Chemical Reactor Stability and Sensitivity

Olegh Bilous and Neal R. Amundson, University of Minnesota, Minneapolis, Minnesota

The purpose of this paper is to consider the well agitated continuous reactor from the standpoint of stability of the steady state. It has been shown in the past that chemical-reaction systems may be unstable in the sense that on slight perturbation they tend to move to a more stable state or that they are stable in their steady states, small perturbations being self-correcting so that the system possesses autoregulation. In this paper methods of developing criteria for the quantitative determination of stability or instability are presented and applied to some simple problems. In order that the effect of large perturbations on the system may be determined, complete solutions of the rigorous equations are obtained on the analogue computer (R.E.A.C.). A complete plot of reaction paths in the concentration-temperature plane may be obtained in this manner. Because of the nonlinearity of the system one cannot predict with certainty what steady state will be approached after a given large perturbation, multiple steady states being assumed possible. From the phase plot of reaction paths the regions in the plane which lead to certain steady states are delineated. Also it is shown that the natural behavior of a reactor is not to approach an unstable state. So far as the reactor is concerned, the unstable state does not exist. The stability of the system is important to the engineer, as control will be easy or difficult and product quality will be satisfactory or not depending upon the relative stability of the steady state. An unstable state would require more elaborate control than a stable state.

The rational design of chemical reactors is a problem of primary interest to the chemical engineer. The theory and practice of catalytic-reactor design is still in a somewhat awkward stage; however, the design of homogeneous reactors can be approached with some confidence whether they be tubular, batch, or the well-agitated continuous type. In particular, the behavior of the continuous stirred tank reactor because of its simplicity and constancy of conditions may be predicted with ease. These reactors have been discussed in detail by MacMullin and Weber(*10*), Denbigh(*2*), Denbigh, Hicks and Page(*3*), Eldridge and Piret(*4*), and Tiller(*16*), all of whom concerned themselves with the steady state. Mason and Piret(*11*) considered the transient behavior of linear systems, that is, isothermal systems in which all reactions are kinetically of the first order. Van Heerden(*17*) considered the nature of the steady state and showed that steady states may be of different types, being stable, autoregulatory, or unstable, the stability manifesting itself in the tendency of the reactor to stay at that state. Salnikov(*15*) has discussed the problem of periodic phenomenon in reaction systems and Frank-Kamenetski(*5, 6, 7*) and Gevart(*7*) have considered similar problems.

It is the purpose of this paper to investigate these problems more deeply and to develop methods of calculation and criteria for the stability or instability of the system. Analytic solutions of the transient behavior will not be developed or needed even though the term *instability* has inherent in it the notion of time. Rather, the methods of nonlinear mechanics as developed and used by Poincare(*13, 14*), Liapounoff(*9*), Minorsky(*12*), and others will be used. These methods are useful in investigating the effect of a small perturbation on the system. In order to investigate the effect of large perturbations an analogue computer has been used to generate solutions of the differential equations and to show very graphically the nature of the approach to the steady state.

It should be pointed out that this paper will deal with the chemical system alone and does not involve instabilities introduced by a control element operating at a time lag. This is another problem altogether and will be treated at another time. The problem here is that of a chemical reaction, exothermic in nature, and the effect on it of large or small perturbations in the conditions under which the reaction is carried out.

In general for stability problems there are two techniques available. The frequency-response technique has been for years widely used by electrical engineers in circuit analysis and feedback amplifier design. Problems in mechanics have been analyzed by perturbation methods. Both these methods will be used in this paper and the succeeding ones. In addition, the whole phase plane may be produced by the use of the analogue computer. These problems should be of interest to the engineer concerned with automatic control, for it is obvious that if the steady state is unstable the difficulty of control will be increased. Stable states, as will be shown, are states in which the reactor tends to remain; the system then possesses autoregulation, and control should be simple.

Most of the analysis, for the sake of illustration only, will be on a very simple system, but the methods do not have this restriction. The perturbation method can be applied to systems of arbitrary complexity, and the use of the analogue computer is limited only by the particular machine available.

THE PERTURBATION METHOD

Consider a well-agitated continuous reactor as shown in Figure 1. This may be a single reactor or it may be one of a series of many such. In a reaction $A \rightarrow B$, irreversible, exothermic, and kinetically of the first order, q is the volumetric flow rate of the influent, k the specific reaction velocity constant, T_s the temperature of operation, T' the average temperature of the coolant in the coil, and U the product of area and heat transfer coefficient. A_0 is the concentration of A in the influent and A_s the concentration in the reactor. If V is the volume of the reactor, a mass balance gives

$$qA_o - qA_s - k_s V A_s = 0$$

from which

$$A_s = \frac{qA_o}{q + k_s V} \tag{1}$$

Implicit here is that T_s has been specified so that k_s is fixed. A steady state heat balance gives

$$qc\rho\,(T_o - T_s) - k_s A_s V\,(\Delta H) - U\,(T_s - T') = 0 \tag{2}$$

and therefore the remainder of the parameter must be fixed in order to satisfy this condition. The two numbers which emerge from the calculation are A_s and T_s.

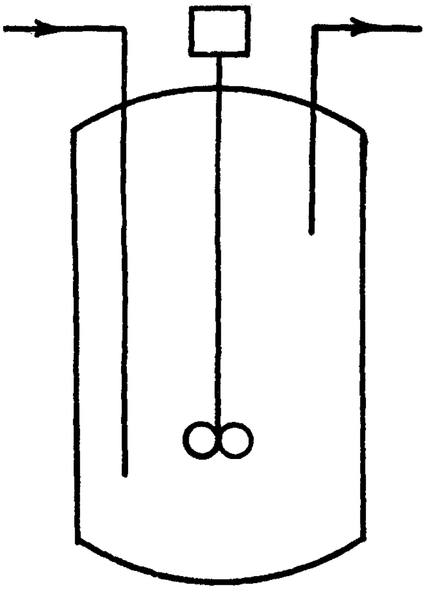
If the parameters which were previously fixed remain fixed except for the temperature T and concentration A, Equations (1) and (2) may then be combined to give a single equation

$$qc\rho\,(T - T_o) - U\,(T' - T) = -V\,(\Delta H) p e^{-E/RT} \frac{qA_o}{q + Vpe^{-E/RT}} \tag{3}$$

where

$$k = pe^{-E/RT}, -\Delta H > 0$$

Olegh Bilous is at present with the Laboratoire Central des Poudres, Paris, France.



↑Fig. 1. Schematic diagram of well-agitated continuous reactor.

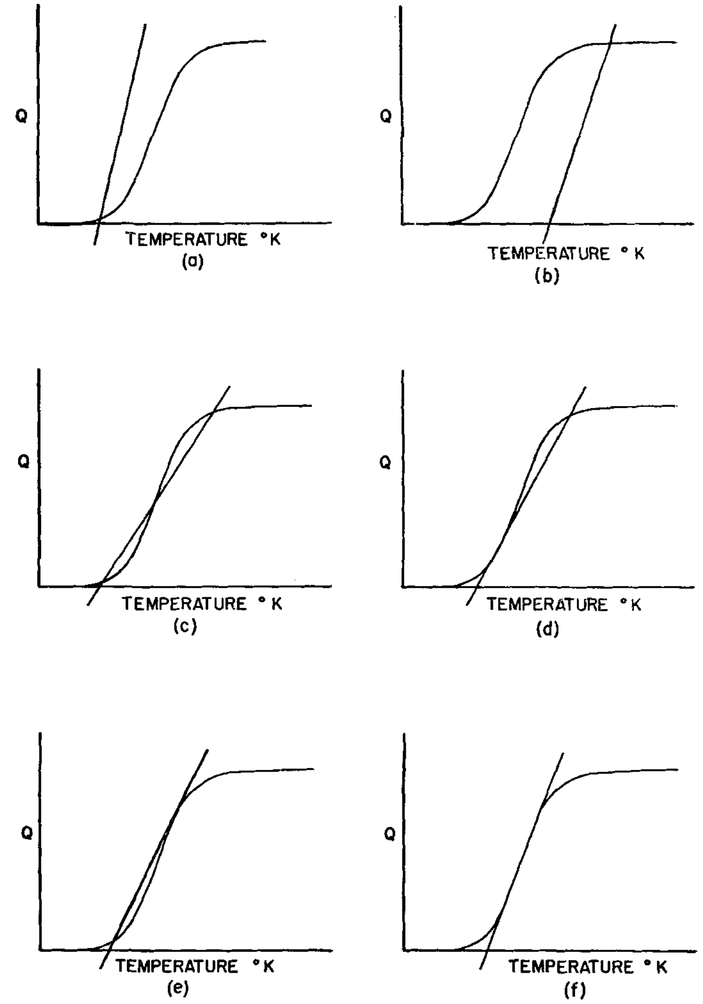
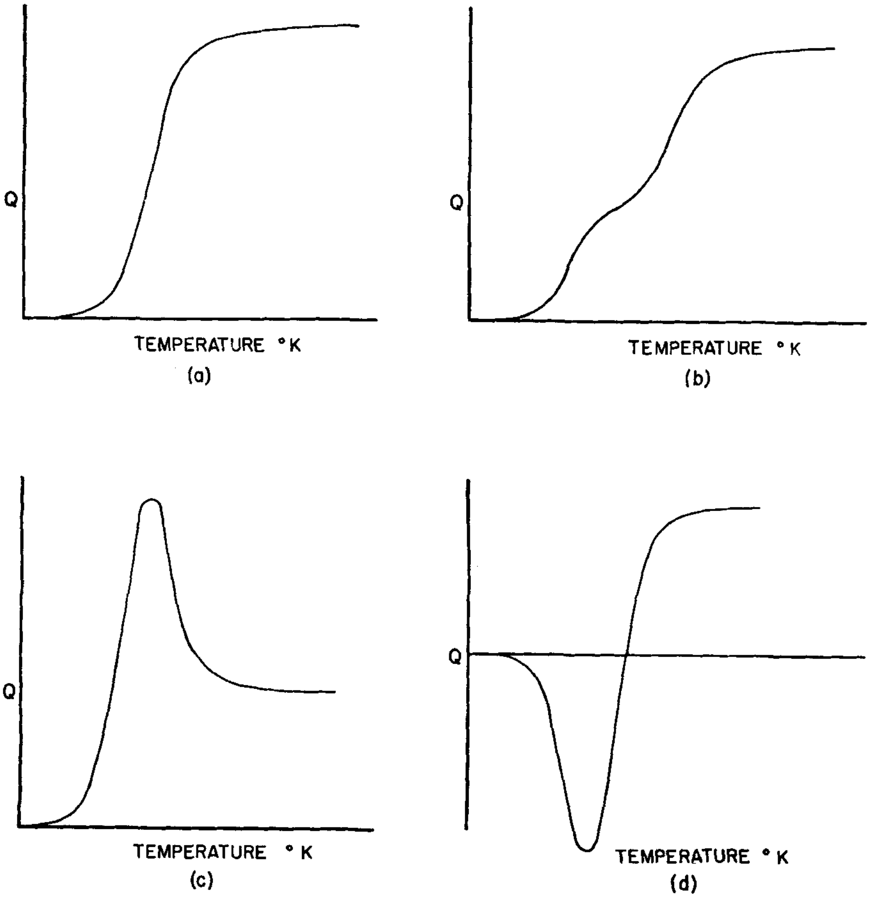


Fig. 2. Schematic plots of heat generation and heat consumption vs. temperature; six possible cases.→

↓Fig. 3. Schematic plots for (a) $A \rightarrow B, -\Delta H > 0$, (b) $A \rightarrow B \rightarrow C$—both reactions exothermal; (c) and (d) $A \rightarrow B \rightarrow C$—one reaction exothermal and one endothermal.



This is an algebraic equation from which one can determine the temperature of operation. The left-hand side of Equation (3) represents the rate of heat consumption in the reactor and the right-hand side is the rate of heat generation. When q, c ρ, U are assumed constants, the left-hand side is a linear function of T and the right-hand side has a sigmodial shape, as shown in Figure 3*a*. Figure 2*a* shows the left- and right-hand sides plotted as functions of T, and the temperature of operation is certainly given by the intersection of the two curves. It is readily apparent that there are six possible cases as shown in Figure 2. The analysis of van Heerden (*17*) may be applied. If there is a single intersection as in Figures 2*a* and *b* the reactor is stable. Three distinct intersections as in Figure 2*c* produce two stable points and the middle unstable point. Figures 2*d* and *e* have each a stable point and a tangency implying a one-sided stability, which really implies instability. Figure 2*f* contains a tangent at the point of inflection, and by van Heerden's analysis is stable although a reactor operated under these conditions would probably show sustained oscillations if perturbed. This point is unsettled at the moment. Thus three distinct intersections always produce one unstable point in the middle. Single intersections are always stable. Other pathological cases produce instabilities which probably would not occur in practice.

Systems of other types may be analyzed by this method although the sigmoidal curve may change its shape under some conditions, usually extreme. In Figure 3 are given three other than the one considered above. They arise from the following situations where the reaction is of the general form:

$$A \xrightarrow{(1)} B \xrightarrow{(2)} C$$

Figure 3*b* $(-\Delta H_1) > 0$, $(-\Delta H_2) > 0$
Figure 3*c* $(-\Delta H_1) > 0$, $(-\Delta H_2) < 0$
Figure 3*d* $(-\Delta H_1) < 0$, $(-\Delta H_2) > 0$

and with suitable activation energies. It is easy to see that a multiplicity of states might arise with stable and unstable states in close proximity. In Figure 3*b* if the number of reactions is increased the number of bumps on the curve may be increased for suitable activation energies, and a profusion of stable and unstable states may result. The existence of a real reaction system as in Figure 3*b* is questionable.

This sort of stability is defined in terms of a small perturbation of the system and the return of the system to its original unperturbed state. If the system exhibits a desire to go elsewhere after slight irritation, perhaps to some more desirable state, the system is said to be unstable. This psychoanalysis of the reactor is essential, since the engineer must choose a control instrument which will live in harmony with the reactor.

In order to investigate the instability analytically, Equations (1) and (2) will be rewritten in their transient forms; thus

$$qA_o - qA - pVe^{-E/RT}A = V\frac{dA}{d\theta} \qquad (4)$$

$$qc\rho\,(T_o - T) - pe^{-E/RT}AV\,(\Delta H) - U\,(T - T') = Vc\rho\frac{dT}{d\theta} \qquad (5)$$

These equations are nonlinear and their analytic solutions probably unobtainable. However, they are of a form which appears in much of the theory of nonlinear mechanics (*12*). The equations can be linearized by taking their first-order linearization by Taylor series about the steady state position. Then it may be supposed that

$$a = A_s - A$$
$$t = T_s - T$$

and the linearization may be taken by the rule

$$f\,(x_o + h, y_o + k) = f\,(x_o, y_o) + h\left(\frac{\partial f}{\partial x}\right)_{x_o,\,y_o} + k\left(\frac{\partial f}{\partial y}\right)_{x_o,\,y_o}$$

Equations (4) and (5) then can be written in the form

$$\frac{da}{d\theta} = -a_{11}\,a - a_{12}\,t \qquad (6)$$

$$\frac{dt}{d\theta} = -a_{21}\,a - a_{22}\,t \qquad (7)$$

with

$$a_{11} = \frac{q}{V} + pe^{-\frac{E}{RT_s}},\ a_{12} = pA_s\frac{E}{RT_s^2}e^{-\frac{E}{RT_s}},\ a_{21} = p\frac{\Delta H}{c\rho}e^{-\frac{E}{RT_s}},$$

$$a_{22} = \frac{q}{V} + p\frac{\Delta H}{c\rho}A_s\frac{E}{RT_s^2}e^{-\frac{E}{RT_s}} + \frac{U}{Vc\rho}$$

Equations (6) and (7) are simple linear equations which may be solved with ease. The solution, however, is not needed. If the steady state is to be stable, that is, if the system is to return to that steady state after being perturbed, these small perturbations, *a* and *t*, must damp out to zero with increasing time. Since the solution to Equations (6) and (7) occurs in the form of exponentials, stability may be expected only if the characteristic equation has roots whose real parts are negative; i.e.

$$\begin{vmatrix} -a_{11} - \gamma & -a_{12} \\ -a_{21} & -a_{22} - \gamma \end{vmatrix} = 0$$

has two roots γ_1 and γ_2 with negative real parts. In this case the characteristic equation is a quadratic

$$\gamma^2 + (a_{11} + a_{22})\,\gamma + a_{11}\,a_{22} - a_{12}\,a_{21} = 0$$

and

$$\gamma_1, \gamma_2 = \frac{-(a_{11} + a_{22}) \pm \sqrt{(a_{11} + a_{22})^2 - 4\,(a_{11}a_{22} - a_{12}a_{21})}}{2}$$

The roots will have negative real parts if, and only if,

$$a_{11} + a_{22} > 0$$

$$a_{11}\,a_{22} - a_{12}\,a_{21} > 0$$

or

$$\frac{2q}{V} + k_s + \frac{U}{Vc\rho} > k_s\left(\frac{-\Delta H}{c\rho}\right)A_s\frac{E}{RT_s^2} \qquad (8)$$

$$\frac{q}{V} + k_s + \frac{U}{Vc\rho} + k_s\frac{U}{qc\rho} > k_s\left(\frac{-\Delta H}{c\rho}\right)A_s\frac{E}{RT_s^2} \qquad (9)$$

and these are necessary and sufficient conditions. Note that the criteria for stability or instability are given in terms of steady state values and no transients need be calculated. Therefore the calculations made for steady state design are also sufficient for the determination of the stability. Equations (8) and (9) taken together give necessary and sufficient criteria for the determination of the stability or instability of the system provided that the linearized equations decribe the nonlinear system. It is not obvious that it should be so, and Liapounoff (*9*) showed that the linearization about the steady state and the subsequent analysis of the linear system was a valid operation and described the physical system in the neighborhood of the steady state, provided the system was either definitely stable or unstable. Perhaps this seems so obvious that the reader doubts the necessity of pressing the point. To illustrate that there is some difficulty here, one sees that if the characteristic equation has pure imaginary roots, i.e., if $a_{11} + a_{22} = 0$, $a_{11}a_{22} - a_{12}a_{21} > 0$, the linear system would exhibit sustained oscillations since the solution would be expressed in terms of trignometric functions, and one would be tempted to say that the nonlinear system must also exhibit oscillations. One has only to recall the treatment of the pendulum in elementary mechanics to fall into such a mistake. However, Liapounoff's theorem holds only for systems which are definitely stable or unstable and it may be shown that when the linearized system exhibits oscillations the nonlinear system may have any of the three behaviors, i.e., stable, unstable, or oscillatory.

Hence in order to examine for stability one must investigate the characteristic equation, to determine the nature of the roots. The system is stable if all roots have negative real parts and unstable if there is one root with a positive real part. For example, if a chemical system has reactions, both simultaneous and consecutive, taking place with chemical species A_i, the system of linearized equations will be of the form

$$\frac{da_1}{d\theta} = a_{11}a_1 + a_{12}a_2 + \cdot\cdot\cdot\cdot\cdot + a_{1,\,n-1}a_{n-1} + a_{1,\,n}t$$

$$\frac{da_2}{d\theta} = a_{21}a_1 + a_{22}a_2 + \quad \cdot\cdot\cdot \quad + a_{2,\,n-1}a_{n-1} + a_{2,\,n}t$$

$$\vdots$$

$$\frac{da_{n-1}}{d\theta} = a_{n-1,\,1}a_1 + a_{n-1,\,2}a_2 + \cdot + a_{n-1,\,n-1}a_{n-1} + a_{n-1,\,n}t$$

$$\frac{dt}{d\theta} = a_{n,\,1}a_1 + a_{n,\,2}a_2 + \quad \cdot\cdot \quad + a_{n,\,n-1}a_{n-1} + a_{n,\,n}t$$

with a_{ij} dependent upon the steady state parameters. If the roots of

$$\begin{vmatrix} a_{11}-\gamma & a_{12} & a_{1,\,n} \\ a_{21} & a_{22}-\gamma & a_{2,\,n} \\ \vdots & & \\ a_{n,\,1} & a_{n,\,2} & a_{n,\,n}-\gamma \end{vmatrix} = 0$$

have negative real parts the system is stable. This is a polynomial of the nth degree of the form

$$b_0\gamma_n + b_1\gamma^{n-1} + \cdot\cdot\cdot + b_{n-1}\gamma + b_n = 0.$$

The Routh-Hurwitz(*8*) criterion may be used to determine the character of the roots. The necessary and sufficient condition that this polynomial have roots with negative real parts is that the successive determinants

$$\Delta_1 = b_1;\ \Delta_2 = \begin{vmatrix} b_1 & b_0 \\ b_3 & b_2 \end{vmatrix};$$

$$\Delta_3 = \begin{vmatrix} b_1 & b_0 & 0 \\ b_3 & b_2 & b_1 \\ b_5 & b_4 & b_3 \end{vmatrix};\text{etc.}$$

and in general

$$\Delta_r = \begin{vmatrix} b_1 & b_0 & 0 & 0 & 0 & 0 & 0 \\ b_3 & b_2 & b_1 & b_0 & 0 & 0 & 0 \\ b_5 & b_4 & b_3 & b_2 & b_1 & b_0 & 0 \\ \vdots & & & & & & \\ b_{2r-1} & b_{2r-2} & b_{2r-3} & & & & b_r \end{vmatrix}$$

should all be positive, it being understood that where $b_r, r > n$ appears in the determinant, it is to be replaced by zero. There are other methods for determining the character of the roots of such an equation, and these can be found in standard works on servomechanism theory. It should be noted that the Routh-Hurwitz criterion leads in the case considered above to Equations (8) and (9). It would be desirable to have a method for the determination of the character of the latent roots of a matrix directly without the polynomial reduction, but no general method is available. There are some special results in this direction, but the matrix of coefficients which arises generally possesses no special simplifying properties.

Example 1. A reactor operates on the simple first-order, irreversible, exothermic reaction, $A \rightarrow B$. The following values of the parameters have been fixed:

$\rho = 1$ g./cc.
$c = 1$ cc./(g.) (°C.)
$q = 10$ cc./sec.
$V = 2000$ cc.
$U = 1.356$ cal./(°C.) (sec.)
$-\Delta H = 10{,}000$ cal./mole
$T_o = 300$°K.
$A_o = 0.005$ mole/liter
$k = 7.86\ (10^{12}) \exp(-22{,}500/RT)$
$T' = 305$°K.

The graphical or algebraic method will show that there are three intersections or steady states with these parameters

$A_s \times 10^3$	T_s	k_s
4.42	306	6.6×10^{-4}
1.67	330	1.00×10^{-2}
1.57	330.8	1.09×10^{-2}

Direct computation will show that Equations (8) and (9) are satisfied simultaneously for the lowest and highest conversions but are not satisfied for the intermediate case. This example is interesting because of the closeness of the two upper states. It is apparent that difficulty of operation would result at any but the state of lowest conversion.

Example 2. Suppose the following reactions are carried out.

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + F, \quad \Delta H_1$$

$$C \overset{k_3}{\rightarrow} E \quad , \quad \Delta H_2$$

The transient equations which describe an arbitrary displacement from the steady state are

$$hA_0 - hA - k_1AB + k_2CF = \frac{dA}{d\theta}$$

$$hB_0 - hB - k_1AB + k_2CF = \frac{dB}{d\theta}$$

$$hC_0 - hC + k_1AB - k_2CF - k_3C = \frac{dC}{d\theta}$$

$$hF_0 - hF + k_1AB - k_2CF = \frac{dF}{d\theta}$$

$$h(T_0 - T) - (k_1AB - k_2CF)\left(\frac{\Delta H_1}{c\rho}\right) - k_3C\left(\frac{\Delta H_2}{c\rho}\right) - \frac{U}{Vc\rho}(T - T') = \frac{dT}{d\theta}$$

If the perturbations from the steady state are defined by

$$t = T - T_s$$
$$a = A - A_s$$
$$b = B - B_s$$
$$c = C - C_s$$
$$f = F - F_s$$

the linearized perturbations about the steady state may be written. These will constitute a homogeneous set of first-order linear differential equations. The matrix whose latent roots must have negative real parts to ensure stability is

$$\begin{bmatrix} -h-k_{1s}B_s & -k_{1s}A_s & k_{2s}F_s & k_{2s}C_s & -X_s \\ -k_{1s}B_s & -h-A_sk_{1s} & k_{2s}F_s & k_{2s}C_s & -X_s \\ k_{1s}B_s & k_{1s}A_s & -h-k_{2s}F_s-k_{3s} & -k_{2s}C_s & -X_s \\ k_{1s}B_s & k_{1s}A_s & -k_{2s}F_s & -h-k_{2s}C_s & X_s \\ M_s & N_s & P_s & Q_s & -h-Z_s \end{bmatrix}$$

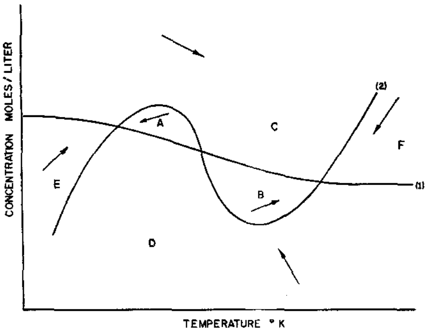


Fig. 4. Qualitative plot showing trends of reaction paths.

where

$$M_s = -k_{1s}B_s\frac{\Delta H_1}{c\rho}$$

$$N_s = -k_{1s}A_s\frac{\Delta H_1}{c\rho}$$

$$P_s = k_{2s}F_s\frac{\Delta H_1}{c\rho} - k_{3s}\frac{\Delta H_2}{c\rho}$$

$$Q_s = k_{2s}C_s\frac{\Delta H_1}{c\rho}$$

$$X_s = k_{1s}A_sB_s\frac{E_1}{RT_s^2} - k_{2s}C_sD_s\frac{E_2}{RT_s^2}$$

$$Y_s = X_s - k_{3s}\frac{E_3}{RT_s^2}C_s$$

$$Z_s = -X_s\frac{\Delta H_1}{c\rho} - \frac{U}{Vc\rho} - k_{3s}\frac{E_3}{RT_s^2}C_s\frac{\Delta H_2}{c\rho}$$

Five equations must be written as the perturbations must be arbitrary. The task of determining the latent roots of a matrix of large order can be carried out with facility with new high-speed computation equipment.

It may be of interest to consider the stability of the corresponding isothermal system; that is, to consider only perturbations which alter the concentrations, on the assumption that temperature control and mixing are instantaneous. The secular determinant is then

$$\begin{vmatrix} -h-\bar{a}-\gamma & -\bar{b} & \bar{c} & \bar{f} \\ -\bar{a} & -h-\bar{b}-\gamma & \bar{c} & \bar{f} \\ \bar{a} & \bar{b} & -h-c-\bar{g}-\gamma & -\bar{f} \\ \bar{a} & \bar{b} & -\bar{c} & -h-\bar{f}-\gamma \end{vmatrix} = 0$$

with

$$\bar{a} = k_{1s}B_s, \bar{b} = k_{1s}A_s, \bar{c} = k_{2s}F_s,$$

$$\bar{f} = k_{2s}C_s, \bar{g} = k_{3s}.$$

This determinant may be expanded to give

$$(h+\gamma)^2\,[(h+\gamma)^2 + (h+\gamma)\,(a+b+c+f+g) + g\,(a+b+f)] = 0$$

and the γ's satisfying this equation have negative real parts. Thus the isothermal system is always stable.

Certainly these methods may be generalized to any chemical system for the continuous stirred reactor, however complex may be the kinetics. The physical mechanism of instability is clear and needs no elucidation. It would be interesting to investigate the oscillatory state, but from a practical point of view this cannot be much more than a curiosity since, seemingly, it would require a coincidental choice of parameters.

NATURE OF THE APPROACH TO THE STEADY STATE

Reactors are generally brought to a steady state in practice by a coaxing and coercing process bringing temperatures and concentrations to the desired point. This may be easy or difficult and it is the purpose of this section to study in detail, not this process, but rather the natural behavior of a reactor in the region or neighborhood of its steady states. For simplicity only the simple case $A \rightarrow B$, first order, will be considered, but the generalization to more complex systems may be carried out. The two transient equations (4) and (5) may be written in the form

$$\frac{dA}{d\theta} = a_1 - b_1A - c_1Ae^{-E/RT} \qquad (10)$$

$$a_i > 0, b_i > 0, c_i > 0$$

$$\frac{dT}{d\theta} = a_2 - b_2T + c_2Ae^{-E/RT} \qquad (11)$$

For the plane A, T, if in Equations (10) and (11) $dA/d\theta$ and $dT/d\theta$ are set equal to zero, two equations result which may be plotted in this A, T plane to give, respectively, the curves 1 and 2 in Figure 4. On curve 1, $dA/d\theta = 0$, and on curve 2, $dT/d\theta = 0$. For fixed T, as A is increased

$$a_1 - b_1A - c_1Ae^{-E/RT}$$

decreases. Similarly, for fixed T, as A is increased

$$a_2 - b_2T + c_2Ae^{-E/RT}$$

increases. Therefore above curve 1 $dA/d\theta < 0$, and below curve 1, $dA/d\theta > 0$, since it is zero on curve 1. Likewise above curve 2, $dT/d\theta > 0$, and below curve 2, $dT/d\theta < 0$. In the six regions of the A, T plane the following values appear:

	$dA/d\theta$	$dT/d\theta$
A	neg	neg
B	pos	pos
C	neg	pos
D	pos	neg
E	pos	neg
F	neg	pos

The steady state for the reactor is defined by the parameters a_i, b_i, and c_i and there are three such states at the three intersections. From the earlier argument the two extreme states are stable but the middle one is unstable. Any point on the A, T plane is a possible transient state for the reactor, and in undergoing the transient the reactor must ultimately end at one of the three states. Attached to every point on this plane is a vector pointing in the direction which the reactor coordinates will move on this plane. In region C, $dA/d\theta < 0$, $dT/d\theta > 0$, and hence the reactor must move in the general direction indicated by the arrow. It must continue to move in this direction until it crosses over into region F, where, because of the sign of the derivatives, it must move as the arrow indicates. In region B the arrow points upward and to the right and it appears that the right-hand steady state will be approached perhaps even by transient states, which are initially closer to the left-hand steady state. In regions A and B the vectors will point away from the unstable state, and hence this appears to be a state toward which a reactor would never naturally tend. It is clear that this method could be made quantitative by a numerical scheme and the whole plane could be filled in with reaction paths. Thus one could consider any point on the plane as an initial point, resulting from start up or from a large perturbation, and could calculate and plot on such a diagram the time history of the reactor in its approach to the steady state. This would be a difficult task and it is easier and quicker to accomplish this on an analogue computer.

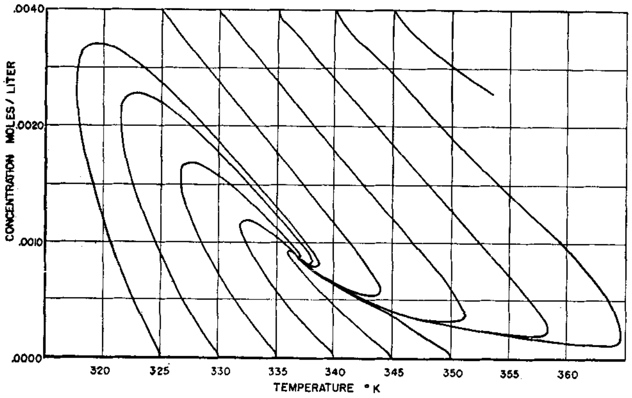


Fig. 5a. Reaction paths for a single stable state.

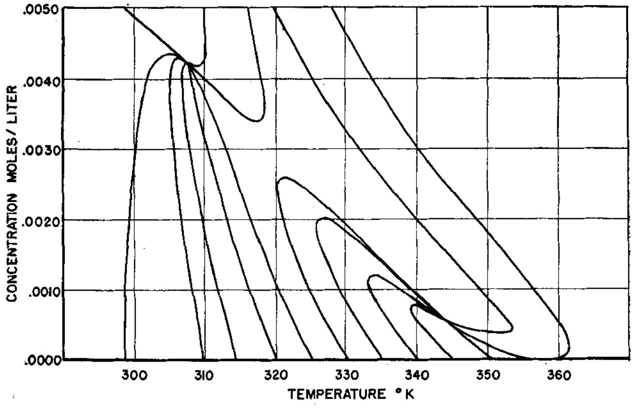


Fig. 5b. Reaction paths for a system with three steady states; $q = 10$ cc./sec.

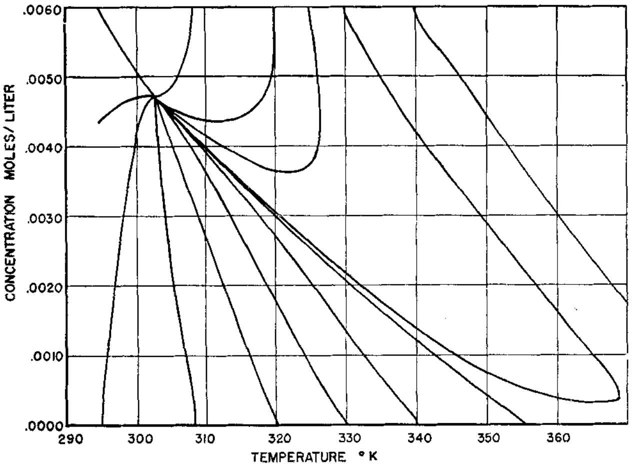


Fig. 5c. Reaction paths for a system with one stable state; data same as in Figure 5b except that $q = 20$ cc./sec.

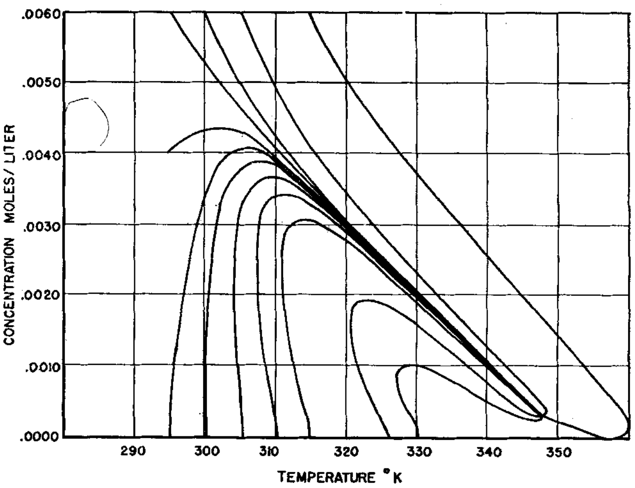


Fig. 5d. Reaction paths for a system with one stable state; data same as in Figure 5b except that $q = 5$ cc./sec.

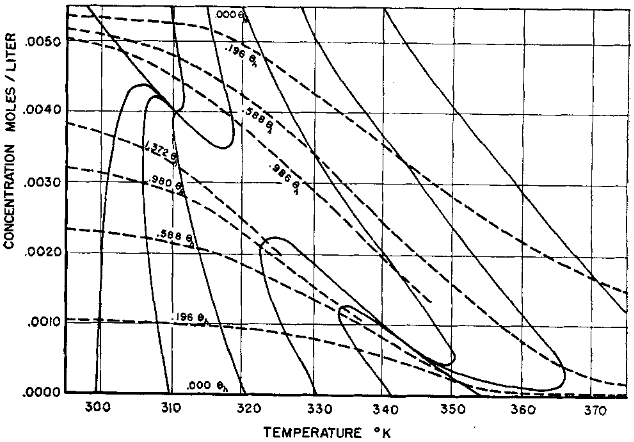


Fig. 5e. Reaction paths for a system with two stable states with a superimposed time grid, $\theta_h = V/q$.

With this end in view Equations (10) and (11) were programmed for the Reeves electronic analogue computer (R.E.A.C.) (*1*) and the reaction paths obtained. Figure 5 was obtained by this method and the curves shown are the actual traces made by the pen on the plotting board. On the R.E.A.C. one may obtain the two plots A vs. θ and T vs. θ, or one may use the plotting board and feed A and T to pens to obtain the reaction paths directly. The latter method was chosen as it illustrates more graphically reactor behavior.

In Figure 5*a* are shown the reaction paths for a single intersection at a high temperature such as in Figure 2*b*. The numerical data used are not important; suffice it to say that they are not much different from those of Example 1. All transient states lead to the same stable steady state. In Figure 5*b* the data would produce three steady states, one of which is unstable. In this case a flow rate of $q = 10$ cc./sec. was used, and this plot bears out the qualitative argument used above. The unstable state is approached on no reaction path and the plane seems to be divided into two domains by a line (not drawn) such that all transients in one part lead to one steady state while all transients in the other part lead to the other steady state. Two transient states

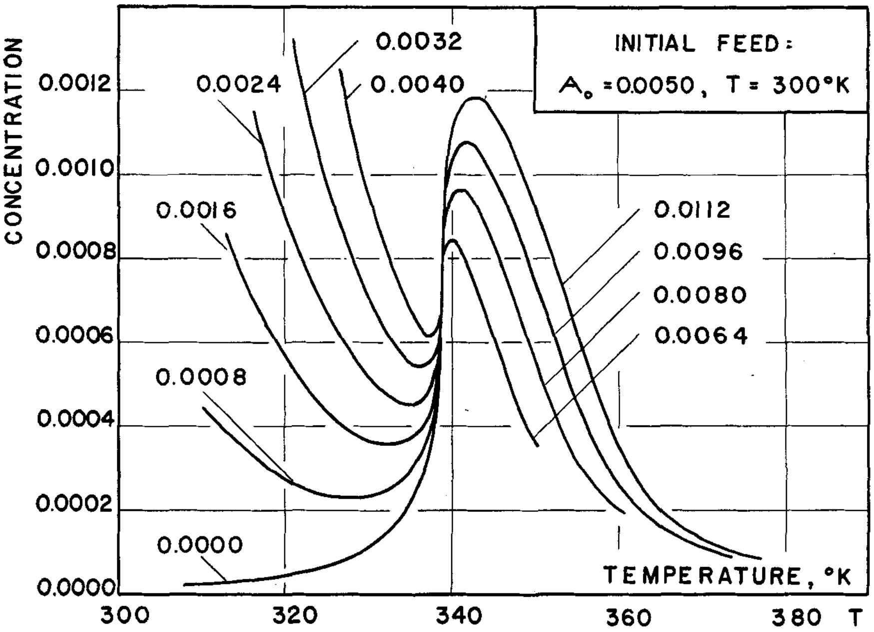


Fig. 6. Transient behavior caused by a step function in the feed showing overshoot. Numbers on curves refer to new feed concentration.

which are very close initially might lead to widely different steady states.

If the data for Figure 5*b* are kept unchanged except that the flow rate is increased to $q = 20$ cc./sec., then Figure 5*c* results. The high-conversion steady state is wiped out completely, as it should be, because the slope of the heat-consumption curve increases. There are some transient states however at which the reactor appears to be seeking a high-conversion steady state. None existing, it must then return to the low conversion state.

If the flow rate instead of being doubled is cut in half, $q = 5$, the low-conversion state is wiped out, and the reactor approaches only the high conversion state, as shown in Figure 5*d*. It appears, however, that transients would prefer to go to a low-conversion steady state but are forced to converge to a high-conversion state.

On each reaction path there is implicit a time scale and in theory it would require infinite time to traverse a single path, the speed along the path becoming less and less as the steady state is approached. This manifests itself on the computer in exactly the same way. In Figure 5*e*, Figure 5*b* is essentially reproduced except that during the course of tracing out the reaction paths a record was kept of the elapsed time and a time grid then superimposed on the totality of reaction paths. In this way the time for various transients can be compared.

One further study was made in connection with the transient from one steady state to another. It was supposed that the reactor had been operated at an influent concentration $A_0 = 0.005$ and $T_0 = 300$°K. At $\theta = 0$ a step change in feed concentration is made. As shown in Figure 6, if the step is positive the concentration in the reactor always increases over the prior steady state value and then damps off to a higher conversion, higher temperature steady state. When the step is negative, these trends are inverted.

All these reaction paths show overshoot and false-start phenomena which seem a little surprising. However such systems have been observed by Denbigh, Hicks, and Page(*3*).

It would be interesting to consider other types of steady states such as were discussed in connection with Figures 3 and 2*d*, *e*, and *f*. Some effort was put on this but the practicality of such a discussion is limited and it was decided to put no more time on it since the technique was now clear and reactor behavior had been illustrated and elucidated. These special states are difficult to produce as they require a coincidental choice of parameters. Systems with a high degree of instability are difficult to simulate on the analogue computer and the reason is not hard to find. For if the simulation is a real analogue, one must expect the electric circuit to become unstable also. This seemed to be the case in some of the work since more often than not the capacity of the machine was exceeded in these special cases. A great deal of time was put on the case corresponding to Figure 2*f*. No conclusive results were obtained but indications were that this case would exhibit oscillatory or periodic (limit cycle) reaction paths.

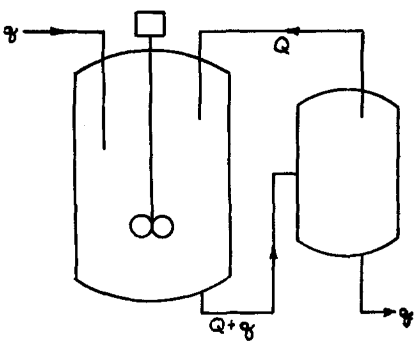


Fig. 7. Schematic diagram of reactor with recycle stream.

In the language of nonlinear mechanics the points of stability appear to be stable nodal points. The points of instability are either saddle points or unstable nodal points. Focal points have not been noticed, but these probably exist in some problems of the type considered here.

One sees thus that the approach to a steady state is not a straightforward procedure but may be rather involved. The unstable state is also recognized as a state which a reactor will not naturally approach. If a perturbation is large, it is also evident that the reactor of its own accord might shift to a new steady state. At stable states the system is autoregulatory, always returning after small perturbations to the same state. Control is thus a simple problem. At unstable states the control must be good as the reactor must be maintained in a state to which it has no natural tendency.

A REACTOR WITH A RECYCLE STREAM

The product from a stirred reactor, *R*, may be supposed to pass to a separating unit, *S*. From this unit a stream rich in unreacted feed is recycled into the reactor while the enriched product passes out. The external and recycle flows are *q* and *Q* respectively. The separating unit might be a distillation column, extractor, crystallizer, settler, etc. The simple reversible reaction, $A \rightleftarrows B$, first order in each direction, is carried out in the schematic system of Figure 7. A linear equilibrium is assumed in the separator and the rate of separation in the separator is the usual one for mass transfer. A and B stand for concentrations as well as chemical species. The transient isothermal equations are easily set up:

$$V\frac{dA}{d\theta} = qA_0 + QA' - (q+Q)A - V(k_1A - k_2B) \qquad (12)$$

$$V\frac{dB}{d\theta} = QB' - (q+Q)B + V(k_1A - k_2B) \qquad (13)$$

$$H\frac{dA'}{d\theta} = (q+Q)A - QA' - SK_A(A' - \alpha A) \qquad (14)$$

$$H\frac{dB'}{d\theta} = (q+Q)B - QB' - SK_B(B' - \beta A_1) \qquad (15)$$

$$h\frac{dA_1}{d\theta} = SK_A(A' - \alpha A_1) - qA_1 \qquad (16)$$

$$h\frac{dB_1}{d\theta} = SK_B(B' - \beta B_1) - qB_1 \qquad (17)$$

The symbols are defined completely at the end of the paper. The first pair of equations describes the reactor. Equations (14) and (15) describe the lean phase where H is the holdup, SK_A is the over-all mass transfer factor, and α is the equilibrium constant for the phase equilibrium. Equations (16) and (17) describe the rich phase. This system of equations could be solved analytically, but the solving of a sixth-order system is a little tedious and so will be omitted. The solution can easily be obtained on the analogue computer, and in fact systems in which the kinetics are more complicated or in which the separation is more complex may also be treated. A particular example will be considered to illustrate what may be done.

Let $\gamma = Q/q$
which may be called a reflux ratio. Suppose

$V = 2000$ liters
$q = 1000$ liters/hr.
$Q = \gamma q$
$h = 500$ liters
$H = 500$ liters
$k_1 = 1.00$ hr.$^{-1}$
$k_2 = 2.00$ hr.$^{-1}$
$SK_A = 1000$ liters/hr.
$SK_B = 2000$ liters/hr.
$\alpha = 5$; $\beta = 0.2$
$A_o = 1$ mole/liter
$B_o = 0$

The transient equations may then be written

$$\frac{dA}{d\theta} + (1.5 + 0.5\gamma)A = 0.5A_0 + 2B + 0.5\gamma A' \qquad (18)$$

$$\frac{dB}{d\theta} + (2.5 + 0.5\gamma)B = A + 0.5\gamma B' \qquad (19)$$

$$\frac{dA'}{d\theta} + (2 + 2\gamma)A' = 2(1 + \gamma)A + 10A_1 \qquad (20)$$

$$\frac{dB'}{d\theta} + (4 + 2\gamma)B' = 2(1 + \gamma)B + 0.8B_1 \qquad (21)$$

$$\frac{dA_1}{d\theta} + 12A_1 = 2A' \qquad (22)$$

$$\frac{dB_1}{d\theta} + 2.8B_1 = 4B' \qquad (23)$$

and the steady state solution is

recycle

$$A_s' = 6A_{1s}$$
$$B_s' = 0.7B_{1s}$$

reactor product

$$A_s = \frac{1+6\gamma}{1+\gamma}A_{1s}$$

$$B_s = \frac{1+0.7\gamma}{1+\gamma}B_{1s}$$

separator product

$$A_s = \frac{2.50 + 1.90\gamma}{3.50 + 7.90\gamma}A_0$$

$$B_{1s} = \frac{1+6\gamma}{3.50 + 7.90\gamma}A_0$$

The product yield increases with the reflux ratio γ,

γ	0	0.50	1.00	2.00	∞
B_1/A_o	0.286	0.537	0.615	0.675	0.760

In practice the reflux ratio would have to be determined by some optimizing process.

The transient, as stated above, was developed on the analogue computer, and Figure 8 shows the effect of a step change in the feed concentration and gives the two concentrations A_1 and B_1 as functions of the time for the case $\gamma = 1$. Each of these curves will become asymptotic to a line which can be calculated from the steady state solution.

In order to study the stability of the system the methods used above could be applied, but it is interesting to approach the problem from the frequency-response technique. For such a system, from control theory, it is known that if L denotes the Laplace transform operator, then the transfer function of the system is

$$G(s) = \frac{L\,(\text{output})}{L\,(\text{input})}$$

where s is the Laplace transform parameter. The product of $G(jw)$, where $j = \sqrt{-1}$ and w is the frequency of the input signal, and the input signal gives the output signal. In this case

$$G(s) = \frac{\begin{vmatrix} 1.5+0.5\gamma+s & -2 & -0.5\gamma & 0 & 0 & 0.5 \\ -1 & 2.5+0.5\gamma+s & 0 & -0.5\gamma & 0 & 0 \\ -2(1+\gamma) & 0 & 2(1+\gamma)+s & 0 & -10 & 0 \\ 0 & -2(1+\gamma) & 0 & 4+2\gamma+s & 0 & 0 \\ 0 & 0 & -2 & 0 & 12+s & 0 \\ 0 & 0 & 0 & -4 & 0 & 0 \end{vmatrix}}{\begin{vmatrix} 1.5+0.5\gamma+s & -2 & -0.5\gamma & 0 & 0 & 0 \\ -1 & 2.5+0.5\gamma+s & 0 & -0.5\gamma & 0 & 0 \\ -2(1+\gamma) & 0 & 2(1+\gamma)+s & 0 & -10 & 0 \\ 0 & -2(1+\gamma) & 0 & 4+2\gamma+s & 0 & -0.8 \\ 0 & 0 & -2 & 0 & 12+s & 0 \\ 0 & 0 & 0 & -4 & 0 & 2.8+s \end{vmatrix}}$$

and after reductions

$$G(s) = \frac{4+24\gamma+(14+2\gamma)\,s+s^2}{P_6(s)}$$

where $P_6(s)$ is a polynomial of the sixth degree in s. System stability may be discussed by applying the Routh-Hurwitz criterion to $P_6(s)$. Also theoretical Nyguist and Bode diagrams may be calculated from the expression for $G(jw)$. If, for example $\gamma = 1$ and the frequency $w = 1$ radian/hr., then

Amplitude ratio $= G(jw) = 0.70$
Phase lag $= \phi = 130°$

These considerations will not be given in more detail here since the elucidation of the method of solution was all that was intended. Clearly the inclusion of heat effects for exothermic reactions, etc., will cause only a complication and in no way alters the method. For recycle systems one should expect instabilities in the system as well as increased sensivity, as a recycle stream in chemical operations would play the same role as feedback in electric circuit and amplifier design.

SUMMARY

In this paper the general character of the steady state operation of the continuous stirred-tank reactor has been considered. It has been shown, after the method of van Heerden, that instabilities may exist in these steady states. Analytical criteria for the determination of stability or instability have been developed. The nature of the approach to the steady state has been investigated both qualitatively and by the use of the R.E.A.C., an analogue computer. It cannot be decided on *a priori* grounds to what steady state a given transient state will lead. This may have been expected by some because of the high degree of nonlinearity of the transient equations. The approach to the steady state is not, in general, simple, and the reaction paths traced by the R.E.A.C. show that unstable states are not approached at all along any reaction paths. As far as the natural behavior of the reactor is concerned, the unstable states do not even exist and, in fact, a reactor which finds itself in the neighborhood of an unstable state makes an effort to leave that neighborhood. This poses problems in the control of such reactors and may explain in part some of the difficulties encountered in their control. It is the conclusion of this paper that steady states should be investigated for stability. It is also the conclusion that an investigation of the reaction path may shorten transient times by a proper juggling of initial conditions.

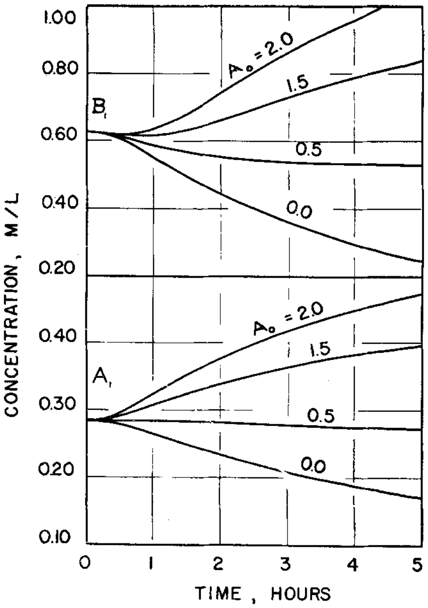


Fig. 8. Effect of step change on the feed with a system with a recycle ratio equal to 1.

The methods of this paper may be extended to systems with arbitrary kinetics and heat effects. The problems were chosen as simply as possible here in order to illustrate the method.

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NOTATION

A,B,C,F, etc. = chemical specie and concentrations in the reactor
A_o,B_o,C_o,F_o, etc. = influent concentration or corresponding specie
A_s,B_s,C_s,F_s, etc. = steady state concentration of corresponding specie
A_1,B_1 = concentration in the rich phase (rich in B)
A',B' = concentration in the lean phase
a,b,c, etc. = perturbations from steady state values
c = specific heat
ΔH = heat of reaction ($-\Delta H>0$, exothermic)
E = activation energy
k = reaction velocity constant
k_s = reaction velocity constant at temperature of steady state
q = influent flow rate
Q = recycle flow rate (recycle problem)
p = frequency factor in reaction velocity constant
SK_A,SK_B = separation-rate constants in separator
T = reactor temperature
T_s = reactor steady state temperature
T' = average coolant temperature in reactor cooling coil
T_o = influent temperature
s = Laplace transform variable
U = product of heat transfer coefficient and surface area in reactor
V = reactor volume

Greek Letters

α,β = equilibrium constant in separator
γ = root of characteristic equation (stability) or recycle ratio (recycle problem)
ρ = density
θ = time

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