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A MODEL FOR OSCILLATING CHEMICAL REACTIONS

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A simple theoretical model for a class of oscillating chemical reactions is investigated, which is inspired by Degn's analysis of the mechanism of Belousov–Zhabotinsky reactions. Although the model involves only one auto catalytic path, as distinct from models presented hitherto, a limit-cycle behaviour is found for the concentrations, corresponding to a definite region in the space of controllable parameters. Characteristics of the coherent oscillations are investigated together with the behaviour in the induction period. The critical slowing-down around the onset of instability is shown to behave very much like that found in the equilibrium phase transition. The existence of an "anti-Curie" point is found as well as the Curie point, corresponding to the fact that the domain for sustained oscillation is closed in certain directions. Possible extensions of the model and ways of improving the theory are discussed.

1. Introduction

Concentration oscillations in chemical reactions under conditions far from equilibrium have only recently become a subject of considerable interest, partly because of their expected relation to biological clocks [1] and to the possible dynamical differentiation of various tissues in living systems [2], although examples were reported quite some time ago (for early references see e.g. [3,4]).

The essential kinetic structure of oscillating reactions has been recognized as the existence of autocatalysis or of feedback channels in multiple reactions. The non-linear differential equations describing a set of reactions are expected, under certain conditions, to have a solution which reveals a limit-cycle behaviour. This type of dynamical order emerges only under certain conditions and particular interest centres around the fact that there are cases in which one can control the situation by changing the boundary conditions. It is expected that such control mechanisms are always operating in living organisms. The understanding of the mechanisms may possibly lead to an external adjustment of the conditions for living organisms.

Early in 1910, Lotka [5] (see also [6]) introduced a model which exhibits periodic behaviour. However, in his model an infinite number of orbits neighbouring one another are found to be stable and in that respect the model is not quite realistic.

In this paper, a theoretical analysis will be given of a simple class of models which is based on Degn's work [7] on a possible mechanism of Belousov–Zhabotinsky reactions. The recent investigations by Noyes et al. [8–11] suggest that Degn's mechanism may not be realistic. Nevertheless, its simplicity motivated us to investigate the details of oscillations predicted by the model. Moreover, as we shall see later, the model can be generalized defining a wide class of mechanisms which are likely to be present in general experimentally realistic situations.

Only the results for the case of homogeneous phases are presented in this paper. The results for the inhomogeneous case will be treated in a separate publication. In sect. 2 a mathematical model is formulated and the steady-state solutions of the model are derived. In sect. 3 the stability of the steady state is discussed and the existance of a particular region is shown in the space of controllable parameters, inside

which sustained oscillations emerge. In sect. 4 the characteristics of sustained oscillations, i.e. amplitudes and phases, are studied both in marginal and off-marginal situations. In sects. 5 and 6 transient behaviours in the evolution to the regime of sustained oscillations of the limit-cycle type are discussed: first, in analogy with the phenomenon of critical slowing-down, and secondly paying special attention to the induction period and the related structure of the space of reference variables. In sect. 7 several possible extensions of the model are briefly discussed. Sect. 8 is devoted to general discussions and concluding remarks.

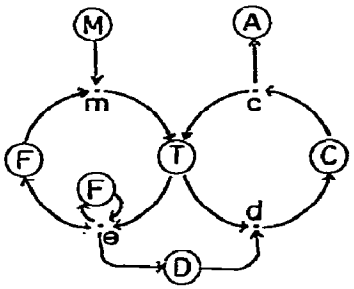

Fig. 1. Diagramatic representation of the model reaction. M: malonic acid, F: Ce^{4+}, T: Ce^{3+}, D: dibromo-malonic acid, C: complex of dibromomalonic acid and Ce^{3+}, A: dibromoacetic acid.

2. The model and steady-state solutions

As Degn himself seems not to be completely definite about the detailed mechanisms of activation and inhibition with respect to the reaction $Ce^{3+} \rightarrow Ce^{4+}$, it would be safer to define a model of our own, though it is mostly based on Degn's wording in his first publication [7].

Our model consists of four elementary reactions and four intermediate chemical components, F, T, D and C, and an input M and an output A. The correspondence between the four reactions in our model and Degn's proposal is as follows (see fig. 1);

(1) "Reaction m" corresponds to the oxidation of malonic acid (M) by ceric ions (F).

(2) "Reaction θ" corresponds to the oxidation of cerous ions (T) by bromate. It is assumed that this reaction has an auto-catalytic activation.

(3) Br_2, which is a product of "reaction θ", reacts very rapidly with malonic acid to form bromomalonic acid (D). "Reaction d", then, corresponds to the formation of complexes (C) of cerous ions (T) and bromomalonic acid (D), which has an inhibiting effect on "reaction θ".

(4) "Reaction c" corresponds to the decomposition of the complexes (C), as a result of which cerous ions (T) reappear, thus closing the second cycle of reaction.

The main assumptions adopted here are as follows:

(1) The inhibition of "reaction θ" is induced by the formation of complexes (C), which results from "reaction d" of dibromomalonic acid (D) with Ce^{3+} (T). "Reaction θ" is recovered when Ce^{3+} (T) is liberated after a time from dibromoacetic acid (A), which has evolved from dibromomalonic acid.

(2) The activation of "reaction θ" is supposed to be a first-order auto-catalysis by Ce^{4+} (F). Without this auto-catalysis the system does not exhibit any oscillatory behaviour.

(3) The concentration of malonic acid (M) is controllable.

Under these assumptions, a closed set of reaction pathways is obtained as is shown in fig. 1. To each of the reactions, there correspond rate constants k_m, k_θ, k_d and k_c, respectively. These rate constants may be taken as the result of renormalizing the effects of probable paths other than those indicated, provided they are proceeding rapidly compared with those under explicit consideration.

The diagram in fig. 1 corresponds to the following set of differential equations, namely,

$$\frac{d}{dt}F = -k_m MF + k_\theta FT, \tag{2.1}$$

$$\frac{d}{dt}T = k_m MF - k_\theta FT - k_d DT + k_c C, \tag{2.2}$$

$$\frac{d}{dt}C = k_d DT - k_c C, \tag{2.3}$$

$$\frac{d}{dt}D = k_\theta FT - k_d DT. \tag{2.4}$$

It is clear thet the sum of eqs. (2.1), (2.2) and (2.3) is zero, therefore

$$F + T + C = \phi, \tag{2.5}$$

where ϕ is a positive constant independent of time.

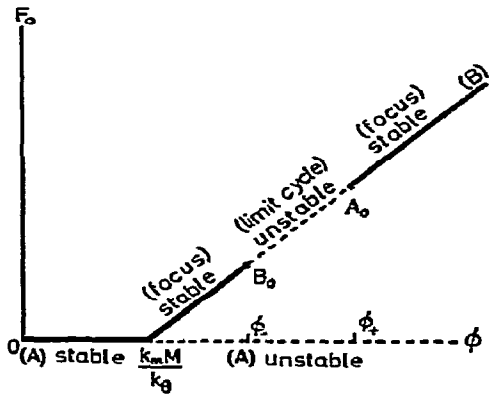

Fig. 2a. Steady state for various ϕ in (ϕ, F) plane. A_0 and B_0 are the marginal steady states corresponding to $\phi=\phi_+$ and $\phi=\phi_-$ respectively.

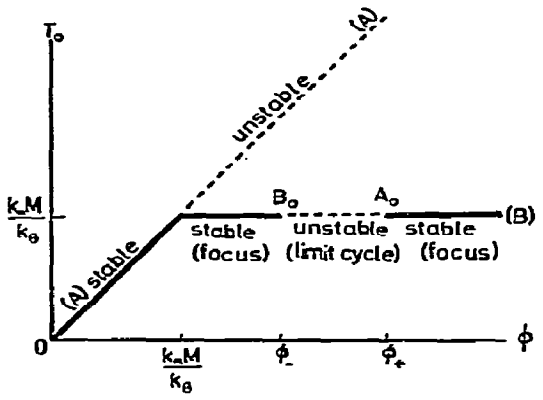

Fig. 2b. Steady state for various ϕ in (ϕ, T) plane.

One finds two sets of steady-state solutions, namely,

$$F_0 = C_0 = D_0 = 0 \quad \text{and} \quad T_0 = \phi \qquad \text{(Case A), (2.6)}$$

and

$$F_0 = k_c\Psi/k_\theta, \quad D_0 = k_c\Psi/k_d, \quad T_0 = k_mM/k_\theta, \quad C_0 = T_0\Psi, \qquad \text{(Case B). (2.7)}$$

where

$$\Psi = (k_\theta\phi - k_mM)/(k_c + k_mM). \qquad (2.8)$$

The steady-state solutions, Case A and Case B, are shown in the (ϕ, F) plane and in the (ϕ, T) plane in fig. 2 as functions of ϕ.

For $\phi < k_mM/k_\theta$, only the steady state (A) exists. For $\phi > k_mM/k_\theta$, the two steady states (A) and (B) appear; the steady state (A) lies on the same line as for $\phi < k_mM/k_\theta$, and the steady state (B) lies on another line which originates at the point $(k_mM/k_\theta, 0, k_mM/k_\theta)$ in (ϕ, F, T) space.

3. Stability and the criterion for the appearance of oscillation

In order to obtain information about the stability of the steady state, one may linearize eqs. (2.1)–(2.4) around the steady state. Suppose a variable X is expressed as

$$X = X_0 + \delta X = X_0 + xe^{\lambda t}, \qquad (3.1)$$

where X_0 stands for a steady state and δX for an infinitesimal deviation from it. Then, using eq. (2.5) the linearized equation may be written as

$$\frac{d}{dt}\begin{bmatrix}\delta F\\ \delta F\\ \delta D\end{bmatrix} = \qquad (3.2)$$

$$\begin{bmatrix} k_\theta T_0 - k_mM, & k_\theta F_0 & 0 \\ k_mM - k_\theta T_0 - k_c, & -k_\theta F_0 - k_dD_0 - k_c, & -k_dT_0 \\ k_\theta T_0, & k_\theta F_0 - k_dD_0, & -k_dT_0 \end{bmatrix}\begin{bmatrix}\delta F\\ \delta T\\ \delta D\end{bmatrix}.$$

In the following, the stabilities of the two steady-state solutions are studied separately.

3.1. Case A

Substituting the steady-state solutions (2.6) into eq. (3.2), one finds a secular equation of the form

$$(\lambda + k_mM - k_\theta\phi)(\lambda + k_c)(\lambda + k_d\phi) = 0. \qquad (3.3)$$

Accordingly, the solution (A) is stable for

$$\phi < k_mM/k_\theta, \qquad (3.4)$$

and it is unstable for

$$\phi > k_mM/k_\theta. \qquad (3.5)$$

In Case A, it is clear that there is no possibility of finding an oscillatory solution. Therefore the solution (A) will be given no further attention in this paper.

3.2. Case B

Substituting the steady-state solution (2.7) into eq. (3.2), one finds a simpler equation,

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix}\delta F\\ \delta T\\ \delta D\end{bmatrix}=\begin{bmatrix}0, & k_c\Psi, & 0\\ -k_c, & -(2\Psi+1)k_c, & -k_dT_0\\ k_\theta T_0, & 0 & -k_dT_0\end{bmatrix}\begin{bmatrix}\delta F\\ \delta T\\ \delta D\end{bmatrix}. \quad (3.6)$$

Then the secular equation is

$$\lambda^3+\{k_c(1+2\Psi)+k_dT_0\}\lambda^2+k_c\{k_dT_0(1+2\Psi)+k_c\Psi\}\lambda + k_dk_c\Psi T_0(k_c+k_\theta T_0)=0. \quad (3.7)$$

By choosing a particular unit of time, one of the rate constants may be put equal to unity without losing generality. Let us therefore choose k_d as a unit, i.e.

$$k_d=1. \quad (3.8)$$

One may further simplify the equation by introducing a scale transformation, such that

$$\lambda=k_c\mu, \quad (3.9)$$

$$T_0=k_c\Theta. \quad (3.10)$$

Then, instead of eq. (3.7) one finds

$$\mu^3+\alpha(\Theta,\Psi)\mu^2+\beta(\Theta,\Psi)\mu+\gamma(k_\theta,\Theta,\Psi)=0, \quad (3.11)$$

where

$$\alpha(\Theta,\Psi)=1+\Theta+2\Psi, \quad (3.12)$$

$$\beta(\Theta,\Psi)=\Theta(1+2\Psi)+\Psi, \quad (3.13)$$

$$\gamma(k_\theta,\Theta,\Psi)=\Theta\Psi(1+k_\theta\Theta). \quad (3.14)$$

From these equations it is clear that

$$\mu=\mu(k_\theta,\Theta,\Psi), \quad (3.15)$$

i.e. μ depends on three independent parameters, which may be alternatively chosen as k_θ, M and ϕ.

The condition under which eq. (3.11) has a purely imaginary solution is given by the equation

$$\alpha(\Theta,\Psi)\beta(\Theta,\Psi)=\gamma(k_\theta,\Theta,\Psi), \quad (3.16)$$

which is explicitly

$$(2\Psi+\Theta+1)\{(2\Theta+1)\Psi+\Theta\}=\Theta(1+k_\theta\Theta)\Psi, \quad (3.17)$$

or

$$2(2\Theta+1)\Psi^2-\{(k_\theta-2)\Theta^2-4\Theta-1\}\Psi+\Theta(\Theta+1)=0. \quad (3.18)$$

One may solve eq. (3.18) for Ψ:

$$\Psi_\pm(k_\theta,\Theta)=\frac{1}{4(2\Theta+1)}\left[\{(k_\theta-2)\Theta^2-4\Theta-1\}\pm\sqrt{\{(k_\theta-2)\Theta^2-4\Theta-1\}^2-8\Theta(\Theta+1)(2\Theta+1)}\right]. \quad (3.19)$$

Under the condition that positive $\Psi_+(k_\theta,\Theta)$ and $\Psi_-(k_\theta,\Theta)$ exist, the stability of the steady-state solutions is shown in figs. 2a and b. ϕ_+ and ϕ_- are defined as [see eq. (2.8)]

$$\Psi_\pm(k_\theta,\Theta)=(k_\theta\phi_\pm-k_mM)/(k_c+k_mM). \quad (3.20)$$

Therefore ϕ_+ and ϕ_- correspond to the marginal situations. The steady state (B) becomes unstable for

$$\phi_-<\phi<\phi_+, \quad (3.21)$$

though it is a stable focus for

$$k_mM/k_\theta<\phi<\phi_- \quad (3.22)$$

and for

$$\phi>\phi_+. \quad (3.23)$$

As discussed before, the steady state (A) is stable for $\phi<k_mM/k_\theta$ and unstable for $\phi>k_mM/k_\theta$.

One should now discuss the condition for the existence of positive $\Psi_+(k_\theta,\Theta)$ and $\Psi_-(k_\theta,\Theta)$.

First, in order for $\Psi_\pm(k_\theta,\Theta)$ to be real, one finds a condition

$$\{(k_\theta-2)\Theta^2-4\Theta-1\}^2\geqslant 8\Theta(\Theta+1)(2\Theta+1). \quad (3.24)$$

In order for $\Psi_\pm(k_\theta,\Theta)$ to be positive, one finds an additional condition

$$(k_\theta-2)\Theta^2-4\Theta-1>0. \quad (3.25)$$

Supposing that both conditions (3.24) and (3.25) are satisfied, then one finds two solutions $\Psi_+(k_\theta,\Theta)$ and $\Psi_-(k_\theta,\Theta)$ for eq. (3.18), which are both real and positive.

The remaining thing is to rewrite (3.24) and (3.25) in terms of k_θ and M. One need only remember that

$$\Theta=\sigma(M)/k_\theta, \quad (3.26)$$

where

$$\sigma(M)=k_mM/k_c. \quad (3.27)$$

In terms of $\sigma(M)$, the above conditions are now

$$\{(k_\theta-2)\sigma^2-4k_\theta\sigma-k_\theta^2\}^2 \geqslant 8\sigma(\sigma+k_\theta)(2\sigma+k_\theta)k_\theta. \tag{3.24a}$$

and

$$(k_\theta-2)\sigma^2-4k_\theta\sigma-k_\theta^2>0. \tag{3.25a}$$

The latter condition (3.25a) is easier to analyse, for it may be rewritten as

$$k_\theta^2-\sigma(\sigma-4)k_\theta+2\sigma^2<0. \tag{3.25b}$$

For fixed σ, (3.25b) is satisfied only if k_θ has a value between two roots of the equation

$$k_\theta^2-\sigma(\sigma-4)k_\theta+2\sigma^2=0, \tag{3.28}$$

namely

$$k_\theta^{\pm}=\tfrac{1}{2}\sigma\{\sigma-4\pm\sqrt{(\sigma-4)^2-8}\}. \tag{3.29}$$

For $k_\theta^{\pm}$ to be real and positive, it is necessary that

$$\sigma\geqslant 4+2\sqrt{2}. \tag{3.30}$$

Suppose that the condition (3.30) is satisfied, then the condition (3.25b) is satisfied only for

$$k_\theta^-<k_\theta<k_\theta^+. \tag{3.31}$$

In physical terms, the inequality (3.31) can be explained as follows: When $k_\theta<k_\theta^-$, "reaction θ" is too slow to generate an inertia of the flow, whereas for $k_\theta>k_\theta^+$, "reaction θ" is too fast to feel the inhibiting effect of "reaction d".

The former condition (3.24a) is obviously more stringent than (3.25a), therefore the resultant criterion is quantitatively more restrictive, although the qualitative structure of the criterion should be similar. Namely,

(i) There exists an absolute lower bound M_* for the value of M.

(ii) For a legitimate value of M, there exists a closed curve in the (k_θ, Ψ) plane and oscillations may appear only inside this closed curve. In fig. 3a the closed curves corresponding to the marginal situations given in eq. (3.19) are shown for various values of σ.

Fig. 3a implies that for a fixed value of σ there exist two values of k_θ, say $k_\theta^+(\sigma)$ and $k_\theta^-(\sigma)$, for which $\Psi_+(k_\theta,\Theta)$ and $\Psi_-(k_\theta,\Theta)$ coincide. From eq. (3.19) one sees that $k_\theta^+(\sigma)$ and $k_\theta^-(\sigma)$ are solutions of an equation for k_θ,

$$[(k_\theta-2)\Theta^2-4\Theta-1]^2-8\Theta(\Theta+1)(2\Theta+1)=0 \tag{3.32}$$

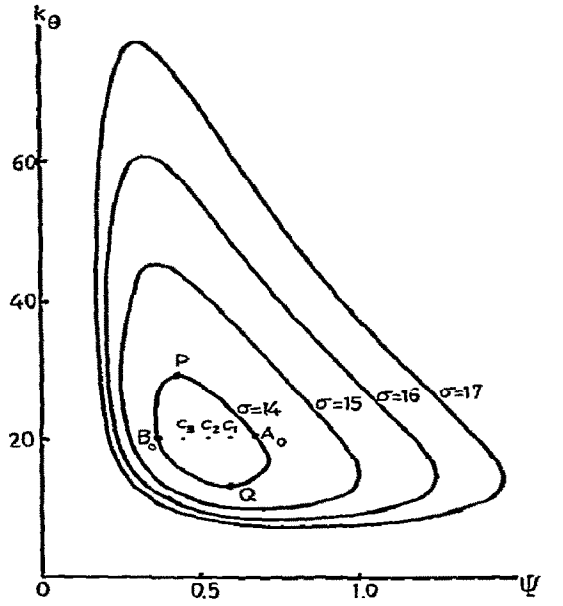

Fig. 3a. The criterion for the existence of oscillations indicated in (k_θ, Ψ) plane. For fixed σ, oscillations may exist only inside the closed curve. For $\sigma = 14$ and $k_\theta = 20$, the points C_1, C_2 and C_3 with $\Psi = 0.6$, 0.525 and 0.45 respectively give rise to the unstable steady states while the points A_0 and B_0 with $\Psi = 0.6827$ and 0.3632, respectively, correspond to the marginal situations. At the points P and Q, the two marginal situations become identical (sect. 3).

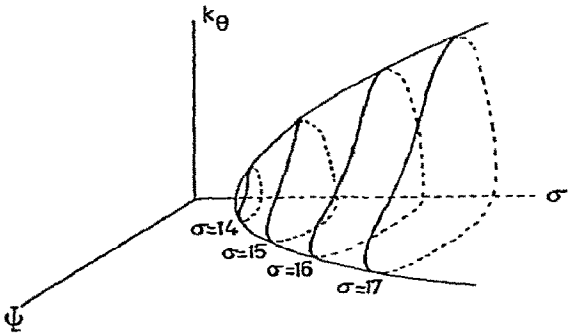

Fig. 3b. The criterion for the existence of oscillations indicated in (k_θ, Ψ, σ) space. Oscillations may exist only inside the volume of horn-like shape.

where $\Theta = \sigma/k_\theta$ [eq. (3.26)]. For example, for $\sigma = 14$, the points P and Q in fig. 3a correspond to such situations.

Furthermore, if one reduces σ, the closed curve in (k_θ, Ψ) plane becomes smaller and finally it collapses into a point. The value $\sigma = \sigma_0$ corresponding to this situation is given as the lower bound for σ, which satisfies the inequalities (3.24) and (3.25). Actually this value σ_0 lies between 13 and 14.

In order to visualize the structure of the space of the controllable parameters k_θ, Ψ and σ, the unstable region is roughly sketched in fig. 3b.

It should be noted that for this model the unstable region in (k_θ, Ψ, σ) space is open in the positive direction of σ. For Belousov–Zhabotinsky reactions, Zhabotinsky et al. [12] reported that experimentally there exists also an upper bound for the concentration of malonic acid which gives rise to oscillations. This point will be discussed in sect. 8.

4. Characteristics of the oscillation

In order to compare the qualification of various similar models in relation to the observed facts, it is often convenient to examine the phase relations and the relative amplitudes among several oscillating quantities.

In our particular example of the oscillation around the steady state (B), it is not difficult to determine these relations in the marginal situations. The oscillation is supposed to be purely sinusoidal with infinitesimal amplitude and its frequency is given by

$$\omega_\pm = \sqrt{\beta(\Theta, \Psi_\pm)}, \tag{4.1}$$

or

$$\omega_\pm = \sqrt{\gamma(k_\theta, \Theta, \Psi_\pm)/\alpha(\Theta, \Psi_\pm)}. \tag{4.2}$$

Accordingly the oscillation around the marginal steady state is expressed as

$$\delta F = f_\pm \sin(\omega_\pm t), \tag{4.3}$$

$$\delta T = \theta_\pm \sin(\omega_\pm t + \eta_\pm), \tag{4.4}$$

$$\delta D = d_\pm \sin(\omega_\pm t + \zeta_\pm). \tag{4.5}$$

In the above the two signs "+" and "−" correspond to the upper and the lower marginal situations.

From eq. (3.6) one finds the relation

$$\omega_\pm \begin{bmatrix} f_\pm \cos(\omega_\pm t) \\ \theta_\pm \cos(\omega_\pm t + \eta_\pm) \\ d_\pm \cos(\omega_\pm t + \zeta_\pm) \end{bmatrix} = \tag{4.6}$$

$$\begin{bmatrix} 0, & k_c\Psi, & 0 \\ -k_c, & -(2\Psi+1)k_c, & -k_d T_0 \\ k_\theta T_0, & 0, & -k_d T_0 \end{bmatrix} \begin{bmatrix} f_\pm \cos(\omega_\pm t) \\ \theta_\pm \cos(\omega_\pm t + \eta_\pm) \\ d_\pm \cos(\omega_\pm t + \zeta_\pm) \end{bmatrix}.$$

Putting $\omega_\pm t + \eta_\pm = 0$, one finds that, in marginal situations,

$$\cos \eta_\pm = 0, \tag{4.7}$$

or

$$\eta_\pm = \tfrac{1}{2}\pi \tag{4.7a}$$

and

$$f_\pm/\theta_\pm = k_c\Psi/\omega_\pm. \tag{4.8}$$

Putting $\omega_\pm t = 0$, one finds that

$$\omega_\pm d_\pm \cos\zeta_\pm = -k_d T_0 d_\pm \sin\zeta_\pm,$$

or

$$\tan\zeta_\pm = -\omega_\pm/k_d T_0, \tag{4.9}$$

accordingly

$$-\tfrac{1}{2}\pi < \zeta_\pm < 0. \tag{4.10}$$

Putting $\omega_\pm t = \frac{1}{2}\pi$, one finds that

$$(\omega_\pm \sin\zeta_\pm + k_d T_0 \cos\zeta_\pm) d_\pm = k_\theta T_0 f_\pm,$$

or

$$f_\pm/d_\pm = (\omega_\pm \sin\zeta_\pm + k_d T_0 \cos\zeta_\pm)/k_\theta T_0. \tag{4.11}$$

In this way, the phase relations and the relative amplitudes in the marginal situations are completely determined, provided the deviations are infinitesimal.

When the situation deviates from the marginal ones by a finite amount, it is expected that both the amplitudes of oscillations and the phase relations are determined by the non-linearity. In fact, the off-marginal oscillation in the range $\phi_- < \phi < \phi_+$ (see eqs. (3.19) and (3.20)), tends to a definite limit cycle and its

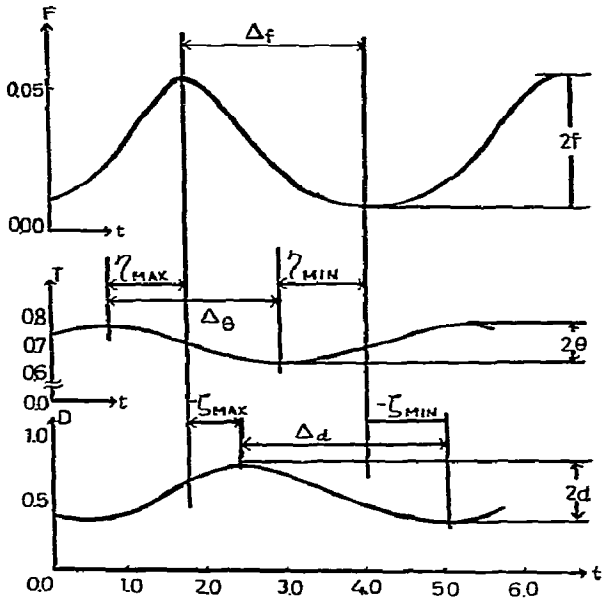

Fig. 4. The limit cycle in an off-marginal situation. The parameters are chosen as $k_c = k_d = 1$, $k_\theta = 20$, $\Psi = 0.525$ and $\sigma = 14$.

behaviour deviates from a pure sinusoidal curve.

In order to see how the oscillation in the off-marginal situation deviates from a sinusoidal curve, it is convenient to introduce the following quantities characterizing the oscillation; with respect to a complete cycle η_{max} and η_{min} are defined as the phase differences between the peaks and depths of $F(t)$ and $T(t)$ respectively. In a similar way ζ_{max} and ζ_{min} are also defined for $F(t)$ and $D(t)$. Δ_f is the phase retardation of the bottom of $F(t)$ after the peak of $F(t)$. Similarly Δ_θ and Δ_d are also defined for $T(t)$ and $D(t)$.

In fig. 4, sustained oscillations of $F(t)$, $T(t)$ and $D(t)$ corresponding to a limit cycle in an off-marginal situation are shown. Here the values of the controllable parameters correspond to the point C_2 in fig. 3a. The definitions of the characteristics Δ_f, Δ_θ, Δ_d, η_{max}, η_{min} etc., are also shown in fig. 4.

Of course, it is expected that *in marginal situations* one has

$$\eta_{max} = \eta_{min} = \eta_{\pm}, \tag{4.12}$$

$$\zeta_{max} = \zeta_{min} = \zeta_{\pm}, \tag{4.13}$$

and

$$\Delta_f = \Delta_\theta = \Delta_d = \pi. \tag{4.14}$$

Δ_f, Δ_θ and Δ_d may show how relaxation and growth of the concentrations of the chemical components are accelerated by the non-linearity in off-marginal situations. If the time dependences of the concentrations are extremely different from sinusoidal ones, as is the case in experiments, the phase retardations Δ_f, Δ_θ and Δ_d lose their meaning. With this reservation, as far as the deformation is not extremely strong, like in fig. 4, one may study the dependences of Δ_f, Δ_θ and Δ_d on Ψ.

As an example, let us examine the case

$$\sigma = 14.0, \quad k_\theta = 20.0, \quad k_c = k_d = 1.0. \tag{4.15}$$

The marginal situations in this case are characterized by

$$\Psi_+ = 0.6827, \tag{4.16}$$

and

$$\Psi_- = 0.3632. \tag{4.17}$$

Accordingly, one may calculate the characteristics of the oscillation given in eqs. (4.8)–(4.11) for the marginal situations. The results of the calculation are shown in tables 1 and 2.

In this case, the steady state (B) given in (2.7) becomes unstable for

$$0.3632 < \Psi < 0.6827, \tag{4.18}$$

and yields a limit cycle for each value of Ψ lying in the interval given in (4.18). Limit cycles for several values of Ψ are studied numerically with the aid of a computer, and the obtained characteristics are shown in tables 1 and 2.

Before analyzing the numerical data in tables 1 and 2, it should be noted here that for the given values of k_c, k_d, σ, k_θ and Ψ, the limit cycle seems to be uniquely determined independently of initial conditions except for trival cases in which particular initial conditions do not drive the system. Physically speaking, k_c, k_d, σ, k_θ and Ψ are controllable parameters and they determine not only the stability of the steady state but also the final sustained oscillation around the steady state uniquely.

Table 1 shows the following features of the oscillation:

Table 1
Frequency and amplitudes. $\omega_{int}^{(1)}$ and $\omega_{int}^{(2)}$ are results of interpolation using the marginal formulae (4.1) and (4.2) respectively. The amplitude f is defined as the difference between the maximum and the minimum of $F(t)$. θ and d are defined in a similar way for $T(t)$ and $D(t)$

Ψ	ω	$\omega_{int}^{(1)}$	$\omega_{int}^{(2)}$	$2f = F_{max}-F_{min}$	$2\theta = T_{max}-T_{min}$	$2d = D_{max}-D_{min}$	f/θ	f/d
0.3632 (calc)	1.254	1.254	1.254				0.289	0.103
0.45	1.276	1.334	1.348	0.0358	0.107	0.328	0.334	0.109
0.525	1.308	1.400	1.416	0.0448	0.121	0.395	0.370	0.114
0.6	1.440	1.463	1.477	0.0432	0.106	0.369	0.405	0.117
0.6827 (calc)	1.529	1.529	1.529				0.447	0.120

(1) The frequency ω is an increasing function of Ψ. In physical terms, it means that the higher the total concentration of F+T+C(cerium ions) is, the more rapidly T(cerous ion) is consumed because of the nature of the auto-catalysis. It should be noted, however, that the rate of increase is fairly slow and in the lowest approximation, the interpolation ω_{int} using the marginal formula (4.1) or (4.2) is not too unrealistic, as is indicated in table 1.

(2) The relative amplitude of $F(t)$ with respect to $T(t)$ as well as to $D(t)$ is also an increasing function of Ψ.

(3) The absolute amplitudes of $F(t)$, $T(t)$ and $D(t)$ become maximum in the off-marginal situation, and they are vanishing when the system tends to the marginal situations. Thus for fixed values of σ and k_θ, the envelope of the limit cycle for various values of Ψ looks like an egg or a cigar.

In fig. 5a the limit cycles for $\Psi = 0.6$, 0.525 and 0.45 and their envelopes are roughly sketched in the (F, T, D) space. In fig. 5b these limit cycles are drawn in the (F, T) plane and in the (F, D) plane. The points A_0 and B_0 in figs. 5a and 5b are the steady states in the marginal situations, namely $\Psi = 0.6827$ and $\Psi = 0.3632$. The points C_1, C_2 and C_3 are the steady states for $\Psi = 0.6$, $\Psi = 0.525$ and $\Psi = 0.45$, respectively. The curves γ_1, γ_2 and γ_3 are the limit cycles corresponding to $\Psi = 0.6$, $\Psi = 0.525$ and $\Psi = 0.45$, respectively.

The surface of the envelope of the limit cycles is an analogue of that of the order-parameter in the case of equilibrium phase transition, for example, spontaneous magnetization in the ferromagnetic phase. The fact that there exist two ends, $\Psi_+(k_\theta, \Theta)$ and $\Psi_-(k_\theta, \Theta)$, to this surface corresponds to the situation in which an anti-Curie point emerges as well as the Curie point in the language of equilibrium phase transition.

Table 2 shows the following features:

(1) In the off-marginal situations, the peaks of $F(t)$ and $T(t)$ tend to be in phase, and their bottoms out of phase. In the off-marginal situations, the peaks of $F(t)$ and $D(t)$ also tend to be in phase and their bottoms out of phase. In physical terms, when $T(t)$

Table 2
Phase relations. The definitions of these characteristics are shown in fig. 4

Ψ	η_{max} ($\times 2\pi$)	η_{min} ($\times 2\pi$)	ζ_{max} ($\times 2\pi$)	ζ_{min} ($\times 2\pi$)	Δ_f ($\times 2\pi$)	Δ_θ ($\times 2\pi$)	Δ_d ($\times 2\pi$)
0.3632 (calc)	0.25	0.25	−0.169	−0.169	0.5	0.5	0.5
0.45	0.217	0.279	−0.150	−0.204	0.517	0.454	0.571
0.525	0.214	0.280	−0.153	−0.205	0.520	0.454	0.572
0.6	0.220	0.275	−0.161	−0.211	0.518	0.466	0.564
0.6827 (calc)	0.25	0.25	−0.181	−0.181	0.5	0.5	0.5

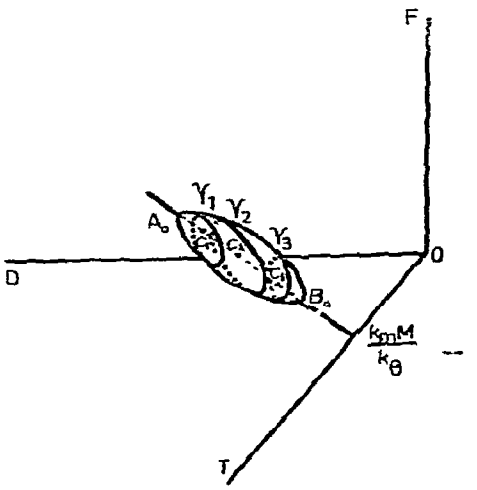

Fig. 5a. The limit cycles and their envelope. The parameters are chosen as $k_c = k_d = 1$, $k_\theta = 20$, $\sigma = 14$ and $\Psi = 0.6$ (the limit cycle γ_1), $\Psi = 0.525$ (the limit cycle γ_2) and $\Psi = 0.45$ (the limit cycle γ_3). The three points C_1, C_2 and C_3 are the unstable steady states corresponding to the points C_1, C_2 and C_3 in fig. 3a. The points A_0 and B_0 are the marginal steady states.

is maximum, the auto-catalytic reaction θ is strongly activated. Thus in the off-marginal situations in which the absolute amplitudes are enhancec, "reaction θ" makes the three components $F(t)$, $T(t)$ and $D(t)$ in phase. The de-phasing of the bottoms is due to the inertia of "reaction θ", which can be seen in the behaviour of Δ_f, Δ_θ and Δ_d.

(2) In the off-marginal situations, Δ_f and Δ_d increase and Δ_θ decreases. Physically, once "reaction θ" is activated, it gains inertia and even after the maximum of activation is attained, "reaction θ" still goes on. Thus $T(t)$ decays sharply and $F(t)$ and $D(t)$ decay slowly.

5. Transient behaviour: critical slowing-down

In the neighbourhood of marginal situations, the real parts of the complex eigenvalues of the matrix in the linearized equation (3.6) become very small. This means that the evolution of the oscillation around the steady state is extremely slow in the vicinity of the marginal situations, which is very much like the phenomena of critical slowing-down in a closed system near equilibrium.

In fact, for a slightly off-marginal situation, one may estimate the real part x as

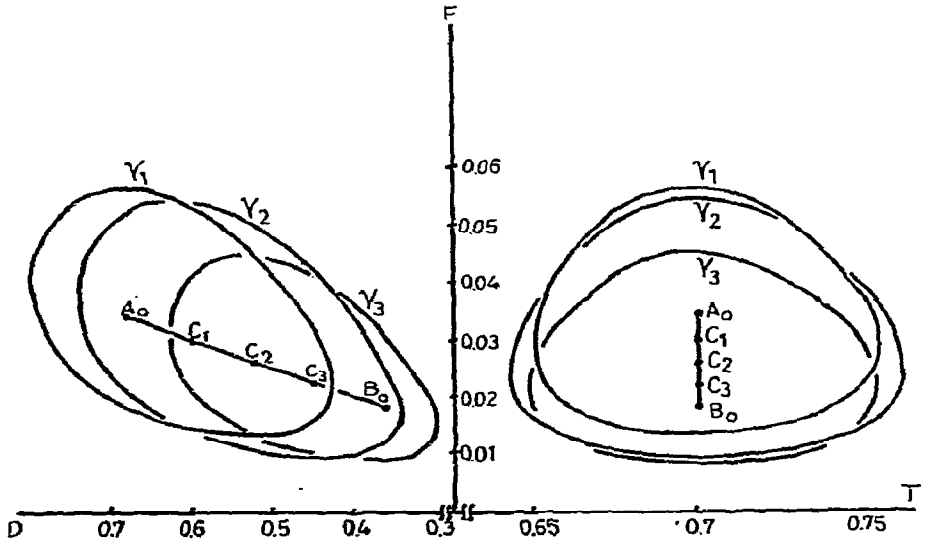

Fig. 5b. The limit cycles γ_1, γ_2 and γ_3 in (F, T) plane and in (F, D) plane. The values of the parameters are given in the caption to fig. 5a.

$$x = \mathrm{Re}\,\lambda_{\pm} = k_c\,\mathrm{Re}\,\mu_{\pm}$$

$$\cong k_c \frac{\gamma(k_\theta,\Theta,\Psi)-\alpha(\Theta,\Psi)\beta(\Theta,\Psi)}{2\{\beta(\Theta,\Psi)+(\alpha(\Theta,\Psi))^2\}}. \qquad (5.1)$$

Supposing in the present case one substitutes

$$\Psi = \Psi_+(k_\theta,\Theta)+\delta\Psi \quad \text{or} \quad \Psi = \Psi_-(k_\theta,\Theta)-\delta\Psi, \qquad (5.2)$$

where $\delta\Psi > 0$, one finds

$$\gamma(k_\theta,\Theta,\Psi)-\alpha(\Theta,\Psi)\beta(\Theta,\Psi) \qquad (5.3)$$

$$\cong -\sqrt{[(k_\theta-2)\Theta^2-4\Theta-1]^2-8\Theta(\Theta+1)(2\Theta+1)}\,\delta\Psi,$$

which indicates that the steady state is stable.

Suppose, on the other hand, one puts

$$\Psi = \Psi_+(k_\theta,\Theta)-\delta\Psi, \quad \Psi = \Psi_-(k_\theta,\Theta)+\delta\Psi, \qquad (5.4)$$

where $\delta\Psi > 0$, naturally one finds

$$\gamma(k_\theta,\Theta,\Psi)-\alpha(\Theta,\Psi)\beta(\Theta,\Psi) \qquad (5.5)$$

$$\cong \sqrt{[(k_\theta-2)\Theta^2-4\Theta-1]^2-8\Theta(\Theta+1)(2\Theta+1)}\,\delta\Psi,$$

which indicates that the steady state is unstable.

The two cases together indicate the appearance of critical slowing-down and that the dynamic critical exponent is unity in the present case with respect to the marginal deviation of the total cerium concentration.

As discussed in sect. 3, for a fixed $\sigma(>\sigma_0)$ one may choose the value of k_θ in such a way that the two marginal values of Ψ, $\Psi_+(k_\theta,\Theta)$ and $\Psi_-(k_\theta,\Theta)$, coincide. In this situation the interval of Ψ, which gives rise to limit cycle, disappears. At the same time, eqs. (5.3) and (5.5) are reduced to

$$\gamma(k_\theta,\Theta,\Psi)-\alpha(\Theta,\Psi)\beta(\Theta,\Psi)$$

$$\cong -(2\Theta^{\pm}+1)(\delta\Psi)^2, \qquad (5.6)$$

where $\Theta^{\pm} = \sigma/k_\theta^{\pm}(\sigma)$, because the coefficient of $\delta\Psi$ vanishes. This means that the steady state is stable and the dynamic critical exponent is 2 around this marginal point.

For $\sigma < \sigma_0$, the marginal situation completely disappears. Accordingly the steady state (B) given in (2.7) is always stable, i.e. the real part x is negative and finite.

In a general off-marginal situation for which $k_\theta^-(\sigma) < k_\theta < k_\theta^+(\sigma)$ holds, a limit cycle is found for each value of Ψ in the interval

$$\Psi_-(k_\theta,\Theta) < \Psi < \Psi_+(k_\theta,\Theta).$$

The way in which the reference variable $F(t)$ tends to the limit cycles is shown in figs. 6a–e for various values of Ψ. Here maxima and minima of $F(t)$ are plotted against the number of cycles. On the abcissa, one puts the numbers 1, 2,...50, which stand for the first period, the second period etc. The horizontal lines show the values to which the maxima and the minima will asymptotically tend. Figs. 6a and 6e correspond to the marginal situations, $\Psi = \Psi_-(k_\theta,\Theta)$ and $\Psi = \Psi_+(k_\theta,\Theta)$, respectively.

The initial conditions are given in the captions to figs. 6a–e. Starting from rather high concentration,

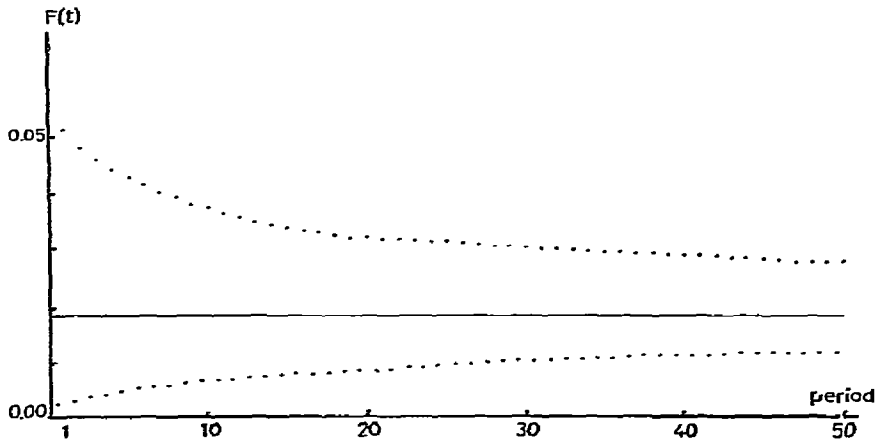

Fig. 6a. Time-dependence of the maxima and minima of $F(t)$. The parameters are chosen as $k_c = k_d = 1$, $k_\theta = 20$, $\sigma = 14$ and $\Psi = 0.3632$. The initial condition is as follows; $F(0) = 0.08816$, $T(0) = 0.63$ and $D(0) = 0.3632$. In figs. 6a through 6e the straight lines stand for the amplitudes of the final limit cycles.

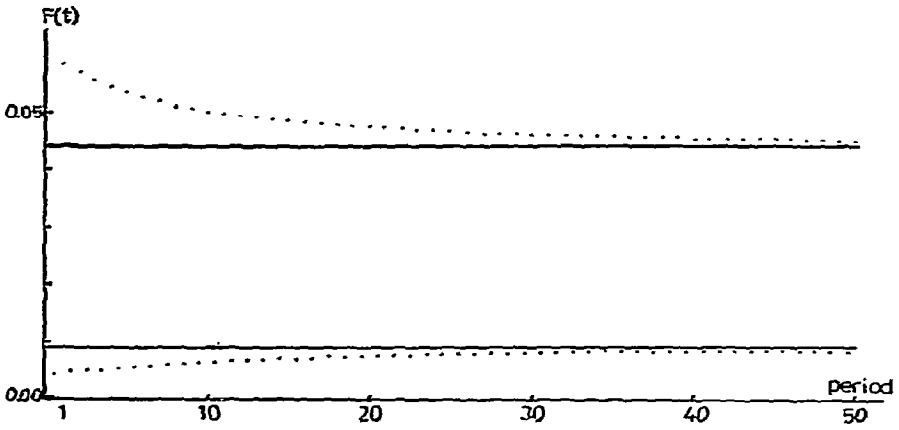

Fig. 6b. Time-dependence of the maxima and minima of $F(t)$. The parameters are chosen as $k_c = k_d = 1$, $k_\theta = 20$, $\sigma = 14$ and $\Psi = 0.45$. The initial conditions are: $F(0) = 0.0925$, $T(0) = 0.63$ and $D(0) = 0.45$.

$F(t)$ decreases rapidly to the bottom of the first period. At this stage the system is supposed to reach an attractor surface in the space of the reference variables (see sect. 6). The first period may be interpreted as the induction period. Now the system begins to oscillate on the attractor surface. The duration of the period of the subsequent oscillation is only slightly shortened as time proceeds.

In figs. 6 one may recognize that the rate of tending towards the stationary orbit becomes slower when one approaches the marginal situations.

6. Structure of the reference variable space

In an off-marginal situation, taking various initial conditions in the space of reference variables, $F(t)$, $T(t)$ and $D(t)$, one finds an interesting structure in the reference variable space.

Trajectories first tend towards a sheet very fast and then approach the limit cycle, turning round on the sheet. The trajectory I in fig. 7 shows this general transient behaviour.

From several numerical results one finds that the

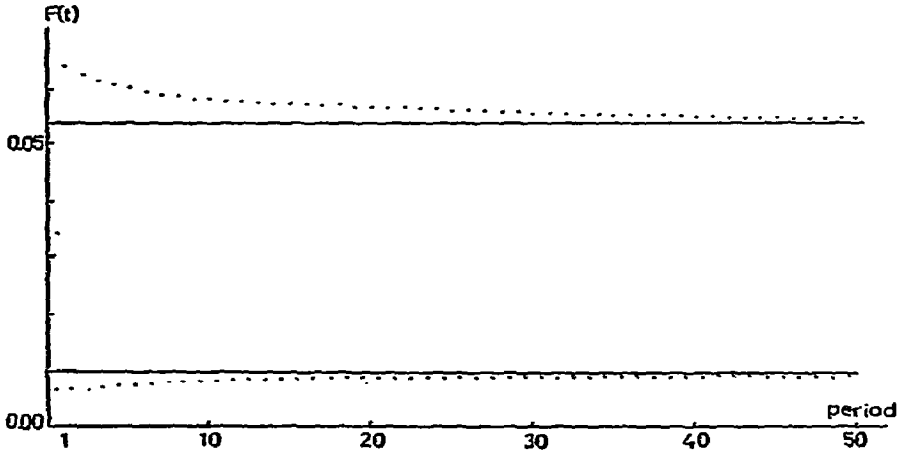

Fig. 6c. Time-dependence of the maxima and minima of $F(t)$. The parameters are chosen as $k_c = k_d = 1$, $k_\theta = 20$, $\sigma = 14$ and $\Psi = 0.525$. The initial condition is as follows; $F(0) = 0.9625$, $T(0) = 0.63$ and $D(0) = 0.525$.

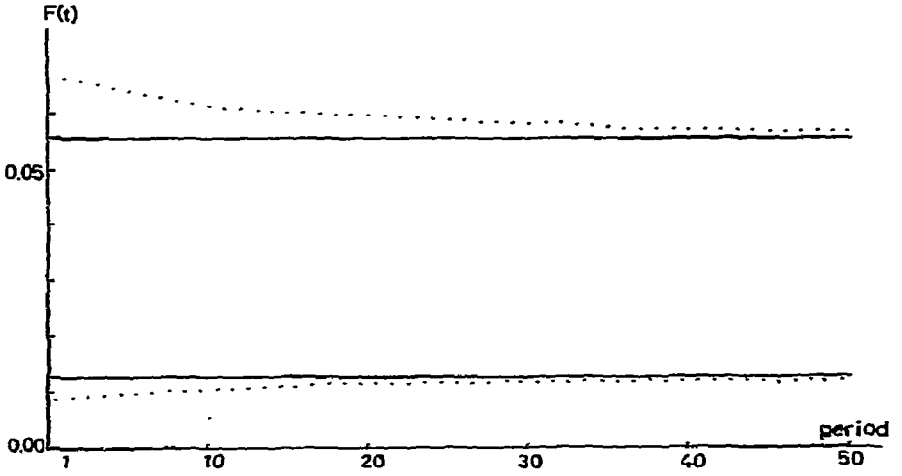

Fig. 6d. Time-dependence of the maxima and minima of $F(t)$. The parameters are chosen as $k_c = k_d = 1$, $k_\theta = 20$, $\sigma = 14$ and $\Psi = 0.6$. The initial condition is as follows; $F(0) = 0.1$, $T(0) = 0.63$ and $D(0) = 0.6$.

part of trajectories corresponding to the initial fast motion towards the sheet forms a fibre space which is separated by the sheet of an attracting surface, and trajectories on one side of the attractor surface will never meet those on the other side except on the attractor surface itself.

Corresponding to the limit cycle, in particular, there exists a fibre bundle which defines a cylindrical pipe-like surface as shown in fig. 7. Trajectories inside this pipe-like surface never meet those outside before they reach the attractor surface.

Thus, to summarize, the whole space may be de-

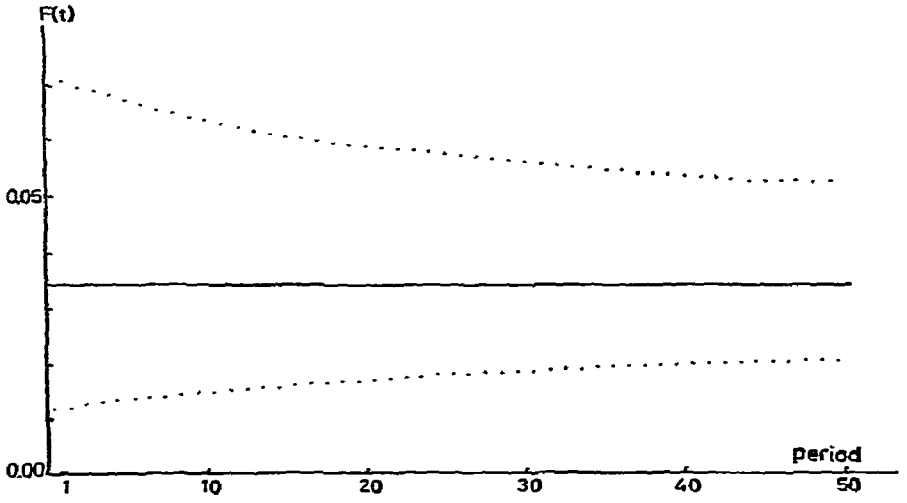

Fig. 6e. Time dependence of the maxima and minima of $F(t)$. The parameters are chosen as $k_c = k_d = 1$, $k_\theta = 20$, $\sigma = 14$ and $\Psi = 0.6827$. The initial condition is as follows; $F(0) = 0.1041$, $T(0) = 0.63$ and $D(0) = 0.6827$.

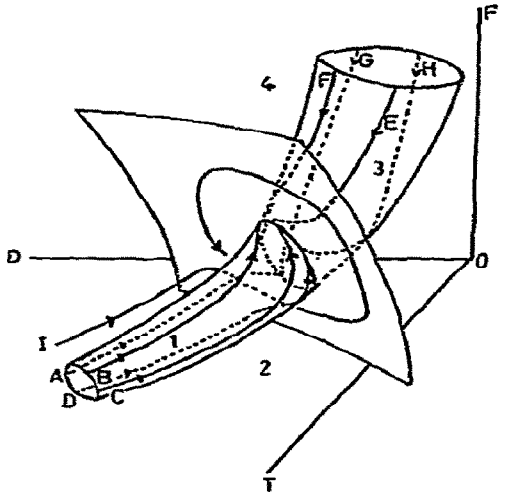

Fig. 7. The structure of (F, T, D) space in an off-marginal situation. The parameters are chosen as $k_c = k_d = 1$, $k_\theta = 20$, $\sigma = 14$ and $\Psi = 0.525$. The four parts are: 1 – inside the pipe below the sheet, 2 – outside the pipe below the sheet, 3 – inside the pipe above the sheet and 4 – outside the pipe above the sheet. The trajectories A, B, C, D, E, F, G, and H are on the surface of the pipe and the trajectory I is off the surface. The initial conditions are as follows; A: $F(0) = 4 \times 10^{-3}$, $T(0) = 1.08975$ and $D(0) = 1.14$; B: $F(0) = 4 \times 10^{-3}$, $T(0) = 1.08975$ and $D(0) = 0.9$; C: $F(0) = 1 \times 10^{-3}$, $T(0) = 1.09275$ and $D(0) = 0.74$; D: $F(0) = 0.3 \times 10^{-3}$, $T(0) = 1.09345$ and $D(0) = 0.91$; E: $F(0) = 0.2516$, $T(0) = 0.3732$ and $D(0) = 0.0046$; F: $F(0) = 0.2055$, $T(0) = 0.3727$ and $D(0) = 0.4201$; G: $F(0) = 0.1221$, $T(0) = 0.3716$ and $D(0) = 0.4307$; H: $F(0) = 0.1630$, $T(0) = 0.2706$ and $D(0) = 0.1111$; I: $F(0) = 5 \times 10^{-3}$, $T(0) = 1.0890$ and $D(0) = 1.8$.

composed into four distinct regions, say, 1, 2, 3 and 4, as shown in fig. 7, among which there exists no transition through natural trajectories.

The above observations lead to an interpretation that the intial fast motion towards the attractor surface corresponds to the induction period and the system begins to oscillate practically after arriving on the attractor surface.

In order to find the shape of the fibre bundle (i.e. the pipe), one looks for trajectories which go over to the limit cycle immediately when they reach the attractor surface. The easiest way to find those trajectories is as follows; because the original differential eqs. (2.1)–(2.4) are autonomous one may change the direction of time simply by changing the sign of the right-hand sides of the differential equations. Then the system returns back on the same trajectory. Now that one knows the limit cycle, one may follow the time-reversed differential equations starting from an initial condition which is very close to the limit cycle. Thus one may roughly trace where the fibre bundle is, by examining the behaviour of the time-reversed trajectories. The trajectories which are supposed to be on the surface of the fibre bundle are shown in the (T, D) plane and in the (F, D) plane in figs. 8a and b. The trajectories A, B, C, D, E, F, G, and H are on the surface while the trajectory I is off the surface. These trajectories are also shown in (F, T, D) space in fig. 7.

It is difficult to determine the shape of the attractor surface either numerically or analytically.

Closing this section, one would say that such a simple structure of the reference variable space makes the model a self-control system of the limit-cycle type. In general the limiting orbit can be a more complex loop even if it exists.

7. Extensions of the model

As has been mentioned earlier, the existence and the multiplicity of auto-catalysis are essential in inducing oscillatory character and also in determining the detailed aspects of oscillations.

In our model, there seems to be two possible reactions which may be auto-catalytic, namely, "reaction θ" and "reaction d".

Suppose the multiplicities of the auto-catalyses are indicated by N_θ and N_d, respectively, then one may define a family of models by an abbreviated notation $\langle N_\theta, N_d \rangle$. The explicit forms of equations corresponding to the system $\langle N_\theta, N_d \rangle$ are as follows;

$$\begin{aligned}
\frac{d}{dt}F &= -k_m MF + k_\theta F^{N_\theta} T, \\
\frac{d}{dt}T &= k_m MF - k_\theta F^{N_\theta} T + k_c C - k_d TDC^{N_d}, \\
\frac{d}{dt}D &= k_\theta F^{N_\theta} T - k_d TDC^{N_d}, \\
\frac{d}{dt}C &= -k_c C + k_d TDC^{N_d}. \qquad (7.1)
\end{aligned}$$

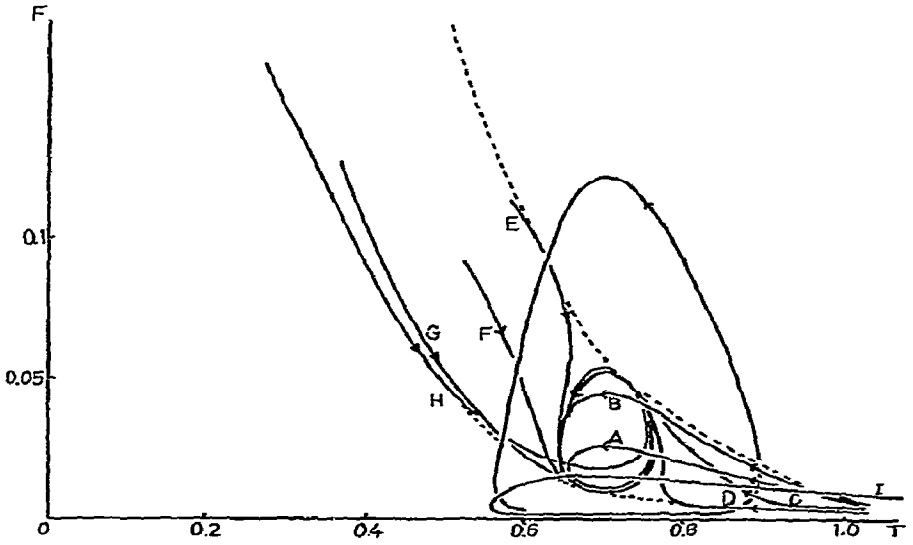

Fig. 8a. The trajectories in fig. 7 projected on (F, T) plane.

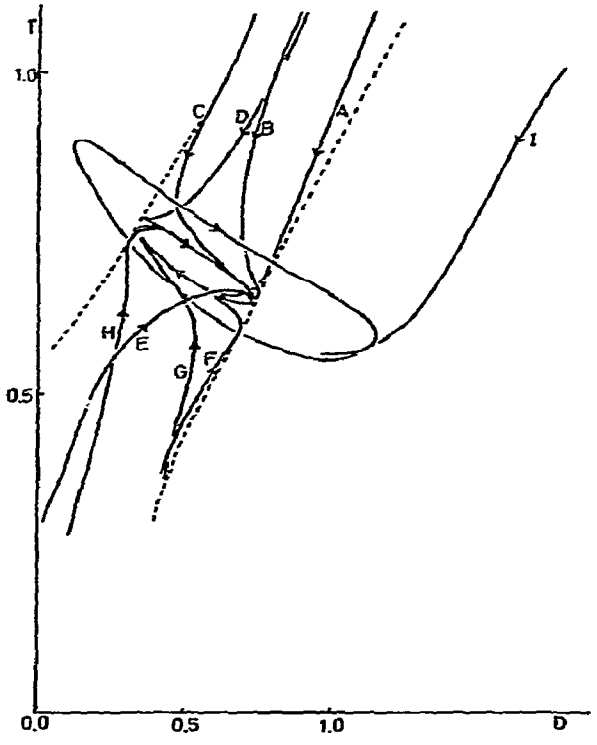

Fig. 8b. The trajectories in fig. 7 projected on (T, D) plane.

It is easily seen that there is a conservation law,

$$F + T + C = \phi = \text{constant}, \tag{7.2}$$

with the aid of which one may reduce the number of reference variables. Several systems will be briefly discussed below.

The system $\langle 0, N_d \rangle$, $N_d = 0, 1, 2, \ldots$, has the following properties:

(1) The system has only one steady state, i.e.

$$k_\theta T_0 = k_m M F_0 \tag{7.3}$$

and $k_c = k_d T_0 D_0 C_0^{N_d - 1}$ $(N_d \neq 0)$,

$$\text{or} \quad k_c C_0 = k_d T_0 D_0 \qquad (N_d = 0). \tag{7.4}$$

(2) For $N_d = 0$ and 1, the steady state is always stable.

(3) For $N_d = 2$, the steady state may become a stable focus or an unstable focus. In the marginal situation, one has an oscillation with infinitesimal amplitude around the steady state, and the phase difference between $F(t)$ and $T(t)$ is given by

$$\tan \eta = \omega / k_m M > 0, \tag{7.5}$$

where ω is the frequency of the infinitesimal oscillation.

In the case of the system $\langle 0, N_d \rangle$, oscillations are due to the inertia of flow in the auto-catalytic reac-

tion d. Thus the large value of N_d makes the system unstable.

The system $\langle 1, N_d \rangle$, $N_d = 0, 1, 2, \ldots$, has the following properties:

(1) The system has two steady-state solutions,

$$\text{(A)} \quad F_0 = C_0 = 0 \quad \text{and} \quad T_0 = \phi, \tag{7.6}$$

$$\text{(B)} \quad k_\theta T_0 = k_m M, \qquad k_\theta F_0 = k_d D_0 C_0$$

$$\text{and} \quad k_c = k_d T_0 D_0 C_0^{N_d - 1} \qquad (N_d \neq 0)$$

$$\text{or} \quad k_c C_0 = k_d T_0 D_0 \qquad (N_d = 0). \tag{7.7}$$

The steady state (B) appears when the inequality $\phi > k_m M / k_\theta$ holds.

(2) For $N_d = 0$, 1 and 2, it is possible to have a situation in which the steady state (A) is unstable and the steady state (B) is an unstable focus or, in a marginal situation, a center.

(3) In the marginal situation, one may have an oscillation with infinitesimal amplitude around the steady state (B). The phase difference η between $F(t)$ and $T(t)$ is given by

$$\cos \eta = 0. \tag{7.8}$$

The system $\langle 2, N_d \rangle$, $N_d = 0, 1, 2, \ldots$, has the following properties:

(1) The system has two steady-state solutions,

$$\text{(A)} \quad F_0 = C_0 = 0 \quad \text{and} \quad T_0 = \phi, \tag{7.9}$$

$$\text{(B)} \quad k_\theta T_0 F_0 = k_m M, \qquad k_\theta F_0^2 = k_d D_0 C_0^{N_d}$$

$$\text{and} \quad k_c = k_d T_0 D_0 C_0^{N_d - 1} \qquad (N_d \neq 0)$$

$$\text{or} \quad k_c C_0 = k_d T_0 D_0 \qquad (N_d = 0). \tag{7.10}$$

(2) For $N_d = 0$, the steady state (A) is always stable and the steady state (B) may become an unstable focus, a center or a stable steady state. In this case it is difficult to have a stable limit cycle around the steady state (B).

(3) For $N_d = 1$ and 2, it is possible to have a situation in which the steady state (A) is unstable and the steady state (B) is an unstable focus, thus a stable limit cycle may exist. In the marginal situation in which the steady state (B) is a center, one may have an oscillation with infinitesimal amplitude around the steady state (B). The phase difference in this case is given by

$$\tan \eta = -\omega / k_m M < 0. \tag{7.11}$$

Eqs. (7.5), (7.8) and (7.11) show that the phase difference η between $F(t)$ and $T(t)$ in the marginal situation is $0 < \eta < \frac{1}{2}\pi$ for the system $\langle 0, 2 \rangle$, $\eta = \frac{1}{2}\pi$ for the system $\langle 1, N_d \rangle$ and $\frac{1}{2}\pi < \eta < \pi$ for the system $\langle 2, N_d \rangle$. Thus the phase difference η depends on the multiplicity N_θ of the auto-catalysis in "reaction θ".

As was discussed above, the system $\langle N_\theta, N_d \rangle$, where $N_\theta \neq 0$, has two steady states, the one (A) is characterized by $F_0 = C_0 = 0$ and the other (B) by $F_0 \neq 0$ and $C_0 \neq 0$. The higher the multiplicity N_θ of the auto-catalysis in "reaction θ", the more the steady state (A) is stabilized. In fact, the supply of $F(t)$ is only from "reaction θ" and its rate is in the form of $k_\theta F(t)^{N_\theta} T(t)$ while the rate of the consumption of $F(t)$ in "reaction m" is $k_m M F(t)$. Thus for a small value of $F(t)$ the consumption prevails over the supply and the system comes back to the steady state (A).

The role of the auto-catalysis in "reaction d" is as follows; when $C(t)$ is small, "reaction d" hardly proceeds for large N_d because its rate is given in the form of $k_d T(t) D(t) C(t)^{N_d}$. Thus only the left-hand cycle of the chemical reactions in fig. 1 begins to work. Then gradually $T(t)$ and $D(t)$ accumulate and "reaction d" opens. Thus the large value of N_d leads to instability of the steady state (A).

In the case of the system $\langle 2, 0 \rangle$, N_θ is too large in comparison with N_d, thus the steady state (A) is stabilized.

The above considerations on possible related extensions of the model throw some light on the mechanism through which a stable chemical oscillation emerges. It is also interesting to note that the phase relation between $F(t)$ and $T(t)$ is clearly governed by the type of the model, rather than numerical magnitudes of individual rate constants.

8. Discussion

Although no quantitative comparison was attempted in this paper between theoretical results and the data referring to a Belousov–Zhabotinsky reaction, the following points would be of help to remember in such a future attempt.

8.1. The closed characteristics of the limit cycle region

In discussing the stability of the steady state solutions of the system ⟨1,0⟩ in sect. 3, it was found that in the space of the controllable parameters the region corresponding to sustained oscillations is open in the positive direction of σ. However, according to Zhabotinsky et al. [12] the region corresponding to sustained oscillation is closed in the space of initial concentrations of malonic acid, ceric ion and bromate ion. Roughly speaking, these initial concentrations may be taken to correspond to our parameters σ, ϕ and k_θ, respectively. Thus our model appears to be at variance with their observation.

In this connection it should be noted that in a slightly modified model ⟨1,1⟩, an upper bound is found for M as well as a lower bound, under fixed values of rate constants, in order that there appear sustained oscillations, i.e.

$$M_-(k_m, k_\theta, k_d, k_c) < M < M_+(k_m, k_\theta, k_d, k_c), \quad (8.1)$$

where

$$M_\pm(k_m, k_\theta, k_d, k_c) = k_\theta^2 (1 \pm \sqrt{1 - 4k_c k_d / k_\theta^2}) / k_m k_d. \quad (8.2)$$

The modified system ⟨1,1⟩ seems, therefore, to indicate one of the possible directions of improvement.

8.2. Phase relations among various oscillating quantities

It was found from the examination of several related extensions of the model that the phase relations among various oscillating quantities are rather sensitive to the model adopted. These relations, therefore, would be of help in identifying the global characteristics of the proper type of model.

8.3. Oscillation characteristics

In many cases the observed oscillation in a Belousov–Zhabotinsky reaction is characterized by a strong relaxation oscillation, which is different from the computed example in fig. 4. However it was found that the characteristics are severely affected by the relative magnitudes of the kinetic parameters of the reactions involved. Oscillation characteristics, therefore, would be of help in determining the relations among various rate constants involved in a particular type of model.

8.4. Propagation of chemical waves

In the experiments on Belousov–Zhabotinsky reactions spatial propagation of concentration waves was observed in an unstirred sample [13–15] as well as the uniform oscillation in a stirred sample. Only the latter case has been treated in this paper, but it is clear that spatial propagation yields important additional information on the diffusion characteristics of various chemical components. The corresponding theoretical analysis is now under way and the results will be presented in a separate paper.

8.5. Other models differing from Degn's type

Zhabotinsky et al. [16] have proposed a set of kinetic equations. However they have introduced several ad hoc assumptions on the rate constants in order to approximate the observed oscillation characteristics. From our point of view it seems necessary to analyze the basis for this assumption.

Recently Noyes et al. [8–11] proposed a detailed network of reactions, together with quantitative information on elementary steps, in order to explain the oscillation mechanism of Belousov–Zhabotinsky reactions. One may reduce his network to get a simpler model by contracting relatively fast steps, thus renormalizing the slow ones. The resulting model is different from the one treated in the present paper. Work is in progress which is aimed at analyzing new model in a method similar to that adopted in this paper. The results will be reported in a forthcoming publication.

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