Multiplicity and Instability of States for Isothermal Homogeneous Reactions in CSTR: Case of Autocatalysis

V. RAVI KUMAR,

B. D. KULKARNI,

and L. K. DORAISWAMY

**National Chemical Laboratory
Poona 411 008, India**

INTRODUCTION

The phenomena of multiplicity, instability, etc. in chemical reactors are known to occur in homogeneous as well as heterogeneous systems both under isothermal and nonisothermal conditions. The significant developments in the area have been summarized in several recent papers and reviews (Noyes, 1980; Gray, 1980; Uppal et al., 1974; Schmitz, 1975; Slinko and Slinko, 1978; Schmitz, 1978). Instability in solid catalyzed reactions under isothermal conditions is generally the result of surface dynamic effects (Belyaev et al., 1974; Pikios and Luss, 1977; Dagonnier and Nuyts, 1976). The presence of the solid component offers at least the possibility of explaining the phenomenon in terms of any one of the causes mentioned in the studies cited above. However, in the case of homogeneous reactions, which are characterized by the absence of surface effects, these phenomena are difficult to explain. In the absence of any thermal feedback or an additional phase (such as a solid catalyst surface), it seems likely that such behavior is caused by intrinsic rates of elementary processes where the products formed from some of the steps interact with those from some of the other steps in the total sequence. The presence of autocatalysis therefore seems a necessary assumption.

The presence of autocatalysis gives rise to a closed chain of actions that generates the feedback necessary for nonunique behavior. Two kinds of autocatalytic behavior have been identified by Franck (1978). In one the product acts as a reactant and the case has been analyzed earlier (Lin, 1979; Kawczynski, 1974; Lopushanskaya et al., 1975).

In the second case the product does not influence the rate directly but affects it through its influence on the rate constant. This kind of situation exists in some biological systems as well as in some gas- and liquid-phase reactions. Froment and Bischoff (1979) also hint that a form different than the conventional one can be used to describe the autocatalytic behavior of some of these systems. This case of autocatalysis is considered in this paper.

A similar situation was found to exist in combustion reactions where the instabilities reported are frequently explained by invoking the theory of branching chain reactions with chain interaction (Gray, 1977; Yang, 1974). The mechanism used here is somewhat similar to this. The difficult task, however, is that the chemical systems of the above types are of considerable complexity, and no reaction mechanism has been clarified completely up to now. It is necessary, therefore, to simplify the situation by presuming that the final product is obtained from the reactants through a sequence of intermediates and develop a theoretical model that would adequately represent the behavior of the system ranging from a unique stable situation to multiplicity behavior and also the instabilities.

The particular reaction scheme analyzed consists of the sequence

$$A \xrightarrow{k_1} A_1 \xrightarrow{k_2} A_2 \xrightarrow{k_3} B \qquad (I)$$
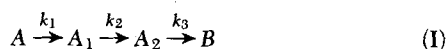
where A_1 and A_2 are regarded as the intermediates. It is clear that for reaction I in CSTR the steady state will be single valued; to generate nonlinearity in the system it is necessary, therefore, to postulate that the intermediate species A_1 and/or A_2 should have

an activating or inhibiting influence on the rate constants. The feedback generated as a result of such autocatalysis/autoinhibition suggests that nonunique behavior may be observed in certain ranges of concentration (Gilles, 1980; Franck, 1978). The kind of situation envisaged here can arise in some biochemical reactions catalyzed using allosteric enzymes. These enzyme molecules have more than one type of active center and the presence of a bound molecule or substrate on one active center can affect the activity of another center in the molecule. Several examples of instabilities in enzymic and multienzymic systems under homogeneous and heterogeneous conditions are cited by Isao et al. (1979). Some of the other examples in the area of homogeneously catalyzed reactions have been noted in the work of Golodov et al. (1980), Kolchinskii and Yatsimirskii (1980), Tikhonova and Zayats (1980), and Tovstokhatko et al. (1980). The mechanism of autocatalysis arising due to chain propagation and interaction has been shown to be responsible for the instabilities.

THEORETICAL ANALYSIS

Let us consider the reaction scheme I carried out in a CSTR. For brevity, let us assume that the component A_1 has an activating influence on the rate constant k_1 which is arbitrarily represented as

$$k_1 = k_1' \exp(\alpha A_1) \qquad (1)$$

The parameter α measures an activating influence of intermediate A_1 on the rate constant for the first step. A relationship of the form of Eq. 1 has been chosen primarily for the following reasons: (1) due to its resemblance to the corresponding form in the heterogeneous case where the parameter α is given the physical significance of surface heterogeneity parameter; (2) the equation suggests a fast response of k to variations in the parameter α; this seems especially desirable in view of the fact that different systems with apparently not-too-large variations in parameter values (e.g., Da etc.) indicate varied behavior ranging from unique stable solution to multiple behaviour and instabilities; and (3) the resemblance of the form used to that of the Semenov law (1935), which postulates exponential autocatalytic accelerations of chemical reactions in branched systems. This law has been followed by diverse chemical reactions (Kondratiev, 1979) and is frequently invoked to explain the characteristic features of branched chain reactions.

The conservation equations for the species, assuming Eq. 1, can now be written in dimensionless form as

$$\frac{da}{d\theta} = a_0 - a - Da_1 a \exp(\alpha a_1) = f_1(a, a_1) \qquad (2)$$
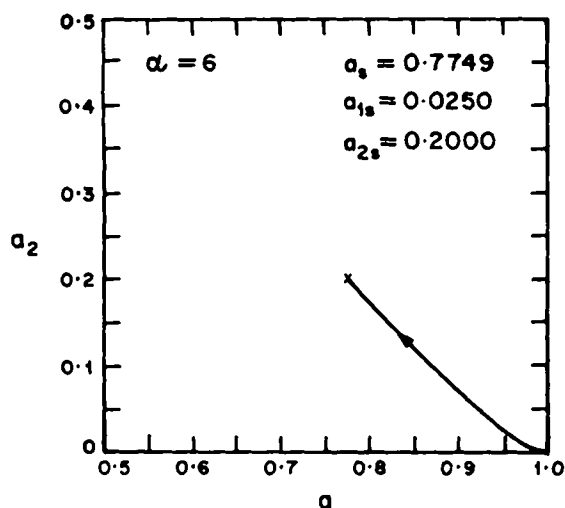
$$\frac{da_1}{d\theta} = a_{10} - a_1 + Da_1 a \exp(\alpha a_1) - Da_2 a_1 = f_2(a, a_1) \qquad (3)$$

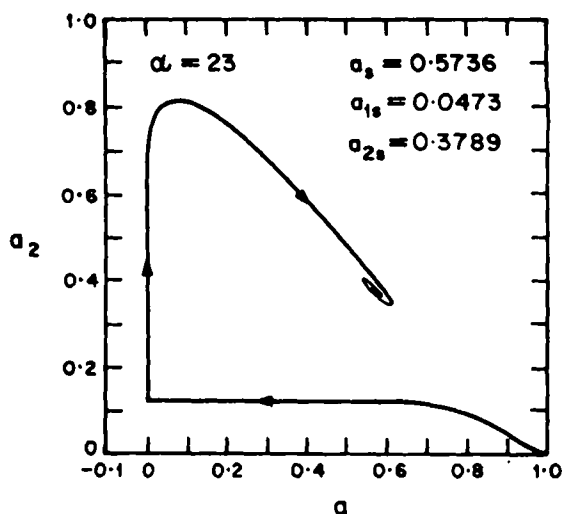$$\frac{da_2}{d\theta} = a_{20} - (1 + Da_3)a_2 + Da_2 a_1 = f_3(a_1, a_2) \qquad (4)$$

with the initial conditions

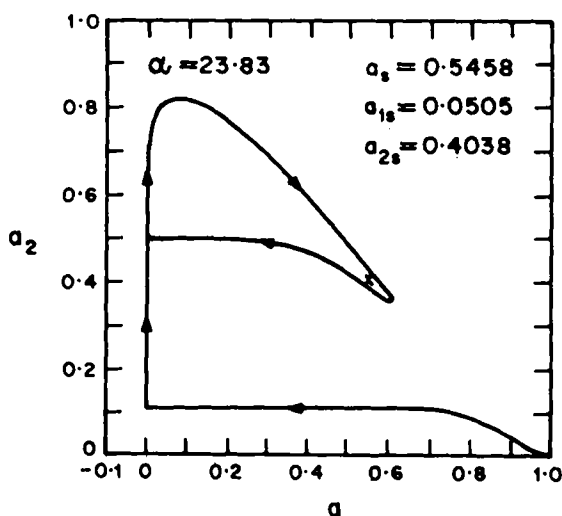$$a = a_0, a_1 = a_{10} \text{ and } a_2 = a_{20} \text{ at } \theta = 0 \qquad (5)$$

The parameters a, a_1 and a_2 respectively represent the dimen-

Figure 1. Effect of varying autocatalytic influence on the nature of phase plane plots (The case of unique stable steady state) (Da_1 = 0.25, Da_2 = 8.00: a_0 = 1, a_{10} = 0, a_{20} = 0)

sionless concentrations of species A, A_1 and A_2 defined with respect to the total inlet concentration. The parameter θ represents dimensionless time defined as $\theta = tF/V$ and the Damkohler numbers Da_i (i = 1, 3) are defined in the notation.

The set of Eqs. 2–4 can be rearranged at steady state to give

$$a_0 = a \left[1 + Da_1 \exp\left(\frac{\alpha(a_{10} + a_0 - a)}{1 + Da_2}\right)\right] \qquad (6)$$

Solution of Eq. 6 gives the desired steady state. Also at steady state the concentrations of various species are interrelated as

$$a_1 = \frac{a_{10} + a_1 - a}{1 + Da_2} \qquad a_2 = \frac{a_{20} + Da_2 a_1}{1 + Da_3} \qquad (7)$$

It is important to note that for certain ranges of parameter values Eq. 6 can possess more than one solution. Mutliplicity of states is therefore possible for certain parameter ranges. The set of Eqs. 2–5 may also have solutions which are not stationary but, for instance, periodic so that sustained oscillations may be observed.

For purposes of linear stability analysis the third order characteristic equation for the system is obtained as

$$\lambda^3 - trM \lambda^2$$
$$+ [\Sigma \text{ minors of diagonal elements of } M]\lambda - detM = 0 \quad (8)$$

where M represents the 3×3 Jacobian matrix formed out of Eqs. 2–4. The number of roots of Eq. 8 with positive real part is equal to the number of sign changes in the sequence (Sattinger, 1973).

$$1, (-trM), \frac{[\Sigma \text{ minors of diag. element}][-trM] + detM}{\Sigma \text{ minors of diag. elements}},$$
$$(-detM) \quad (9)$$

The criteria 9 can thus be used to check the stability of the solution of Eq. 6.

RESULTS AND DISCUSSION

The set of Eqs. 2–5 have been numerically solved for various parameter values to obtain the transient behavior of the system. The problem requires the solution of a set of stiff differential equations and the semiimplicit method proposed by Michelsen (1976) has been found suitable for the present work. The results obtained using this method are summarized in Figures 1–5.

Figure 1 shows the activating influence of the intermediate on the course of reactor behaviour. For α = 6 (Figure 1a) the reactor steady state is approached almost straight and only short transients are involved. On increasing the value of α (Figure 1b) long transients develop and the trajectory goes round the steady state before
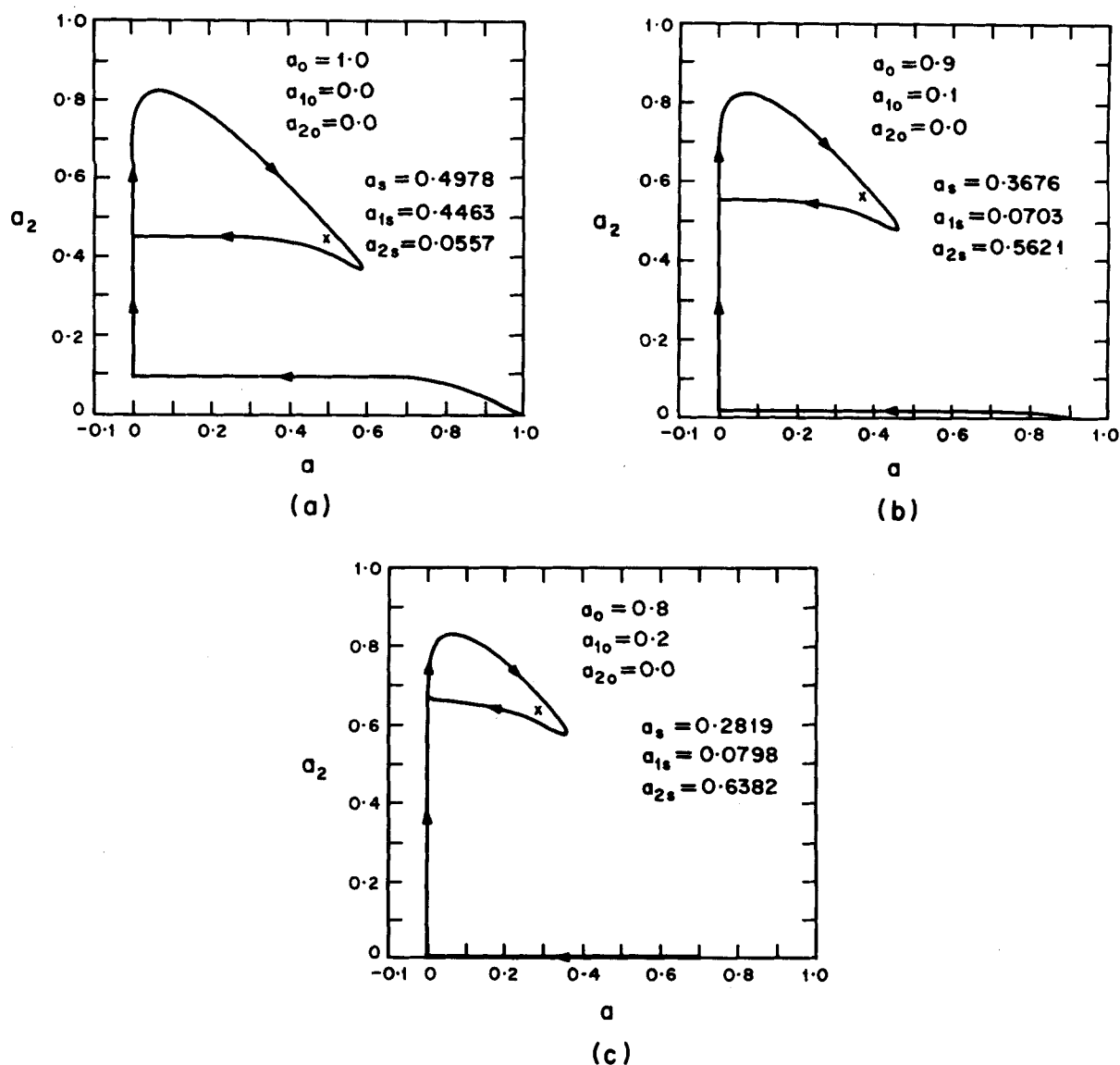
Figure 2. Effect of varying inlet conditions on the nature of phase plane plots (The case of unique unstable steady state) ($Da_1 = 0.25$, $Da_2 = 8.00$, $\alpha = 25.00$, $Da_3 = 0.0$).

approaching it. On further increase in the value of α (Figure 1c), while much of the qualitative nature of the trajectory is retained, the trajectory finally winds up in a closed circuit representing limit cycle behaviour. It is important to note that the linear stability analysis (Eq. 9) of the cases in Figure 1 show them to be unique stable solutions. Figure 1c therefore clearly provides an example of a limit cycle existing when linear stability analysis indicates the presence of a unique stable solution. Such a situation is feasible as already known (Aris, 1979; Bruns et al., 1973) and points to the shortcomings of linear stability analysis where a small region close to the steady state only is examined. Examination of Figures 1a,b,c therefore indicates that for a fixed set of parameter values, progressively increasing the autocatalytic influence has the effect of weakening the global stability of the steady state. A critical value of α depending on the other parameters of the system exists for which the steady state, though asymptotically stable, becomes globally unstable and gives rise to a stable limit cycle.

On increasing the value of α still further even the asymptotic stability of the steady state vanishes and we have a unique unstable steady state. Clearly limit cycle behaviour is expected for this case, and Figures 2a,b,c show the trajectories for different inlet compositions to the reactor. It is clearly seen that the limit cycle region dimensions with decrease in concentration of the main reactant
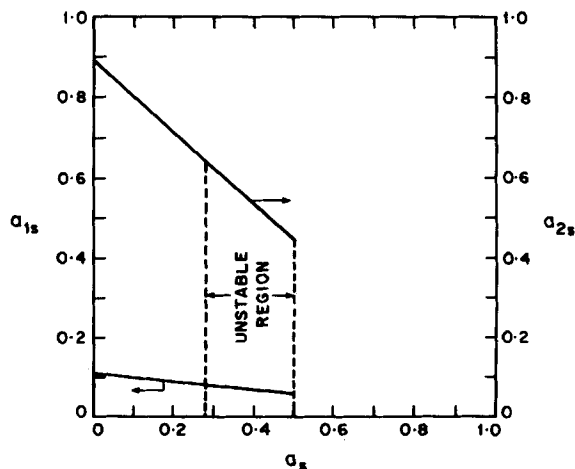

Figure 3. Plots of steady-state solutions for varying inlet conditions in a and a_1. Unstable region indicated. ($Da_1 = 0.25$, $Da_2 = 8.00$, $\alpha = 25$: $a_{20} = 0$, $Da_3 = 0.0$).
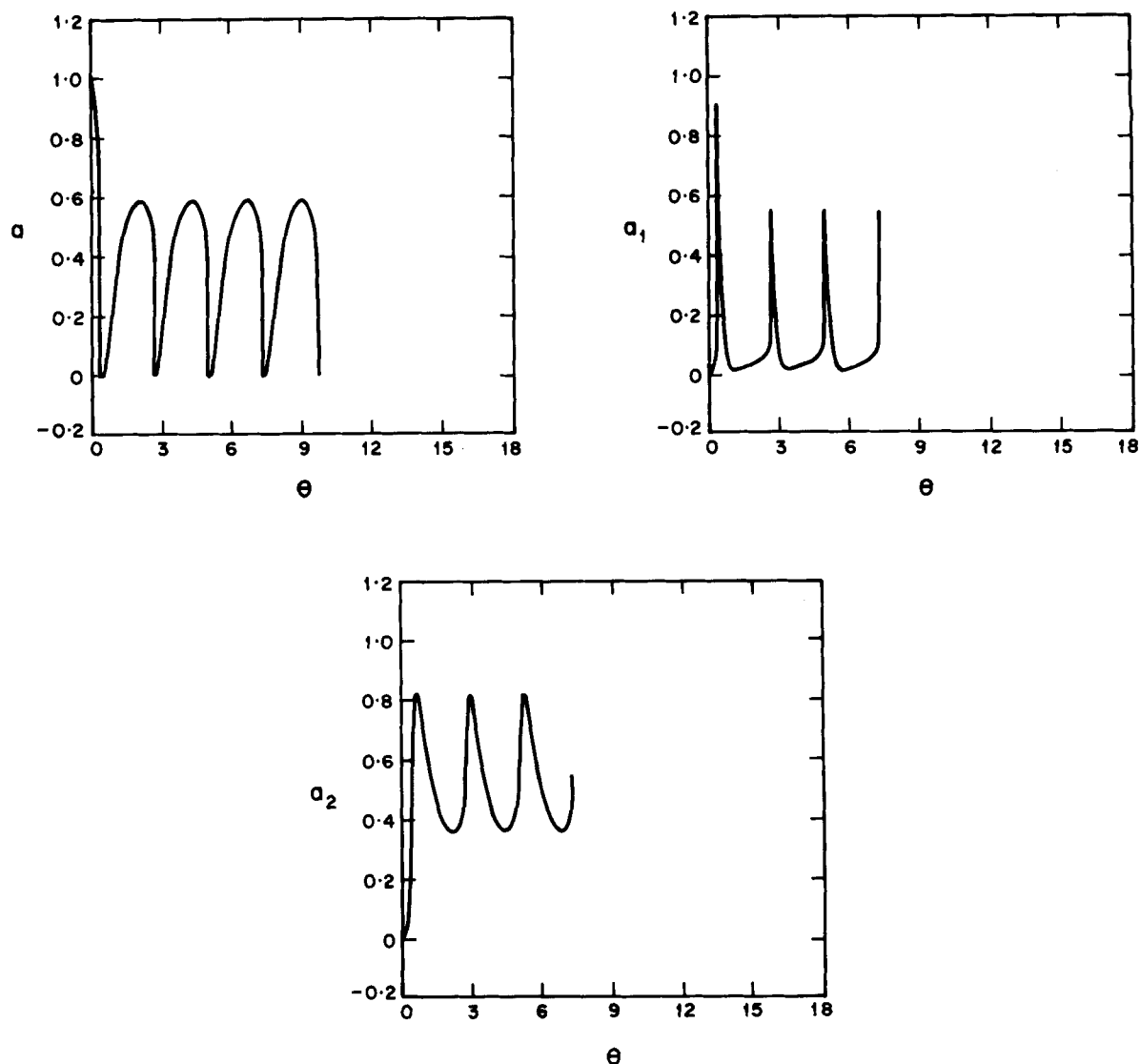
Figure 4. Amplitude of oscillations for the reactant and products (Da_1 = 0.25, Da_2 = 8.00, α = 25: a_0 = 1.0, a_{10} = 0, a_{20} = 0, Da_3 = 0.0).
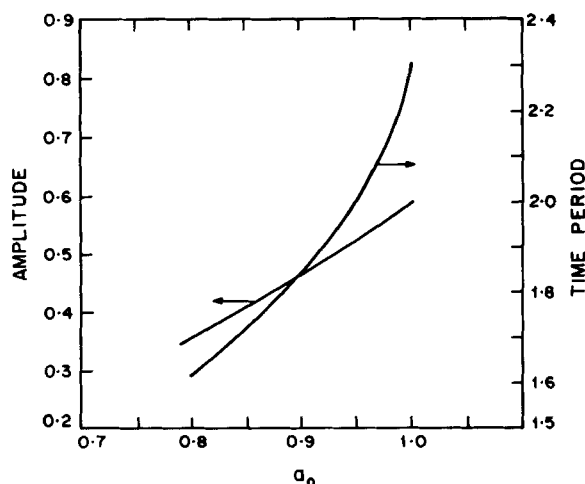

Figure 5. Dependence of amplitude and period of oscillations on the inlet composition. (Da_1 = 0.25, Da_2 = 8.00, α = 25: a_{20} = 0, Da_3 = 0.0).

or increase in the concentration of intermediate that has an activating influence on the first reaction. A further decrease in the concentration of the main reactant leads to a situation where the limit cycle region totally vanishes and we have a unique stable solution. Figure 3 shows the steady-state concentrations of the species A, A_1 and A_2 for different inlet compositions to the reactor. The region of unique stable and unstable solution is clearly marked on this figure.

For the set of parameter values corresponding to the unique unstable solution, Figure 4 shows the concentration profiles for the reactant and intermediates with respect to time. The three sets of the profiles have been generated for different inlet compositions of the reactor and show almost similar trends. The amplitude and period of oscillations are seen to depend on the inlet composition to the reactor. This is brought out more clearly in Figure 5 where it is seen that both the period and amplitude of oscillations decrease with decrease in concentration of the main reactant. Similar behavior has been observed in the combustion of n-heptane-isooctane mixture (Bykov et al., 1980; Stepanskii et al., 1980).

The influence of the other parameters such as the Damkohler numbers for the individual steps has also been examined. Thus for a set of parameter values Da_1 = 0.05, Da_2 = 1, Da_3 = 0, α = 15,

three steady-state solutions are obtained. The linear stability analysis of these solutions indicates two stable and one unstable steady states. On decreasing the value of Da_1 ($= 0.01$) for the same values of other parameters, the multiplicity still remains; however, we now have two unstable steady-state solutions, and only one of the three steady states is a stable solution.

CONCLUSIONS

A method has been presented for analyzing the occurrence of instability, multiplicity and limit cycle behavior in homogeneous isothermal systems. It appears that the presence of autocatalysis will have to be invoked for the purpose. It is likely that the methodology used may be helpful in describing the behavior of several biological reactions, catalyzed and uncatalyzed homogeneous reactions, reactions in combustion and oxidation of hydrocarbons, and branching chain reactions.

NOTATION

A	= reactant species
A_1, A_2	= intermediate/product species
a	= dimensionless concentration of reactant species
a_1, a_2	= dimensionless concentration of intermediate/product species
B	= product species
Da_1	= Damkohler number defined as $k_1' V/F$
Da_2, Da_3	= Damkohler number defined as $k_i V/F$ ($i = 2,3$)
F	= flow rate
f_1, f_2, f_3	= functions defined in Eqs. 2–4
k_1, k_2, k_3	= rate constants for the successive steps in Scheme I
k_1'	= rate constant for the first step in Scheme I in the absence of autocatalytic effects
M	= Jacobian matrix
t	= time parameter
V	= volume of reactor

Greek Letters

α	= parameter defined in Eq. 1
θ	= dimensionless time
λ	= roots of the characteristic equation in Eq. 8

Subscripts

0	= value of the parameter at $\theta = 0$
s	= value of the parameter at steady state

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