bar{x}^2/(k_3 N_1) , \tag{23}$$

where $\bar{x}$ is given by the roots of the fourth order polynomial

$$N_1 P_1 + N_2 P_2 = 0 \tag{24}$$

with

$$\alpha = k_2/k_{-1} , \tag{25}$$

$$\beta = k_{-2}/k_3 , \tag{26}$$

$$N_1 = 1 + (\alpha + \beta) x , \tag{27}$$

$$N_2 = k_6 + k_{-5} c + k_4 x , \tag{28}$$

$$P_1 = k_{-4} b (k_6 + 3 k_{-5} c) + k_{-6} d (2 k_{-5} c - k_4 x) - k_5 x^2 (3 k_4 x + 2 k_6) , \tag{29}$$

$$P_2 = x^2 (\alpha k_1 a - \beta k_{-3} x) . \tag{30}$$

Generally, (24) can yield more than one stationary state, but in the part of parameter space of current interest there is only one non-negative real root of (24), i.e. the stationary state is unique.

The rate expression of reaction (9) can be retrieved by assuming that $z = w \approx 0$, so that (11 a) can be written

$$\dot{x} = P_2/N_1 . \tag{31}$$

When $(\alpha + \beta) x \ll 1$, expansion of the right-hand side of (31) in powers of x yields

$$x = \alpha k_1 a x^2 + \sum_{n=3}^{\infty} (-x)^n \cdot [\beta k_{-3} (\alpha + \beta)^{n-3} + \alpha k_1 a (\alpha + \beta)^{n-2}] , \tag{32}$$

and the rate expression of reaction (9) (with reverse reaction) is found by discarding all terms of order x^4 and higher. Escher's system is in fact reached exactly in the limit

$$\alpha \to 0 , \quad \beta \to 0 , \quad k_{-5} = 0 , \tag{33a}$$

$$\alpha k_1 a \ \text{constant (i.e.}\ k_1 a \to \infty) , \tag{33b}$$

where the entire sum in (32) disappears. If k_{-5}, α and β are chosen small but non-zero the limit cycles are still roughly planar and elliptic, but they do not lie in a plane parallel to the x-y-plane, as can be seen in the projections into x-y-z- and x-y-w-space. The time constants for movement perpendicular to this plane are roughly five orders of magnitude smaller than those associated with movement parallel to it.

The stability of the stationary state is determined by the signs of the real parts of the eigenvalues of the jacobian matrix

$$J = \begin{pmatrix} -k_1 a - 4k_{-3}x - k_4 y - 4k_5 x & -k_4 x + 2k_{-5}c & k_{-1} & 2k_3 \\ -k_4 y + 2k_5 x & -k_4 x - k_{-5}c - k_6 & 0 & 0 \\ k_1 a - k_2 z + k_{-2} w & 0 & -k_{-1} - k_2 x & k_{-2} x \\ k_2 z - k_{-2} w + 2k_{-3} x & 0 & k_2 x & -k_{-2} x - k_3 \end{pmatrix} \tag{34}$$

evaluated at the stationary state. The eigenvalues λ_i $(i = 1-4)$ are the roots of the fourth-order polynomial

$$\mathrm{Det}\,(J - \lambda I) = 0\,. \tag{35}$$

Similarly, for the three-dimensional model the stationary states are given by

$$\bar{y} = g\,(\bar{x})\,, \tag{36}$$

$$\bar{z} = h\,(\bar{x})\,, \tag{37}$$

where

$$g\,(x) = (k_{-4} b + k_{-6} d + k_5 x^2)/(k_4 x + k_{-5} c + k_6)\,,$$

$$h\,(x) = k_{-8} x^2/k_8\,, \tag{39}$$

and where $\bar{x}$ is a root of the fourth-order polynomial

$$(k_7 a - k_{-7} x)\,h\,(x) - k_4 x\,g\,(x) + k_{-4} b$$
$$- 2\,(k_5 x^2 - k_{-5} c\,g\,(x))\,. \tag{40}$$

One of the roots is real and negative for all values of *a*, *b*, *c*, and *d*.

The jacobian matrix is

$$J = \begin{pmatrix} -k_{-7} z - 4k_{-8} x - k_4 y - 4k_5 x & -k_4 x + 2k_{-5} c & k_7 a - k_{-7} x + 2k_8 \\ -k_4 y + 2k_5 x & -k_4 x - k_{-5} c - k_6 & 0 \\ 2k_{-8} x & 0 & -k_8 \end{pmatrix}. \tag{41}$$

The eigenvalues are here the roots of the third order polynomial corresponding to (35).

As pointed out above, a positive real part of any eigenvalue to the jacobian matrix evaluated in the stationary state indicates instability of the stationary state.

VI. Simulation Results

The numerical investigations [13] are based upon a reference case with the following parameter values: $k_1 = 100$, $k_{-6} = 10^6$, $k_2 = 700$, $k_{-2} = k_4 = k_6 = 1.0$, $k_3 = 10^6$, $k_{-3} = 0.01$, $k_{-4} = 0.15$, $k_5 = 2.5$, $k_{-5} = 10^{-4}$, $k_{-6} = 0.275$, $k_7 = 10^3$, $k_{-7} = 10^{-3}$, $k_8 = 7000$, $k_{-8} = 0.1$, $b = c = d = 10$. The reference value of *a* is 100 for the four-dimensional model and 490 for the three-dimensional. From projections of the trajectories onto appropriate planes in *x*-*y*-*z*-*w*-space it is clear that the limit cycle is almost planar in both models and that it has an elliptic character. This is not surprising since the reference case values are deliberately chosen to be very close to the values used by Escher. The properties of the models are here found by letting the concentrations *a*, *b*, *c*, and *d* vary from zero to 10^4, one at a time, keeping all other parameters at the reference values. (The reference case was also chosen so that the stationary state would be unique during these variations.) The range of parameter values where qualitative changes in the dynamical behaviour occur are in all cases close to the reference case.

In the four-dimensional model two of the roots of (35) have a negative real part of the order of 10^6 throughout, indicating a very fast approach to the surface in which the limit cycle/stationary state resides. The locus of the other two roots as a function of the concentration *b* is shown in Figure 1. Since the locus is symmetric with respect to the real axis only one root is shown, $\mathrm{Im}\,(\lambda\,(b)) > 0$. The locus shows two Hopf bifurcations, one at $\mathrm{Im}\,(\lambda) = 0.8007$ for $b = 9.7887$ and one at $\mathrm{Im}\,(\lambda) = 3.134$ for $b = 63.4$. The corresponding periods of the oscillations are 7.85 and 2.00 (time units). (The period of the oscillation is 7.66 for the reference case.) This range is simple to treat numerically. Since *B* also participates in a reaction which contains both the main variables *X* and *Y*, the properties of the system for different *b* values are investigated in

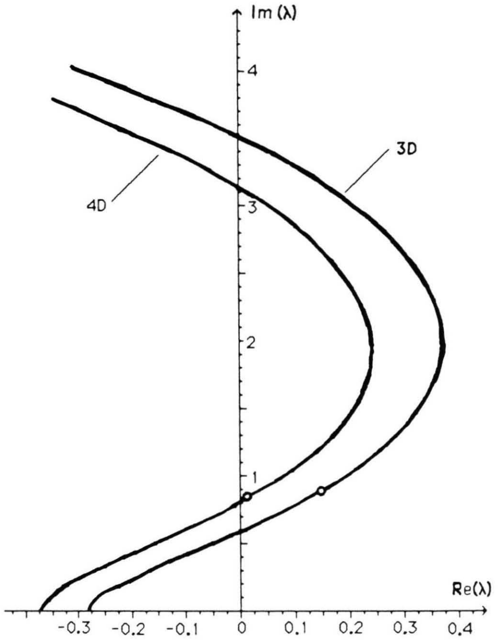

Fig. 1. Root-locuses $\lambda(b)$, showing only the branch with non-negative imaginary parts of the close-to-the-origin eigenvalues of the stationary state jacobian matrix. The three and four-dimensional models are indicated by "3D" and "4D", respectively. The circles mark the reference cases. The locuses return to the real axis for $b = 1521$ (4D) and $b = 1777$ (3D) and stay on the negative real axis thereafter.

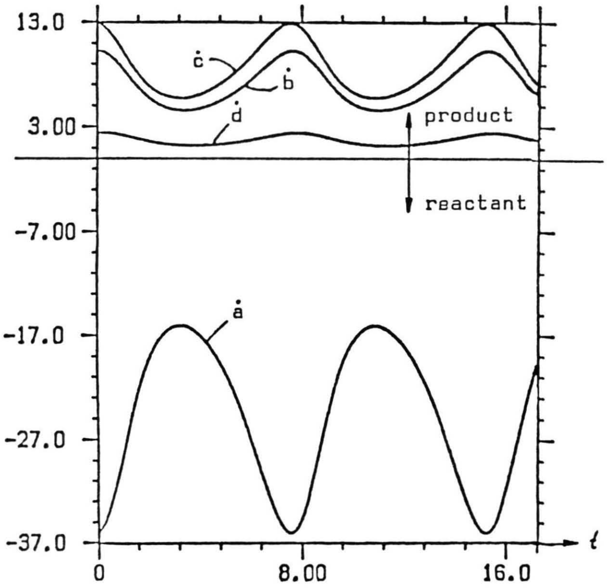

Fig. 2. Flows of A, B, C, and D as functions of time on the four-dimensional reference case closed trajectory. Positive values indicate positive outflow, i.e. production inside the system.

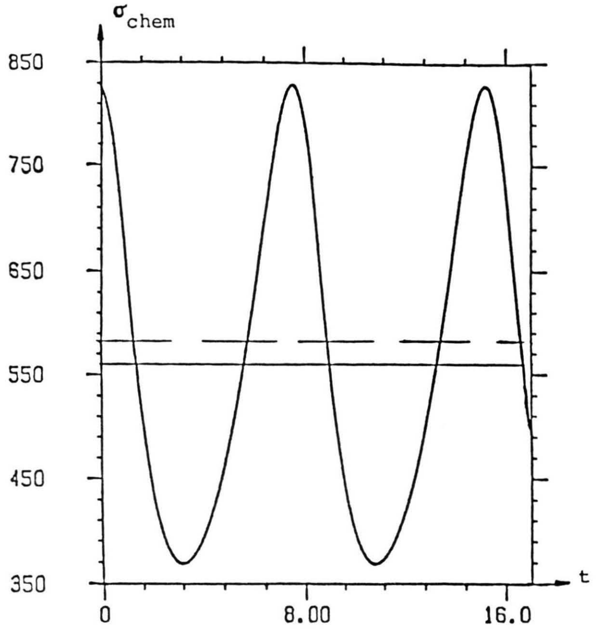

Fig. 3. Entropy production rate in the chemical reactions as a function of time on the four-dimensional reference case closed trajectory. The solid line indicates the time-average on the trajectory, the dashed line the production rate in the unstable stationary state.

more detail than for variations of a, c, and d. The reference case is close to one of the Hopf bifurcations (where the complex conjugate roots cross the imaginary axis) where the limit cycle oscillation comes into existence. The locus $\lambda(a)$ also has two Hopf bifurcations, one at $\mathrm{Im}(\lambda) = 0.834$ for $a = 99.96$ and one at $\mathrm{Im}(\lambda) = 419$ for $a = 133.1$. The corresponding periods of the oscillations are 7.53 and 0.015. Due to difficulties in handling the smaller period time numerically this range has not been investigated in detail. The locus $\lambda(c)$ has one Hopf bifurcation, at $\mathrm{Im}(\lambda) = 0.823$ for $c = 2.5$. The corresponding period time of the oscillation is 7.63. The locus $\lambda(d)$ also has one Hopf bifurcation, also at $\mathrm{Im}(\lambda) = 0.823$ for $d = 10.04$. In this case the stability increases with increasing d and the oscillations exist also when $d = 0$, i.e. when the back reaction in (10f) is excluded.

From the time-variation of the flow rates of A, B, C, and D on the reference case trajectory (see Fig. 2) it is clear that A is invariably consumed (reactant) while B, C, and D are produced (products).

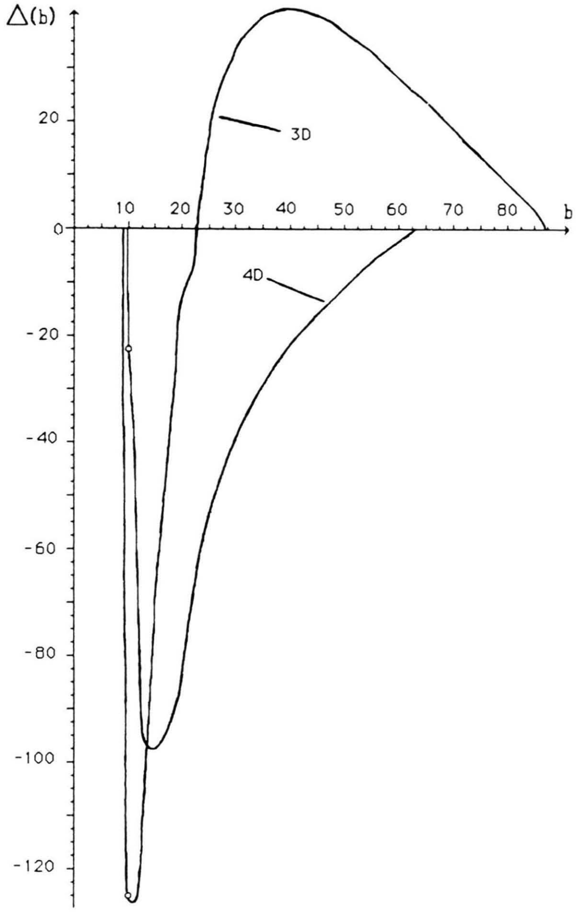

Fig. 4. The differences Δ (b) between the chemical entropy production rate in the stationary state and the time average on the limit cycle as a functions of the concentration parameter b. All other parameters are reference case values. The circles indicate the reference cases ($b = 10$). The difference is negative everywhere for the four-dimensional model (curve labelled "4D") but changes sign for the three-dimensional (3D) one.

The result of the reference case simulation for the chemical contribution to the entropy production rate as a function of time is shown in Fig. 3, with the stationary state value σ^{stat} and the time average $\bar{\sigma}$ also indicated. It is obvious that the entropy production rate difference Δ is quite small compared to the variations during a cycle. (Another feature, not shown in the figure, is that the entropy production rate can be given as a simple function of x with good accuracy.)

Figure 4 shows Δ as a function of b. It is consistently negative, i.e. the four-dimensional system *decreases* the chemical entropy production rate by leaving the unstable steady state and going into the oscillating mode for all values of b.

The three-dimensional model is dynamically similar, with one eigenvalue of the jacobian matrix being real, negative and of the order of 10^5. The locus λ (b) (see Fig. 1) also shows two Hopf bifurcations, one at $\text{Im}(\lambda) = 0.59$ for $b = 8.96$ and one at $\text{Im}(\lambda) = 3.517$ for $b = 88.8$, with corresponding period times of 10.65 and 1.79, respectively. Noteworthy is that the locus λ (a) has only one Hopf bifurcation in this model, and λ (c) has none ($\text{Re}(\lambda(c)) > 0$ for all values of c).

The entropy production rate difference, also shown in Fig. 4, is different from the one for the four-dimensional system by becoming zero and then positive as b is increased toward the second Hopf bifurcation.

VII. Discussion

It is certainly worthwhile to find out whether there are simple evolution principles governing the behavior of open chemical systems, and especially principles with a clear connection to thermodynamics and statistical mechanics. It might then become possible to describe evolution in thermodynamical terms, maybe using such concepts as "structure" and "order" which could be quantified with the help of information theory. It is also possible to analyze the evolutionary properties of systems using information-theoretical methods [14].

Previously some thermodynamic evolution criteria have been found to apply to certain classes of systems, e.g. the "minimum entropy production theorem" in linear thermodynamics [1]. The previous studies have mostly concerned themselves with the thermodynamic properties in the neighborhood of non-equilibrium stationary states. The present investigation differs by studying open, homogenous, non-linear and oscillating chemical systems. One of the simplest rules possible for such systems is that a chemical oscillator has a lower average entropy production rate in the oscillating state than in the unstable stationary state.

It has been proved here that this rule is not valid. The derivation in Sect. II of the properties in the neighborhood of a Hopf bifurcation indicates that both signs of the entropy production rate difference are possible, and the three-dimensional model proves that there are actually systems where the sign of the difference depends on a parameter. Thus the rule is disproved by counterexample. (The same obviously applies to the version with "higher" instead of "lower".)

The derivation shows that a simple algorithm can be used to find out which way the entropy production rate difference turns as the oscillating mode is created in a Hopf bifurcation. The algorithm involves the jacobian matrix J and the hessian matrix M at the stationary state, and it is therefore not necessary to integrate the equations of motion to find the sign of Δ in the neighborhood of the bifurcation. Nothing is said about the behavior away from the bifurcation, and the three-dimensional model shows that Δ can change sign. (One can say that the algorithm is local both in state space and parameter space.)

In conclusion we have seen that an evolution principle which favors low entropy production rate would not necessarily favor an oscillating mode (although it might do so, as in the four-dimensional model). It remains to be seen whether there are any rules that can identify certain classes of chemical oscillators as negentropy-savers. This is a stimulating topic for further investigation.

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[1] G. Nicolis and I. Prigogine, Self-organization in Nonequilibrium Systems, John Wiley, New York 1977.

[2] A. R. Peacocke, The Physical Chemistry of Biological Organization, Oxford University Press, Oxford 1983.

[3] S. R. de Groot and P. Mazur, Non-equilibrium Thermodynamics, North-Holland, Amsterdam 1962.

[4] H. Haken, Advanced Synergetics, Springer-Verlag, Berlin 1984.

[5] J. E. Marsden and M. McCracken, The Hopf Bifurcation and its Applications, Springer-Verlag, Berlin 1976.

[6] C. Escher, J. Chem. Phys. **70,** 4435 (1979).

[7] C. Escher, Z. Phys. B **35,** 351 (1979).

[8] C. Escher, Ber. Bunsenges. Phys. Chem. **84,** 387 (1980).

[9] C. Escher, Z. Phys. B **40,** 137 (1980).

[10] C. Escher, Chem. Phys. **63,** 337 (1981).

[11] C. Escher, Chem. Phys. **67,** 239 (1982).

[12] J. J. Tyson and J. C. Light, J. Chem. Phys. **59,** 4164 (1973).

[13] The equations of motion were solved using the Merson variable-steplength integration method and also the procedure described in L. Lapidus, J. H. Seinfeld, Numerical Solution of Ordinary Differential Equations, Academic Press, New York 1971, pp. 64–65.

[14] M. Eigen and P. Schuster, The Hypercycle, Springer-Verlag, Berlin 1979.