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Multiplicity Criteria for Multireaction Networks

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A general method is developed for a systematic determination of criteria predicting steady-state multiplicity in lumped-parameter systems in which many irreversible reactions occur simultaneously. The method enables use of criteria derived for simple reaction networks to predict the behavior of more complex networks. The available multiplicity criteria for the single- and two-reaction networks can always be used to write down sufficient multiplicity criteria for any multireaction system. Several examples illustrate the power of the proposed technique.

SCOPE

Most practical control and start-up problems associated with steady-state multiplicity are encountered in systems in which several chemical reactions occur simultaneously and are due to the "taking over" by an undesired reaction, whose rate is negligible at the normal operating conditions. It is of practical and academic interest to have simple criteria predicting in terms of simple observable quantities the conditions for which multiplicity exists in multireaction systems. At present exact criteria are available only for predicting the conditions under which multiplicity exists in a lumped-parameter system in which either a single or two chemical reactions occur (Aris, 1969; Michelsen, 1977; Balakotaiah and Luss, 1982a).

The steady-state equation describing N first-order reactions occurring in a lumped-parameter system is of the form

$$F(y,p^*,Da) = 0$$

where y is the dimensionless temperature, p^* is a vector of parameters and Da is a vector of N Damköhler numbers. The large number of parameters and the highly nonlinear nature of the steady-state equation prevent, in general, a direct prediction if multiplicity occurs for some p^* and Da. Instead, we suggest to derive first criteria predicting the conditions that p^* has to satisfy so that multiplicity occurs for some Da. When at least one of these criteria is satisfied we can construct the exact boundaries of the multiplicity region and check if the specific Da is within the region.

The goal of this work is to reveal the structure of the criteria that guarantee multiplicity for some Da and to present a systematic method of determining them for any chemical reaction network. Moreover, we show how the available criteria for simple reaction networks can be utilized to predict multiplicity of more complex reaction networks.

CONCLUSIONS AND SIGNIFICANCE

When N reactions occur in a lumped-parameter system, the conditions that the parameter vector p^* has to satisfy so that multiplicity exists for some Da, can be derived by analyzing systematically the limiting cases in which only j reactions proceed at a finite rate while each of the remaining $N - j$ reactions is either instantaneous ($Da_i \to \infty$) or occurs at a negligible rate ($Da_i = 0$). This scheme generates at most $3^N - 2^N$ multiplicity criteria, some of which are implied by others and can be discarded. This procedure enables one to incorporate in the analysis of any multireaction network all the available criteria about simpler reaction networks. Thus, the available criteria for the single- and two-reaction cases can always be utilized to write down some sufficient multiplicity criteria for any multireaction network. A simple scheme is derived for determining the boundaries of the multiplicity region for the case that it exists for some Da. The procedure described here is expected to become the standard tool for predicting multiplicity in multireaction systems.

Three examples are used to illustrate the application of the technique to different multireaction networks. These examples led to the derivation of simple necessary and sufficient conditions predicting when multiplicity exists for some Da in the case of N simultaneous or parallel reactions. It is proven that when N simultaneous first-order reactions occur in a CSTR multiplicity can occur for some Da if and only if it can exist when only two of the N reactions occur.

The interaction between chemical and physical rate processes may lead to steady-state multiplicity in chemically reacting systems. Comprehensive reviews of the subject were presented by Schmitz (1975), Endoh et al. (1977), Hlavacek and Votruba (1978), Eigenberger (1981), and Luss (1980, 1981). Balakotaiah and Luss (1982b) developed a method for predicting the maximal number of steady-state solutions in lumped-parameter chemically-reacting systems and a technique for dividing the global parameter space into regions with different number of solutions.

Most practical problems caused by steady-state multiplicity are encountered in systems in which several chemical reactions occur simultaneously. Thus, it is of practical importance to have criteria predicting the conditions under which steady-state multiplicity exists in multireaction systems.

This work presents an analysis of the structure of the multiplicity criteria for lumped-parameter systems in which several reactions occur simultaneously. We consider an arbitrary reaction network of N irreversible, first-order reactions with an Arrhenius temperature dependence occurring in a lumped-parameter system. The steady-state equations consist of N species balances and an energy balance. The N-independent concentrations appear in a linear fashion in the N species balances. These can be solved and the result substituted into the energy balance, giving a single steady-state equation of the form

$$F(y,\mathbf{Da},\mathbf{p}^*) = 0 \tag{1}$$

where y is the dimensionless steady-state temperature, $\boldsymbol{Da}$ is a vector of N Damköhler numbers ($Da_i = Vk_i(T_o)/q$) and $\boldsymbol{p}^*$ is a vector of parameters describing the various dimensionless activation energies and heats of reaction.

It can be proven that the steady-state Eq. 1 has at least one solution for any feasible parameter values and that one can always find a set of parameters $\boldsymbol{p}^*$ for which a unique solution exists for all $\boldsymbol{Da}$. Moreover, F is continuously differentiable with respect to y, $\boldsymbol{p}^*$ and $\boldsymbol{Da}$, dF/dy does not vanish on the boundaries of the feasible y values and there exists at least one parameter (for example, the flow rate q) with respect to which Eq. 1 represents a one to one mapping next to the boundaries of the feasible y values.

The implicit function theorem can be used to prove that for a given $\boldsymbol{p}^*$, the boundaries of the region of $\boldsymbol{Da}$ values for which multiplicity exists must be on the hypersurface defined by the simultaneous solution of Eq. 1 and

$$\frac{dF}{dy}(y,\boldsymbol{Da},\boldsymbol{p}^*) = 0. \tag{2}$$

For certain $\boldsymbol{p}^*$ values the simultaneous solution gives values of $\boldsymbol{Da}$ which are either complex or negative, i.e., values which are outside the feasible region ($0 < Da_i < \infty$). For these $\boldsymbol{p}^*$, Eq. 1 has a unique solution for all $\boldsymbol{Da}$.

Necessary and sufficient multiplicity criteria can be obtained by finding all the conditions that $\boldsymbol{p}^*$ has to satisfy so that Eqs. 1 and 2 are satisfied for some feasible y and $\boldsymbol{Da}$. Unfortunately, algebraic difficulties usually make this derivation of exact multiplicity criteria for multireaction systems extremely difficult and often impossible. We present here a method for a systematic derivation of sufficient multiplicity criteria which are a subset of the set of the exact criteria.

We start with a brief review of the available criteria for the single- and two-reaction cases and of the strategy used to derive them. This information is essential for understanding the generalized technique, and it will be utilized to predict multiplicity in multireaction systems.

MULTIPLICITY CRITERIA FOR THE SINGLE-REACTION CASE

The dimensionless steady-state temperature, y, of a lumped-parameter system, such as a cooled CSTR, in which a first-order, exothermic reaction occurs is governed by:

$$y - 1 = Da_1(1 + \beta_1 - y)X_1 \tag{3}$$

where

$$X_1 = \exp[\gamma_1(1 - 1/y)],$$

β_1 is the dimensionless temperature rise, γ_1 the dimensionless activation energy, and Da_1 is the ratio between the residence time in the reactor and the characteristic reaction time. Equation 3 may be rewritten as

$$F(y) \triangleq \frac{(1 + \beta_1 - y)X_1}{y - 1} = \frac{1}{Da_1} \tag{4}$$

It was shown by Aris (1969) that Eq. 4 has multiple solutions for some values of Da_1 if and only if

$$\gamma_1 > \gamma_m(\beta_1) \triangleq 4(1 + 1/\beta_1) \qquad \beta_1 > 0 \tag{5}$$

Consider a case in which the feed releases instantaneously upon entry to the reactor Q units of heat per unit volume of feed (in addition to the heat generated by the reaction). The corresponding dimensionless steady-state equation is

$$y - 1 - \beta_s = Da_1(1 + \beta_1 + \beta_s - y)X_1 \tag{6}$$

where

$$\beta_s = \frac{Q}{\rho c_p(T_o + HT_c)}.$$

Steady-state multiplicity occurs in this case for some Da_1 if and only if

$$\left(\frac{\gamma_1}{1 + \beta_s}\right) > \gamma_m\left(\frac{\beta_1}{1 + \beta_s}\right) \tag{7}$$

or equivalently when

$$\gamma_1 > \Gamma_m(\beta_1 + \beta_s, \beta_s) \tag{8}$$

where

$$\Gamma_m(\beta_i,\beta_j) \triangleq \left[\frac{1}{\gamma_m(\beta_i)} - \frac{1}{\gamma_m(\beta_j)}\right]^{-1} \tag{9}$$

Note that

$$\Gamma_m(\beta_i,0) = \gamma_m(\beta_i) \tag{10}$$

and that

$$\frac{d\Gamma_m(\beta_i + \beta_s,\beta_s)}{d\beta_s} > 0 \tag{11}$$

so that instantaneous cooling ($\beta_s < 0$) decreases the value of γ_1 for which multiplicity exists for some Da_1.

Whenever condition 5 is satisfied, steady-state multiplicity exists for all Da_1 bounded in $(1/F(y_1), 1/F(y_2))$ where

$$y_{1,2} = \frac{\gamma_1(2 + \beta_1) \pm \sqrt{\gamma_1\beta_1[\gamma_1\beta_1 - 4(1 + \beta_1)]}}{2(1 + \beta_1)} \tag{12}$$

The analysis may be generalized to the case of any nth order reaction (Chang and Calo, 1979; Tsotsis and Schmitz, 1979; Leib and Luss, 1981). Here multiplicity exists for some Da_1 if and only if

$$\gamma_1 > \gamma_m(\beta_1, n) \tag{13}$$

where $\gamma_m(\beta_1, n)$ is the largest root of the cubic equation

$$\gamma_1^3\beta_1^2 - 2\eta_1^2\beta_1 h_1(\beta_1,n) + \gamma_1 h_2(\beta_1,n) - 4(1 + \beta_1)(1 + \beta_1 - n)^3 = 0 \tag{14}$$

and

$$h_1(\beta_1,n) = (1 - 2n)\beta_1^2 + 2(2 - n)\beta_1 + 1 - n$$

$$h_2(\beta_1,n) = \beta_1^4 + 4(3 - 5n)\beta_1^3 - 2(4n^2 + 11n - 11)\beta_1^2 + 4\beta_1(1 - n)(3 + 2n) + (1 - n)^2 \tag{15}$$

Figure 1 describes the dependence of γ_m on β_1 and the reaction order.

MULTIPLICITY CRITERIA FOR TWO CONSECUTIVE OR PARALLEL REACTIONS

The dimensionless steady-state temperature of a lumped-parameter system in which two consecutive first-order reactions

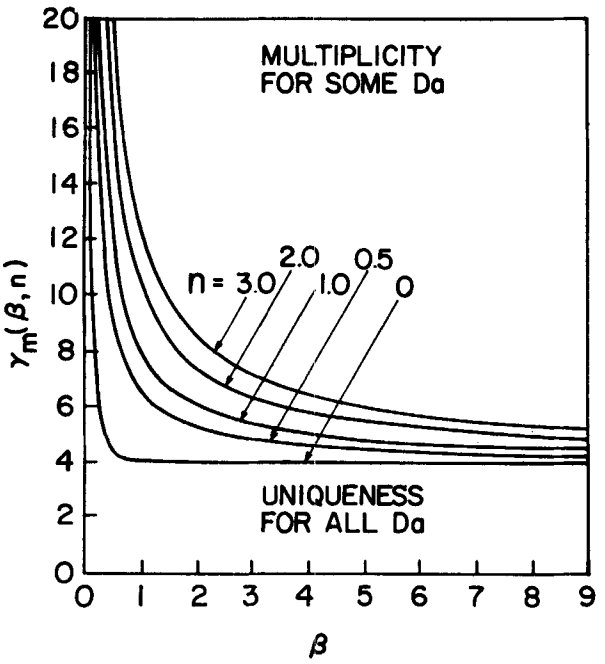


Figure 1. The dependence of the maximal dimensionless activation energy, for which a unique solution exists for all *Da*, on the reaction order and β.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

occur is given by (Balakotaiah and Luss, 1982a)

$$y - 1 = \frac{\beta_1 Da_1 X_1}{1 + Da_1 X_1}\left(1 + \frac{\sigma Da_2 X_2}{1 + Da_2 X_2}\right) + \frac{\beta_2 Da_2 X_2}{1 + Da_2 X_2} \quad (16)$$

or

$$F(y,p) = 0 \quad (17)$$

where

$$\mathbf{p} = (Da_1, Da_2, \gamma_1, \gamma_2, \beta_1, \beta_2, \sigma) \quad (18)$$

When the term multiplying σ in Eq. 16 is deleted, or equivalently if we assume $\sigma = 0$, Eq. 16 describes the dimensionless steady-state temperature for a system in which the two parallel reactions

$$A \xrightarrow{k_1} D \qquad B \xrightarrow{k_2} C$$

occur. Pikios and Luss (1979) proved that multiplicity can occur only if at least one of the reactions is exothermic. We consider here cases in which at least one reaction is exothermic. We assume that the dimensionless heat of reaction of any endothermic reaction satisfies the practical constraint $\beta_i > -1$.

It is rather difficult to derive criteria predicting directly whether multiplicity exists for a given $\boldsymbol{p}$. Balakotaiah and Luss (1982a) circumvented this difficulty by determining first the exact conditions the parameters vector $\boldsymbol{p}^* \triangleq (\gamma_1, \gamma_2, \beta_1, \beta_2, \sigma)$ has to satisfy so that multiplicity exists for some nonnegative Da_1 and Da_2. When any of these conditions is satisfied, one constructs a map of the multiplicity region in the $Da_1 - Da_2$ plane and checks if the specific point is within that region.

Balakotaiah and Luss (1982a) found that multiplicity exists for some Da_1 and Da_2 if and only if at least one of the following criteria is satisfied

$$\gamma_1 > \gamma_m(\beta_1) \qquad \beta_1 > 0 \quad (19)$$

$$\gamma_2 > \gamma_m(\beta_2) \qquad \beta_2 > 0 \quad (20)$$

$$\gamma_1 > \Gamma_m(\beta_1 + \sigma\beta_1 + \beta_2, \beta_2) \qquad \beta_1 + \sigma\beta_1 > 0 \quad (21)$$

$$\gamma_2 > \Gamma_m(\sigma\beta_1 + \beta_2 + \beta_1, \beta_1) \qquad \sigma\beta_1 + \beta_2 > 0 \quad (22)$$

$$g_2(\gamma_1, \gamma_2, \beta_1, \beta_2, \sigma) > 0 \quad (23)$$

where g_2 is an implicit criteria defined by Balakotaiah and Luss (1982a).

The above criteria have a simple physical meaning and each of the four conditions 19–22 corresponds to a limiting situation in which only one of the two reactions proceeds at a finite rate. It is important to comprehend these limiting cases to understand the analysis of the general case presented later.

Let us define

$$Da_i^* = Da_i/(1 + Da_i) \quad (24)$$

then the physically realizable values of the Damköhler numbers are within the unit square

$$0 \le Da_i^* \le 1 \qquad i = 1,2 \quad (25)$$

Each of the four boundaries of this unit square represents a limiting case for which only one reaction proceeds at a finite rate. For example, the edge $Da_2^* = 0$ describes a case for which the rate of the second reaction is negligible so that the steady-state equation degenerates into that for a single reaction. According to the analysis for the single-reaction case, this equation will have multiple solutions for some Da_1 if and only if criterion 19 is satisfied. In other words, the multiplicity region in the unit $\boldsymbol{Da^*}$ square will intersect the edge $Da_2^* = 0$ if and only if criterion 19 is satisfied. Similarly, criterion 20 guarantees that the multiplicity region for the two reactions intersects the edge $Da_1^* = 0$.

The edge $Da_2^* = 1$ represents the case in which the second reaction is instantaneous so that all the B present in the feed is converted instantaneously, raising the feed temperature to $1 + \beta_2$. The dimensionless temperature rise corresponding to the complete conversion of A is $\beta_1 + \sigma\beta_1$ as all the B that is formed is immediately converted to C by the consecutive reaction. Criterion 21 predicts when the multiplicity region intersects the edge ($Da_2^* = 1$), while criterion 22 predicts when it intersects the edge $Da_1^* = 1$ which represents the limiting case in which the first reaction is instantaneous.

Criterion 23 constrains the values of $\boldsymbol{p}^*$ so that if only this condition is satisfied the multiplicity region is entirely within the unit square and does not interest any edge. Thus, it describes cases in which both reactions occur at a finite rate and that the interaction between the two is the cause of the multiplicity. For two consecutive reactions this criterion is a cumbersome implicit function. For parallel reactions this condition can be satisfied only if both reactions are exothermic. It predicts that multiplicity exists for some Da_1 and Da_2 if and only if

$$\gamma_1 > \gamma_m(\beta_1) \quad \text{if } \gamma_2 \le 4(1 + \beta_1)/(2 + \beta_1) \quad (26)$$
$$\gamma_2 > \gamma_m(\beta_2) \quad \text{if } \gamma_1 \le 4(1 + \beta_2)/(2 + \beta_2)$$

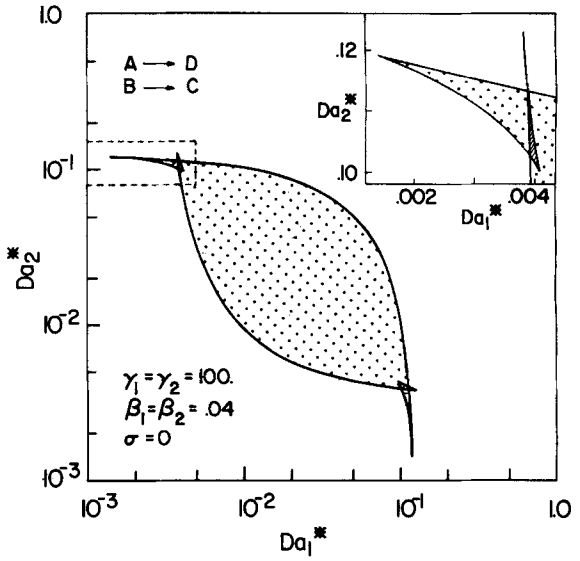


Figure 2. Map of the multiplicity region in the $Da_1^* - Da_2^*$ plane for two parallel reactions which satisfy only criterion 23. (Three steady-state solutions exist for all Da_1^* and Da_2^* in the dotted region and five in the hatched region).

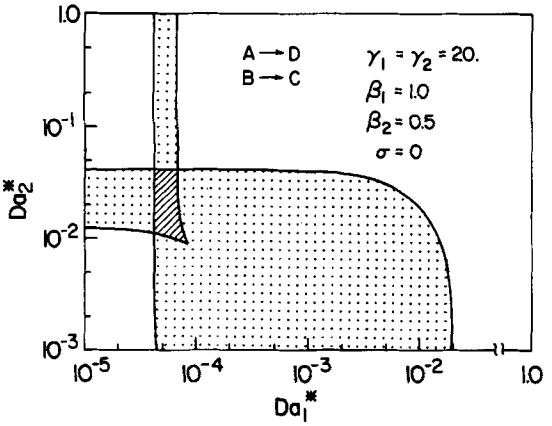


Figure 3. Map of the multiplicity region for two parallel reactions when criteria 19, 20, 21 and 23 are satisfied.

and in all other cases if

$$(\gamma_2\beta_1 + \beta_1\beta_2)\gamma_1^2 + [\gamma_2\beta_2 - 2\beta_1\beta_2 - 4(1 + \beta_1 + \beta_2)]\gamma_2\gamma_1 + \gamma_2^2\beta_1\beta_2 > 0 \quad (27)$$

In the special case of $\gamma_1 = \gamma_2$ criterion 27 reduces to

$$\gamma_1 = \gamma_2 > \gamma_m(\beta_1 + \beta_2) \quad (28)$$

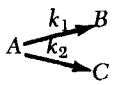
which is equivalent to the one obtained for a single reaction with a dimensionless reaction heat of $\beta_1 + \beta_2$.

When one or more of the five criteria is satisfied multiplicity must exist for some Da_1 and Da_2 values. As mentioned before each of the four edges of the unit square represents a limiting case in which only one reaction proceeds at a finite rate. The range of Damköhler numbers for which multiplicity exists on any edge can be determined by the technique used for the single-reaction case. When only criterion 23 is satisfied the multiplicity region does not intersect any edge of the unit square.

Balakotaiah and Luss (1982a) presented a systematic method of constructing the exact multiplicity region and described all the possible shapes the map of the multiplicity region can have. Figure 2 describes a case for which only criterion 23 is satisfied, while Figure 3 describes a case for which criteria 19, 20, 21 and 23 are satisfied. Three steady-state solutions exist for all Da_1 and Da_2 in the dotted regions while five solutions exist for all Da_1 and Da_2 in the hatched regions. It can be proven that no more than five solutions exist for this reaction network.

MULTIPLICITY CRITERIA FOR TWO SIMULTANEOUS REACTIONS

When two simultaneous first-order reactions



occur in a lumped-parameter system the dimensionless steady-state temperature satisfies the equation

$$y - 1 = Da_1(1 + \beta_1 - y)\exp[\gamma_1(1 - 1/y)] + Da_2(1 + \beta_2 - y)\exp[\gamma_2(1 - 1/y)] \quad (29)$$

Michelsen (1977) proved that for all the practical cases in which $\beta_1 > -1$ and $\beta_2 > -1$ Eq. 29 has multiple solutions for some Da_1 and Da_2 if and only if at least one of the following three criteria is satisfied

$$\gamma_1 > \gamma_m(\beta_1) \qquad \beta_1 > 0 \quad (30)$$

$$\gamma_2 > \gamma_m(\beta_2) \qquad \beta_2 > 0 \quad (31)$$

$$\gamma_2 - \gamma_1 > \Gamma_m(\beta_2,\beta_1) \qquad \beta_2 > \beta_1 \quad (32)$$

Here again the criteria correspond to limiting cases. Criterion 30 predicts when the multiplicity region intersects the edge $Da_2^* = 0$ and corresponds to the limiting case in which only the first reaction occurs. Similarly, criterion 31 predicts when the multiplicity region intersects the edge $Da_1^* = 0$ and corresponds to the case that only the second reaction occurs. The multiplicity region cannot intersect any of the other two edges ($Da_1^* = 1$ and $Da_2^* = 1$) as they correspond to cases in which one reaction is instantaneous. When one reaction is very fast it consumes all the reactant so that the second reaction cannot occur and lead to multiplicity.

Criterion 32 describes cases for which the interaction between the two reactions leads to multiplicity. When only this criteria is satisfied the multiplicity region is completely within the unit square. Surprisingly, this condition may be satisfied when both simultaneous reactions are endothermic. It is interesting to note that this criterion can be derived readily by examining the special case of

$$Da_1 \to \infty \quad Da_2 \to \infty \quad \mu = Da_2/Da_1$$

for which Eq. 29 simplifies to

$$y - 1 - \beta_1 = \mu(1 + \beta_2 - y)\exp[(\gamma_2 - \gamma_1)(1 - 1/y)] \quad (33)$$

Equation 33 describes a single reaction in a CSTR whose dimensionless feed temperature is $1 + \beta_1$. Condition 32 guarantees that this equation has multiple solutions for some μ.

Michelsen (1977) has shown that the boundary of the multiplicity region in the $Da_1 - Da_2$ plane is given parametrically by:

$$Da_1 = \frac{-P_2(y)}{P_3(y)}\exp(\gamma_1 - \gamma_1/y)$$

$$Da_2 = \frac{P_1(y)}{P_3(y)}\exp(\gamma_2 - \gamma_2/y) \quad (34)$$

where

$$P_i(y) = (\gamma_i + \beta_i)y^2 - \gamma_i(2 + \beta_i)y + \gamma_i(1 + \beta_i) \qquad i = 1,2$$

$$P_3(y) = [(\gamma_2 - \gamma_1) + (\beta_2 - \beta_1)]y^2 - (\gamma_2 - \gamma_1)(2 + \beta_1 + \beta_2)y + (\gamma_2 - \gamma_1)(1 + \beta_1)(1 + \beta_2) \quad (35)$$

and y is within the domain of interest.

The range of Damköhler numbers for which the multiplicity region exists on the edges $Da_1^* = 0$ and $Da_2^* = 0$ can be determined

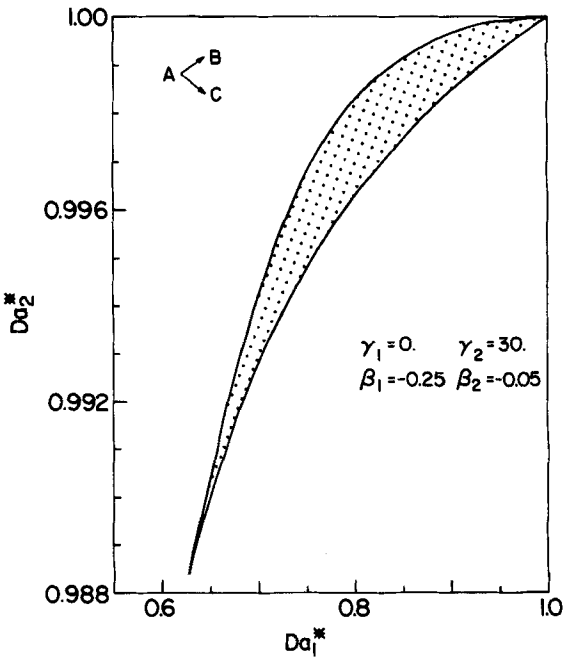


Figure 4. Map of the multiplicity region in the $Da_1^* - Da_2^*$ plane for two simultaneous endothermic reactions which satisfy only criterion 32.

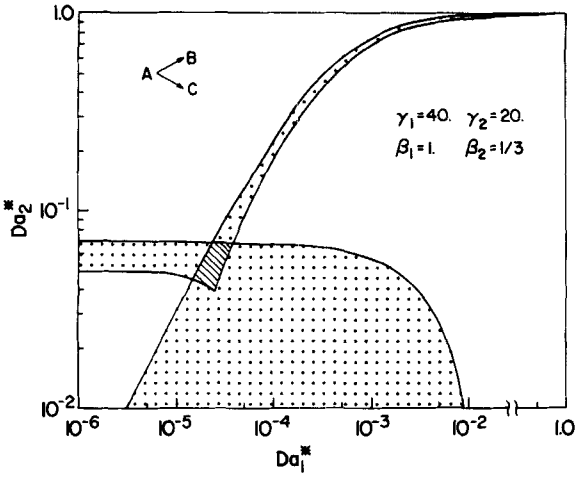


Figure 5. Map of the multiplicity region in the $Da_1^* - Da_2^*$ plane for two simultaneous reactions which satisfy criteria 30, 31 and 32.

by the technique developed for the single-reaction case. Whenever only criterion 32 is satisfied the multiplicity region exists at points very close to the corner formed by the edges $Da_1^* = 1$ and $Da_2^* = 1$.

Figure 4 illustrates the multiplicity region for a case of two endothermic reactions for which only criterion 32 is satisfied. Figure 5 describes the multiplicity region for a case of two exothermic reactions for which the three criteria 30, 31 and 32 are satisfied. There exists in this case a region of Damköhler numbers with five steady-state solutions. It can be proven that no more than five steady states exist for this reaction network.

CRITERIA FOR MULTI-REACTION NETWORKS

We describe here a systematic method of deriving criteria predicting when multiplicity occurs for some $\boldsymbol{Da}$ for any arbitrary reaction network of N irreversible, first-order reactions. We assume that the first M reactions are exothermic ($\beta_i > 0$), while the remaining $N - M$ reactions are endothermic ($\beta_i < 0$). We restrict the analysis to cases for which

$$\sum_{i=M+1}^{N} \beta_i > -1$$

which is probably satisfied for any practical system.

Any feasible $\boldsymbol{Da}$ value is represented by a point in the N-dimensional unit hypercube

$$o \le Da_i^* \le 1 \qquad i = 1,2,\ldots N$$

The boundary of this hypercube can be divided into $N - 1$ subsets of j-dimensional regions. Each subset describes a limiting case in which j reactions proceed at a finite rate while the remaining $N - j$ reactions are either instantaneous or have negligible rate. Each subset may be used to derive a different class of multiplicity criteria.

The first subset consists of $\binom{N}{1}2^{N-1}$ one-dimensional segments of length unity (edges of the hypercube). Each edge describes a limiting situation for which the rate of one reaction is finite, while the rate of each of the other $N - 1$ reactions is either instantaneous ($Da_i^* = 1$) or negligible ($Da_i^* = 0$). The instantaneous reactions affect only the feed's temperature and multiplicity may be caused only by the reaction with the finite rate. We can use criterion 8 to write down for each edge a condition that guarantees multiplicity. It should be noted that for some special cases, such as for a simultaneous reactions network, multiplicity may not exist for the conditions represented by some edges. Obviously, it is not possible to derive a multiplicity criterion corresponding to these edges. We conclude that knowledge of the multiplicity criterion for the single reaction case enables us to write down up to $\binom{N}{1}2^{N-1}$ sufficient multiplicity criteria for the N-reaction case.

The second subset consists of $\binom{N}{2}2^{N-2}$ two-dimensional surfaces. Each surface represents a limiting situation in which the Damköhler numbers of $N - 2$ reactions are either zero or unbounded, while the Damköhler numbers corresponding to the surface can assume any positive value. The previous analysis of the two-reaction cases revealed that there exists always a single condition predicting when the interaction between two reactions with finite Damköhler numbers may lead to multiplicity. After accounting for the change in the temperature caused by the instantaneous reactions, we can use the available criteria for the two-reaction networks to write down a multiplicity criterion for each surface. Thus, the set of surfaces which describes the interaction between pairs of reactions leads to the derivation of up to $\binom{N}{2}2^{N-2}$ multiplicity criteria for the N-reaction network.

The jth subset consists of $\binom{N}{j}2^{N-j}$ j-dimensional regions representing the limiting cases that j reactions proceed at a finite rate while the rates of the remaining $N - j$ reactions are either negligible or instantaneous. The instantaneous reactions affect the temperature of the feed. There exists in general a criterion, say $g_j(\boldsymbol{p}^*) > 0$ so that if only it is satisfied, the region of the Damköhler number for which multiplicity exists is within the j-dimensional region and does not intersect its boundaries. Obviously, there exist up to $\binom{N}{j}2^{N-j}$ criteria of this type.

The above analysis describes all the limiting cases for which the multiplicity region intersects the boundary of the N-dimensional hypercube. The corresponding criteria were derived by considering the limiting cases for which only j reactions ($1 \le j \le N - 1$) proceed at a finite rate. It should, however, be noted that for certain values of β_i and γ_i the multiplicity region may not intersect the boundary of the hypercube. There exists in general some criterion which restricts the set of γ_i and β_i values so that if only it is satisfied the multiplicity region is completely within the N-dimensional hypercube and does not intersect its surface. In such cases the multiplicity is caused by the interaction among N reactions each of which proceeds at a finite rate.

The analysis indicates that the maximal number of multiplicity criteria of the various types is

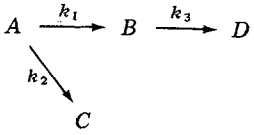
$$L = \sum_{j=1}^{N} \binom{N}{j} 2^{N-j} = 3^N - 2^N \tag{36}$$

For many reaction networks the number of criteria which guarantee multiplicity for some $\boldsymbol{Da}$ is much less than L. For example, when a species is converted by several simultaneous reactions, multiplicity cannot occur when one of them is instantaneous. This reduces the number of limiting cases and corresponding criteria. Moreover, in many applications some of the criteria are implied by others so that they can be discarded.

We present now three specific examples to illustrate further the proposed strategy of deriving the multiplicity criteria for multireaction systems and of discarding the criteria which are implied by others. The examples illustrate also the unexpected result that in certain cases the available criteria for the single- and two-reaction networks are sufficient for determining the necessary and sufficient conditions for multiplicity for some $\boldsymbol{Da}$ for networks with an arbitrary large number of reactions.

Example 1

Consider a cooled CSTR in which the following three first-order reactions occur



The species and energy balances are:

$$q(A_o - A) = V(k_1 + k_2)A \tag{37}$$

$$q(B_o - B) = V(k_3B - k_1A) \tag{38}$$

$$q\rho c_p(T - T_o) + Ua(T - T_c) = AV[k_1(-\Delta H_1) + k_2(-\Delta H_2)] + BVk_3(-\Delta H_3) \quad (39)$$

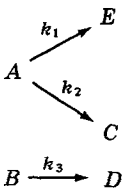
The dimensionless steady-state temperature is the solution of

$$y - 1 = \frac{\beta_1 Da_1 X_1 + \beta_2 Da_2 X_2}{1 + Da_1 X_1 + Da_2 X_2} + \frac{\sigma' \beta_1 Da_1 Da_3 X_1 X_3}{(1 + Da_3 X_3)(1 + Da_1 X_1 + Da_2 X_2)} + \frac{\beta_3 Da_3 X_3}{1 + Da_3 X_3} \quad (40)$$

where

$$T_m = (T_o + HT_c)/(1 + H) \qquad H = Ua/q\rho c_p$$
$$\beta_1 = \frac{(-\Delta H_1)A_o}{\rho c_p(T_o + HT_c)} \qquad \beta_2 = \frac{(-\Delta H_2)A_o}{\rho c_p(T_o + HT_c)}$$
$$\beta_3 = \frac{(-\Delta H_3)B_o}{\rho c_p(T_o + HT_c)} \qquad \sigma' = \frac{\Delta H_3}{\Delta H_1}$$
$$X_i = \exp(\gamma_i(1 - 1/y)) \qquad \gamma_i = E_i/RT_m \quad (41)$$

If we delete from Eq. 40 the term multiplied by σ'; it describes the reaction network



We start by writing down the single-reaction criteria predicting the values of $\boldsymbol{p}^*$ for which the multiplicity region intersects at least one edge of the unit cube. The edge, describing the case that the ith reaction proceeds at a finite rate while the rate of the other two is negligible, is cut by the multiplicity region if and only if

$$\beta_i > 0 \text{ and } \gamma_i > \gamma_m(\beta_i) \qquad i = 1, 2, 3. \quad (42)$$

The multiplicity region intersects the edge corresponding to $Da_1^* = 1$ (first reaction being instantaneous) and $Da_2^* = 0$ if and only if

$$\gamma_3 > \Gamma_m(\beta_3 + \sigma'\beta_1 + \beta_1, \beta_1) \quad (43)$$

Similarly, it intersects the edge $Da_2^* = 1$ and $Da_1^* = 0$ if and only if

$$\gamma_3 > \Gamma_m(\beta_3 + \beta_2, \beta_2), \quad (44)$$

the edge $Da_3^* = 1$ and $Da_1^* = 0$ if and only if

$$\gamma_2 > \Gamma_m(\beta_2 + \beta_3, \beta_3), \quad (45)$$

and the edge $Da_3^* = 1$ and $Da_2^* = 0$ if and only if

$$\gamma_1 > \Gamma_m(\beta_1 + \sigma'\beta_1 + \beta_3, \beta_3) \quad (46)$$

It can be easily established that multiplicity cannot occur for any of the cases represented by the remaining five edges of the unit cube. Thus, knowledge of the single-reaction criterion led to the writing down of seven sufficient multiplicity criteria in this case.

Next we establish the conditions for which the multiplicity region intersects any of the six surfaces of the cube. When $Da_3^* = 0$ the interactions between the simultaneous reactions 1 and 2 will lead to multiplicity for some Da_1 and Da_2 if and only if

$$\gamma_2 - \gamma_1 > \Gamma_m(\beta_2, \beta_1). \quad (47)$$

If the third reaction is instantaneous ($Da_3^* = 1$) this will occur if and only if

$$\gamma_2 - \gamma_1 > \Gamma_m(\beta_2 + \beta_3, \beta_1 + \sigma'\beta_1 + \beta_3) \quad (48)$$

The surface $Da_1^* = 0$ describes the case for which A and B are converted by two parallel independent reactions. Steady-state multiplicity exists in this case for some Da_2 and Da_3 if and only if

$$g_2(\gamma_2, \gamma_3, \beta_2, \beta_3, 0) > 0 \quad (49)$$

where g_2 is defined by Eq. 23.

Similarly, the surface $Da_2^* = 0$ represents the case for which A and B are converted by two consecutive reactions. The corresponding multiplicity criterion is

$$g_2(\gamma_1, \gamma_2, \beta_1, \beta_2, \sigma') > 0 \quad (50)$$

The surfaces $Da_1^* = 1$ or $Da_2^* = 1$ describe cases for which only the reaction $B \rightarrow D$ occurs at a finite rate. Thus, the multiplicity region does not intersect these surfaces, even though it may intersect the edges describing the single reaction $B \rightarrow D$. Thus, knowledge of the two-reaction criteria enabled us to write down four conditions that guarantee multiplicity for this reaction network. This example illustrates a case for which multiplicity criteria can be obtained from those for the single- and two-reaction networks.

We wish to comment that for this special reaction network it is possible to derive a condition predicting parameter values for which multiplicity exists within the unit cube at points arbitrarily close to the corner for which $Da_1^* = Da_2^* = 1$ by considering the special case of

$$Da_1 \rightarrow \infty \qquad Da_2 \rightarrow \infty \quad (51)$$

and

$$Da_2/Da_1 = \mu$$

Here, the steady-state Eq. 40 simplifies to

$$y - 1 = \frac{\beta_1 + \beta_2 \mu X_2/X_1}{1 + \mu X_2/X_1} + \frac{\sigma' \beta_1 Da_3 X_3}{(1 + Da_3 X_3)(1 + \mu X_2/X_1)} + \frac{\beta_3 Da_3 X_3}{1 + Da_3 X_3} \quad (52)$$

which can be rearranged to

$$y' - 1 = (1 + \beta_1' - y')\mu X_2/X_1 + (1 + \beta_2' - y')Da_3 X_3 + (1 + \beta_1' + \sigma''\beta_1' + \beta_2' - y')Da_3 X_3 \mu X_2/X_1 \quad (53)$$

where

$$y' = y/(1 + \beta_1) \qquad \sigma'' = \sigma'\beta_1/(\beta_1 - \beta_2)$$
$$\beta_1' = (\beta_2 - \beta_1)/(1 + \beta_1) \qquad \beta_2' = (\sigma'\beta_1 + \beta_3)/(1 + \beta_1) \quad (54)$$

Eq. 53 is identical in form to the steady-state equation describing two consecutive reactions. Thus, multiplicity exists only for parameters $\boldsymbol{p}^*$ which satisfy

$$g_2\left(\frac{\gamma_2 - \gamma_1}{1 + \beta_1}, \frac{\gamma_3}{1 + \beta_1}, \frac{\beta_2 - \beta_1}{1 + \beta_1}, \frac{\beta_3 + \sigma'\beta_1}{1 + \beta_1}, \frac{\sigma'\beta_1}{\beta_1 - \beta_2}\right) > 0 \quad (55)$$

The analogy between the derivation of criterion 55 and the derivation of Eq. 32 from Eq. 33 leads us to conjecture that multiplicity can exist for this reaction network for some Da if and only if $\boldsymbol{p}^*$ satisfies at least one of the 11 criteria defined by Eqs. 42–50 and 55. We have not succeeded to prove the "only if" part of this conjecture.

Example 2

Consider a cooled CSTR in which a reactant is consumed by N simultaneous first-order reactions

$$A \xrightarrow{k_i} B_i \qquad i = 1,2,3, \ldots, N.$$

The corresponding species and energy balances are

$$q(A_o - A) = VA \sum_{i=1}^{N} k_i \quad (56)$$

$$q\rho c_p(T - T_o) + Ua(T - T_c) = Va \sum_{i=1}^{N} (-\Delta H_i)k_i \qquad (57)$$

Defining

$$Da_i = Vk(T_m)/q \qquad \gamma_i = E_i/RT_m$$
$$\beta_i = \frac{A_o(-\Delta H_i)}{\rho c_p T_m} \qquad y = T/T_m$$
$$X_i = \exp[\gamma_i(1 - 1/y)] \qquad (58)$$

we obtain a single equation for the dimensionless temperature

$$y - 1 = \sum_{i=1}^{N} Da_i(1 + \beta_i - y)X_i. \qquad (59)$$

When any one of the simultaneous reactions is instantaneous then the reactant is completely consumed and a unique steady state corresponding to complete conversion of A by that reaction exists. Thus, the multiplicity region cannot intersect any edge or surface for which $Da_i^* = 1$ for any i.

The multiplicity region intersects the edge representing the case that reaction i proceeds at a finite rate, while the rate of the remaining $N - 1$ reactions is negligible ($Da_j^* = 0$ for $j = 1, 2, i - 1, i + 1, N$), if and only if

$$\beta_i > 0 \text{ and } \gamma_i > \gamma_m(\beta_i) \qquad i = 1,2, \ldots,N. \qquad (60)$$

Consider now the $\binom{N}{2}$ surfaces representing cases in which the rate of two simultaneous reactions is finite while the rates of the remaining $N - 2$ simultaneous reactions is negligible. Capitalizing on the knowledge of criterion 32 we can predict that the multiplicity region intersects any of these surfaces if and only if

$$\gamma_i - \gamma_j > \Gamma_m(\beta_i,\beta_j) \qquad i \neq j = 1,2, \ldots,N. \qquad (61)$$

Thus, we are able to write down $N + (N/2)$ criteria predicting the values of $\boldsymbol{p}^*$ for which multiplicity exists for some $\boldsymbol{Da}$. We prove in the appendix the surprising result that the above criteria are actually necessary and sufficient for multiplicity for some $\boldsymbol{Da}$ in this reaction network. This result implies that if no single reaction or pair of simultaneous reactions can lead to multiplicity then a unique solution exists for any $\boldsymbol{Da}$ for the N simultaneous reactions case.

Example 3

Consider N-independent, irreversible, first-order parallel reactions

$$A_i \xrightarrow{k_i} B_i \qquad i = 1,2, \ldots,N$$

occurring in a cooled CSTR. The dimensionless steady-state temperature satisfies the equation

$$y - 1 = \sum_{i=1}^{N} \frac{\beta_i Da_i X_i}{1 + Da_i X_i} \qquad (62)$$

To simplify the algebraic manipulations we assume that the activation energies of all the reactions are equal, i.e.,

$$\gamma_i = \gamma, \qquad X_i = X = \exp[\gamma(1 - 1/y)] \qquad i = 1,2, \ldots,N \qquad (63)$$

so that the steady-state Eq. 62 reduces to

$$F(y) \triangleq y - 1 - \sum_{i=1}^{N} \frac{\beta_i Da_i X}{1 + Da_i X} = 0 \qquad (64)$$

The standard procedure is to determine systematically all the criteria which guarantee multiplicity for some $\boldsymbol{Da}$ when i reactions occur ($i = 1,2, \ldots,N$) while the remaining $N - i$ reactions are either instantaneous or proceed at a negligible rate. Usually, some of these criteria are implied by others and may be discarded. We shall prove that a single criterion predicts the necessary and sufficient condition which the vector $\boldsymbol{p}^*$ has to satisfy so that Eq. 64 has multiple solutions for some $\boldsymbol{Da}$.

Assume that the first M reactions are exothermic ($\beta_i > 0$), while the remaining $N - M$ reactions are endothermic ($\beta_i < 0$). According to the implicit function theorem the boundary (if it exists) of the region of $\boldsymbol{Da}$ values for which steady-state multiplicity exists must satisfy the two equations

$$F(y) = F'(y) = 0. \qquad (65)$$

Elimination of y between these two equations gives that on this boundary

$$\gamma = \frac{\left(1 + \sum_{i=1}^{M} \frac{\beta_i z_i}{1 + z_i} + \sum_{i=M+1}^{N} \frac{\beta_i z_i}{1 + z_i}\right)^2}{\sum_{i=1}^{M} \frac{\beta_i z_i}{(1 + z_i)^2} + \sum_{i=M+1}^{N} \frac{\beta_i z_i}{(1 + z_i)^2}} \qquad (66)$$

where

$$z_i \triangleq Da_i X.$$

Our purpose is to find the set of z_i for which γ has the smallest positive value, say γ_m. Inspection indicates that the smallest value of the r.h.s. of Eq. 66 is obtained when all the z_i for the endothermic reactions are as large as possible, i.e., when the endothermic reactions are instantaneous. Thus,

$$\gamma_m = \underset{z_i}{Min} \frac{\left(1 + \sum_{i=1}^{M} \frac{\beta_i z_i}{1 + z_i} + \sum_{i=M+1}^{N} \beta_i\right)^2}{\sum_{i=1}^{M} \frac{\beta_i z_i}{(1 + z_i)^2}} \qquad (67)$$

Partial differentiations of the r.h.s. of Eq. 67 shows that this minimum is obtained when

$$z_i \triangleq Da_i X = \frac{1 + \sum_{M+1}^{N} \beta_i}{1 + \sum_{i=1}^{N} \beta_i} \qquad \text{for all } i = 1,2,M. \qquad (68)$$

Substitution of Eq. 68 into Eq. 67 shows that the necessary and sufficient condition for multiplicity to occur for some $\boldsymbol{Da}$ is that

$$\gamma > \Gamma_m\left(\sum_{i=1}^{N} \beta_i, \sum_{i=M+1}^{N} \beta_i\right). \qquad (69)$$

In the special case that all the reactions are exothermic ($N = M$) Eq. 69 becomes

$$\gamma > \gamma_m\left(\sum_{i=1}^{N} \beta_i\right). \qquad (70)$$

CONSTRUCTION OF THE MULTIPLICITY REGION FOR MULTIREACTION NETWORKS

When one or more of the sufficient multiplicity criteria are satisfied, there exists a region of Damköhler numbers for which multiple steady states exist. We show here how to construct this region.

The points which satisfy both Eqs. 1 and 2 form the so called *singular set* in the (y, $\boldsymbol{Da}$, $\boldsymbol{p}^*$) space. The projection of this set onto the ($\boldsymbol{Da}$, $\boldsymbol{p}^*$) parameter space is referred to as the *bifurcation set*. The construction of this multidimensional surface is very difficult. An easier task is the construction of a cross section of the bifurcation set in the N dimensional $\boldsymbol{Da}$ space for a specific $\boldsymbol{p}^*$. This $N - 1$ dimensional cross section divides the $\boldsymbol{Da}$ space into regions with different number of steady-state solutions. The construction of this $N - 1$ dimensional section of the bifurcation set is very complex and tedious for $N \geq 3$ as it requires finding all the sets of N Da_i which satisfy Eqs. 1 and 2. However, for $N = 2$ the construction of the cross sections of the bifurcation set is very easy as shown by Michelsen (1977) for two simultaneous reactions and Balakotaiah and Luss (1982a) for two parallel or consecutive reactions. Sections of the bifurcation sets constructed by these methods are shown in Figures 2–5.

In applications one is often interested in determining if multiplicity exists for a specific situation. The solution of this problem does not require the construction of the complete multidimensional

bifurcation set. If all the parameters $\boldsymbol{p}^*$ and $\boldsymbol{Da}$ are known one can plot $F(y)$ vs. y and determine all its zeros, which are steady-state solutions. In many applications it is necessary to check the influence of changes (or uncertainties) in the values of some parameters on the possible solutions. When the values of p^* and $N-1$ Damköhler numbers are known, one can solve Eqs. 1 and 2 for y and the remaining Damköhler number to determine the region of multiplicity (if it exists). Similarly, if p^* and $N-2$ Damköhler numbers are known one can solve Eqs. 1 and 2 for the remaining Damköhler numbers for all the feasible y values. The corresponding pairs of Damköhler numbers are used to construct a two-dimensional map of the multiplicity region. One can then check if a specific $\boldsymbol{Da}$ is within this region.

CONCLUDING REMARKS

The analysis shows that conditions predicting when steady-state multiplicity occurs for some $\boldsymbol{Da}$ in multireaction systems can be derived in a systematic fashion by examining the limiting cases in which i reactions ($i = 1,2, \ldots, N$) proceed at a finite rate while each of the remaining $N-i$ reactions are either instantaneous or occur at a negligible rate. Thus, the available criteria for the single- and two-reaction cases enable us always to write down several sufficient multiplicity criteria for any reaction network. Moreover, the scheme described here enables us to utilize the knowledge of multiplicity criteria for simple reaction networks to construct criteria for more intricate reaction networks.

The derivation of exact multiplicity criteria for most multireaction systems with $N \geq 3$ is extremely difficult, and in most cases it is impossible to obtain explicit criteria. The major advantage of the scheme proposed here is the simplicity and ease by which it can give some sufficient multiplicity criteria for any reaction network. Moreover, the available expressions for determining the Damköhler numbers for which multiplicity exists in the single- and two-reaction networks can be used to determine values of $\boldsymbol{Da}$ for which multiplicity exists on the surface of the unit hypercube for any multireaction system.

The analysis presented here is for a system of first-order reactions for which it is always possible to derive a single equation describing the steady-state temperature. When the rate expressions are nonlinear, such as nth order or Langmuir-Hinshelwood rate expressions, the steady-state temperature has in general to satisfy a set of equations. However, the proposed scheme of getting sufficient multiplicity criteria from the analysis of limiting cases can be still used For example, Figure 1 can be used to predict the values of γ_i for which the multiplicity region intersects any edge of the N dimensional unit cube when the reactions are of any order $n \geq 0$. Thus, this scheme should become a standard tool in the analysis of multiplicity in multi-reaction networks.

ACKNOWLEDGMENT

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NOTATION

A = species A
a = heat transfer area
B = species B
c_p = heat capacity
Da_i = Damköhler number $(Vk_i(T_m)/q)$
Da_i^* = normalized Damköhler number defined by Eq. 24
E_i = activation energy
H = dimensionless heat transfer coefficient defined by Eq. 41
$(-\Delta H_i)$ = heat of reaction
k_i = reaction rate constant
N = number of reactions
n = reaction order
$P_i(y)$ = polynomials defined in text ($i = 1,2,3$)
$\boldsymbol{p}, \boldsymbol{p}^*$ = parameter vectors defined in text
q = flow rate
Q = instantaneous heat release by feed
R = universal gas constant
T = absolute temperature
T_c = coolant temperature
T_m = reference temperature defined by Eq. 41
U = heat transfer coefficient
V = volume of reactor
X_i = function defined by Eq. 41
y = dimensionless temperature (T/T_m)
z_i = quantity defined by Eq. 66

Greek Symbols

β_i = dimensionless heat of reaction
γ_i = dimensionless activation energy
$\gamma_m(\beta_i)$ = function defined by Eq. 5
$\gamma_m(\beta_i,n)$ = function defined by Eq. 14
$\Gamma_m(\beta_i,\beta_j)$ = function defined by Eq. 9
ρ = density
σ = $\Delta H_2/\Delta H_1$
σ', σ'' = ratio of heats of reaction defined in text
μ = ratio of Damköhler numbers (Da_2/Da_1)

Subscripts

i = referring to ith reaction
o = inlet conditions

APPENDIX: PROOF CONCERNING INTERACTIONS AMONG / SIMULTANEOUS REACTIONS (EXAMPLE 2)

Defining

$$s = 1 - 1/y \qquad z_i = \beta_i/(1+\beta_i) \tag{A1}$$

Eq. 59 can be written as

$$F(s,\mathbf{Da},\mathbf{p}^*) = \sum_{i=1}^{N} \frac{Dai}{1-z_i}(z_i - s)\exp(\gamma_i s) - s = 0 \tag{A2}$$

It can be proven that Eq. A2 has at least one solution for every physically feasible $\boldsymbol{Da}$ and $\boldsymbol{p}^*$. When all $Da_i \to 0$, $s \to 0$ is a unique solution of Eq. A2. According to the implicit function theorem a change in the number of solutions can occur in this case only for parameter values satisfying

$$F(s,\mathbf{Da},\mathbf{p}^*) = \frac{dF}{ds}(s,\mathbf{Da},\mathbf{p}^*) = 0 \tag{A3}$$

These Eqs. are of the form

$$\sum_{i=1}^{N} a_i Da_i = 1 \tag{A4}$$

$$\sum_{i=1}^{N} b_i Da_i = 1 \tag{A5}$$

where

$$a_i = \frac{(-1 + z_i/s)}{1-z_i}\exp(\gamma_i s) \tag{A6}$$

$$b_i = \frac{\gamma_i(z_i - s) - 1}{1-z_i}\exp(\gamma_i s) \tag{A7}$$

Thus, for a specific $\boldsymbol{p}^*$ a unique steady state exists for all $\boldsymbol{Da}$ if the two Eqs. A4 and A5 have no feasible solution ($Da_i \geq 0$ for all i). We prove now that Eqs. A4–A5 cannot have a feasible solution for any $N \geq 3$ unless at least one pair of criteria 60–61 (which are obtained from Eqs. A4–A5 for $N = 2$) are satisfied.

Equations A4 and A5 have a feasible solution

$$Da_i > 0 \qquad i = 1,2,..,N \tag{A8}$$

if and only if the hyperplane defined by these equations intersects at least one of the planes bounding the positive region. Thus, at least one set of equations

$$a_iDa_i + a_jDa_j = 1 \tag{A9}$$

$$b_iDa_i + b_jDa_j = 1 \qquad i \neq j = 1,2,..,N \tag{A10}$$

has to be satisfied. These equations have a feasible solution only if reactions i and j can lead to multiplicity for some Dai and Daj. Thus, unless at least one of the $N(N + 1)/2$ criteria (Eqs. 60 and 61) is satisfied multiplicity cannot occur.

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Chain-of-Rotators Equation of State

An equation of state is obtained to describe the fluid state from the supercritical gas to subcritical vapor and liquid for small and large molecules of organic and inorganic substances. The perturbation theory of the fluid state is extended to include rotational contribution of molecular motion in addition to translational and the attractive force contributions. Three equation constants describe a substance and values are presented for 22 substances. Application is made to mixtures with emphasis on their phase equilibria.

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SCOPE

The design of processes involving fluid mixtures, especially separation processes, requires quantitative information about the thermodynamic properties of fluids and their mixtures. The diversity of fluid mixtures encountered in such processes precludes a compilers approach to estimating fluid properties. Likewise extensive experimental data are seldom available except for a limited number of mixtures and even then restricted in range of composition, temperature and pressure. There continues to be a need to interpolate and extend fragmentary data to predict and design processes. Equations of state are useful to satisfy this need.

The objective of this work is to develop an equation of state generally useful for molecular fluids over a wide range of fluid states including the supercritical gas and the subcritical vapor and liquid of pure fluids and fluid mixtures. Perturbation theory of fluid state is extended to chain molecules with the introduction of a new partition function to describe the rotational contribution of molecules to configurational properties. An equation of state, called the chain-of-rotators (COR) equation, is obtained from the partition function. Only three substance-specific parameters are required to be known for a fluid to be described by the new equation. Values of the parameters have been determined and are reported here for 22 substances.

The new equation is applied to mixtures with the use of Van der Waals one fluid mixing rules.

CONCLUSIONS AND SIGNIFICANCE

The new equation of state gives a generally good description of fluid states for molecular fluids. Good results are obtained in pVT, vapor pressure, and enthalpy calculations.

The new equation describes fluid-phase equilibrium for diverse mixtures including azeotrope-forming systems. Symmetric mixtures of comparable components as well as asymmetric