ENTROPY AND DISSIPATIVE STRUCTURE

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CHAPTER I.   INTRODUCTION

These lectures are devoted to the problem of structure formation in systems beyond thermodynamic equilibrium. Classical thermodynamics implies that macroscopic structures may arise at equilibrium beyond the phase transition point. A crystal is an example. Once such a structure is formed, it is maintained without any exchange of energy and matter with its surroundings. We shall show that beyond thermodynamic equilibrium new types of critical phenomenon, such as structure formation may occur. These structures are maintained only through exchange of energy (and in some cases of matter) with the outside world. They are "dissipative structures" [1].

Consider a thermodiffusion cell in which a gradient of concentration is maintained by a flow of energy. This exchange of heat leads to an entropy lowering, hence, to an increase of organization. However, the increase occurs gradually with the increase of the gradient of temperature.

The so-called "Benard problem" of classical hydrodynamics is an example of discontinuous changes in structure due to dissipative processes. If a horizontal fluid layer is heated from below, maintaining an "adverse gradient" (to $\vec{g}$) of temperature, for small values of this gradient the fluid remains at rest. But for a critical value of the gradient, there is an abrupt onset of convection, leading to the well known "Benard cell" problem [2].

Dissipative structures are also possible in chemical systems.
Let us consider a sequence of reactions such as

$$A \rightleftharpoons [X, Y, Z] \rightleftharpoons F$$
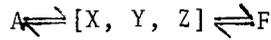
where the concentrations of the initial and final components A and F
are maintained constant. X, Y, Z are intermediate components. The
parameter which expresses the thermodynamic constraint may be taken
as the ratio of A and F. If this ratio is taken in accordance with
the law of mass action, the system will evolve to equilibrium.

If the scheme of reactions is non-linear, there may be different
time-independent solutions of the kinetic equations describing the
system

$$\frac{dX}{dt} = 0 \qquad \frac{dY}{dt} = 0 \qquad \frac{dZ}{dt} = 0 \; ,$$

all satisfying the physical condition that the concentrations must be
real and positive quantities.

For given values of A and F one of these solutions contains, as
a special case, the equilibrium solution corresponding to the minimum
of free energy. Will this solution be stable for large deviation
from equilibrium?

The occurences of dissipative structures is associated with the
fact that the continuation of the equilibrium branch of the kinetic
equations becomes unstable and is replaced by another branch. Thus
dissipative structures may occur only in non-linear systems for which
more than one solution of the kinetic equations exists.

In addition, dissipative structures will occur only at a finite
distance from thermodynamic equilibrium as the stability of thermo-
dynamic solution must extend over at least some non equilibrium region.

The preceding remarks lead us to the study of stability
properties far beyond equilibrium states.

CHAPTER II.   STABILITY OF THERMODYNAMIC SYSTEMS

A.   Fluctuations and Balance Equation for Entropy

The structure beyond an instability point in a macroscopic system
originates in a fluctuation. Far from the point of instability a
fluctuation is followed by a response which brings the system back to
the unperturbed state. On the contrary at the point of formation
of a new structure the fluctuations are amplified. There is a well
known method; normal modes analysis, for the study of these
instabilities. However, we want to deduce an independent stability
theory based on thermodynamics of irreversible processes and deduce
the same information as in normal mode analysis. To this end we have
to build a generalized thermodynamic theory of stability which also
includes a macroscopic theory of fluctuations.

The starting point is the basic Einstein formula for an isolated
system [3]. The probability, P_r, of a fluctuation to some state far
from equilibrium is

$$P_r \sim \exp \frac{\Delta S}{k} \qquad , \qquad (2.1)$$

where ΔS is the change of entropy associated with fluctuations. For
small fluctuations (2.1) gives

$$P_r \sim \exp \frac{1}{2k} \delta^2 S \quad . \qquad (2.2)$$

Here $\delta^2 S$ is the curvature of the entropy surface at the equilibrium
state. Assuming local equilibrium (see below) it can be shown that
(2.2) remains valid even for fluctuations in non-equilibrium condi-
tions. This has been substantiated recently by detailed calculations
based on stochastic models [4,5]. It has been shown that the
generalized Einstein formula (where the equilibrium values are replaced
by steady state values) remains valid whenever there exists a separa-
tion of the time scales between the fluctuating system and the "outside
world". Such separation is always implied when well defined boundary
conditions are prescribed for the macroscopic systems. Now if we

derive a balance equation for $\delta^2 S$ and study its evolution in time, we establish a link between fluctuations and the stability theory.

We shall assume for the remainder of the lectures the validity of the "local equilibrium" assumption. Therefore, the local entropy per unit mass s, is the same function of the local macroscopic variables as given by Gibbs' law at equilibrium [6]:

$$s = s(e, v, N_\gamma)$$

with

$$(\frac{\partial s}{\partial e})_{v,N_\gamma} = T^{-1}; \quad (\frac{\partial s}{\partial v})_{e,N_\gamma} = pT^{-1}; \quad (\frac{\partial s}{\partial N_\gamma})_{e,v,N_\gamma} = -\mu_\gamma T^{-1}$$

$$(N_\gamma = \frac{m_\gamma}{m}; \quad \sum_\gamma N_\gamma = 1; \quad \gamma = 1,\ldots,c) \quad . \tag{2.3}$$

The local equilibrium assumption implies that the effect of collisions must be sufficiently dominant to exclude large deviations from statistical equilibrium ; an assumption that cannot be maintained for rarefied gases. The balance equation for entropy is [7]:

$$dS = d_e S + d_i S \tag{2.4}$$

where $d_e S$ denotes the contribution of the outside world and $d_i S$ denotes the entropy production due to the irreversible processes inside the system. The second law of thermodynamics postulates that

$$d_i S \geq 0 \quad . \tag{2.5}$$

The equality sign corresponds to equilibrium situations where entropy production vanishes.

Now assuming local equilibrium the explicit form of entropy production can be obtained by using the balance equations for mass, momentum, and energy. Then one gets a bilinear expression for the entropy production per unit time [8]:

$$P = \frac{d_i S}{dt} = \int_V dV \sum_\alpha J_\alpha X_\alpha \geq 0 \quad . \tag{2.6}$$

J_α are the flows (or rates) of the irreversible processes and X_α the corresponding forces.

B. Classical Stability Theory of Thermodynamic Equilibrium

The Gibbs-Duhem stability criterion is a formulation of the second law, valid for closed systems at uniform pressure and temperature [6]:

$$\delta E + p\delta V - T\delta S \geq 0 \qquad . \tag{2.7}$$

When this inequality is satisfied, any macroscopic deviation from equilibrium is impossible as inconsistent with a positive entropy production.

For infinitesimal perturbations this gives:

$$(\delta^2 S)_{eq} < 0 \ . \tag{2.8}$$

This kind of approach cannot be extended to the study of non-equilibrium situations due to the lack of thermodynamic potentials.

A more general approach to equilibrium stability valid for all boundary conditions compatible with the maintainance of equilibrium will now be presented.

C. Equilibrium Stability Theory and Entropy Balance Equation

Let us combine (2.4) and (2.6). We get (for more details see ref. 9):

$$P[S] = \int_V dV \sum_\alpha J_\alpha X_\alpha = \partial_t S + \Phi [S] \geq 0 \qquad . \tag{2.9}$$

$\Phi [S]$ is the entropy flow through the surface of the system. Now we separate in the r.h.s. of (2.9) terms of first and second order. The entropy production is a quantity of second order with respect to the deviations from equilibrium. We get

$$\left[\frac{\partial}{\partial t} (\Delta S)\right]^{(1)}_{eq} = - \Phi [S]_{eq} \qquad , \tag{2.10}$$

and

$$\frac{1}{2} \left[\frac{\partial}{\partial t}(\Delta S)\right]^{(2)}_{eq} = P[S] - \Delta \Phi [S] . \tag{2.11}$$

Eq. (2.10) is a generalized equilibrium condition.

By taking appropriate boundary conditions (2.11) reduces to

$$\frac{1}{2} \left[\partial_t (\Delta S)\right]^{(2)}_{eq} = P[S] \geq 0 . \tag{2.12}$$

According to the Gibbs-Duhem definition of stability, if no perturbation can satisfy the inequality, (2.12) the system will remain in equilibrium. The stability condition is therefore:

$$\frac{1}{2}(\delta^2 S)_{eq} = \int_0^t P[S]dt = \int_0^t d_i S = \Delta_i S < 0. \tag{2.13}$$

Let us look for the explicit form of the equilibrium stability conditions. It can be shown [see ref. 9] that

$$\delta^2 s = -\frac{1}{T} \left[\frac{C_V}{T}(\delta T)^2 + \frac{\rho}{\chi} (\delta v)^2_{N_\gamma} + \sum_{\gamma\gamma'} \mu_{\gamma\gamma'} \delta N_\gamma \delta N_{\gamma'}\right] \tag{2.14}$$

with

$$\chi = -\frac{1}{v}(\frac{\partial v}{\partial p})_{T,N_\gamma} ; \quad (\delta v)_{N_\gamma} = (\frac{\partial v}{\partial T})_{p,N_\gamma} \delta T + (\frac{\partial v}{\partial p})_{T,N_\gamma} \delta p; \tag{2.15}$$

$$\mu_{\gamma\gamma'} = (\frac{\partial \mu_\gamma}{\partial N_{\gamma'}})_{T,p,(N_\gamma)}$$

and

$$(\delta^2 S)_{eq} = \int_V dV \, \rho_{eq}[\delta^2 s]_{eq} < 0 , \tag{2.16}$$

this inequality must be verified for arbitrary perturbations. It implies:

$$[\delta^2 s]_{eq} < 0 \tag{2.17}$$

therefore

$$C_V > 0; \quad \chi > 0; \quad \Sigma \mu_{\gamma\gamma'} x_\gamma x_{\gamma'} > 0 . \tag{2.18}$$

These are the classical conditions of equilibrium stability.

D. Stability of Non-Equilibrium States

This study shall be limited to small perturbations with respect to some reference state (the details of this section can be found in reference 8). The entropy production is no longer a second order quantity, so we cannot split the second law as in preceding sections. However we shall take that local equilibrium assumption subsists and equilibrium is stable. Thus inequalities (2.17) and (2.18) remain valid. Therefore, we assume

$$\delta^2 s < 0 \qquad\qquad (2.19)$$

even for states far from thermodynamic equilibrium. This property suggests an approach to thermodynamic stability which is closely related to the ideas underlying Ljapounov's theory.[*] We consider $(-\delta^2 s)$ as a Ljapounov function. According to classical stability theory, if

$$\dot{\delta^2 s} > 0 \quad\text{and}\quad \delta^2 s < 0 , \qquad\qquad (2.20)$$

are valid for all times t, the reference state is stable

More explicitly

$$\frac{1}{2} \dot{\delta^2 s} = \delta T^{-1} \delta \dot{e} + \delta(pT^{-1}) \delta \dot{v} - \sum_\gamma \delta(\mu_\gamma T^{-1}) \delta \dot{N}_\gamma \geq 0 , \qquad (2.21)$$

the "dot" denotes a time derivative in the space of the independent variables e, v, N_γ.

Since a local formulation of stability theory is not appropriate for a description of systems submitted to given boundary conditions, we need a global formulation.

Using the local formulation one can show [8,9] that a global stability condition is:

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[*]For a discussion of this see La Salle, J. and Lefschetz, S., Stability by Ljapounov's Direct Method, Acad. Press Inc. (New York, 1961).

$$\delta^2 S < 0; \quad \partial_t \delta^2 S \geq 0 \quad . \tag{2.22}$$

To investigate the stability of a given non-equilibrium state by means of this criterion it remains to establish the explicit form of the entropy-balance equation associated with small perturbations. We shall use the balance equations for mass, momentum, energy and assuming the system is in mechanical equilibrium, we get:

$$\frac{1}{2} P[\delta^2 S] = \int_V dV \sum_\alpha \delta J_\alpha \delta X_\alpha \geq 0 \quad . \tag{2.23}$$

We shall call this important quantity the excess <u>entropy production</u>. The similarity in structure with the entropy production (2.6) is striking. However, while the very formulation of the second law of thermodynamics prescribes a positive value of P, the sign of the excess entropy production depends on the kinetic laws relating the fluxes J_α and the generalized forces X_α

An especially interesting case is the one of chemical reactions, where the laws between reaction rates and chemical affinities are generally non linear. The stability condition (2.23) becomes:

$$\sum_\rho \delta\omega_\rho \delta(A_\rho T^{-1}) \geq 0 \quad , \tag{2.24}$$

where ω_ρ are the chemical reaction rates, and A_ρ the corresponding affinities.

CHAPTER 3. CHEMICAL EXAMPLES

We shall study the behavior of chemical reactions in open systems, far from equilibrium, and look for possible new effects beyond instability. We shall show that the dissipation may give rise to space and time order. We shall consider systems exhibiting the following behavior:

        a) oscillations occur on the thermodynamic branch, but no instability appears (Lotka - Volterra Model),

        b) oscillations occur after an instability point (on a new non thermodynamic branch),

        c) there is structure formation beyond an instability point.

In this section we combine the results of the thermodynamic analysis outlined in previous sections and derive the behavior of a single normal mode around the steady state.

We take fluctuations of the form

$$\delta\omega_\rho = \delta\omega^o{}_\rho \ \exp[(\omega_1 + i\omega_2)t]$$

$$\delta A_\rho = \delta A^o{}_\rho \ \exp[(\omega_1 + i\omega_2)t] \ . \tag{3.1}$$

Using (2.24) and (3.1) it can be shown that [8].

$$\frac{1}{2} \int dV\{\omega_1 \sum_\rho (\delta\omega_\rho{}^* \delta A_\rho + \delta\omega_\rho \delta A^*{}_\rho) + i\omega_2 \sum_\rho (\delta\omega_\rho{}^* \delta A_\rho - \delta\omega_\rho \delta A^*{}_\rho)\}$$

$$= \omega_1 \ \delta_m P + i\omega_2 \delta_m \Pi \le 0 \ . \tag{3.2}$$

$\delta_m P$ may be associated with the approach to the steady state, and $\delta_m \Pi$ with rotation around this state. It can easily be seen that the stability condition may be written as [9].

$$\omega_1 \delta_m P \le 0 \ \ . \tag{3.3a}$$

At the same time one can obtain a criterion for the onset of oscillations

$$\omega_2 \delta_m \Pi \le 0 \ \ . \tag{3.3b}$$

A. Oscillation On Thermodynamic Branch

Let us consider the following scheme of reactions which contains an autocatalytic step [8,10]

$$A + X \xrightarrow{k_1} 2X$$

$$X + Y \xrightarrow{k_2} 2Y \qquad\qquad (3.4)$$

$$Y \xrightarrow{k_3} E$$

where the values of initial and final products A and E are held constant.

The corresponding kinetic equations are:

$$\frac{dX}{dt} = k_1 AX - k_2 XY$$

$$\qquad\qquad (3.5)$$

$$\frac{dY}{dt} = k_2 XY - k_3 Y$$

They admit a single non zero steady state solution.

We perform a standard normal mode analysis around this stationary state. The dispersion equation indicates that small fluctuations around the steady state are periodic with frequency

$$\omega = i(k_1 \, k_3 \, A)^{1/2} \, .\qquad\qquad (3.6)$$

Moreover, a Thermodynamic analysis shows that [8]

$$\delta_m P = 0 \qquad\quad \text{and} \qquad\quad \delta_m \Pi \geq 0 \, . \qquad (3.7)$$

Consequently, one may conclude that the system is in a state of "marginal stability"; fluctuations can neither decay nor grow.

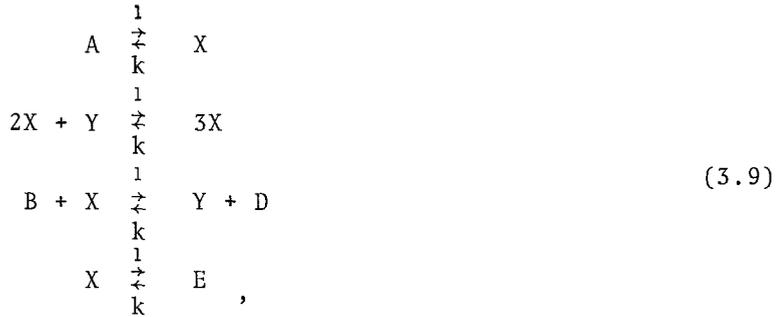Upon integrating the kinetic equations one gets:

$$X^{-1} \, e^X = e^K \, Y \, e^{-Y} \qquad\qquad (3.8)$$

where K is an arbitrary constant, and is fixed by the initial
conditions. A particular value of K gives a corresponding closed
curve in the X,Y plane; therefore, even large fluctuations around the
steady state are periodic. This time however the periods depend on
the initial conditions.

B. Oscillation Past An Instability: Limit Cycles

Let us study a case of instability for which the excess entropy
production first vanishes and then changes sign for a finite value of
the overall affinity. The thermodynamic branch then becomes stable.

We consider the following scheme of reactions [8,10,11]

$$
\begin{aligned}
A &\underset{k}{\overset{1}{\rightleftarrows}} X \\
2X + Y &\underset{k}{\overset{1}{\rightleftarrows}} 3X \\
B + X &\underset{k}{\overset{1}{\rightleftarrows}} Y + D \\
X &\underset{k}{\overset{1}{\rightleftarrows}} E \quad,
\end{aligned}
$$
(3.9)

where A, B, D, E are held constant. The kinetic equations are
(if we take k=0):

$$\frac{dX}{dt} = A + X^2Y - BX - X$$

$$\frac{dY}{dt} = BX - X^2Y .$$
(3.10)

The steady state values of X and Y are

$$X_o = A \qquad\qquad Y_o = B/A$$
(3.11)

the usual normal mode analysis considering again only homogeneous
perturbations yields

$$\omega^2 + (X_o^2 + B + 1 - 2X_oY_o)\omega + X_o^2 = 0.$$
(3.12)

The value of B for which the coefficient of ω in (3.12) vanishes corresponds to a transition point. Beyond this point $(B > B_c)$ the system becomes unstable. We find

$$B_c = 1 + A^2 . \tag{3.13}$$

In addition, Poincaré has shown that differential equations of the form (3.10) beyond a point of instability such as given by (3.13) may admit solutions represented by closed curves in the phase plane (hence periodic solutions) which are such that another trajectory which is also closed is necessarily at a finite distance from the former: these are the <u>limit cycles</u>. The fundamental importance of limit cycles is to represent self sustained oscillatory motion in non linear, non conservative systems. This can be seen on Figure 1.
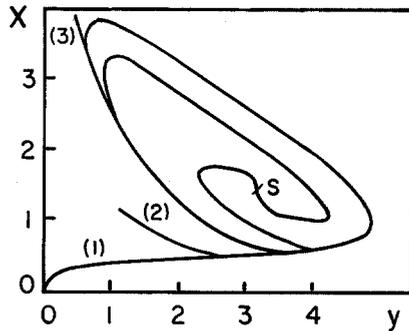

FIGURE 1

Figure 1 shows the typical behavior of the system in a region where a limit cycle is observed. Whatever the initial conditions (1,2,3) the system reaches the same periodic behavior.

Let us evaluate $\delta_m P$ around the steady state. We obtain [ref. 8]

$$\delta_m P = \frac{1}{AB} [B(1-B)\delta X \delta X^* + A^4 \delta Y \delta Y^*] . \tag{3.14}$$

$B\delta X\delta X^*$ is due to the autocatalytic step and is the "dangerous" contribution. For $B \leq 1$ (3.14) is positive definite and the system is stable.

It can be shown that for $B = B_c$, $\delta_m P$ vanishes and $\delta_m \Pi \geq 0$.

The thermodynamic criterion therefore gives the same information in a concise form, as the kinetic methods.

C. Symmetry Breaking Instabilities

So far we have discussed the problem of stability in chemical systems with respect to homogeneous fluctuations. Both the unperturbed and perturbed systems were assumed homogeneous. The problem of stability with respect to diffusion will now be considered.

Let us return to the scheme (3.9). In the kinetic equations (3.10), we have to add $D_X \dfrac{\partial^2 X}{\partial^2 r^2}$ and $D_Y \dfrac{\partial^2 Y}{\partial r^2}$ in order to take account of diffusion. We take a perturbation of the form

$$X(t) - X_o = x \ \exp\ (\omega t + \frac{ir}{\lambda})$$

$$Y(t) - Y_o = y \ \exp\ (\omega t + \frac{ir}{\lambda})$$

It can then be shown that the homogeneous stationary state becomes unstable (for the details of this section see refs. [8,12]), for a critical wave length λ_c, and B_c.

$$\lambda^2_c = \frac{1}{A} \ (D_x D_y)^{1/2}$$

$$B_c = [1 + A(\frac{D_x}{D_y})^{1/2}]^2 \tag{3.15}$$

Since the computational problem involved in the study of the time evolution beyond the instability is rather involved, we shall consider rather than disturbances of arbitrary wavelength a two box model. In this system the initial and final products are distributed homogeneously in the system whereas X and Y may diffuse freely between the two parts. We now have four equations:

$$\frac{dX_1}{dt} = A + X_1^2 Y_1 - BX_1 - X_1 + D_x(X_2 - X_1)$$

$$\frac{dX_2}{dt} = A + X_2^2 Y_2 - BX_2 - X_2 + D_x(X_1 - X_2)$$

$$\frac{dY_1}{dt} = BX_1 - X_1^2 Y_1 + D_y(Y_2 - Y_1)$$

$$\frac{dY_2}{dt} = BX_2 - X_2^2 Y_2 + D_y(Y_1 - Y_2) \ . \qquad (3.16)$$

The time independent homogeneous solution is

$$X_i = A \qquad Y_i = B/A \qquad (i = 1,2) \qquad (3.17)$$

We make the following choice of numerical values for the diffusion
coefficient of X and for A

$$D_x = 1 \qquad A = 2 \ .$$

There remains two arbitrary parameters whose values determine the
properties of the steady states. The steady state equations are:

$$3X_2^5 - 30X_2^4 + [96 + 2D_y(B+3)]X_2^3 - [96 + 12D_y(B+3)]X_2^2 + 16D_y(6+B)X_2 - 96D_y = 0$$

$$X_1 = 4 - X_2$$

$$Y_2 = B(8X_2^2 - 4D_y - 16X_2 - X_2^3)/[8X_2^3 - 3X_2^2 - (D_y + 8) + 8D_y(X_2 - 2) - X_2^4]$$

$$Y_1 = Y_2 + (X_2^2 Y_2 - BX_2)/D_y \ . \qquad (3.18)$$

This system has two types of solutions: the homogeneous steady state
solution given by (3.17) and an inhomogeneous solution which because
of the symmetry of the model may be written in two equivalent ways.

$$X_1 > X_2, \qquad Y_1 < Y_2 \qquad (3.19)$$

or

$$X_1 < X_2, \qquad Y_1 > Y_2$$

The stability analysis of the steady state solutions of (3.18) has been performed both for homogeneous and inhomogeneous fluctuations. One finds that the homogeneous state is unstable with respect to homogeneous perturbation when

$$B > 5 \tag{3.20}$$

and with respect to inhomogeneous perturbations when

$$B > B_c = \frac{1}{2D_y} (6D_y + 12) \quad . \tag{3.21}$$

These results combined with those obtained for the inhomogeneous steady state are shown in Figure 2.
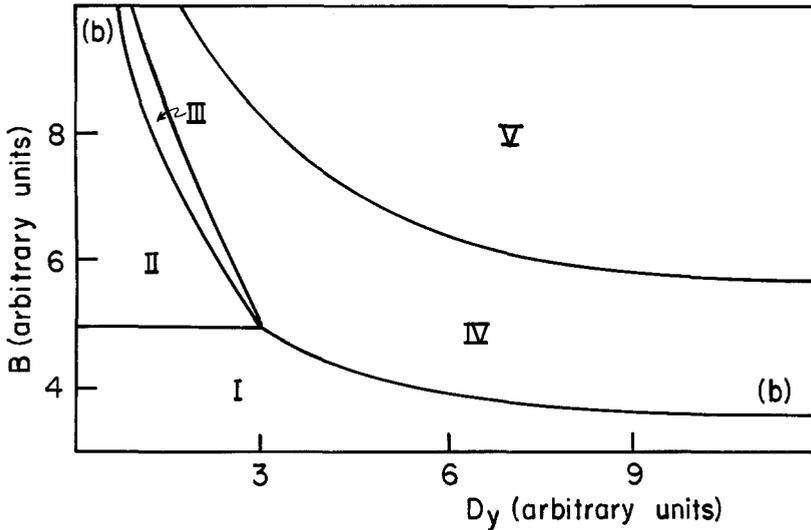

FIGURE 2

Conditions (3.20) and (3.21) define a domain I where only the homogeneous steady state exists and is stable. This state becomes unstable with respect to homogeneous perturbations in II and with respect to inhomogeneous perturbations beyond the curve (b). In regions II, III, V no time independent, stable state exists, but in region IV the inhomogeneous steady state is stable. This region, therefore, corresponds to what we call a dissipative structure. It is particularly interesting to investigate how such an inhomogeneous

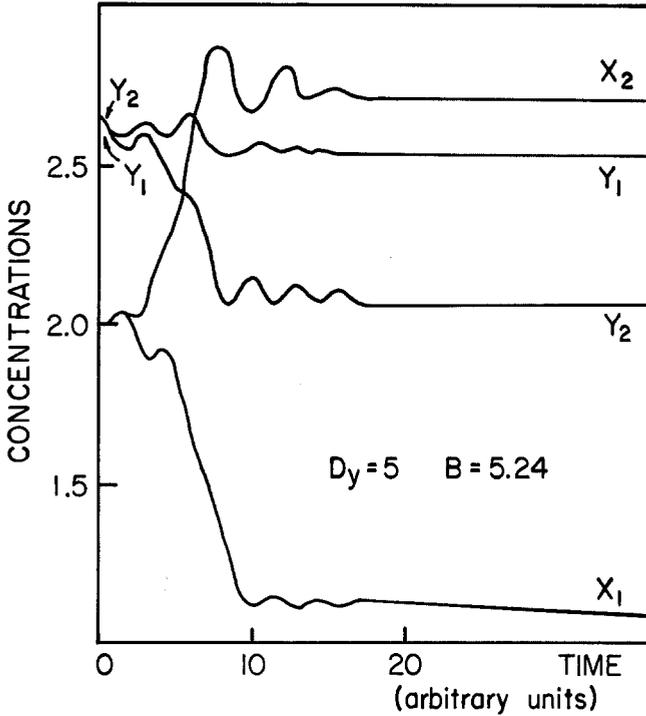state is reached. A typical result is reported in Figure 3.

FIGURE 3

The homogeneous state corresponding to $X_1 = X_2 = 2$ and $Y_1 = Y_2 = 2.62$ is destroyed by a small fluctuation $Y_2 - Y_1 = 0.04$. It is clearly seen how the initial perturbation is magnified until the inhomogeneous steady state is reached. The configuration (3.19) chosen by the system depends crucially on the nature of the initial perturbation. The thermodynamic analysis yields

$$\delta_X P = (1 - B)\frac{X^2}{A} + \frac{A^3}{B} Y^2 + \frac{D_X}{\lambda^2 A} x^2 + \frac{D_Y}{\lambda^2 B} y^2 . \qquad (3.22)$$

Again, in agreement with our general discussion, a negative term, $-\frac{B}{A} X^2$, due to the auto catalytic action of X, appears. This is the "dangerous contribution".

The explicit contribution of diffusion is positive and proportional to $\frac{D}{\lambda^2}$. Therefore, if there is an instability, increasing values of D must give rise to increasing values of the critical wavelength. If not, the contribution of diffusion to (3.22) would become dominant and $\delta_X \dot{P}$ would be always positive. Diffusion has a second role - the manifold of perturbations which we may introduce into (3.22) is now increased by the consideration of inhomogeneous systems.

Dissipative structures have been observed experimentally. We will not describe them here but the reader is referred to papers by Zhabotinsky [12], Busse [13] and Herschkowitz-Kaufman [14].

References

[1] I. PRIGOGINE: "Structure, Dissipation and Life" in
Theoretical Physics and Biology, ed. M. Marois (Amsterdam:
North Holland Publishing Co., 1969)
I. PRIGOGINE: "Dissipative Structures in Biological Systems"
Second International Conference on 'Theoretical Physics and
Biology', Versailles (July 1969)

[2] S. CHANDRASEKHAR: Hydrodynamic and Hydromagnetic Stability
(Oxford: Clarendon Press, 1961)

[3] L. D. LANDAU AND E. M. LIFSHITZ: Statistical Physics
(New York: Addison-Wesley, 2nd ed. 1969) Ch. XII

[4] G. NICOLIS AND A. BABLOYANTZ: J. Chem. Phys. 51, 2632 (1969)

[5] A. BABLOYANTZ AND G. NICOLIS: J. Stat. Phys. 1,

[6] I. PRIGOGINE AND R. DEFAY: Thermodynamique Chimique
Editions Desoer, Liege (1950)

[7] I. PRIGOGINE: Introduction to Thermodyanmics of Irreversible
Processes, 3rd edition (New York: Interscience, John Wiley
and Sons, 1967)

[8] P. GLANSDORFF AND I. PRIGOGINE: Generalized Thermodynamics
(in press) Wiley, Interscience (1970)

[9] P. GLANSDORFF AND I. PRIGOGINE: Physica 46, 344 (1970)

[10] I. PRIGOGINE AND G.NICOLIS: J. Chem. Phys. 46, 3542 (1967
G. NICOLIS: Adv. Chem. Phys., to appear 1970
R. LEFEVER, G. NICOLIS, AND I. PRIGOGINE: J. Chem. Phys.
47, 1045 (1967)

[11] I. PRIGOGINE AND R. LEFEVER: J. Chem. Phys. 48, 1605 (1968)
R. LEFEVER: J. Chem. Phys. 49, 4977 (1968)
Bull. Cl. Sci. Acad. Roy. Belg. 54, 712 (1968)

[12] A. M. ZHABOTINSKY: Dokl. Acad. Nauk. U.S.S.R. 152, 392 (1964)
Biofizika 9, 306 (1964)

[13] H. BUSSE: J. Phys. Chem. <u>73</u>, 750 (1969)

[14] M. HERSCHKOWITZ-KAUFMAN: C.R. Acad. Sc. Paris <u>270</u>, 1049
       (1970)