Chemical Reactor Stability by Liapunov's Direct Method

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It is necessary in the course of reactor design to determine such quantities as the heat and mass transfer coefficients and the kinetics of the reacting system under consideration. Usually this design is based on steady state analysis which does not consider the effect of transients on reactor operation. While this approach is satisfactory for many purposes, it cannot provide answers to questions regarding reactor stability, behavior which is by its nature dependent on dynamic characteristics.

A reactor operating at some steady state is subject to a number of disturbances which cause this condition to change. If following such a disturbance the reactor variables (say temperature and concentration) remain within some bounded range, the system is called "stable." If in addition the system approaches its steady state condition with increasing time, it is termed asymptotically stable. If on the other hand the system behaves such that a given disturbance produces a runaway (unbounded) response, it is called "unstable" with respect to that disturbance. The stability of a given reactor is in general dependent on its initial condition and on the form and magnitude of the disturbances.

It is convenient to think of the reactor condition geometrically as a point in a state space whose coordinates are the dependent variables of interest. If the reactor condition can adequately be characterized for example by a temperature and a single composition, the state space is a two-dimensional phase plane. Changes in temperature and concentration will describe a trajectory in the phase plane from any initial condition through each subsequent state. In the arguments that follow the disturbances are considered to be step or impulse inputs, or in general such that they can be expressed as an equivalent change in initial conditions of the state variables. In order to have asymptotic stability there must exist some region about the steady state in which all trajectories converge to that state. Since it is not known a priori how small this region may have to be, asymptotic stability of this sort is called "local stability."

This concept can be extended to develop definitions for stability over larger regions. If a system steady state is stable for inputs of any magnitude, that is if trajectories from any initial condition converge on a steady state, the system is called "globally asymptotically stable." In many cases of practical interest this behavior can only be demonstrated for a restricted set of initial conditions. The system is then said to be asymptotically stable in a bounded region.

Chemical reactor dynamic models can conveniently be divided into two categories according to whether total or partial differential equations are used. They are then described as lumped parameter and distributed parameter models, respectively. The first of these is best exemplified by the continuous-flow stirred vessel. This model has been the subject of a great deal of analytical study. It is complicated primarily by reaction kinetics terms which are almost universally nonlinear, especially with respect to temperature. Amundson and his co-workers have explored a series of important stability and control problems: criteria for the stability of the steady state (*1*), stability of a recycle reactor (*4*), and closed loop stability with control (*2*). Bilous, Block, and Piret (*5*) have analyzed cascade control for continuous flow reactors, and Aris and Amundson (*3*) have investigated the effect of random inputs.

Generally these analyses have been numerical or by linearization. The linearized approach is limited in one important respect, the result can only provide information on local stability. For practical design a guarantee that a particular steady state is locally stable is not as useful as quantitative information showing stability over at least a region of interest because from local stability alone it is not possible to establish whether a small disturbance can produce instability. In this paper the nonlinear kinetics are retained by using a Liapunov function to study stability. The method is variously called "Liapunov's second method" or "Liapunov's direct method". Kalman and Bertram (*8*) have described this technique and applied it to several circuit problems. Gurel and Lapidus (*6*) have used related techniques in a digital computer study of limit cycles in chemical reactor operations.

THE SYSTEM EQUATIONS

The system under consideration is a well-stirred reactor in which a homogeneous reaction is taking place. The reactants are fed continuously, and effluent is continually removed. This system can be described by one heat balance and one material balance:

$$\left.\begin{aligned} \rho V C_p \frac{dT}{dt} &= \Delta H V r - U A_r (T - T_A) - \rho q C_p (T - T_o) \\ V \frac{dc}{dt} &= - V r - q\,(c - c_o) \end{aligned}\right\} \quad (1)$$

Two transformations are necessary to put these equations into a form amenable to the subsequent analysis. First, following Aris and Amundson (*2*), the equations are normalized and abbreviated by letting

$$\left.\begin{aligned} \eta &= \rho C_p T / \Delta H c_o \\ y &= c/c_o \\ a &= \rho V C_p \\ b &= U A_r + \rho q C_p \\ \tau &= V/q \\ \tau_o &= \rho V C_p / U A_r \end{aligned}\right\} \quad (2)$$

Substitution in Equation (1) results in

$$\left.\begin{aligned} \frac{d\eta}{dt} &= \frac{r}{c_o} - \frac{b}{a}\eta + \frac{\eta_A}{\tau_o} + \frac{\eta_o}{\tau} \\ \frac{dy}{dt} &= -\frac{r}{c_o} - \frac{1}{\tau}(y-1) \end{aligned}\right\} \quad (3)$$

A second transformation is necessary to form a system of equations in which the steady state has the vector coordinate zero. This is accomplished by a simple translation. Let

$$\left.\begin{array}{l}\hat{\eta} = \eta - \eta_{ss} \\ \hat{y} = y - y_{ss} \\ \hat{r} = r - r_{ss}\end{array}\right\} \quad (4)$$

In the new coordinates Equations (3) reduce to

$$\left.\begin{array}{l}\dfrac{d\hat{\eta}}{dt} = \dfrac{\hat{r}}{c_o} - \dfrac{b}{a}\hat{\eta} \\ \dfrac{d\hat{y}}{dt} = -\dfrac{\hat{r}}{c_o} - \dfrac{1}{\tau}\hat{y}\end{array}\right\} \quad (5)$$

which has the steady state solution $\hat{\eta} = \hat{y} = 0$.
In terms of a two-dimensional state vector $\mathbf{x}$ the steady state is at $\mathbf{x} = \mathbf{0}$. The only nonlinear term in these equations is the rate term, whose complexity is the source of difficulty.

LIAPUNOV'S SECOND METHOD

The Liapunov approach provides a method by which it is possible to study the stability of a set of nonlinear differential equations without resort to integration. In its various forms the second method can be used to prove global stability, local stability, stability in a bounded region, or instability.

When possible it is desirable to demonstrate global asymptotic stability, that is in the whole T, c plane. This most fortunate condition can be guaranteed for a system (*8, 10*) if it is possible to formulate a scalar function (named for Liapunov) with continuous first partial derivatives such that

$$\left.\begin{array}{lll}\text{(i)} & \mathcal{V}(\mathbf{x}) = 0 & ,\ \mathbf{x} = \mathbf{0} \\ \text{(ii)} & \mathcal{V}(\mathbf{x}) > 0 & ,\ \mathbf{x} \neq \mathbf{0} \\ \text{(iii)} & \mathcal{V}(\mathbf{x}) \to \infty & ,\ \|\mathbf{x}\| \to \infty \\ \text{(iv)} & \dot{\mathcal{V}}(\mathbf{x}) = (d\mathcal{V}/dt) < 0 & ,\ \mathbf{x} \neq \mathbf{0}\end{array}\right\} \quad (6)$$

where as above $\mathbf{x}$ is the generalized state vector. In case it is not possible to find a function that meets all these requirements, it may be necessary to compromise for weaker conclusions. LaSalle and Lefschetz (pp. 58 to 59, reference *10*) have shown that if conditions i, ii, and iv of Equation (6) apply within a bounded region defined by $\mathcal{V}(\mathbf{x}) < K$, then the system is asymptotically stable in that bounded region. These same conditions are also sufficient to establish the local stability of the steady state, since the small neighborhood required for this local condition is contained within the larger region, referred to above. If the inequality condition on $\dot{\mathcal{V}}(\mathbf{x})$ is reversed, the steady state is necessarily unstable (*8, 10*).

The second method does nevertheless have several limitations which are of basic importance. The first limitation is inherent. The restrictions which assure the various stabilities or instability are sufficient, but not necessary. If these conditions are violated for a particular choice of $\mathcal{V}(\mathbf{x})$, that Liapunov function cannot be the basis of any conclusions about system behavior. The second limitation lies in the details of choosing a Liapunov function for a system. There is no general method available by which a Liapunov function may be constructed except for linear systems, or nonlinear systems of certain restricted kinds. This difficulty is compounded by the third limitation; a system may have any number of Liapunov functions, some of which may be more satisfactory than others from the standpoint of the regions in state space for which they may be useful.

One important class of nonlinear systems can be treated systematically. If the system equations can be written in the form

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}),\ \mathbf{f}(\mathbf{0}) = \mathbf{0} \quad (7)$$

they will be subject to a theorem due to Krasovskii (*9*). If $\mathbf{f}$ has continuous first partial derivatives and its Jacobian matrix $\mathbf{F}(\mathbf{x}) = [\partial f_i/\partial x_j]$ satisfies the condition that

$$\hat{\mathbf{F}}(\mathbf{x}) = \mathbf{F}(\mathbf{x}) + \mathbf{F}^T(\mathbf{x}) \quad (8)$$

is negative definite, then the steady state $\mathbf{x}_{ss} = \mathbf{0}$ of the system is asymptotically stable in the large, and

$$\mathcal{V}(\mathbf{x}) = \|\mathbf{f}(\mathbf{x})\|^2 \quad (9)$$

is a Liapunov function for the system. In the course of proving this theorem (*8*), it is shown that the sign of $\dot{\mathcal{V}}(\mathbf{x})$ depends on the sign definiteness of the matrix $\hat{\mathbf{F}}(\mathbf{x})$. If the $\hat{\mathbf{F}}(\mathbf{x})$. matrix is negative definite, then the scalar $\dot{\mathcal{V}}(\mathbf{x})$ will be negative. In the analysis that follows it is found that for the system of Equations (5) $\hat{\mathbf{F}}(\mathbf{x})$ is only negative definite is a bounded region of the T, c plane. Accordingly certainty concerning the sign of $\dot{\mathcal{V}}(\mathbf{x})$ is similarly restricted, and only stability in a bounded region can be established.

ANALYSIS BY KRASOVSKII'S THEOREM

Equations (5) may now be analyzed by Krasovskii's theorem. If the rate term is treated as an implicit function of concentration and temperature, $r = r(T, c) = r(\hat{\eta}, \hat{y})$, the Jacobian matrix is

$$\mathbf{F} = \begin{bmatrix} -\left(\dfrac{b}{a} - \dfrac{1}{c_o}\dfrac{\partial \hat{r}}{\partial \hat{\eta}}\right) & \dfrac{1}{c_o}\dfrac{\partial \hat{r}}{\partial \hat{y}} \\ -\dfrac{1}{c_o}\dfrac{\partial \hat{r}}{\partial \hat{\eta}} & -\left(\dfrac{1}{c_o}\dfrac{\partial \hat{r}}{\partial \hat{y}} + \dfrac{1}{\tau}\right)\end{bmatrix} \quad (10)$$

As indicated by the theorem it is necessary to examine $\hat{\mathbf{F}}(\mathbf{x})$, the sum of $\mathbf{F}(\mathbf{x})$ and its transpose. To avoid repeated minus signs the condition that $\hat{\mathbf{F}}(\mathbf{x}) < \mathbf{0}$ can be restated as $-\hat{\mathbf{F}}(\mathbf{x}) > \mathbf{0}$:

$$-\hat{\mathbf{F}} = \begin{bmatrix} 2\left(\dfrac{b}{a} - \dfrac{1}{c_o}\dfrac{\partial \hat{r}}{\partial \hat{\eta}}\right) & \dfrac{1}{c_o}\left(\dfrac{\partial \hat{r}}{\partial \hat{\eta}} - \dfrac{\partial \hat{r}}{\partial \hat{y}}\right) \\ \dfrac{1}{c_o}\left(\dfrac{\partial \hat{r}}{\partial \hat{\eta}} - \dfrac{\partial \hat{r}}{\partial \hat{y}}\right) & 2\left(\dfrac{1}{c_o}\dfrac{\partial \hat{r}}{\partial \hat{y}} + \dfrac{1}{\tau}\right)\end{bmatrix} \quad (11)$$

In order that the matrix $-\hat{\mathbf{F}}$ shall be positive definite its elements must satisfy Sylvester's inequalities (*7*):

$$\left.\begin{array}{l}\dfrac{b}{a} - \dfrac{1}{c_o}\dfrac{\partial \hat{r}}{\partial \hat{\eta}} > 0 \\ 4\left(\dfrac{b}{a} - \dfrac{1}{c_o}\dfrac{\partial \hat{r}}{\partial \hat{\eta}}\right)\left(\dfrac{1}{c_o}\dfrac{\partial \hat{r}}{\partial \hat{y}} + \dfrac{1}{\tau}\right) - \dfrac{1}{c_o^2}\left(\dfrac{\partial \hat{r}}{\partial \hat{\eta}} - \dfrac{\partial \hat{r}}{\partial \hat{y}}\right)^2 > 0\end{array}\right\} \quad (12)$$

When transformed back into T, c coordinates and simplified Sylvester's inequalities take the form

$$b - \Delta HV \frac{\partial r}{\partial T} > 0 \tag{13}$$

$$\frac{4}{a\tau}\left(b - \Delta HV \frac{\partial r}{\partial T}\right) + \frac{4b}{a}\frac{\partial r}{\partial c} > \left[\frac{\Delta HV}{a}\frac{\partial r}{\partial T} + \frac{\partial r}{\partial c}\right]^2 \tag{14}$$

The key to an interpretation of these inequalities lies in recalling that the sign of $\dot{V}(\mathbf{x})$ is fixed by the sign definiteness of the matrix $\hat{\mathbf{F}}(\mathbf{x})$. If in a region of the T, c plane these inequalities are satisfied, then $\dot{V}(\mathbf{x})$ is negative in that region. To check the other conditions for asymptotic stability in a bounded region it is necessary to examine the Liapunov function for this system in order to find the largest possible region $V(\mathbf{x}) < K$ that lies within the region in which $\dot{V}(\mathbf{x}) < 0$. From Equations (5) and (9)

$$V(\hat{\eta}, \hat{y}) = \left(\frac{\hat{r}}{c_o} - \frac{b}{a}\hat{\eta}\right)^2 + \left(\frac{\hat{r}}{c_o} + \frac{1}{\tau}\hat{y}\right)^2 \tag{15}$$

where the variables y and η are implicit in $r(\eta, y)$. A brief investigation of this function confirms that

$$\left.\begin{array}{lll} \text{(i)} & V(\hat{\eta}, \hat{y}) = 0 & , \ \hat{\eta} = \hat{y} = \hat{r} = 0 \\ \text{(ii)} & V(\hat{\eta}, \hat{y}) > 0 & , \ \hat{\eta}, \hat{y}, \hat{r} \text{ not all} = 0 \\ \text{(iii)} & V(\hat{\eta}, \hat{y}) \rightarrow \infty & , \ \hat{\eta}, \hat{y}, \text{or } \hat{r} \rightarrow \infty \end{array}\right\} \tag{16}$$

conditions which according to Letov (*11*) show that a graph of $V = K$ is a closed contour in the phase plane.

GEOMETRIC INTERPRETATION

The argument for asymptotic stability in a bounded region may be followed with reference to the T, c plane. In Figure 1 three $V = K$ contours are shown for a hypothetical Liapunov function. An increase in K will produce contours that enclose larger areas in the plane. Each of inequalities (13) and (14) defines a line below which the inequalities are satisfied and above which they are contradicted. In the figure these lines are labeled as the first and second separatrix, respectively. At any point in the region of the plane which lies below both lines $\dot{V}(\mathbf{x})$ will be negative. Therefore any region that is both within a $V = K$ contour and below both separatrices satisfies all the requirements of the LaSalle and Lefschetz theorem and is a region of asymptotic stability (RAS).

As a corollary it may also be concluded that any steady state (T_{ss}, c_{ss}) below both separatrices is locally stable, since it is always possible to find a neighborhood about that point that is within a $V = K$ contour.

The largest RAS which can be established by use of a particular Liapunov function is determined by the smallest value of K that produces an intersection of the $V = K$ contour with one of the separatrices. With reference to the curves of Figure 1 for example the curve $V = K_1$ gives an RAS which includes point A. This indicates that disturbances to this point will ultimately decay, and the system will return to its steady state. The curve for $V = K_2$ shows that the same conclusion is valid for point B. The area included within $V = K_2$ is the largest possible RAS

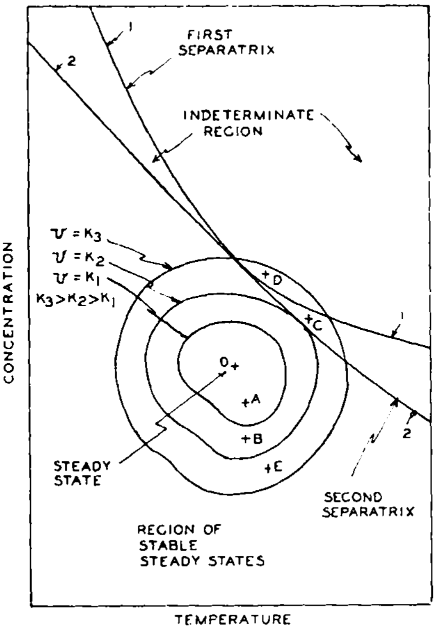

Fig. 1. Stability regions in the T — c plane.

for this particular Liapunov function, for if $V = K_3$ is chosen, the contour encloses areas in the plane for which $\dot{V}$ is indeterminate in sign. Points C and D for example are in a region of indeterminate behavior as regards this Liapunov function. Because any $V > K_2$ is unacceptable, the behavior of the trajectory from point E is similarly indeterminate; although E is in the region of locally stable steady states, it cannot be included in the RAS. It may be possible however to find another Liapunov function for which an RAS includes such points as C, D, and E.

To illustrate the difficulty of finding a satisfactory Liapunov function it is instructive to examine an alternative proposal. Suppose to satisfy conditions (16)

$$V(\hat{\eta}, \hat{y}) = \hat{\eta}^2 + \hat{y}^2 \tag{17}$$

Then

$$\dot{V}(\hat{\eta}, \hat{y}) = 2\left[\hat{\eta}\frac{d\hat{\eta}}{dt} + \hat{y}\frac{d\hat{y}}{dt}\right] \tag{18}$$

and from Equations (5) one can obtain

$$\dot{V}(\hat{\eta}, \hat{y}) = -2\left[+\frac{b}{a}\hat{\eta}^2 + \frac{1}{\tau}\hat{y}^2 - \frac{\hat{r}}{c_o}(\hat{\eta} - \hat{y})\right] \tag{19}$$

This derivative can be guaranteed negative [condition iv, Equation (6)] by requiring that

$$\frac{b}{a}\hat{\eta}^2 + \frac{1}{\tau}\hat{y}^2 > \frac{\hat{r}}{c_o}(\hat{\eta} - \hat{y}) \tag{20}$$

but this separatrix passes through the steady state, where $\hat{\eta} = \hat{y} = \hat{r} = 0$. Any separatrix that shows this behavior will not be satisfactory for establishing an RAS, because in the graph analogous to Figure 1 the contour $V = K$ will enclose part of the separatrix for any $K > 0$.

NTH ORDER KINETICS WITH ARRHENIUS TEMPERATURE DEPENDENCE

To this point no restriction has been placed on the form of the rate equation. In this section a most important special case is considered:

$$r = A\, e^{-Q/T}\, c^n \qquad (21)$$

From Equation (21) the necessary partial derivatives for inequalities (13) and (14) are

$$\left.\begin{aligned} \frac{\partial r}{\partial T} &= \frac{AQ}{T^2}\, e^{-Q/T}\, c^n = \frac{Q}{T^2}\, r \\ \frac{\partial r}{\partial c} &= nAe^{-Q/T}\, c^{n-1} = \frac{n}{c}\, r \end{aligned}\right\} \qquad (22)$$

Substitution into inequalities (13) and (14) yields the following:

$$\left.\begin{aligned} & b - (\Delta HVQr/T^2) > 0 \\ & \frac{4}{a_T}\left(b - \Delta HV\frac{Q}{T^2}\, r\right) + \frac{4bnr}{ac} > \left(\frac{\Delta HV}{a}\, \frac{Q}{T^2}\, r + \frac{nr}{c}\right)^2 \end{aligned}\right\} \qquad (23)$$

These relationships [together with Equation (21)] determine the two separatrices in the T, c plane. When used with the Liapunov function of Equation (15) they are adequate to fix the RAS about an arbitrary steady state.

A NUMERICAL EXAMPLE

The application of inequalities (23) will be demonstrated for a first-order reaction. The assumption of first-order kinetics does not linearize the equation, since the Arrhenius temperature dependence remains. Let the system constants be chosen as follows, for some hypothetical homogeneous reaction:

$A = 10^8$ hr.$^{-1}$	$C_p = 1.0$ B.t.u./lb. °F.
$Q = 10^4$ °R.	$\rho = 50$ lb./cu. ft.
$U = 5$ B.t.u./hr. sq.ft. °F.	$T_o = T_A = 530$°R.
$A_r = 100$ sq. ft.	$\Delta H = 10^4$ B.t.u./lb. mole
$V = 100$ cu. ft.	$q = 200$ cu. ft./hr.

Choose $T_{ss} = 550$°R. From Equation (1) $r_{ss} = 0.210$ lb. moles/cu. ft. hr. From Equation (21) $c_{ss} = 0.165$ lb. moles/cu. ft. With the constants chosen inequalities (23) become

$$\left.\begin{aligned} & c < 1.05 \times 10^{-14}\, T^2\, e^{10^4/T} \\ & 16.8 - \frac{16 \times 10^{14} c}{T^2\, e^{10^4/T}} + \frac{8.4 \times 10^8}{e^{10^4/T}} > \left(\frac{2 \times 10^{14} c}{T^2\, e^{10^4/T}} + \frac{10^8}{e^{10^4/T}}\right)^2 \end{aligned}\right\} \qquad (24)$$

These inequalities divide that T, c plane into stable and indeterminate regions as shown in Figure 2. Again it should be emphasized that the designation of indeterminate refers only to the particular $\mathcal{V}(\mathbf{x})$ used here. The Liapunov function for this system is

$$\mathcal{V}(T, c) = [r - 0.0105\,(T - 550) - 0.210]^2 + [r + 2.0c - 0.54]^2 \qquad (25)$$

For this Liapunov function $K = 0.006$ yields the RAS shown in Figure 3. This system will exhibit asymptotic stability for disturbances in temperature as great as ±15°F. or disturbances in composition as large as ±0.02 lb. moles/cu. ft.

DISCUSSION

The stability criteria presented are valid in particular only for disturbances which can be expressed in the form of changed initial conditions. Many practical inputs do fit this category. If a reactor in steady state operation is disturbed by an impulse, say in flow rate, the effect is to move the system to a new point in the T, c plane. The reactor will return to the original steady state, if the new T, c point is in the RAS. This may also be the case if the new point is out of the RAS, but this cannot be proved with the given Liapunov function (again sufficient but not necessary). In the event that the disturbance is a step change in one of the input variables, the system will have a new steady state after the input change. A phase plane diagram such as Figure 3 may then be most readily interpreted by taking the steady state point to represent the new condition; the trajectory is then understood to move from the T, c point that was the former steady state.

The relatively simple equations developed depend on the supposition that the system can be adequately described by only two state variables. This requirement is met for the continuous-flow well-stirred, homogeneous re-

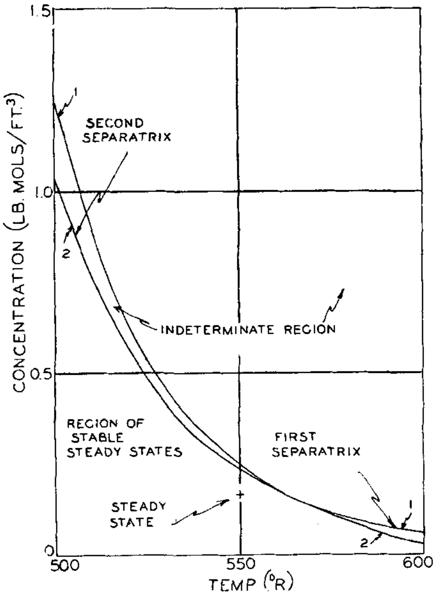

Fig. 2. Stability regions for a first-order reaction with Arrhenius temperature dependence.

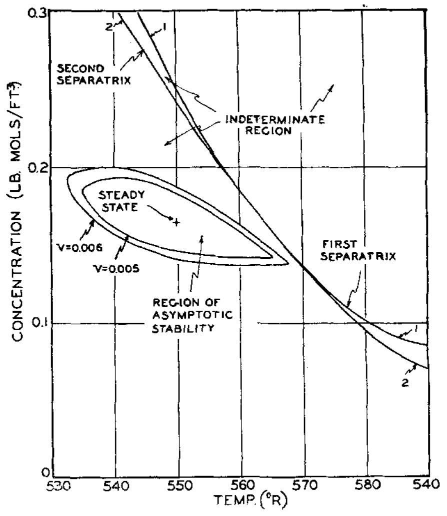

Fig. 3. A region of asymptotic stability for a chemical reactor.

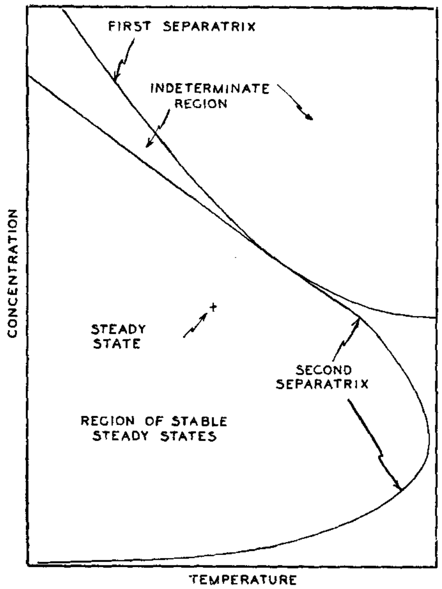

Fig. 4. Stability regions in the $T - c$ plane for orders of reaction less than unity.

actor where the rate is always expressible as a function of a single composition and temperature (2). For more complicated systems it would be necessary to increase the number of state variables. While this is not a restriction in principle, it does of course complicate numerical analysis.

There is an additional restriction concerning the type of kinetics that can be studied by this method. Consider the following unsimplified form of the two Sylvester inequalities:

$$\left.\begin{array}{l} b - \Delta HV \dfrac{\partial r}{\partial T} > 0 \\ \dfrac{4}{a}\left(b - \Delta HV \dfrac{\partial r}{\partial T}\right)\left(\dfrac{\partial r}{\partial c} + \dfrac{1}{\tau}\right) - \left(\dfrac{\Delta HV}{a}\dfrac{\partial r}{\partial T} - \dfrac{\partial r}{\partial c}\right)^2 > 0 \end{array}\right\} \quad (26)$$

If these two are to hold simultaneously it is necessary also that

$$\left(\frac{\partial r}{\partial c} + \frac{1}{\tau}\right) > 0 \quad (27)$$

For kinetic rate equations of the form of (21) this is assured for all reactions of order zero or higher; nevertheless inequality (27) might play an important role for kinetic systems of very different sort.

Because of their obvious importance to stability it is of some interest to examine the effect of reaction order on the shape of the separatrices. For kinetics following rate Equation (21) the equation of the first separatrix is

$$c = (b/\Delta HVQA)\, T^{2/n}\, e^{Q/nT} \quad (28)$$

A change in n will not affect the shape of the curve materially but will shift it in the T, c plane. Regardless of the order of reaction the curve will go through a minimum at a temperature of $T = Q/2$. In the numerical example considered above this minimum occurs at 5,000 °R. If activation energies are moderate to large, the position of this minimum has no material effect on the RAS in cases of practical interest. The minimum composition on the first separatrix is found from Equation (28):

$$c_{\min} = (b/\Delta HVA)\, 4^{-1/n}\, Q^{(2/n)-1}\, e^{2/n} \quad (29)$$

The effect of reaction order on the shape of the second separatrix can be seen by examining inequality (23). Let the concentration become vanishingly small at constant temperature. For all orders of reaction equal to or greater than unity the second inequality reduces to $(4b/a\tau) > 0$. Since this inequality is always true, the T axis is included in the region of stable steady states. Such a separatrix is shown in Figure 3. If the order of reaction is less than unity, the same argument leads to

$$(4b/a) > e^{-Q/T}\, c^{n-1} \rightarrow \infty \quad (30)$$

This inequality can never be true because a and b are necessarily finite. In this case the points on the T axis must violate the second Sylvester inequality, and the second separatrix must be shaped as shown in Figure 4.

The two separatrices possess a unique intersection at one point in the T, c plane. From inequalities (12) it is seen that this intersection occurs at the point where the square term vanishes:

$$\frac{\Delta HV}{a}\frac{\partial r}{\partial T} = \frac{\partial r}{\partial c} \quad (31)$$

Combining this with the equation of the first separatrix one gets the following equation for the intersection temperature:

$$2(n-1)\ln T - \frac{Q}{T} = \ln\left[\frac{b}{A}\frac{(\Delta HVQ)^{n-1}}{(an)^n}\right] \quad (32)$$

For the numerical example considered above this intersection occurs at $T = 565$°R.

Of the two separatrices derived from this Liapunov function the second is more restrictive; it always reduces the region of stable steady states allowed by the first. The fact that the separatrices meet at a point can however be used for rapid local stability estimates, if the steady state of interest is located in the vicinity of this common point. In this special case the more restrictive second Sylvester inequality can be ignored and calculations based on the simpler first inequality. For a steady state to be below the first separatrix

$$b - (V\Delta HQr_{ss}/T_{ss}^2) > 0 \quad (33)$$

where from Equation (1)

$$r_{ss} = \frac{1}{\Delta HV}(bT_{ss} - UA_rT_A - \rho q C_p T_o) \quad (34)$$

Combining (33) and (34) one obtains the following inequality:

$$T_{ss}^2 - Q\,T_{ss} + [Q(\tau T_A + \tau_o T_o)/(\tau + \tau_o)] > 0 \quad (35)$$

Permissible steady state temperatures are thus limited by a quadratic inequality. For the previous numerical example inequality (35) results in $T_{ss} < 570$°R., $T_{ss} >$ 9,432 °R. Of these restrictions only the first is of practical interest.

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NOTATION

A = frequency factor
A_r = reactor area
a,b = constants defined in Equation (2)

C_p = specific heat
c = concentration
$\mathbf{F}$ = Jacobian matrix
$\hat{\mathbf{F}}$ = $\mathbf{F} + \mathbf{F}^T$
$\mathbf{f}$ = autonomous vector function
ΔH = heat of reaction
K = constant for Liapunov function contour
n = order of reaction
Q = activation energy divided by the gas constant
q = volumetric flow rate
r = rate of reaction per unit volume
T = temperature
t = time
U = overall heat transfer coefficient
V = reactor volume
$\mathcal{V}$ = Liapunov function
$\mathbf{x}$ = general state vector
y = normalized concentration
η = normalized temperature
ρ = density
τ = time constant defined in Equation (2)

Subscripts and Superscripts

$\wedge$ = deviation from steady state
$\cdot$ = total time derivative
$\| \|$ = norm of a vector
ss = steady state
A = heat sink
o = input
1,2,3 = specific values of K
T = transpose

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The Effect of Feedback Control on Chemical Reactor Stability

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In a previous paper (*1*) an analysis of a wide class of chemical reactors established criteria for computing a region of asymptotic stability (RAS). Sufficient conditions were given for treating arbitrary nonlinear kinetics for a system that can be described by two state variables, temperature and concentration. These criteria were established for the reactor operating without control, but in virtually all cases of practical interest some mode of control is desirable to help improve stability and performance. The choice of a particular control action is most often a decision based wholly on past experience with related problems. This paper is concerned with establishing criteria by which the stability effects of many linear or nonlinear control modes may be analyzed. The analysis is based on the second method of Liapunov and Krasovskii's theorem (*3*), techniques which are described fully in the reference cited above.

THE SYSTEM EQUATIONS

The system under consideration is a well-stirred reactor in which a homogeneous reaction is taking place. It can be described by energy and material balances which yield

$$\left.\begin{aligned} \rho V C_p \frac{dT}{dt} &= \Delta H V r - U A_R (T - T_A) - \rho q C_p (T - T_o) \\ V \frac{dc}{dt} &= -Vr - q(c - c_o) \end{aligned}\right\} \quad (1)$$

The dependent variables, temperature and/or concentration, are to be controlled in this system. A feedback controller responds to changes in these variables and improves system behavior through its effect on another variable of the system called a "manipulating" variable. A typical control scheme might control reactor temperature for example by manipulating the heat transfer coefficient. For this system there are eight possible combinations of the control variables (T, c) and the principle manipulating variables (T_o, T_A, c_o, U) if the controller input and output are taken one variable at a time. A sizable increase in this number will result if the control or manipulating variables are to act or respond in concert. Since such control schemes require very rapid computational facilities, this last consideration raises questions concerning the applicability of computers to control. In what follows all eight simple loops and some combination controls are discussed. It is simplest to study each possible manipulating variable in a sequence of cases. The flow variable q is not included; it is straightforward in principle but does not seem to be of any practical interest.