Chemical Engineering Communications
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454788

ANALYSIS OF BISTABLE AND OSCILLATING REACTION SYSTEMS IN PRESENCE OF AN EXTERNAL NOISE

V. Ravi Kumar[a]; B. D. Kulkarni[a]
[a] Chemical Engineering Division, National Chemical Laboratory, Poona, India

To cite this Article Kumar, V. Ravi and Kulkarni, B. D.(1985) 'ANALYSIS OF BISTABLE AND OSCILLATING REACTION SYSTEMS IN PRESENCE OF AN EXTERNAL NOISE', Chemical Engineering Communications, 39: 1, 69 — 90
To link to this Article: DOI: 10.1080/00986448508911663
URL: http://dx.doi.org/10.1080/00986448508911663

Chem. Eng. Commun. Vol. 39 pp. 69–90
0098-6445/85/3906-0069$25.00/0

ANALYSIS OF BISTABLE AND OSCILLATING REACTION SYSTEMS IN PRESENCE OF AN EXTERNAL NOISE

V. RAVI KUMAR and B.D. KULKARNI†

Chemical Engineering Division,
National Chemical Laboratory,
Poona 411 008, India

(*Received October 19, 1984; in final form February 27, 1985*)

The paper analyses a bistable and an oscillatory reaction system in the presence of an external noise. The analysis of a bistable system shows that in the normal way the inclusion of noise destroys all the deterministic solutions. In other words, the stochastic system does not admit any solution. With imposition of certain restraints it is possible, however, to get stochastic solutions in a certain region of parameter space, which in general shrinks with the extent of noise. The modality of diminishing the region of solutions is different for white and nonwhite noise and has been discussed.

The paper also evaluates the influence of white and nonwhite noise on the behavior of an oscillating system and illustrates it by considering two case examples. One example indicates the conflicting role of white and nonwhite noise in bringing about the transitions from the oscillatory behavior while the second example shows no influence of white and nonwhite noise on the oscillating solution.

The implications of the role of noise in analysing bistable and oscillatory systems is discussed.

I. INTRODUCTION

The phenomenological description of chemically reacting systems can generally be described by a set of differential equations and the stationary as well as the dynamic characteristics of the systems can be understood by their study. Typical equations such as

$$\frac{dc}{dt} = f(\alpha_i, C) \tag{1}$$

are commonly involved in the analysis of reactions taking place in reactors under well stirred conditions and these have been investigated for different forms of the function $f(\alpha_i, C)$. The parameter α_i in this equation represent external parameters such as input- output flow-rates, exchange coefficients, kinetic rare constants etc., and it may be brought out that conventional treatments assume these parameters as constants during analysis. In reality, however, all these parameters could be varying about a certain mean value; thus for instance an input-output flow rate k_f used in an analysis represents a statistical mean value obtained over a length of

† To whom the correspondence should be made.
NCL Communication No. 3563/3654
Submitted for publication by J. J. Ulbrecht.

time. At any time therefore the actual k_f value can in general be different from its mean value and it would be more appropriate to write it as

$$k_f = \bar{k}_f + \xi(t) \tag{2}$$

where $\xi(t)$ represents some random noise and $\bar{k}_f$ the mean value of the flow rate. Similarly, values of other parameters such as exchange coefficients or rate constants represent statistical average values which have been calculated from the results of a set of sufficiently large number of experiments. Therefore, at any specific time t, the parameters α_i cannot be considered to be constants but should be assumed to vary around their mean value obtained over a period of time. A logical way to take into account such variations is to write these parameters, in accordance with Eq. (2) as

$$\alpha_i = \bar{\alpha}_i + \xi(t) \tag{3}$$

where $\bar{\alpha}_i$ represents the mean value and $\xi(t)$ a random contribution usually termed as the fluctuating or noise term.

Equation (3), while simple from a conceptual viewpoint, presents considerable difficulties from the mathematical viewpoint, since the original deterministic equation describing the physical system on incorporation of Eq. (3) becomes a differential equation involving random coefficients and no easy methods for solving it exist. To circumvent the mathematical difficulties—at least to a certain extent—it can be presumed that $\xi(t)$ represents a Gaussian white noise having zero mean with a certain variance around this mean value. White noise, however, is an idealization and practical systems require the consideration of real noise. Coloured noise with finite-time correlation effects are known to approximate real noise better. Therefore during analysis of systems of interest it is practical to regard $\xi(t)$ in Eq. (3) as a coloured noise. In our study, however, we shall consider cases when white and coloured types of noises are present in the system for the sake of comparison.

The incorporation of Eq. (3) in Eq. (1) helps to reform the phenomenological Eq. (1) as a stochastic differential equation provided the noise term $\xi(t)$ is defined. As is known, the resulting stochastic differential equation can be interpreted either by the Ito or Stratanovich rules. While mathematical techniques have been developed for the Ito form, the Stratanovich interpretation of the stochastic equation is considered to be physically more meaningful (Bulsara *et al.*, 1981). It, therefore, becomes necessary to treat the stochastic equation formulated from the phenomenological equation in a Stratonovich form and then convert it into an Ito form for subsequent mathematical treatments. In what follows, therefore, we have adopted this convention. For more information regarding the general methodology in formulating and obtaining the solutions of these equations the readers can refer to the standard texts and reviews (Arnold, 1973; Seinfeld and Lapidus, 1974; Van Kampen, 1976).

The methodology outlined as above works well when $\xi(t)$ is treated as a white noise (i.e. with no time-correlation effects) since the stochastic differential equation describing the Markovian process can be converted into an equivalent

Fokker–Planck equation which describes the probability of evolution. This equation can be easily solved to obtain the stationary probability distribution. Incorporation of coloured noise however makes the process non-Markovian. It is no more possible then to write a simple Fokker-Planck equation as is the case for the white noise. Only if the coloured noise itself follows a Markovian process one can work within the framework of the Markovian theory. Even so, one has now to deal with a multivariate Fokker-Planck equation involving the state variables ($\bar{C}$) and the noise as its constituent variables. The difficulties associated with such multivariate Fokker-Planck equations are well known and many a time the stationary probability distributions cannot be uniquely obtained.

We note from the above discussion that the consideration of coloured noise leads to complex formulations even for single variable systems. In recent years, several attempts to provide easier methods of solutions to such problems have been evident. Thus Sancho and San Miguel (1979) and Horsthemke and Lefever (1980) have provided a perturbative expansion in terms of the correlation time of the noise. The method permits calculation of the stationary probability density of stochastic systems subjected to wide band external coloured noise. Lindenberg and West (1983) have also developed a renormalization scheme to obtain the influence of time correlation effects of coloured noise on the steady state distribution of single variable systems. In chemical engineering literature Ligon and Amundson (1981a,b,c) have considered the effect of gamma distributed noise and evaluated its influence numerically. Sancho *et al.* (1982) have suggested a method to obtain an approximate Fokker-Planck equation for a non-Markovian process in the presence of coloured noise. This method quickly gives the influence of time-correlation effects on the stationary distribution. The scheme of Sancho *et al.* (1982) valid for small correlation times is extremely useful and will be followed in analysing a one variable bistable system, the results of which are presented in Section II.

The present paper is also concerned with the presence of external noise in a two-variable reacting system specifically when its deterministic analysis indicates the occurrence of oscillatory solution. A large number of skeleton models that explain the oscillatory behavior of chemically reacting systems have been proposed in the literature and the more recent work of Kevrekidis *et al.* (1984) generalises some of these models. Their study on these models reflect the fact that none of the models are exactly solvable and recourse to numerical methods becomes necessary. To seek the influence of external noise on these models introduces additional numerical complications and the results obtained become specific to the model chosen for analysis. A few such cases, (de la Rubia *et al.*, 1984, Tambe *et al.* 1984b), have respectively considered the basic oscillatory models of Takoudis *et al.* (1978) and Pikios and Luss (1977). These analyses reveal interesting results of the role of white and coloured noise in generating new transitions in reacting systems.

In the present paper we start with an exactly solvable case of a limit cycle and study the influence of external noise on the system behavior. This would help to obtain more insight into the behavior of system in the presence of noise than those considered above. The results for the two-component oscillatory system are presented in Section III while Section IV provides a summary and concluding remarks on the results obtained.

II. ANALYSIS OF A BISTABLE REACTION SYSTEM (SINGLE VARIABLE CASE)

To ascertain the role of white and nonwhite noise on chemical reacting systems that possess phenomenological equations of the form of Eq. (1) we shall treat the case of an autocatalytic reaction with exponential acceleration in the rate. This type of autocatalytic rate form has been analysed earlier from a macroscopic point of view by Ravikumar *et al.* (1984). They have cited several examples of systems following this rate model. In this type of rate model it is presumed that for a reaction scheme

$$A \xrightarrow{k_1} A_1 \xrightarrow{k_2} \qquad (I)$$

the rate of consumption of A follows the rate law

$$r_A = k_1[A]\exp(\alpha_1[A_1]) \qquad (4)$$

where the product species A_1 is accelerating or decelerating the rate of its own formation in an exponential way with α_1 as some arbitrary constant. For the present analysis let us assume that such a reaction occurs in a CSTR, wherein the concentration of species A can be maintained constant. The phenomenological equation describing the concentration evolution of species A_1 can then be written as

$$V\frac{d[A_1]}{dt_1} = k_f([A_{10}]-[A_1]) + Vk_1A \exp \alpha_1[A_1] - k_2V[A_1] \qquad (5)$$

which can be nondimensionalised to obtain

$$\frac{da_1}{dt} = a_{10} - a_1 + Da_1 \exp(\alpha a_1) - Da_2 a_1 \qquad (6)$$

where

$$t = \frac{k_f[A_{10}]t}{V}, \qquad Da_1 = \frac{k_1V}{k_f}, \qquad Da_2 = \frac{k_2V}{k_f[A]}, \qquad a_1 = \frac{[A_1]}{[A]}, \qquad \alpha = \alpha_1[A] \qquad (7)$$

For no autocatalytic species in the feedstream and $Da_2 = 0$, we can write the associated stochastic differential as

$$\frac{da_1}{dt} = -a_1 + \overline{Da}_1 \exp(\alpha a_1) + \exp(\alpha a_1)\xi(t) \qquad (8)$$

where it is presumed that the parameter Da_1 fluctuates around the mean value as

$Da_1 = \overline{Da}_1 + \xi(t)$. Equation (8) can be generally written as

$$\frac{da_1}{dt} = f(a_1) + g(a_1)\xi(t) \tag{9}$$

The associated Fokker-Planck equation can now be written for the white noise case as

$$\begin{aligned}\frac{\partial p(a_1, t)}{\partial t} &= -\frac{\partial}{\partial a_1} f(a_1)p(a_1, t) + D\frac{\partial}{\partial a_1} g(a_1)\frac{\partial}{\partial a_1} g(a_1)p(a_1, t)\\ &= -\frac{\partial}{\partial a_1}[-a_1 + \overline{Da}_1 \exp(\alpha a_1)]p(a_1, t)\\ &\quad + D\frac{\partial}{\partial a_1}\exp(\alpha a_1)\frac{\partial}{\partial a_1}\exp(\alpha a_1)p(a_1, t)\end{aligned} \tag{10}$$

where D represents the intensity of the noise.

The stationary solution to Eq. (10) can be obtained only if the model possesses certain boundary conditions. It is known that the stochastic system possesses solution only if the boundaries are natural, reflecting or periodic. Details of the classification of boundaries can be found in Horsthemke and Lefever (1984), Gardiner (1983) and Risken (1984). Let us now test whether the boundaries for the present example are natural. In this case it is expected that the process never reaches its boundaries, that is the probability flux at the boundaries is zero. The fact is equivalent to the analytical condition

$$J = \int \exp\left\{-\int_\delta^{a_1} \frac{2f(z)}{g^2(z)}\, dz\right\} da_1 = \infty,\ \delta > 0 \tag{11}$$

where the first integral for the lower and the upper boundary is evaluated over the range $(0, \delta)$ and $(\delta, a_{1\infty})$. The function $f(z)$ and $g(z)$ in this equation are those identified in Eq. (9) and $a_{1\infty}$ represents the upper bound for the variable a_1. Evaluating the inner integral in this equation leads to

$$J = \int \exp\left[\frac{2\overline{Da}_1 \exp(-2\alpha Z)}{\alpha} - \frac{z\exp(-2\alpha Z)}{\alpha} - \frac{\exp(-2\alpha Z)}{2\alpha^2}\right]_\delta^{a_1} da_1 \tag{12}$$

Clearly this integral tends to finite values at the boundaries $(0, a_{1\infty})$ signifying that the system does not possess natural boundaries. As would be evident the system does not have either periodic or reflecting boundaries.

The Fokker-Planck Eq. (10) therefore does not possess a stationary solution and we obtain a simple result that the presence of white noise destroys all the deterministic solutions. It is possible, however to create artificial boundaries by imposing certain restrictions on the physical model. Thus for instance, if we suppose that the activating influence (α) vanishes for no autocatalytic species in the system (i.e. $\alpha = 0$ for $a_1 = 0$) we have a natural lower boundary. Likewise for $\overline{Da}/\alpha \to \infty$ for $\alpha_1 = a_{1\infty}$ creates a natural boundary at the other end. Note that these constraints can be easily applied to the physical model described by Eq. (6)

which now needs to be supplemented by additional equations valid at the boundaries.

In the presence of these restrictions the Fokker-Planck Eq. (10) possesses the stationary solution given by

$$p_a(a_1, \infty) = \frac{N}{\exp(\alpha a_1)} \exp\left[-\frac{1}{D}\left\{\frac{(1+2\alpha a_1)}{4\alpha}\exp(-2\alpha a_1) + \frac{\overline{Da}_1}{\alpha}\exp(\alpha a_1)\right\}\right] \quad (13)$$

where N represents the normalization constant to be obtained subject to the condition $\int_0^1 p(a_1, t)\, da_1 = 1$. When $\xi(t)$ is treated as a white noise, the process $a_1(t)$ described by Eq. (8) is known to be Markovian. The fundamental solution given by Eq. (11) therefore also describes the transition probability of the process. In the event when $\xi(t)$ is considered as a coloured noise this property is lost and simple formulation as above is not possible. Sancho *et al.* (1982) have been able to develop an approximate Fokker-Planck equation especially for cases where the coloured noise can be described by an Ornstein-Uhlenbeck process with small time-correlation effects and the equation can be written as

$$\frac{\partial p(a_1, t)}{\partial t} = -\frac{\partial}{\partial a_1} f(a_1)p(a_1, t) + D\frac{\partial}{\partial g_1} g(a_1)\frac{\partial}{\partial a_1} h(a_1)p(a_1, t) \quad (14)$$

where

$$h(a_1) = g(a_1)\left[1 + \tau g(a_1)\frac{d}{da_1}[f(a_1)/g(a_1)]\right] \quad (15)$$

τ in Eq. (15) represents the correlation-time for the Ornstein-Uhlenbeck noise. This approximate formulation given by Eq. (14) is difficult to solve and Sancho *et al.* (1982) give the following solution to this equation in terms of the white noise solution

$$p_{st}(a_1, \infty) = p_0(a_1, \infty)[1 + \tau(E_1 - E_2 - E_3)] \quad (16)$$

where

$$E_1 = -\frac{1}{2D}\int_{a_{1-}}^{a_{1+}} \frac{f^2(a_1)}{g^2(a_1)} p_0(a_1, \infty)\, da_1$$
$$E_2 = g(a_1)\frac{d}{da_1}\left[\frac{f(a_1)}{g(a_1)}\right], \quad \text{and} \quad E_3 = \frac{1}{2D}\left[\frac{f(a_1)}{g(a_1)}\right]^2 \quad (17)$$

The stationary solution in the present case can thus be obtained by using these equations as

$$p_{st}(a_1, \infty) = p_0(a_1, \infty)\left[1 + \tau\left\{E_1 + 1 - a_1 - \frac{1}{2D}\left[\frac{-a_1 + \overline{Da}_1 \exp(\alpha a_1)}{\exp(\alpha a_1)}\right]^2\right\}\right] \quad (18)$$

Equations (13) and (18) respectively give the effect of incorporating the white and coloured noise in the deterministic system. The results obtained using these equations are discussed below.

Results and Discussion

The results obtained by solving the unrestrained macroscopic Eq. (6) are presented in Figure 1 as a bifurcation diagram in the $\alpha - Da_1$ parameter space, for the case when $Da_2 = 0$ and when no autocatalytic species is fed in the input stream. The figure clearly reveals the existence of regions where no solution, single solution and two solutions prevail. The stationary concentration distributions as a function of α for several values of Da_1 are presented in Figure 2. The multiplicity pattern shown in the bifurcation diagram is clearly evident in this figure too. As may be noted from this figure the region where two solutions exist is spread over a wider region in the $a_1 - \alpha$ space for lower values of Da_1. Thus for instance for a value of $Da_1 = 0.02$ the region where two solutions exist lasts up to $\alpha = 18$ while for $Da_1 = 0.4$ the two-solution region is almost nonexistent. The stability of the solutions as obtained by linear stability analysis is also indicated in the figure.

The stochastic solution to the restrained problems has been obtained using Eq. (18). The typical probability distribution curves for two sets of values of D and τ are presented in Figures 3 and 4. In both the cases the other parameter values (listed in legends to the figures) were chosen such that we are operating in the two-solution region (cf. Figure 1). The maximum and minimum in these curves correspond to the stable and unstable solutions. The region marked in the Figure 3 is magnified for sake of clarity and is shown as an inset within the figure. The

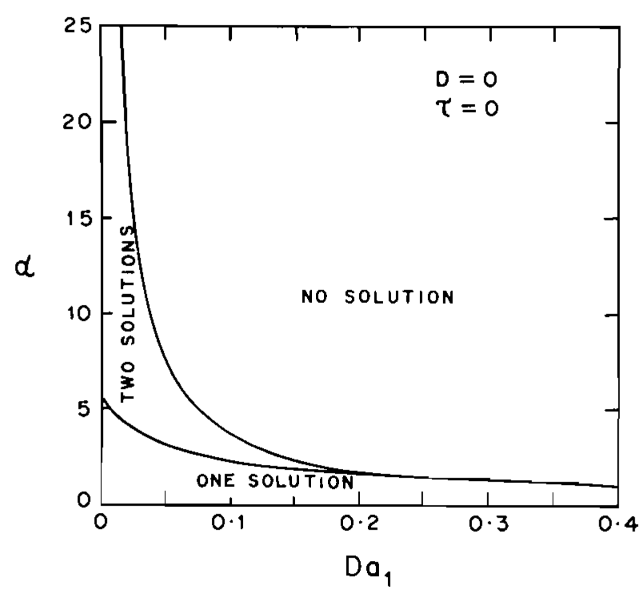

FIGURE 1 Bifurcation plot in the $\alpha - Da_1$ parameter space.

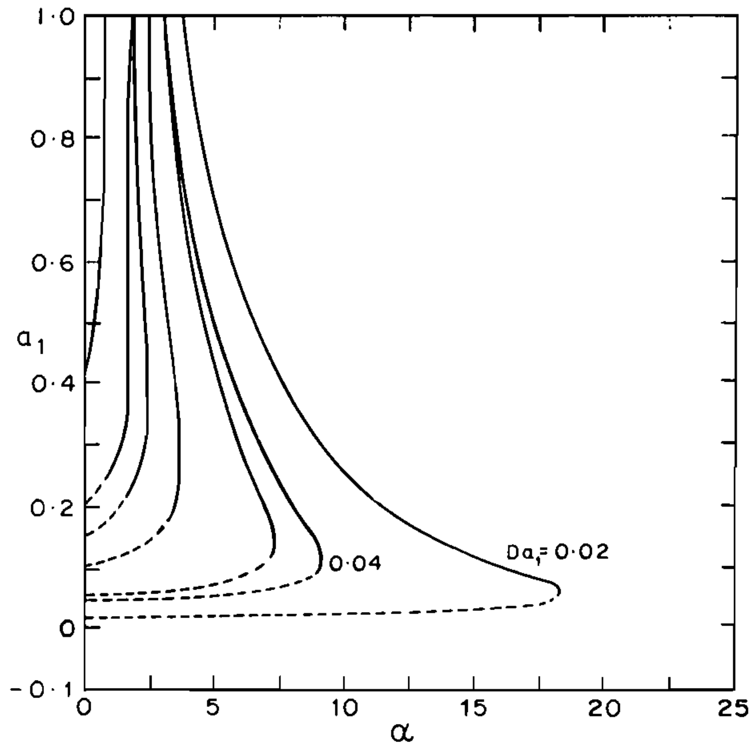

FIGURE 2 $a_1-\alpha$ plots for various Da_1 values (deterministic analysis).

maximum and the minimum thus obtained for several sets of parameter values have been subsequently used to prepare plots of $a_1-\alpha$ for a given value of Da_1 (=0.02), and different values of D and τ. The typical plot shown in Figure 5 also indicates whether the solutions are stable or unstable. For sake of comparison the unrestrained deterministic solution is also included. The results indicate that, in general, with inclusion of noise in the system, the parameter space wherein solutions exist narrows down.

In accordance with the deterministic solutions the stochastic solutions also indicate the existence of a stable and an unstable branch of solutions. Both the stable and unstable solution branches of the stochastic solution, however, lie below that for the deterministic case suggesting a shrinkage in the region of two solutions. This trend continues as the value of τ is increased for the same value of D.

The typical curve for $D=0.001$ and a higher value of τ (=0.1) is indicated in Figure 6. Comparison with Figure 5 shows the influence of τ.

In order to understand the influence of τ on the system behavior, the stable solution branch in Figure 5 is marked by points A, B and C. The curve ABC is the stable solution branch and the point C marks the end of the stable solution branch. The effect of τ as seen in Figure 6 is to bend the stable solution branch to create a point of maximum. The general trends regarding the movements of the

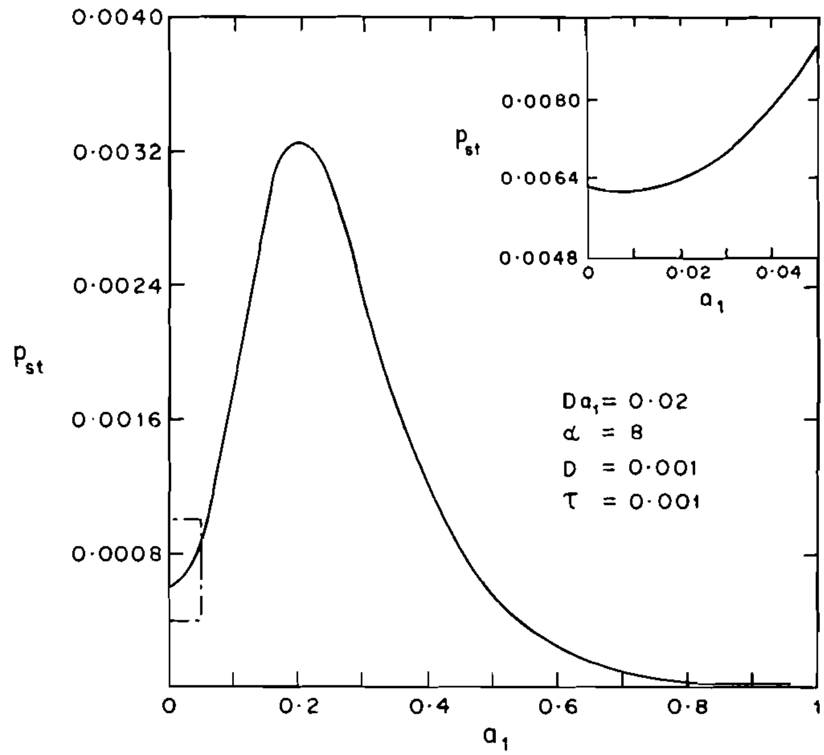

FIGURE 3 Stationary probability density distribution.

points A, B and C on increase in τ is evident in the Figures 7 and 8 where curves for the same value of D, and $\tau = 0.5$ and 1.0, are respectively plotted. The point A in general moves towards higher values of α implying that the system now possesses a solution only at higher values of α. The point C moves to the left on the α axis implying that the region of two solutions now exists over a smaller range of α values. The point of maximum indicated by point B moves down with increase in τ. Thus the final picture that emerges is that with increase in τ the three points move towards each other narrowing the region of parameter space contained within them. Eventually they merge into each other, and there is also a total shrinkage of the region wherein solutions can prevail. The system would obviously not possess any solution for values of τ greater than this critical value. Calculations with higher and lower values of D were found to require lower or higher values of τ respectively to complete this task. The qualitative features, however, essentially remain the same.

Figure 9 shows the influence of variations in the intensity of white noise (D) where $a_1 - \alpha$ curves are plotted for one value of Da_1. It is apparent from the figure that increasing the intensity of white noise, also has the similar influence of diminishing the parameter region where two solutions can prevail. There is, however, a difference when compared to the effects observed in the presence of coloured noise (i.e. both D and τ). As noticed, the white noise does not cause any

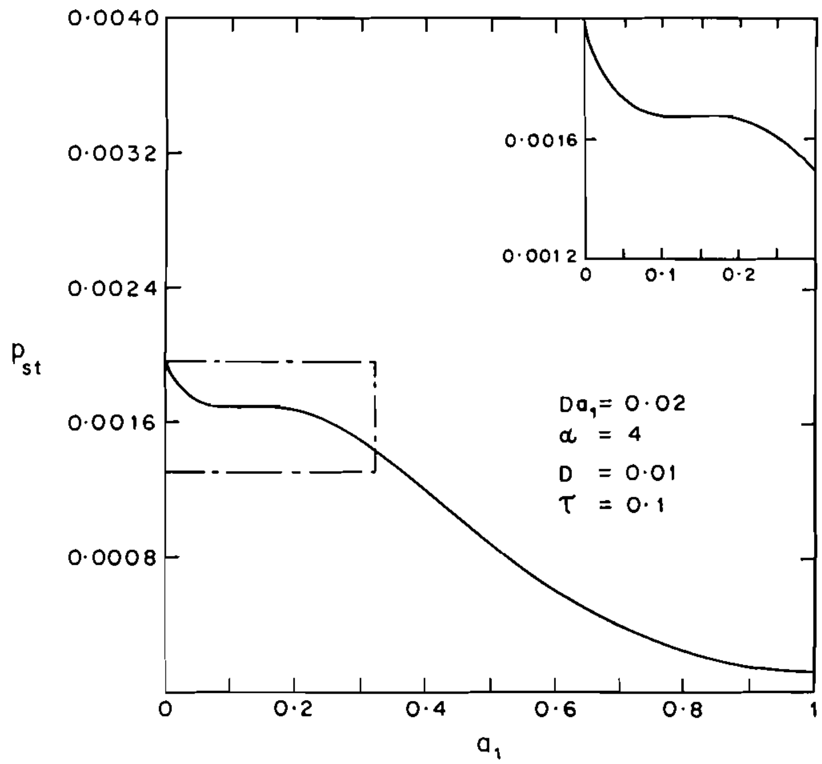

FIGURE 4 Stationary probability density distribution.

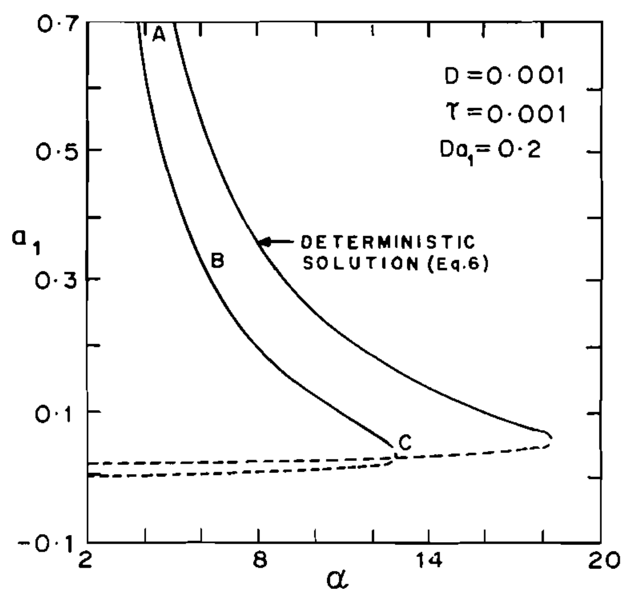

FIGURE 5 $a_1-\alpha$ plot in the presence of coloured noise.

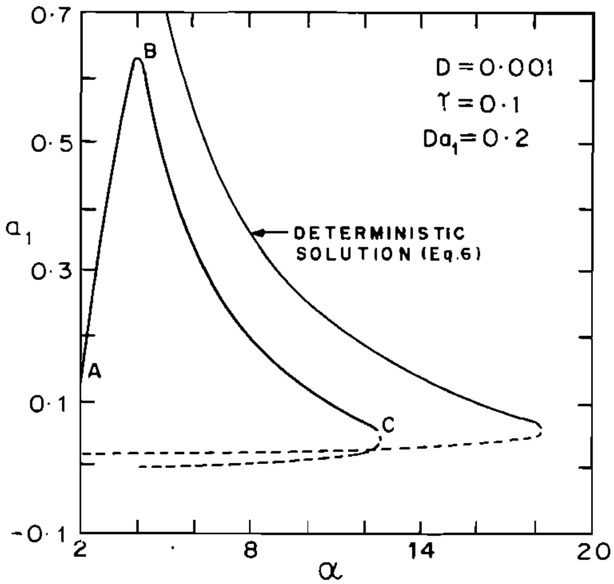

FIGURE 6 $a_1-\alpha$ plot in the presence of coloured noise.

bending of the stable solution branch and in consequence does not produce any point of maximum in it. The point A of the stable solution branch, however, moves to the left on the α axis indicating that the two-solution region now begins at an earlier value of α. The point C also moves to the left. The region where two solutions prevail, therefore, is compressed and moves from right to left. Note the

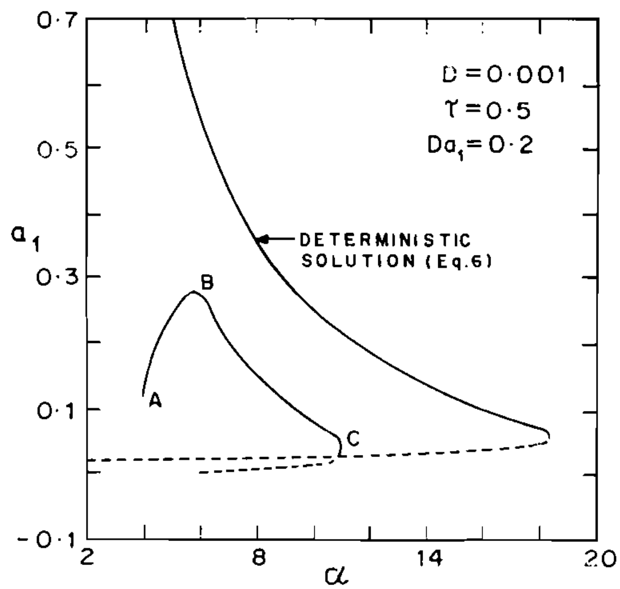

FIGURE 7 $a_1-\alpha$ plot in the presence of coloured noise.

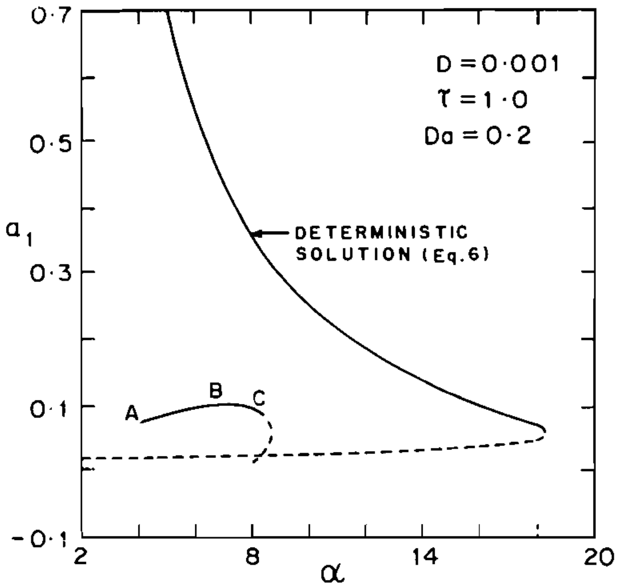

FIGURE 8 $a_1-\alpha$ plot in the presence of coloured noise.

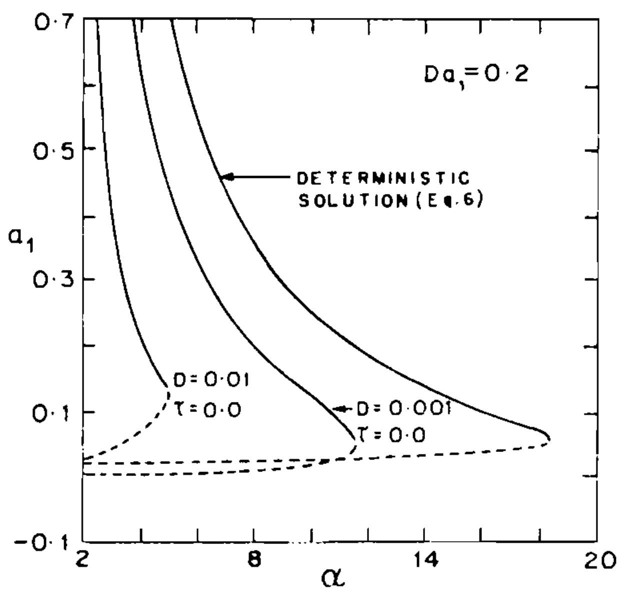

FIGURE 9 $a_1-\alpha$ plot for different values of intensity of noise (white noise case).

contrast in comparison to the effect of coloured noise where point A moves to the right while C moves to the left.

III. ANALYSIS OF AN OSCILLATORY SYSTEM (TWO-VARIABLES CASE)

In the present section we start with an exactly solvable case of a limit cycle and study the influence of external noise on the system behavior. This would help to obtain more insight into the behavior of system in the presence of noise than those involving more complex models. A general criterion for the deterministic system to possess an exactly solvable elliptical limit cycle has been presented by Escher (1979) who also presents by way of illustrations, several examples of such chemically reacting systems. An ellipse can be described in terms of a general equation as

$$ax^2+by^2+cx+dy+exy+f=f(x, y)=H \tag{19}$$

where $a \cdots f$ represents the constants that can be chosen appropriate to the reaction scheme. Equation (19) being the equation for the limit cycle should also satisfy the governing deterministic equations

$$\frac{dx}{dt}=f_1(x, y), \qquad \frac{dy}{dt}=f_2(x, y) \tag{20}$$

which possess the limit cycle described by Eq. (19) as their solution. In view of Eq. (19), Eq. (20) can be written in terms of $H(x, y)$ as

$$\frac{dH}{dt}=\frac{\partial H}{\partial x}\frac{\partial x}{\partial t}+\frac{\partial H}{\partial y}\frac{\partial y}{\partial t}=f(H, \alpha') \tag{21}$$

where α' represents some parameter. The effective idea in writing Eq. (20) in the form of Eq. (21) is to reduce the original two-variable system to that of a single variable case and one can now apply known methods for analysis.

Ebeling and Engel-Herbert (1980) have considered another class of systems that is exactly solvable. The original deterministic equations (Eq. 20) possessing a closed trajectory can be written for this class of systems as

$$\frac{\partial x}{\partial t}=\frac{\partial H}{\partial y}+f(H, \alpha')\frac{\partial H}{\partial x}, \qquad \frac{\partial y}{\partial t}=-\frac{\partial H}{\partial x}+f(H, \alpha')\frac{\partial H}{\partial y} \tag{22}$$

where $H(x, y)$ represents the Hamiltonian and $f(H, \alpha')$ in general some nonlinear function of H and external parameter α'. To incorporate the effect of variations in the parameter α', Eq. (3) is substituted in Eq. (22) to obtain

$$\frac{\partial x}{\partial t}=\frac{\partial H}{\partial y}+f(H, \bar{\alpha}')\frac{\partial H}{\partial x}+g(H)\xi(t) \tag{23}$$

$$\frac{\partial y}{\partial t}=-\frac{\partial H}{\partial x}+f(H, \bar{\alpha}')\frac{\partial H}{\partial y}+g(H)\xi(t) \tag{24}$$

where $g(H)$ represents some function of H that is associated with the parameter and depends on the specific form of $f(H, \bar{\alpha}')$ and $\xi(t)$ represents the noise. It is convenient in most cases to treat the noise $\xi(t)$ as a delta correlated Gaussian white noise with zero mean. The white noise is, however, an idealization that suits mathematical convenience but is rarely possible in physical systems. It becomes necessary then to treat $\xi(t)$ as a coloured noise to understand the role of fluctuations in practical systems.

Using Eqs. (23) and (24) in Eq. (21) renders a single equation in H as

$$\frac{dH}{dt} = h(H)[f(H, \bar{\alpha}') + g(H)\xi(t)] \tag{25}$$

where

$$h(H) = (\partial H/\partial x)^2 + (\partial H/\partial y)^2$$

Ebeling and Engel-Herbert have solved the stochastic differential Eq. (25) on the assumption of white noise. The method of solution involves writing a Fokker-Planck equation corresponding to Eq. (25) that is interpreted in the Strantanovich sense. The stationary probability distribution is then obtained as

$$p_0(H, \infty) = \frac{N}{h(H)g(H)} \exp \int_{H_1}^{H_2} \frac{1}{D} \frac{f(H, \bar{\alpha}')}{h(H)g^2(H)} dH \tag{26}$$

where N represents the normalisation constant to be obtained subject to condition $\int_{H_1}^{H_2} p_0(H, \infty)\, dH = 1$ and D the intensity of white noise. The limits of integration H_1 and H_2 represents the lower and upper bound for the values of variable H.

The simple treatment as above becomes invalid if $\xi(t)$ represents a coloured noise where the nonvanishing correlation time of the noise (τ) renders the temporal evolution of a system as a non-Markovian process. It is still possible, however, to work within the framework of a Markovian theory provided the noise itself is Markovian. This can be achieved using a two-dimensional process described in terms of the state variable (H) and the external fluctuating parameter. As we see here, the original advantage of working with a one dimensional system, as in Eq. (25) is, however, lost. Alternatively one can proceed with the non-Markovian process and, indeed as shown elsewhere, (Sancho *et al.* 1982) obtain an equivalent description of Fokker-Planck equation valid for small correlation times as

$$\frac{\partial p(H, t)}{\partial t} = -\frac{\partial}{\partial H}[h(H)f(H, \bar{\alpha}')]p(H, t) + D\frac{\partial}{\partial H} h(H)g(H) \frac{\partial}{\partial H} l(H)p(H, t) \tag{27}$$

where in obtaining the above equation the noise $\xi(t)$ is assumed to be of the Ornstein-Uhlenbeck form characterised by a correlation function defined as equal to $D/\tau[\exp -(t-t')/\tau]$. Such a noise is known to approximate the real noise in physical processes better than the white noise. As may be noted in the limit $\tau \rightarrow 0$ we recover the correlation function for the white noise. τ in this function represents the correlation time and D the noise intensity while the function $l(H)$ in Eq. (27) is defined as

$$l(H) = h(H)g(H)\left[1 + \tau h(H)g(H)\frac{d}{dH}\left(\frac{f(H, \bar{\alpha}')}{g(H)}\right)\right] \tag{28}$$

The stationary solution to Eq. (27) can be obtained as

$$P_{st}(H, \infty) = p_0(H, \infty)\{1 + \tau[E_1 - E_2 - E_3]\} \tag{29}$$

where

$$\begin{aligned} E_1 &= -\frac{1}{2D}\int_{H_1}^{H_2} \frac{f^2(H, \bar{\alpha}')}{g^2(H)} p_0(H, \infty)\, dH, \\ E_2 &= h(H)g(H)\frac{d}{dH}\frac{f(H, \bar{\alpha}')}{g(H)} \\ E_3 &= -\frac{1}{2D}\frac{f^2(H, \bar{\alpha}')}{g^2(H)} \end{aligned} \tag{30}$$

Equation (29) gives the stationary probability distribution of H in presence of Ornstein-Uhlenbeck noise.

Equation (26) has been used by Ebeling and Engel-Herbert (1980) to analytically show the influence of white noise on the oscillatory system. The effect of coloured noise as contained in Eq. (29), however, has not been reported so far. In what follows, we shall demonstrate this effect by considering illustrative examples.

Example 1

As a first example, we shall take the several functions in Eq. (25) as $h(H) = 2H$, $g(H) = (2H)^{-1/2}$, $f(H, \bar{\alpha}') = (\bar{\alpha}' - 2H)(2H)^{-1/2}$. The specific forms of the functions correspond to a set of deterministic equations of the form of Eq. (20) which possess a stable limit cycle described by $2H = x^2 + y^2 = \bar{\alpha}'$. Clearly $H = \bar{\alpha}'/2$ then represents the deterministic solution. In order to obtain a stochastic solution to this case, we first obtain the stationary probability distribution using Eq. (26) as

$$p_0(H, \infty) = N(2H)^{-1/2} \exp\left\{\frac{1}{D}[\bar{\alpha}'(2H)^{1/2} - \tfrac{1}{3}(2H)^{3/2}]\right\} \tag{31}$$

Recollecting that the points of maxima of this probability distribution correspond to the stable states while the minima to the unstable states we can differentiate Eq. (31) with respect to H to obtain the external points as

$$\frac{dp_0(H, \infty)}{dH} = 0 = (2H)^{1/2}(\bar{\alpha}' - 2H) - D \tag{32}$$

Clearly for $D = 0$, that is in the absence of white noise the system possesses a solution at $2H = \bar{\alpha}'$ which as brought out earlier is the deterministic solution. For finite values of D, the equation admits another root indicating new transitions generated due to white noise. In fact as noted by Ebeling and Engel-Herbert an unstable limit cycle gets generated inside a stable orbit, which eventually annihilates the solutions completely. For values of D lying beyond a critical value $D_c(=0.4)$ the system then does not possess any solution.

We have investigated the effect of coloured noise on this system by using Eq. (29) where $\bar{\alpha}'$ has been assigned a value of one. The fixation of $\bar{\alpha}'$ helps to fix up the bounds on H which now varies between 0 and 1. The lower limit arises due to the consideration that x and y which represent the concentrations of species cannot take negative values. The results obtained are displayed in Figures 10 and 11 which show the stationary solutions for varying values of correlation time (τ) as the value of the intensity of noise (D) is increased. Let us first concentrate on the results shown in Figure 10 for the case of $D=0, 1$. It is evident from the figure that at low values of τ ($\tau \to 0$) the system possesses two solutions one of which is stable. The case $\tau=0$, of course, corresponds to the white noise case. As the value of τ is increased, the stable solution that begins at $H=0.445$ shifts towards the deterministic solution ($H=0.5$). The unstable solution branch shows a decreasing tendency. The branch, however, disappears abruptly at around $\tau=0.15$. In this region $\tau=0$ to 0.15, we therefore have two stationary solutions to the system. One of these solutions corresponds to a stable limit cycle while the other one to the unstable limit cycle. Between $\tau=0.15$ to 0.3 the system possesses only one solution that corresponds to the stable limit cycle. At $\tau=0.3$ the system shows bifurcation to two other solutions. For $\tau>0.3$ the system therefore possesses three solutions two of which are stable and one unstable. While the numerical analysis in this region of τ indicates the existence of the unstable branch it should be remarked that the probability of its occurrence always lies very close to zero.

Let us now seek the influence of increase in the intensity of noise on the behavior of this system. As noted in the figure for $D=0.2$, for $\tau=0$ the system again possesses two solutions which corresponds to a stable and an unstable limit cycle. The stable and the unstable solutions in this case have, however, moved closer to each other in comparison when $D=0.1$. As before stable branch moves towards the deterministic solution with increase in τ. The unstable branch shows a declining tendency and eventually disappears at $\tau=0.3$. After $\tau=0.3$ the system then possesses only one solution which corresponds to a stable limit cycle. Note that the deterministic stable limit cycle corresponds to $H=0.5$ while the limit cycle in this case tries to approach the deterministic one with increase in τ. In fact for $\tau>0.8$, the stochastic solution yields $H=0.49001$.

As the value of D is further increased to ($D=0.3$) we note the following observations. At $\tau=0$, the stable and unstable solutions have moved further closer together. The stable branch tries to approach the deterministic solution with increase in τ. The unstable branch declines with increase in τ and finally disappears at $\tau=0.4$. A comparative assessment of the cases for these three values of D indicates that with increase in D for a given value of τ the stable solution decreases while the unstable solution in the region where it exists has risen. Thus for $\tau=0$ the stable solution of $H=0.445$ for $D=0.1$ decreases to 0.385 for $D=0.2$ and further decreases to $H=0.31$ for $D=0.3$. The general trend continues until at some value of D the two solutions merge annhilating each other. This occurs for example at $D=0.4$ where for $\tau=0$, the system possesses no

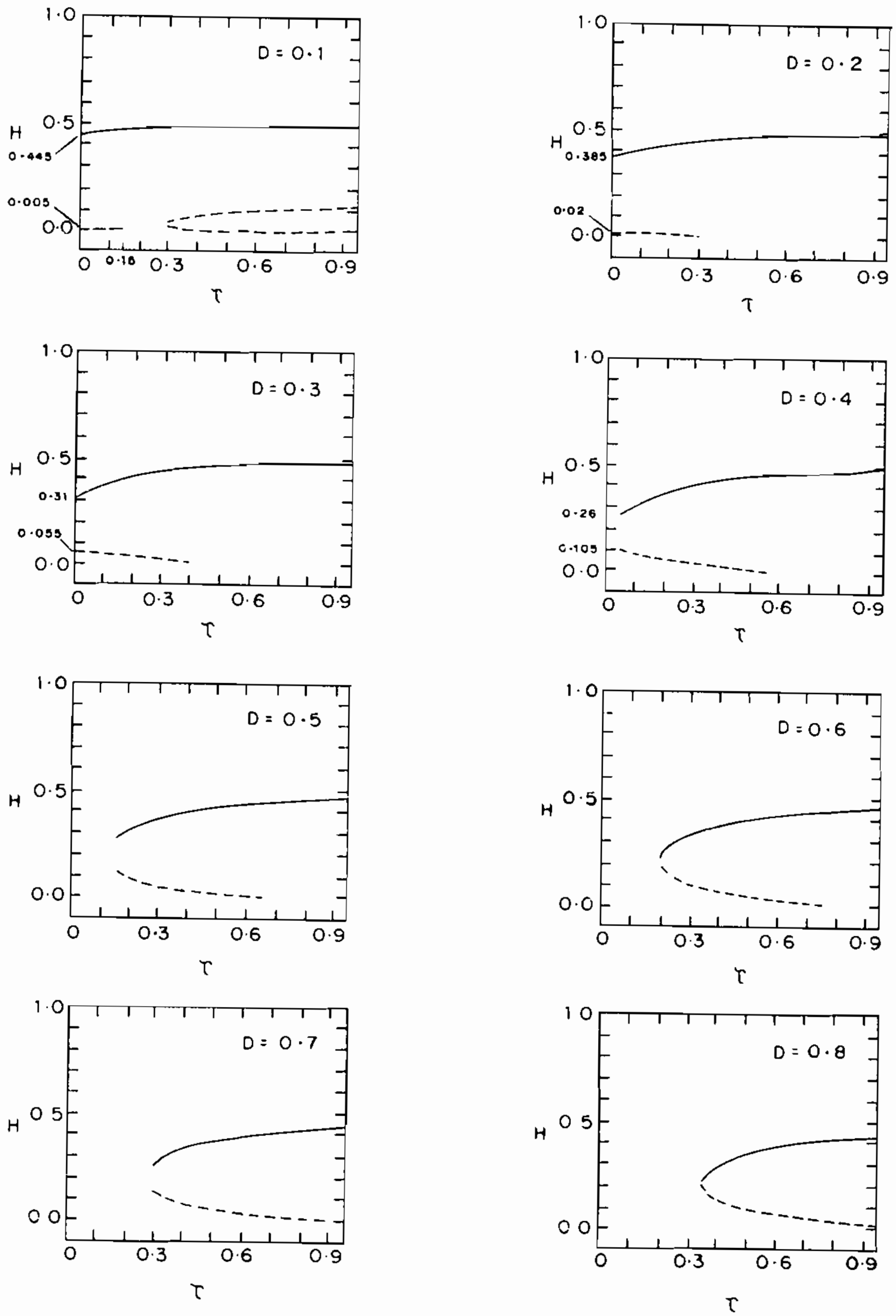

FIGURE 10 Stationary solutions for varying noise parameters (D and τ).

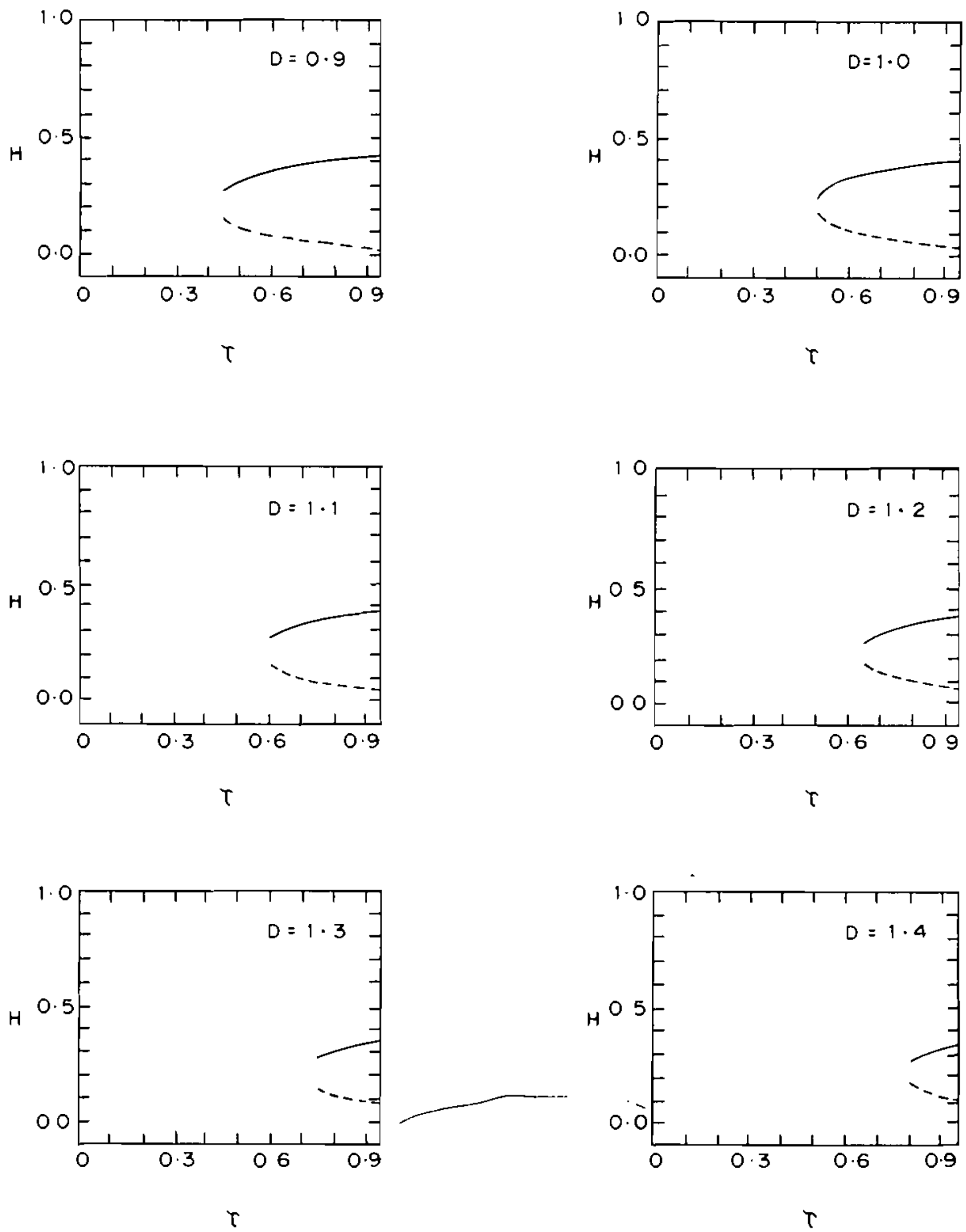

FIGURE 11 Stationary solutions for varying noise parameters (D and τ).

solution. The stable and unstable branch now appears only at $\tau = 0.05$ and even here in accordance with the general trend in the previous cases the stable branch starts at a further lower value of $H = 0.26$ while the unstable branch at a corresponding higher value of $H = 0.105$. With further increase in τ the stable branch tries to approach the deterministic solution while the unstable branch decays and eventually disappears at $\tau = 0.55$. After this value of τ the system then possesses only one stable limit cycle as its solution.

The remaining figures for progressively higher values of D essentially bring-forth the same pattern. As the value of D is further increased the initial region where no solutions exist increases. Thus for $D = 0.6$ the no solution region extends from $\tau = 0$ to 0.2 as against $\tau = 0$ to 0.05 for $D = 0.4$. The figures also indicate that the stable and unstable solution branches begin at higher values of τ as D is increased. The unstable solution branch that decays consequently requires larger values of τ with increase in D to completely disappear. The stable branch that tries to approach to the deterministic solution also requires larger values of τ with increase in D to approach the deterministic limit cycle.

To sum up, the results of the present case indicate conflicting roles of D and τ. For a deterministic system with one stable limit cycle as its solution, incorporation of D (i.e. white noise alone) brings about an additional solution that corresponds to the unstable limit cycle. The increase in the value of D helps to grow the unstable solution while the stable solution is brought down. Eventually for some value of D the two solutions merge annihilating each other and the system possesses no solutions after this critical value of D. The incorporation of coloured noise (D and τ both) for a given value of D acts the other way. Increasing the correlation time of the noise for the fixed value of its intensity (D) favours the stable solution which it helps to grow towards the deterministic solution. The unstable solution decays with increase of correlation time.

Example 2

As a second example we consider the several functions in Eq. (25) as $f = (\bar{\alpha}' - 2H)(2H)^{-1}$, $g(H) = (2H)^{-1}$ and $h(H) = 2H$. These functions again corresponds to a deterministic set of equations that possess the limit cycle described by $2H = x^2 + y^2 = \bar{\alpha}'$. In this case also, $H = \bar{\alpha}/2$ then represents the deterministic solution. To obtain a stochastic solution to the case we obtain the probability distribution in the presence of white noise according to Eq. (26) as

$$p_0(H, \infty) = N \exp\left[\frac{H}{D}(\bar{\alpha}' - H)\right] \tag{33}$$

where N represents the normalisation constant. The points of maxima of this equation indicates that the maxima always occur at $H = \bar{\alpha}'/2$ which corresponds to the deterministic solution. The analysis, therefore indicates that presence of white noise has no influence on the deterministic solution. Let us now investigate the role of coloured noise. According to Eq. (29) the stationary probability distribution is obtained as

$$P_{st}(H, \infty) = p_0(H, \infty)[1 + \tau(E_1 - E_2 - E_3)] \tag{34}$$

where

$$E_1 = -\frac{1}{2D}\int_0^1 (\bar{\alpha}' - 2H)^2 p_0(H_1, \infty)\, dH, \qquad E_2 = 2, \qquad E_3 = \frac{1}{2D}(\bar{\alpha}' - 2H)^2 \tag{35}$$

The stationary probability distribution calculated using Eqs. (34) and (35) also always indicate that the maxima occurs at $H = \bar{\alpha}'/2$ for any combination of D and τ. The coloured noise also therefore has no influence on the deterministic solution. In other words the original deterministic system remains unaltered in the presence of white and also coloured noise.

IV. SUMMARY AND CONCLUDING REMARKS

In summary the present paper has analysed the influence of incorporating coloured and white noise in a reacting system that possess bistability and oscillatory behavior. As noted, in the analysis of bistable system the inclusion of noise destroys the unrestrained deterministic solutions completely. However, if we impose artificial natural boundaries by proper identification of physical constraints on the deterministic model, the stochastic solutions exist and follow different trends for the white and coloured noise. The modality of diminishing the region of solutions in the two cases is seen to be very different. In this case we also note that both D and τ tend to have their effects acting in the same direction—viz. increasing both D and/or τ seems to always diminish the region of solutions. This is in contrast to the effect of D and τ on an oscillating system, where it has been shown in section III that the two act in opposite directions.

Section III in this paper presents an analytical evaluation of the role of external fluctuations on the dynamic behavior of oscillating systems. Two case examples have been studied to illustrate the role of the fluctuations. The first example illustrates the conflicting role of white and coloured noise in bringing about transitions from the originally oscillating system. The white noise tends to generate an additional solution which enhances with noise intensity (D) and finally annihilates the original solution. The system at this critical value of D experiences a transition from two solution region to no solution region. The presence of coloured noise for a fixed value of D, on the other hand tries to preserve the system close to deterministic solution. This is generally achieved for a large enough value of correlation time τ. In general, higher values of D require higher values of τ for such a stabilisation to occur. For higher values of D, even when finite time correlation effects are present (i.e. $\tau > 0$), the solutions are inundated in the initial region of τ values and a solutionless region prevails. In general, the extent of this region is enhanced with the extent of noise intensity.

The second example is included to show that situations might exist where both white and coloured noise have no influence on the original behavior of the system. Noise has no effect in such cases.

The present paper treats only simple model systems. The analysis however, can be extended to more complex situations. As noted in the case examples studied the influence of noise can bring about drastic variations to no variation in the deterministic solutions depending on the nature of functions. Real systems always involve the noise and as shown in this analysis its influence can vary from system to system and even for the same system with the region of parameter space. Trying to fit a deterministic model alone, therefore may sometimes lead to wrong formulations and subsequent information derived from them. Thus, for instance, in situations such as example 1 where one stable and one unstable limit cycle exists, if a deterministic model is to be proposed it would be far more complex and different than the simple deterministic model that actually pertains to the system. The knowledge of the nature and extent of noise is therefore an essential tenet in modelling such systems.

NOTATION

A, A_1	chemical species
$[A]$	concentration of species A
$[A_{10}]$	initial concentration of species A_1 in CSTP
a_1	dimensionless concentration defined in Eq. (7)
$a \cdots f$	constant in an equation for an ellipse (Eq. (19))
a_{10}	dimensionless initial tank concentration of species A defined as A_{10}/A
a_{1-}, a_{1+}	lower and upper bounds for the variable a_1
$\bar{C}$	averaged out concentration
D	intensity of white noise
Da_1, Da_2	Damkohler numbers defined in Eq. (7)
$\overline{Da}_1$	averaged out Damkohler number
E_1, E_2, E_3	parameters defined by Eq. (17)
$f(\ ), g(\ ), h(\ )$	function of terms in brackets
H	transformed variable such as in Eq. (19)
H_1, H_2	lower and upper bounds on the variable H
k_f	flow rate
$\bar{k}_f$	averaged out flow rate
k_2, k_2	rate constants for successive steps in scheme I
N	normalization constant
$p[a_1, t]p[H, t]$	probability density function for single and two component cases
$p_{st}(a_1, \infty)$ $p_{st}(H, \infty)$	stationary probability density in presence of coloured noise for for single and two component cases
$p_0(a_1, \infty)$ $p_0(H, \infty)$	stationary probability density in presence of white noise for for single and two component cases
t, t_1	dimensionless times as appropriately defined in the text
x, y	concentration of species X and Y
V	volume of CSTR

Greek Letters

α	constant defined in Eq. (7)
α_1	arbitrary constant in Eq. (4)
α_i	general notation to denote external parameters
$\bar{\alpha}_i$	averaged out external parameter

τ	correlation time
$\xi(t)$	time dependent noise term

REFERENCES

Arnold, L., 1973, *Stochastic differentialgleichungen*, Munchen-Oldenburg.
Bulsara, A.R., Lindenberg, K., Seshadri, V., Shuler, K.E., and West, B.J., Stochastic processes with non-additive fluctuations—II. Some applications of Ito and Stratonovich calculus, *Physica*, 1979, 234–243.
De la Rubia, F.J., Garcia-Sanz, J., and Velarde, M.G., Role of multiplicative non-white noise in a surface catalyzed reaction with oscillations, *Surf. Sci.*, 1984, **143,** 1–10.
Ebeling, W., and Engel-Herbert, H., The influence of external fluctuations on self sustained temporal oscillations, *Physica*, 1980, **104A,** 378–396.
Escher, C., Models of chemical reaction systems with exactly evaluable limit cycle oscillations, *Z. Physik B.*, 1979, **35,** 351–361.
Gardiner, C.W., Handbook of stochastic methods for physics, chemistry and natural sciences, Springer Verlag, Berlin, 1984.
Horsthemke, W., and Lefever, R., A perturbation expansion for external wide band Markovian noise. Application to transitions induced by Ornstein-Uhlenbeck noise, *Z. Physik B.—Condensed Matter*, 1980, **40,** 241–247.
Horsthemke, W., and Lefever, R., Noise induced transitions, Springer series in Synergetics, vol. 15, Springer Verlag, Berlin, 1984.
Kevrekidis, I., Schmidt, L.D., and Aris, R., Rate multiplicity and oscillations in single species surface reactions, *Surf. Sci.*, 1984, **137,** 151–166.
Ligon, J.R., and Amundson, N.R., Modelling of fluidized bed reactors—Part XVI. An analysis of chemical reactors stability and control—Part XVI. The stochastic stirred pot. *Chem. Engng. Sci.*, 1981a, **36,** 673–685.
Ligon, J.R., and Amundson, N.R., Modelling of fluidized bed reactors—Part VI(a). An isothermal bed with stochastic bubbles, *Chem. Engng. Sci.*, 1981b, **36,** 661–671.
Ligon, J.R., and Amundson, N.R., Modelling of fluidized bed reactors— Part VI(b). The nonisothermal bed with stochastic bubbles, *Chem. Engng. Sci*, 1981c, **36,** 661–667.
Lindenberg, K., and West, B.J., Finite correlation time effects in nonequilibrium phase transitions—I. Dynamic equation and steady state properties, *Physica*, 1983, **119A,** 485–503.
Pikjos, C.A., and Luss, D., Isothermal concentration oscillations on catalytic surfaces, *Chem. Engng. Sci.*, 1977, **32,** 191–194.
Ravi Kumar, V., Kulkarni, B.D., and Doraiswamy, L.K., Multiplicity and instability of states for isothermal homogeneous reactions in CSTR. Case of autocatalysis, *AIChE J.*, 1984, **30,** 649–653.
Risken, H., The Fokker-Planck equation. Methods of solution and applications, Springer Verlag, Berlin, 1984.
Sancho, J.M., San Miguel, M., Katz, S.L., and Gunton, J.D., Analytical and numerical studies of multiplicative noise, *Phys. Rev. A.*, 1982, **26,** 1589–1609.
Sancho, J.M., and San Miguel, M., External nonwhite noise and nonequilibrium phase transitions, *Z. Phys.*, 1979, **B36,** 357–364.
Seinfeld, J.H., and Lapidus, L., 1974, *Mathematical methods in chemical engineering*, Prentice Hall, Inc., Englewood Cliffs, NJ.
Takoudis, C.G., Schmidt, L.D., and Aris, R., Isothermal sustained oscillations in a very simple surface reaction, *Surf. Sci.*, 1978, 705, 119.
Tambe, S.S., Ravi Kumar, V., Kulkarni, B.D., and Doraiswamy, L.K., Sustained isothermal oscillations on catalytic surfaces, *Chem. Engng. Sci.*, 1984, (In press).
Van Kampen, N.G., Stochastic differential equations, Phys. Report C, 1976, **24C,** 171–228.