Parametric Sensitivity and Runaway in Tubular Reactors

Parametric sensitivity of tubular reactors is analyzed to provide critical values of the heat of reaction and heat transfer parameters defining runaway and stable operations for all positive-order exothermic reactions with finite activation energies, and for all reactor inlet temperatures. Evaluation of the critical values does not involve any trial and error.

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SCOPE

The knowledge of temperature and concentration profiles along a nonisothermal tubular reactor plays a fundamental role in the design, operation and control of such reactors. Specifically, in exothermic gas-solid reactions, the temperature may exhibit sudden sharp increases along the reactor length. When such a phenomenon occurs, the reactor is said to operate in a "runaway" condition, with the associated presence of the so-called "hot spot," which can adversely affect reactor performance.

This problem was first studied by Bilous and Amundson (1956), who pointed out that in some cases, the temperature profile is extremely sensitive to the operational and physicochemical parameters involved; they termed such a reactor condition "parametric sensitivity."

Although a variety of subsequent papers have been devoted to establishing relationships among the reaction and reactor operation conditions governing reactor runaway, previous works have been incomplete and have also required trial and error procedures to obtain such relationships.

Our purpose is to provide easily applicable exact criterion of reactor runaway condition for all positive-order exothermic reactions, using the full Arrhenius temperature dependence of the reaction rate, and for all values of the inlet temperature.

CONCLUSIONS AND SIGNIFICANCE

Based on the method of isoclines, a necessary and sufficient condition for reactor runaway is identified. For all positive-order exothermic reactions, using the full Arrhenius temperature dependence of the reaction rate, and for all reactor inlet temperatures, a simple procedure to obtain critical values of the heat of reaction and heat transfer parameters defining runaway and non-runaway (i.e., "stable") operations is derived. The procedure is explicit, and requires only a single numerical integration to obtain the critical values.

All other parameters being fixed, reactor runaway is more likely as the reaction order decreases, the reaction activation energy increases, or as the inlet temperature of the reaction mixture increases.

INTRODUCTION

Almost simultaneously with the appearance of the work of Bilous and Amundson (1956), Chambré (1956) applied the method of isoclines to establish qualitative features of the nonlinear differential equations that govern steady state behavior of the reactor in the temperature-conversion phase plane. Barkelew (1959) used the same method to integrate these equations for many different cases, and derived empirical criteria between the heat of reaction and reactor cooling parameters to define runaway condition.

Adler and Enig (1964) in studying the mathematically similar problem of combustion of solid materials with finite heats of reaction, defined the occurence of an inflection point in the temperature-conversion phase plane as a criterion for the critical explosion condition. The relation between the critical values of the parameters, for a first-order reaction and large activation energy was obtained numerically.

Due to the large amount of computation involved in this approach, various approximations have been suggested by different authors (Hlaváček et al., 1969; Dente and Collina, 1964; Van Welsenaere and Froment, 1970) in order to obtain simple explicit (although approximate) expressions of the critical parameters.

Some numerical solutions of the problem for different orders of reaction and finite values of the activation energy have been reported by Dente et al. (1966). The criterion derived by these authors is based on the observation that at critical conditions, the temperature versus reactor distance profile has an inflexion point, where also the third derivative vanishes. However, this criterion, as pointed out by Adler and Enig (1964), is always implied by the one based on the temperature-concentration phase plane, while the converse is not true.

Apparently unaware of the work of Adler and Enig (1964), Oroskar and Stern (1979) have recently derived a procedure to determine exact conditions leading to runaway reactor operation for a first-order reaction, using the Frank-Kamenetskii approximation to describe the temperature dependence of the reaction rate.

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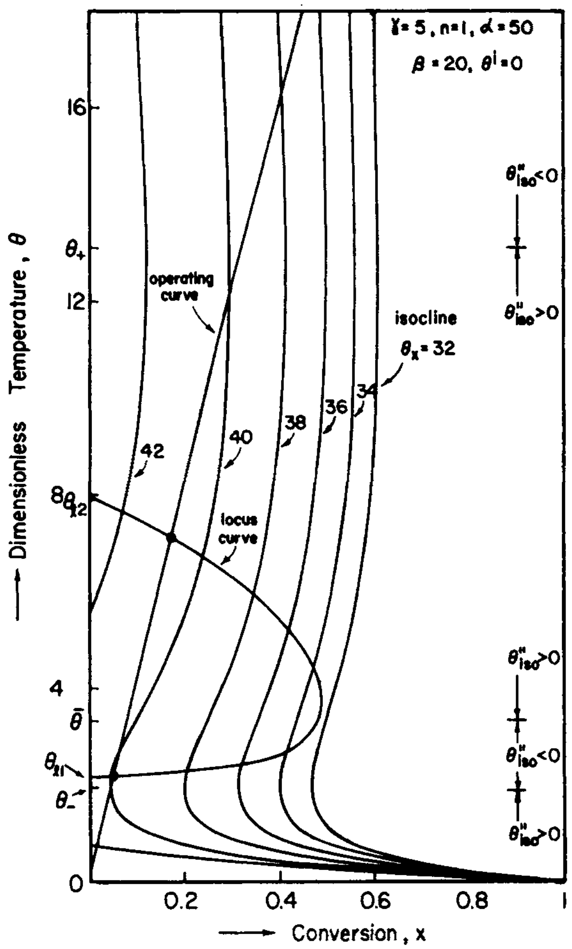


Figure 1(a). Phase plane behavior for an unstable case of a first order reaction with finite activation energy, γ. [● = inflexion point].

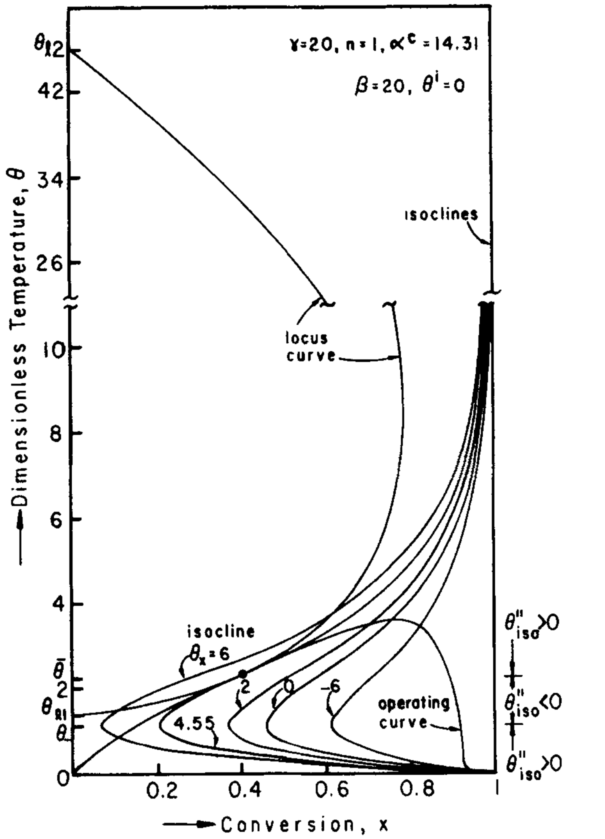


Figure 1(b). Phase plane behavior for a case of criticality (α^c = 14.31) for a first-order reaction with finite activation energy, γ. At the point indicated by ●, the locus curve, the operating curve and the isocline defined by θ_x = 4.55 are *all* tangent. Note that θ_+ = 358.9, and is therefore not shown.

The present paper provides an easily applicable exact criterion of reactor runaway for all positive-order exothermic reactions, using the full Arrhenius dependence of the reaction rate on temperature, and for all reactor inlet temperatures. Based on the method of isoclines, a simple strategy is presented to evaluate, in a *single* numerical integration, the critical values of the heat of reaction and heat transfer parameters which define the separation between runaway and non-runaway (i.e., "stable") reactor operations. This procedure does not involve any trial-and-error required by previous authors (Adler and Enig, 1964; Dente et al., 1966; Hlaváček et al., 1969; Oroskar and Stern, 1979) and therefore considerably reduces the amount of computation required for the evaluation of the critical parameters.

It is worth stressing that this classic parametric sensitivity and runaway problem pertains to the *steady state* character of the tubular reactor, and *not* to its transient behavior.

BASIC EQUATION

Consider an ideal nonisothermal pseudohomogeneous (i.e., a one-phase plug-flow model) tubular reactor operating in the steady state, in which an n-th order reaction occurs. The relation between the temperature and conversion along the reactor length is given by the equation (Aris, 1965):

$$\frac{d\theta}{dx} = \alpha - \beta \frac{\theta g(\theta)}{(1-x)^n} \tag{1}$$

with the initial condition: $\theta = \theta^i$ at $x = 0$, where

$$\alpha = \frac{(-\Delta H)y_A^i}{C_p T_w} \frac{E}{RT_W}; \beta = \frac{4U}{C_p D P^n k_w (y_A^i)^{n-1}}$$

$$\gamma = \frac{E}{RT_w}; \theta = \frac{T - T_w}{T_w} \frac{E}{RT_w} \tag{2}$$

$$k_w = A \exp\left(\frac{-E}{RT_w}\right); g(\theta) = \exp\left[-\frac{\theta}{(1+\theta/\gamma)}\right]$$

and the temperature of the cooling medium (T_w) is assumed constant.

DEFINITIONS AND OBSERVATIONS

Following previous notation (Chambré, 1956; Oroskar and Stern, 1979), we define the following curves:

Operating curve (θ_o) is the solution of Eq. 1.

Isocline (θ_{iso}) is obtained from Eq. 1 considering $d\theta/dx$ as a constant parameter (θ_x):

$$x = 1 - \left[\frac{\beta\theta g(\theta)}{(\alpha - \theta_x)}\right]^{1/n} \tag{3}$$

Each point on this curve, $\theta = \theta_{iso}(x)$, gives the value of the slope of the operating curve at that point, and therefore is very useful for graphical solution of Eq. 1.

Locus curve (θ_l) is the locus of points where the tangent to the isocline at that point, θ'_{iso}, is equal to the value of the parameter θ_x that defines the isocline itself (Figure 1a). In other words, this is the locus of the points where the operating curve is tangent to the isocline. The locus curve $\theta = \theta_l(x)$ is therefore given by the solution of the system:

$$\theta_x = -n\left[\frac{(\alpha - \theta_x)}{\beta\theta g(\theta)}\right]^{1/n} \frac{\theta(1+\theta/\gamma)^2}{[(1+\theta/\gamma)^2 - \theta]} \tag{4a}$$

$$x = 1 - \left[\frac{\beta\theta g(\theta)}{(\alpha - \theta_x)}\right]^{1/n} \tag{4b}$$

It is useful for what follows, to note some characteristics of these curves:

1. The derivative of the isocline

$$\frac{dx}{d\theta} = -\left[\frac{\beta\theta g(\theta)}{(\alpha - \theta_x)}\right]^{1/n} \frac{[(1 + \theta/\gamma)^2 - \theta]}{n\theta(1 + \theta/\gamma)^2} \tag{5}$$

vanishes for two values of θ (Figure 1):

$$\theta_{\pm} = \gamma \frac{(\gamma - 2) \pm [\gamma(\gamma - 4)]^{1/2}}{2} \tag{6}$$

Thus, $d\theta/dx \leq 0$ when $\gamma \leq 4$; so, there is no possibility of runaway for any values of the other parameters. When $\gamma > 4$, $d\theta/dx > 0$ for $\theta_- < \theta < \theta_+$, and < 0 for $\theta > \theta_+$ or $\theta < \theta_-$; also, $d\theta/dx = \infty$ at $\theta = \theta_{\pm}$.

2. All the isoclines defined by values of θ_x smaller than a specific θ_x^* are located in a region of space enveloped by the isocline defined by θ_x^* itself (Figure 1a). This follows from the observation that

$$\left(\frac{\partial x}{\partial \theta_x}\right)_{\theta\, =\, \text{constant}} < 0 \text{ for all } \theta > 0.$$

3. The locus curve has an asymptote at $\theta \to \theta_-$ from above and $\theta \to \theta_+$ from below, as $x \to -\infty$. Recalling that when $\theta \to \theta_-$, $(1 + \theta/\gamma)^2 - \theta \to 0$; it follows from Eq. 4a that $\theta_x \to \alpha$ from below; so from Eq. 4b, $x \to -\infty$. At $x = 0$, the system of Eqs. 4a and 4b has either two solutions, at θ_{l_1} and θ_{l_2}, or no solutions for $\theta \epsilon [\theta_-, \theta_+]$. Therefore, in the range $[\theta_-, \theta_+]$, the locus curve is located in the positive x region of the $\theta - x$ phase plane only for $\theta_{l_1} < \theta < \theta_{l_2}$; if real values θ_{l_1} and θ_{l_2} do not exist, the locus curve is always restricted in the negative x region. It is worth noting that for $0 < \theta < \theta_-$ and for $\theta > \theta_+$, from Eq. 4a, each point on the locus curve is defined by negative values of the parameter θ_x; this means that the locus curve travels in a region where all the isoclines are defined by negative θ_x.

4. The locus curve increases monotonically in the range of $\theta > 0$ where the first derivative of the isocline, θ'_{iso} is positive, and the second derivative, θ''_{iso} is negative. This can be observed from Figure 1a, and readily shown as follows. Recall that the locus curve θ_l is the locus of all points on the isoclines where θ'_{iso} equals θ_x that defines the isocline itself. For a fixed θ, θ'_{iso} is independent of x from Eq. 5. From observation 2 above, for a fixed value of $\theta > 0$, increasing values of x encounter isoclines with smaller θ_x. Thus in the region where $\theta''_{iso} < 0$, increasing values of x require higher θ_{iso} values to be on the locus curve. The locus curve θ_l thus must increase monotonically in the region where $\theta''_{iso} < 0$.

5. Directly from Eq. 1, the operating curve θ_o has values of x, for a given θ, that decrease with increasing α. In other words, as the heat of reaction (α) increases, the same temperature level (θ) is achieved at smaller conversion (x).

6. In the region of the phase plane where $\theta'_{iso} > 0$, for constant θ, the value of x on the locus curve increases with increasing α. This follows from the fact that from Eqs. 4a and 4b:

$$\left(\frac{\partial x}{\partial \alpha}\right)_{\theta\, =\, \text{constant}} > 0 \text{ for } \theta_- < \theta < \theta_+.$$

CRITERIA FOR RUNAWAY CONDITION

The problem under consideration is a *steady state* problem, and so we are not concerned with transient features at all. The problems of instability present in well-agitated reactors are not present in plug-flow tubular reactors. In the former, they arise due to steady state multiplicity; the plug-flow reactor always has a unique steady state which is globally stable to transient perturbations. Non-adiabatic plug-flow tubular reactors, on the other hand, exhibit the phenomenon of parametric sensitivity and runaway (a type of instability, distinct from temporal ones), which are examined here. It is worth reiterating that both these features are for the *steady-state* model.

Before any conditions on the physicochemical parameters that define runaway can be derived, one first needs a definition of runaway itself. It is generally agreed that the occurrence of a "hot spot" in the temperature profile along with the presence of a positive second derivative in the profile of temperature versus conversion *before* the hot spot is a runaway condition for the reactor (Adler and Enig, 1964; Van Welsenare and Froment, 1970). From this definition, it follows that a maximum in the temperature profile along the reactor length is a *hot spot*, but *runaway* operation occurs only with those hot spots which are accompanied by a positive second derivative in the temperature vs. conversion profile *before* the temperature reaches a maximum at the hot spot. The purpose of this study is to identify a relation between the parameters α, β, γ, and θ^i that give rise to a positive second derivative in the temperature-conversion profile.

For the case of $\theta^i < 0$, it can be shown that the value of θ''_o at $\theta = 0$ is always negative. Therefore, runaway condition can only occur in the region of positive θ. This observation allows us to consider in the following only the positive portion of the $\theta - x$ phase plane also for $\theta^i < 0$.

If

$$\theta^i g(\theta^i) \geqslant \alpha/\beta \tag{7}$$

from Eq. 1, $\theta'_o \leqslant 0$ at $x = 0$ and, because the $\theta - x$ profile cannot have a minimum (Varma and Amundson, 1972), the value of θ always decreases; thus, in such cases, runaway can never occur. In what is to follow, we therefore only have to consider conditions violating Eq. 7; i.e., $\theta^i g(\theta^i) < \alpha/\beta$.

It can also be easily observed from Eqs. 1, 4a and 4b that the sign of θ''_o at $x = 0$ and $\theta = \theta^i > 0$ is positive only in the range $\theta_{l_1} < \theta^i < \theta_{l_2}$, and is always negative if θ_{l_1} and θ_{l_2} do not exist; the latter is the case when the locus curve does not intersect the θ-axis in the range $[\theta_-, \theta_+]$ (observation 3). Therefore, if $\theta^i \epsilon\ (\theta_{l_1}, \theta_{l_2})$ runaway condition occurs soon after the reactor entrance, and in the following we need to consider only the case $\theta''_o < 0$ at $x = 0$.

Necessary and Sufficient Condition for Runaway

The necessary and sufficient condition for runaway is that the operating curve is tangent (with positive slope) to an isocline at a point where $\theta''_{iso} < 0$. This means that the operating curve intersects the locus curve at a point where the isocline has negative second derivative.

Proof

To show the *necessary* part, if there is a runaway condition somewhere along the reactor length, the sign of θ''_o must turn from negative (at $x = 0$) to positive. (If θ''_o is positive at $x = 0$, then the reactor is already in runaway condition right at the reactor inlet.) At the transition point $\theta''_o = 0$, and so the operating curve is tangent to the isocline. After the transition $\theta''_o > 0$, due to runaway, and as a consequence of observation 2, the operating curve has to remain above the isocline. Therefore, at the transition point $\theta''_o > \theta''_{iso}$, and so $\theta''_{iso} < 0$.

On the other hand, if the operating curve is tangent to an isocline, then at that point $\theta''_o = 0$. If $\theta''_{iso} < 0$, $\theta''_{iso} < \theta''_o$, and therefore the operating curve will be located in a region above the isocline and, as a consequence of observation 2, after the tangency point, $\theta''_o > 0$; this is runaway condition by definition, and shows the *sufficient* part of the argument.

CRITICALITY CONDITION

Recalling from observations 3 that the locus curve for $\theta < \theta_-$ and $\theta > \theta_+$ is defined by negative values of θ_x, it follows that the operating curve can intersect the locus curve in the range mentioned above, only with a negative slope and so runaway cannot occur. Thus the operating curve, in order to give rise to runaway condition, must intersect the locus curve at values of θ in the range $[\theta_-, \theta_+]$. This observation allows us to define the operating condition of the reactor in some particular cases without solving Eq. 1.

From observation 3 we recall that if the locus curve does not intersect the θ-axis; i.e., the values of θ_{l_1} and θ_{l_2} do not exist, the locus curve for $\theta \epsilon [\theta_-, \theta_+]$ is always restricted in the region of negative conversion; therefore there is again no possibility of runaway. On the other hand, if θ_{l_1} and θ_{l_2} exist, the following possibilities arise:

i) $0 < \theta^i < \theta_{l_1}$: $\theta_0 < 0$ at $x = 0$, and the operating curve may intersect the locus curve in the region $[\theta_{l_1}, \theta_{l_2}]$—giving rise to runaway condition—depending on the values of the parameters.

ii) $\theta_{l_1} \leq \theta^i \leq \theta_{l_2}$: $\theta_o'' \geq 0$ at $x = 0$, and so runaway condition occurs soon after the reactor entrance, as already noted before.

iii) $\theta^i > \theta_{l_2}$: $\theta_o'' < 0$ at $x = 0$, the operating curve (observation 3) cannot intersect the locus curve in the range $\theta \in [\theta_{l_1}, \theta_{l_2}]$ with a positive slope; therefore no runaway can occur.

From the above analysis, it follows that only for the case i) and for $\theta^i \leq 0$ is it not possible, at this stage, to define the operating condition of the reactor. In the following we consider the case:

$$\theta^i < \theta_{l_1} \tag{8}$$

where for $\theta^i \geq 0$, $\theta_o'' < 0$ at $x = 0$, while for $\theta^i < 0$, $\theta_o'' < 0$ at $\theta = 0$ as noted before.

Let us define the point $(\bar{x}, \bar{\theta})$ on the locus curve where the isocline passing through this point has an inflexion, and furthermore

$$\theta_{iso}'' < 0 \text{ for all } \theta \in [\theta_-, \bar{\theta}) \tag{9}$$

The existence of such a point will be shown shortly; at the moment it is worthwhile to note that both θ_- and $\bar{\theta}$ are independent of α. This is clear for θ_- from Eq. 6; for $\bar{\theta}$, the examination of the expression for θ_{iso}'', which in the following is studied in more detail (Eq. 16), shows that the value of θ at which $\theta_{iso}'' = 0$, i.e., $\bar{\theta}$, is a function only of γ and n. Now, assume that, for a given set of values of β, γ, n and θ^i, it is possible to find a value α^c for α, such that the operating curve passes through the point $(\bar{x} = \bar{x}^c, \bar{\theta})$ on the locus curve.

In this case for all values of $\alpha > \alpha^c$, as a consequence of observation 5, the operating curve will reach the value $\bar{\theta}$ for $x < \bar{x}^c$. From Eq. 9 and observation 4, the locus curve increases monotonically in the range $\theta_- < \theta < \bar{\theta}$, and from observation 3 it follows that

$$\theta_- < \theta_{l_1} \tag{10}$$

Therefore, recalling that $\theta^i < \theta_{l_1}$ from Eq. 8, the operating curve intersects the locus curve defined for α^c in the region $\theta_{l_1} < \theta < \bar{\theta}$. From observation 6, the operating curve must also intersect the locus curve defined for all values of $\alpha > \alpha^c$ in the same region, wherein from Eqs. 9 and 10, $\theta_{iso}'' < 0$; this implies runaway from the necessary and sufficient condition discussed above.

For all values of $\alpha < \alpha^c$, from similar arguments it follows that the operating curve can intersect the locus curve only at $\theta > \bar{\theta}$, where $\theta_{iso}'' > 0$. This implies that runaway condition cannot occur. Therefore, α^c will be called the *critical value* of α for a given set of values of β, γ, n and θ^i.

The relative disposition of the locus and operating curves, along with several isoclines, for a specific case of criticality is shown in Figure 1b.

Note that we still need to prove the assumption that there exists the point $(\bar{r}, \bar{\theta})$ defined by Eq. 9, and the corresponding value of α^c. For this purpose, we consider separately the cases of $n = 1$ and $n \neq 1$.

Case 1: $n = 1$

From Eq. 3, the second derivative of an isocline is given by

$$\theta_{iso}'' = -\theta_{iso}' \frac{(\alpha - \theta_x)}{\gamma\beta g(\theta)} \frac{2\gamma + \theta(2-\gamma)}{[(1+\theta/\gamma)^2 - \theta]^2} \tag{11}$$

which has a unique inflexion point at

$$\bar{\theta} = \frac{2\gamma}{(\gamma - 2)}, \tag{12}$$

and $\bar{x}$ is obtained by substituting this in Eqs. 4a and 4b, which also provide the θ_x that defines the specific isocline. It is easily observed from Eqs. 11 and 12 and Figure 1a that $\theta_{iso}'' < 0$ for all $\theta_- < \theta < \bar{\theta}$. Noticing from Eqs. 6 and 12 that $\theta_- < \bar{\theta} < \theta_+$, it is therefore apparent that the point $(\bar{x}, \bar{\theta})$ satisfying the requirements of Eq. 9 does indeed exist.

Substituting

$$z = \alpha(1 - x) \tag{13}$$

in Eq. 1, it follows that

$$\frac{d\theta}{dz} = \beta \frac{\theta g(\theta)}{z} - 1 \tag{14}$$

with the initial condition $\theta = \theta^i$ at $z = \alpha$. Operating in the same way on Eqs. 4a and 4b, for $\bar{\theta} = 2\gamma/(\gamma - 2)$:

$$\bar{z} = \frac{2\gamma}{(4-\gamma)(\gamma-2)} [\beta(4-\gamma)\exp(-2) - \gamma] \tag{15}$$

It is worth reiterating at this stage that given a fixed set of β, γ and θ^i, the operating curve passes through the point $(\bar{x}, \bar{\theta})$, and so in transformed coordinates, through $(\bar{z}, \bar{\theta})$, for $\alpha = \alpha^c$. The critical value of α [i.e., α^c] is then merely the α value that forces the solution of Eq. 14 through two fixed points in the phase plane: (α^c, θ^i) and $(\bar{z}, \bar{\theta})$. The existence of α^c is assured, because from Eq. 4a, $(d\theta/dx) > 0$ at $\theta = \bar{\theta}$, this means $d\theta/dx > 0$ for $\theta \in (\theta^i, \bar{\theta})$, which implies that $d\theta/dz < 0$ for θ in the same range, and so θ decreases as z increases. Thus when Eq. 14 is integrated with the initial condition $\theta = \bar{\theta}$ at $z = \bar{z}$, as z increases, a value of $\theta = \theta^i$ is guaranteed to be reached at some value of z which is by definition α^c.

In the limit $\gamma \to \infty$, $\bar{\theta} \to 2$ from Eq. 12. This limiting value of $\bar{\theta}$ matches with that of Adler and Enig (1964), and Oroskar and Stern (1979). However, even in this limiting case, they required a laborious trial and error along with numerical integration of Eq. 1 to obtain α^c which is here obtained with a *single* integration of Eq. 14. The fact that a single integration is sufficient derives from the existence of explicit formulae for $\bar{z}$ and $\bar{\theta}$, which can be obtained as shown above by the method of isoclines. The other methods employed heretofore (Dente et al., 1966; Hlaváček et al., 1969) do not lend themselves to such a simple technique for evaluation of α^c.

Case 2: $n > 0$ and $\neq 1$.

The procedure becomes somewhat more complex when $n \neq 1$. Since we seek the point $(\bar{x}, \bar{\theta})$ we need to first find the inflexion points of an isocline. From Eq. 3,

$$\theta_{iso}'' = n \left[\frac{\alpha - \theta_x}{\beta\theta g(\theta)}\right]^{2/n} \frac{\theta(1+\theta/\gamma)^2}{\gamma^4[(1+\theta/\gamma)^2 - \theta]^2} \frac{\phi(\theta)}{[(1+\theta/\gamma)^2 - \theta]} \tag{16}$$

where

$$\phi(\theta) = \sum_{n=0}^{4} a_n \theta^n \tag{17}$$

and

$$a_0 = (n-1)\gamma^4,\ a_1 = 2[2(n-1) + \gamma]\gamma^3$$

$$a_2 = [2(n-1)(3-\gamma) - \gamma(\gamma-2)]\gamma^2,\ a_3 = 2\gamma(n-1)(2-\gamma) \tag{18}$$

$$a_4 = (n-1)$$

and so

$$\text{sign}[\theta_{iso}''] = \text{sign}\left[\frac{\phi(\theta)}{(1+\theta/\gamma)^2 - \theta}\right] \tag{19}$$

since we are interested only in $\theta > 0$; as noted before, runaway cannot occur with $\theta < 0$. Note in passing that $\theta > 0$ implies $\alpha > \theta_x$ from Eq. 1, assuring the existence of the $2/n$ root on the rhs of Eq. 16.

From observation 1 of Eq. 6 (also Figure 1) $\theta_{iso}'' \to +\infty$ as $\theta \to \theta_+$ from below; $\theta_{iso}'' \to -\infty$ as $\theta \to \theta_+$ from above. Also, since the poles of the rhs of Eq. 19 are precisely $\theta_\pm$, this equation implies $\phi(\theta_+) < 0$. Similarly, $\phi(\theta_-) > 0$ by a consideration of θ_{iso}'' as $\theta \to \theta_-$ from above or below.

It now becomes necessary to separate the subcases $n > 1$ and $0 < n < 1$.

Subcase 1: $n > 1$. From Eq. 18,

$$\phi(0) > 0 \text{ and } \phi(\theta) \to \infty \text{ as } \theta \to \infty.$$

With this, and the fact that $\phi(\theta_-) > 0$, $\phi(\theta_+) < 0$, it is assured that $\phi(\theta) = 0$ for at least two positive values of θ: one in the interval $\theta_- < \theta < \theta_+$ and the other at $\theta > \theta_+$. Further, from Descartes rule of signs, $\phi(\theta)$ has at most two positive real roots. Thus it is clear that

$\phi(\theta)$ has precisely two positive real roots, and the one larger than θ_+ is outside the range of interest since $\theta'_{iso} < 0$ for $\theta > \theta_+$ (observation 1).

Thus, there is a unique $\bar{\theta}$ in the range $\theta_- < \theta < \theta_+$ where $\theta''_{iso} = 0$. The exact evaluation of $\bar{\theta}$ is numerical, since it is the solution of the quartic $\phi(\theta) = 0$, but its existence and uniqueness in the bounded interval $\theta_- < \theta < \theta_+$ is now assured.

The question of $\bar{x}$ and α^c still remains, but since the procedure for their evaluation is identical for $n > 1$ or $0 < n < 1$, the latter subcase is now considered first.

Subcase 2: $0 < n < 1$. From Eq. 18,

$$\phi(0) < 0 \text{ and } \phi(\theta) \to -\infty \text{ as } \theta \to \infty.$$

However, since $\phi(\theta_-) > 0$ and $\phi(\theta_+) < 0$, there are again at least two positive real roots of $\phi(\theta)$: at least one in the range $0 < \theta < \theta_-$ and at least one in $\theta_- < \theta < \theta_+$. This time, however, Descartes rule does not limit the number of roots of $\phi(\theta)$ to two; so there could be either four or two positive real roots. $\theta'_{iso} < 0$ for the root(s) in the interval $0 < \theta < \theta_-$, and so there could still be at most three but at least one values of $\bar{\theta}$ in the desired range $\theta_- < \theta < \theta_+$.

From the definition of $\phi(\theta)$:

$$\phi''(\theta) = 12a_4\theta^2 + 6a_3\theta + 2a_2, \tag{20}$$

a quadratic whose discriminant is

$$\Delta = -12\gamma^3(1-n)[2(\gamma-2) - (3\gamma-8)(1-n)] \tag{21}$$

It is thus evident that if

$$2(\gamma - 2) - (3\gamma - 8)(1 - n) \geq 0, \tag{22}$$

then $\phi'' \leq 0$ always, and so there will be a unique $\bar{\theta}$ in the range $\theta_- < \theta < \theta_+$.

Equation 22 is satisfied for

$$\text{either } n \geq 1/3, \tag{23a}$$

$$\text{or if } 0 < n < 1/3, \text{ then } \gamma \leq 4\frac{(1-2n)}{(1-3n)} \tag{23b}$$

Thus, although this does not appear to be feasible from a physical viewpoint, the possibility of three values of $\bar{\theta}$ in the permissible range $\theta_- < \theta < \theta_+$ is not eliminated if

$$0 \leq n < 1/3 \text{ and } \gamma > 4\frac{(1-2n)}{(1-3n)} \tag{24}$$

For reaction parameters satisfying Eq. 24, the two inflexion points of $\phi(\theta)$ are indeed in the range $\theta_- < \theta < \theta_+$; however, numerical results indicate that there is only one value of $\bar{\theta}$ in this range. The special cases of $n = 0$ and $\gamma = \infty$ are examined separately in detail in the Appendix.

Thus, summarizing, there is always a unique value of $\bar{\theta}$ in the interval $\theta_- < \theta < \theta_+$ where $\theta''_{iso} = 0$ for both subcases, and we can now return to the main case $n > 0$ and $\neq 1$.

The next item is to prove Eq. 9 for this case. This is readily done from Eq. 19 now that uniqueness of $\bar{\theta}$ is assured. From the qualitative behavior of $\phi(\theta)$, $\phi(\theta) > 0$ for $\theta_- < \theta < \bar{\theta}$ and the denominator of the rhs of Eq. 19 is negative. The rhs being

$$< 0, \theta''_{iso} < 0 \text{ for } \theta_- < \theta < \bar{\theta}.$$

As for the $n = 1$ case, $\bar{x}$ is obtained by substituting $\bar{\theta}$ in Eqs. 4a and 4b.

Again as before, it is more convenient to work with the $\theta - z$ equations. The substitutions:

$$z = (1 - x)\beta^{1/(1-n)},\ \delta = \alpha\beta^{-1/(1-n)} \tag{25}$$

transform Eq. 1 to

$$\frac{d\theta}{dz} = \frac{\theta g(\theta)}{z^n} - \delta \tag{26}$$

with the initial condition

$$\theta = \theta^i \qquad \text{at } z = \alpha/\delta \tag{27}$$

Equations 4a and 4b for the locus curve give the value of $\bar{z}$, with $\theta = \bar{\theta}$, as the solution of the nonlinear equation:

$$\Psi = -n\frac{\bar{\theta}(1+\bar{\theta}/\gamma)^2}{(1+\bar{\theta}/\gamma)^2 - \bar{\theta}}\left[\frac{\delta - \Psi}{\bar{\theta}g(\bar{\theta})}\right]^{1/n} \tag{28a}$$

$$\bar{z} = \left[\frac{\bar{\theta}g(\bar{\theta})}{\delta - \Psi}\right]^{1/n} \tag{28b}$$

where

$$\Psi = \theta_x\beta^{-1/(1-n)} \tag{28c}$$

Since θ_x lies in $(0, \alpha)$, Ψ is assured to be in $(0, \delta)$. Note that Eq. 28a has a unique solution for Ψ.

Similar to the $n = 1$ case, the critical value of α, i.e., α^c, forces the solution of Eq. 26 through the points $(\alpha^c/\delta, \theta^i)$ and $(\bar{z}, \bar{\theta})$. α^c is again obtained in a *single* numerical integration as follows:

Given a set of γ, n and θ^i,

1. Solve Eq. 17 to give $\bar{\theta} \epsilon (\theta_-, \theta_+)$.
2. Choose a value for δ.
3. Solve Eq. 28a to give $\Psi \epsilon (0, \delta)$, and substitute in Eq. 28b to yield $\bar{z}$.
4. Integrate Eq. 26 with initial condition $(\bar{z}, \bar{\theta})$ for increasing values of z till $\theta = \theta^i$ is reached. The value of z where this occurs is α^c/δ.
5. From the chosen value of δ, this gives α^c, and from the definition of δ, the corresponding β is obtained.

The existence of α^c is assured by arguments identical to those made before for $n = 1$.

NUMERICAL RESULTS AND DISCUSSION

Using the numerical procedure outlined above, the critical value α^c was calculated as a function of β, for various sets of the parameters n, γ and θ^i. The plots of the critical values of α vs. β, reported in the next few figures, divide the α–β plane in two portions: the runaway and the non-runaway ("stable") regions.

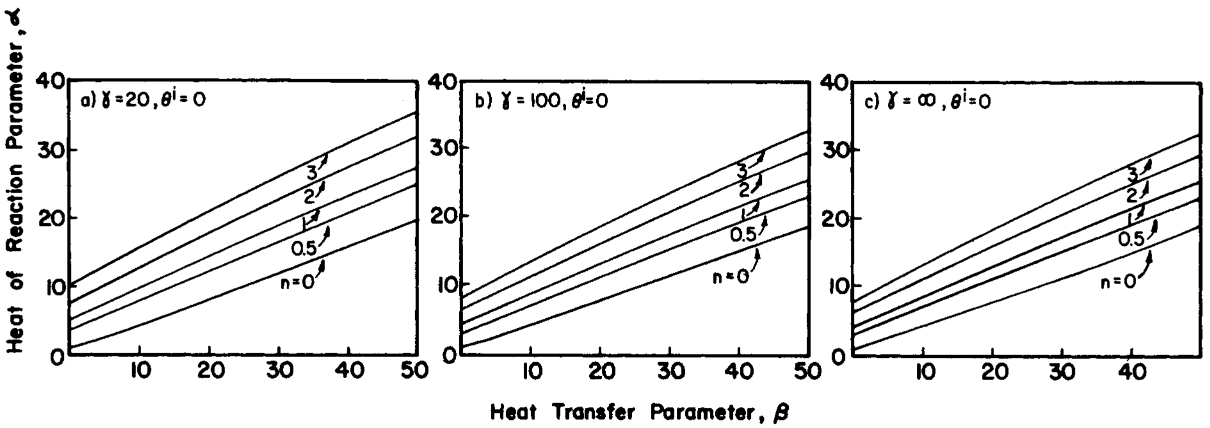
The effect of the activation energy γ, for different orders of reaction n, on the critical value α^c is shown in Figures 2a–c for the *inlet temperature of the reaction mixture*, $\theta^i = 0$. The dependence of the reaction rate on temperature increases with increasing γ, and thus for a fixed heat transfer parameter β and reaction order n, runaway occurs at a smaller value of α. This result is quite expected, and has been numerically observed before (Dente et al., 1966; Hlaváček et al., 1969; Van Welsenaere and Froment, 1970). These same Figures 2a–c also show the effect of reaction order n; runaway is less likely for larger reaction orders.

The effects of γ and n on parametric sensitivity of tubular reactors follow the same trend as multiplicity of steady states in lumped or distributed parameter chemically reacting systems (Van den Bosch and Luss, 1977; Tsotsis and Schmitz, 1979). Thus pathological reactor behavior is always more likely with larger activation energy and lower reaction orders.

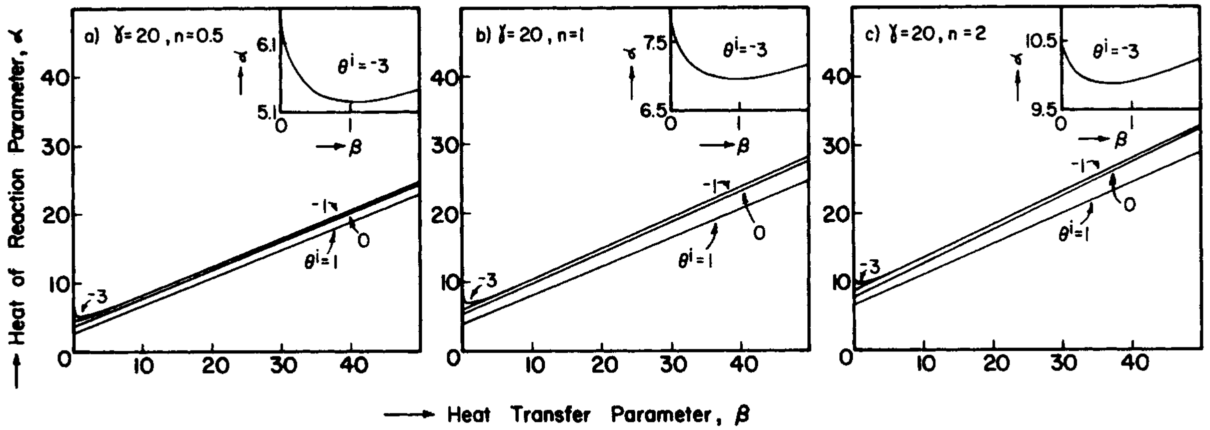
The effect of θ^i is reported in Figures 3a–c. Recalling that $d\theta/dz < 0$ for $\theta \epsilon (\theta^i, \bar{\theta})$, it is apparent that decreasing θ^i, keeping n, γ and β (or δ) constant, for $n = 1$ Eq. 14 gives a larger value of α^c, and for $n \neq 1$ Equation 26 gives a larger value of the ratio α^c/δ. For $n \neq 1$, therefore, α^c increases, but because δ is constant, β also changes according to the equation:

$$d\beta = \frac{\beta(1-n)}{\alpha}d\alpha \tag{29}$$

which is readily derived from the definition of δ in Eq. 25. Thus the critical curve $\alpha^c = \alpha(\beta)$ for $n \geq 1$ certainly moves upward for decreasing inlet temperatures θ^i implying that runaway is less likely, which is intuitively proper. For $0 < n < 1$ the movement of the critical line is not as obvious because *both* α^c and β increase with decreasing θ^i. However for $\beta \to 0$, from Eq. 29, $d\beta \to 0$ and therefore the critical line moves upward for all values of n, as $\beta \to 0$. Noting now that these curves cannot intersect (due to the uniqueness of the Initial Value problem), it follows that the critical line moves upward for all β, also for $0 < n < 1$. Therefore de-



Figures 2(a–c). Critical values of the heat of reaction parameter (α^c) as a function of the heat transfer parameter (β) for various values of the reaction order (n). For each n, the runaway region is above the curve, and the non-runaway (i.e. "stable") region below the curve.



Figures 3(a–c). Critical values of the heat of reaction parameter (α^c) as a function of the heat transfer parameter (β) for different values of the inlet temperature (θ^i). For each θ^i, the runaway region is above the curve, and the non-runaway (i.e. "stable") region below the curve.

creasing values of θ^i reduce the runaway region, as can be expected, for all values of n (Figures 3a–c).

An interesting feature can be observed in these Figures 3a–c. For θ^i sufficiently negative, the critical curve $\alpha^c(\beta)$ has a minimum at relatively low β values. This means that over a small range of the heat transfer parameter β, for a fixed heat of reaction parameter α, decreasing or increasing β results in non-runaway operations. This is because for sufficiently low inlet temperatures relative to the wall, a decrease in β reduces the influence of the hotter wall resulting in stability; for higher β, of course, the normal situation prevails; i.e., an increase of β causes stability.

In Figures 4, 5 and 6, the temperature profiles in the $\theta - x$ phase plane in non-runaway, critical and runaway operating conditions, are shown for various θ^i values. Note that despite the small differences between the values of α, the temperature profiles increase dramatically when runaway occurs (i.e., for $\alpha > \alpha^c$), which testify to the reasonableness of the definition of runaway. In Figure 5 it is shown that the value $\alpha = 13$, which for $\theta^i = 0$ corresponds to a

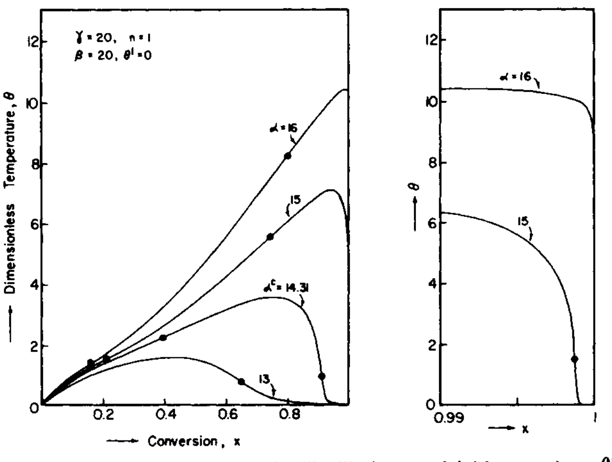


Figure 4. Operating curves around criticality for zero inlet temperature, θ^i. [● = inflexion point].

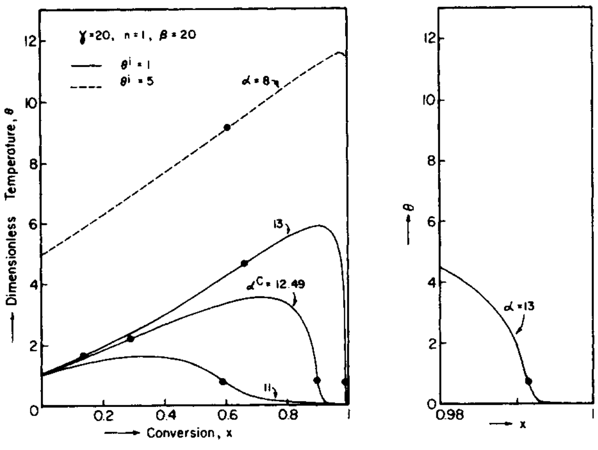


Figure 5. Operating curves around criticality for positive inlet temperature, θ^i. [● = inflexion point].

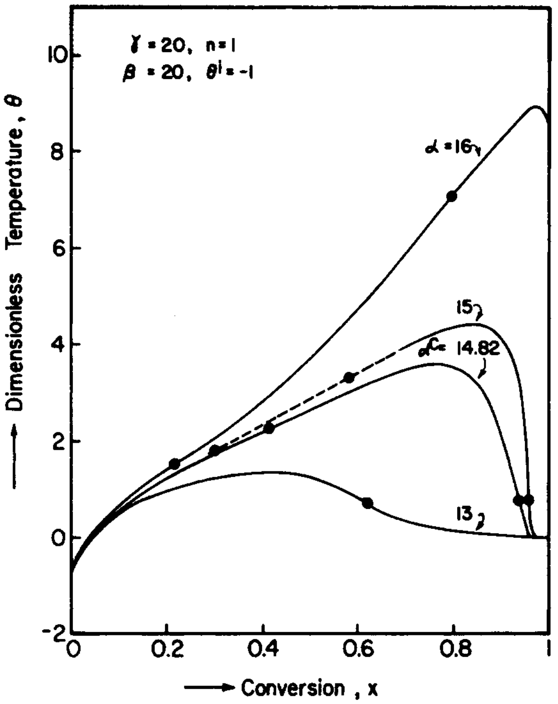


Figure 6. Operating curves around criticality for negative inlet temperature, θ^i. [● = inflexion point].

non-runaway condition (Figure 4), for $\theta^i = 1$ gives rise to runaway. It is apparent that an increase of one in the inlet temperature θ^i causes the temperature at the hot spot to increase by a factor greater than four. On the other hand, for $\theta^i = -1$, the value of $\alpha = 13$ corresponds to a non-runaway condition and as shown in Figure 6, a decrease in the inlet temperature by the same amount as before, this time gives rise to a decrease of the maximum temperature by only about 0.25.

In Figures 4 and 5, expanded versions of the $\theta - x$ portraits are also shown for conversions near one, to point out that $\theta \rightarrow 0$ with zero slope as $x \rightarrow 1$ (except for $n = 0$, as shown in the Appendix); this fact can also be directly verified by investigating the temperature and conversion versus reactor length equations (from which Eq. 1 is derived) linearized about the equilibrium point $\theta = 0$, $x = 1$.

The profile of θ, in a case with sufficiently large θ^i so that $\theta_o'' > 0$ at $x = 0$, which implies runaway right at the reactor inlet, is also shown in Figure 5. It can be observed that despite the relatively low value of α, the $\theta - x$ curve is in this case qualitatively similar to those in runaway conditions of Figures 4 and 5.

Finally, it is worth clarifying that the term "runaway" has been used in other contexts as well. For example, Kimura and Levenspiel (1977) investigated an adiabatic tubular reactor in the limit of large recycle, where it behaves similar to an adiabatic stirred-tank reactor. As is well-known, multiple steady states are possible in such a case. When steady state multiplicity is present, depending on the perturbations, the reactor can move from a low-conversion state to the high-conversion state, causing thereby a temperature increase. They termed such behavior as "runaway."

It should be obvious that the present work deals with a different problem.

ACKNOWLEDGMENT

M. Morbidelli thanks the "Stazione Sperimentale per i Combustibili; Borsa di Studio L. Miani" for financial support during the course of this study.

NOTATION

A	= preexponential factor in Arrhenius rate equation
a_i (i = 1,4)	= coefficients defined by Eq. 18
C_p	= mean specific heat
D	= diameter of the reactor tube
E	= activation energy
g	= $\exp[-\theta/\{1 + (\theta/\gamma)\}]$
ΔH	= heat of reaction
k	= reaction rate constant
n	= reaction order
P	= total pressure
R	= ideal gas constant
T	= temperature
U	= overall heat transfer coefficient
x	= reactant conversion
y	= molar fraction
z	= integration variable

Greek Letters

α	= dimensionless heat of reaction, defined by Eq. 2
β	= dimensionless heat transfer parameter, defined by Eq. 2
γ	= dimensionless activation energy, E/RT_w
δ	= constant, defined by Eq. 25
θ	= dimensionless temperature, $[(T - T_w)/T_w]\gamma$
θ_x	= parameter characteristic of an isocline
$\theta_\pm$	= roots of Eq. 6
ϕ	= function of θ, defined by Eq. 17
Ψ	= parameter, defined by Eq. 28c

Subscripts

A	= reactant
o	= operating curve
iso	= isocline
l	= locus curve
w	= wall

Superscripts

i	= inlet value
c	= critical value

APPENDIX

Case 1: $n = 0$

From Eq. 1, the operating curve is given by

$$\frac{d\theta}{dx} = \alpha - \beta\theta g(\theta) \qquad \text{(A1)}$$

The isoclines are horizontal lines, where the value of θ, for each θ_x, is given by

$$\theta g(\theta) = (\alpha - \theta_x)/\beta \qquad \text{(A2)}$$

The function $[\theta g(\theta)]$ has a maximum at θ_- and a minimum at θ_+, where $\theta_\pm$ are given by Eq. 6. Therefore, the pattern of the isoclines in the $\theta - x$ plane is of the form shown in Figure 7, where the arrows represent increasing values of the parameter θ_x defining each isocline. From Figure 7 and the definition of an isocline follows that the second derivative of the operating curve is positive in the range $\theta_- < \theta < \theta_+$, and negative for $\theta < \theta_-$ or $\theta > \theta_+$.

From the same arguments as in the $n \neq 0$ case, Eq. 7, and also from Figure 7, it is apparent that if $\theta_o' < 0$ at x = 0, i.e., $\theta^i g(\theta^i) \geq \alpha/\beta$, the operating curve always decreases and therefore runaway condition cannot occur. If $\theta^i g(\theta^i) < \alpha/\beta$, the following possibilities can arise:

i) $\theta^i < \theta_-$: $\theta_o'' < 0$ at $x = 0$, runaway occurs if the operating curve intersects the straight line $\theta = \theta_-$.

ii) $\theta_- \leq \theta^i \leq \theta_+$: $\theta_o'' \geq 0$ at $x = 0$, runaway occurs soon at the reactor entrance.

iii) $\theta^i > \theta_+$: $\theta_o'' < 0$ for all θ values, the operating condition of

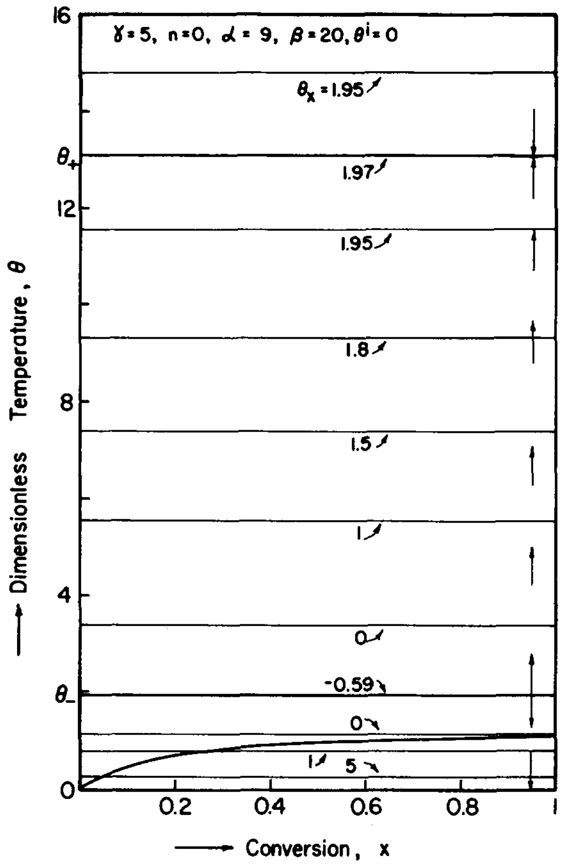


Figure 7. Phase plane behavior for a stable case of a zeroth order reaction with finite activation energy, γ.

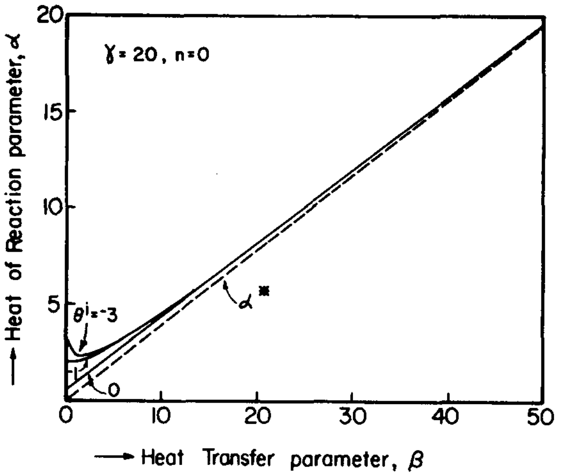


Figure 8. Critical values of the heat of reaction parameter (α^c) as a function of the heat transfer parameter (β) for a zeroth order reaction. For each θ^i, the runaway region is above the curve, and the non-runaway (i.e. "stable") region below the curve.

the reactor is always non-runaway (i.e., "stable"). We consider now, as in the $n \neq 0$ case, only the case i). It is apparent that if the isocline defined by $\theta_x = 0$ is located below the value θ_-, the operating curve cannot intersect such an isocline, and is therefore restricted in the region $\theta < \theta_-$, where $\theta\lambda_{iso}'' < 0$—thus, there is no runaway. The value of α at which this isocline coincides with the straight line $\theta = \theta_-$ is obtained from Eq. A2 by setting $\theta_x = 0$ and $\theta = \theta_-$:

$$\alpha^* = \beta\theta_- g(\theta_-) \qquad \text{(A3)}$$

It follows that for all values of $\alpha < \alpha^*$ the runaway condition cannot occur.

It is worthwhile to note that the rate of a zeroth order reaction has the anomaly of being positive and finite at $x = 1$; therefore, when the reactant is fully consumed, the rate has to be set equal to zero, giving rise to a discontinuity in the derivatives of θ and x versus reactor length profiles. [It should also be noted that physically a zeroth order reaction model cannot be sustained until extremely low values of the reactant concentration, and therefore in reality, this discontinuity will never occur.] After this point the reactant concentration remains constant at $x = 1$, and the reaction contribution in the heat balance disappears. Equation A1 is then no longer valid; the reactor simply acts like a heat exchanger after this point, following the equation:

$$\frac{d\theta}{dt} = -\beta\theta \qquad \text{(A4)}$$

where t is proportional to the reactor length. Thus for larger lengths, the temperature decreases until $\theta = 0$, due to the cooling effect. It follows that, while the operating curve can approach the $\theta_x = 0$ isocline (but not cross it, by definition), this discontinuity can occur at a value of θ well below it. Therefore, the condition $\alpha < \alpha^*$, where α^* is given by Eq. A3, is *sufficient*, but not necessary, to assure non-runaway operating condition for the reactor. The same result as in Eq. A3 was obtained by Hlaváček et al. (1969) using the occurrence of an inflexion point in the temperature-reactor length profile as a runaway criterion, and approximating the reactant concentration constant along the reactor.

We have already noted that at $\theta = \theta_-$ the operating curve has an inflexion point in the $\theta - x$ phase plane, therefore the necessary *and* sufficient condition for runaway, according to our definition, is that the operating curve intersect the line $\theta = \theta_-$ in the range $x \in [0, 1]$. It follows then that the value of α^c is that value of α which forces the solution of Eq. A1, with the initial condition $\theta = \theta^i$ at $x = 0$, to pass through the point $\theta = \theta_-$ at $x = 1$. Converting to $\theta - z$ coordinates, using the same substitution (Eq. 13) as in the $n = 1$ case, it is possible to evaluate α^c, for a given set of values γ, θ^i and β, again with a single integration. The results obtained for different values of γ are shown in Figures 2a–c.

The critical curves of α vs. β are shown in Figure 8 for various θ^i. The same feature of the α^c curve having a minimum for sufficiently negative θ^i, observed before in Figures 3a–c, is more readily apparent here. The operating curve in the temperature-conversion phase plane is shown in Figure 9 for three specific values of β around the minimum; $\beta = 0.1$ and 7 result in non-runaway operation, while $\beta = 2.5$ is in runaway regime.

A comparison between α^*, obtained from Eq. A3, and α^c is also shown in Figure 8. It can be observed that α^* is a rather good ap-

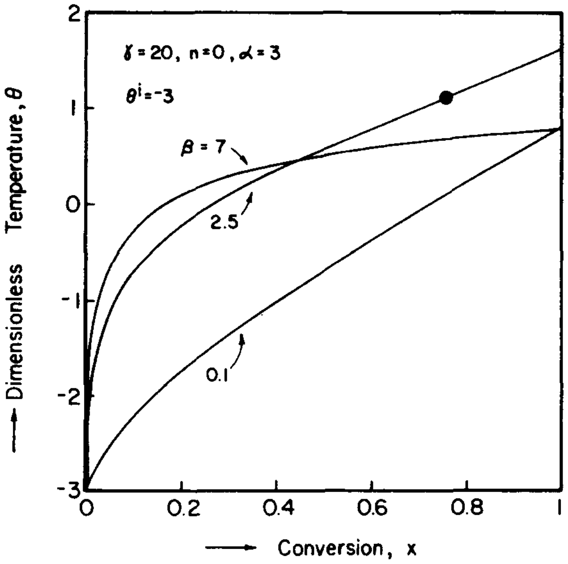


Figure 9. Operating curves for a fixed value of the heat of reaction parameter, α and various values of the heat transfer parameter, β. [● = inflexion point].

proximation of α^c (except for very negative θ^i in the region of low β), and that $\alpha^c \to \alpha^*$ for larger values of the heat of reaction. The latter is due to the fact that for highly exothermic reactions the operating curve approaches the isocline $\theta_x = 0$ at relatively lower conversions, and so criticality is well approximated by insisting that the $\theta_x = 0$ isocline coincide with θ_-. Increasing values of the inlet temperature have the same effect on the operating curve; i.e., they also give rise to values of α^c closer to α^*.

Case 2: $\gamma = \infty$

In this case

$$g(\theta) = \exp(-\theta),$$

and so the operating curve equation becomes:

$$\frac{d\theta}{dx} = \alpha - \beta \frac{\theta \exp(-\theta)}{(1-x)^n}$$

and the isocline equation is:

$$x = 1 - \left[\frac{\beta\theta \exp(-\theta)}{(\alpha - \theta_x)}\right]^{1/n} \quad \text{(A5)}$$

Differentiating Eq. A5:

$$\frac{d\theta_{iso}}{dx} = n\left[\frac{(a - \theta_x)}{\beta\theta \exp(-\theta)}\right]^{1/n} \frac{\theta}{(\theta - 1)} \quad \text{(A6)}$$

where it is apparent that for $\theta > 1$, $\theta'_{iso} > 0$. This result coincides with the general case noting from Eq. 6

$$\lim_{\gamma \to \infty} \theta_- = 1; \quad \lim_{\gamma \to \infty} \theta_+ = +\infty$$

The locus curve equation is given by

$$\theta_x = \frac{n\theta}{\theta - 1}\left[\frac{(\alpha - \theta_x)}{\beta\theta \exp(-\theta)}\right]^{1/n} \quad \text{(A7)}$$

$$x = 1 - \frac{n\theta}{\theta_x(\theta - 1)} \quad \text{(A8)}$$

It is readily observed, setting $x = 0$ in Eqs. A7 and A8, that the value of θ, at which the locus curve intersects the θ-axis is given by the solution of the equation

$$L(\theta) \equiv \beta\theta \exp(-\theta) = \{\alpha - n\theta/(\theta - 1)\} \equiv R(\theta) \quad \text{(A9)}$$

Noting that for the rhs of Eq. A9, $R(\theta)$: $R(1) = -\infty$, $R(\infty) = \alpha - n$, and $R' > 0$, while for the lhs, $L(\theta)$: $L(1) > 0$, $L(\infty) = 0$, $L' < 0$ for $\theta > 1$; it then follows that Eq. A9 has at most one solution (θ_{l_1}) in the range $\theta > 1$, and that the necessary and sufficient condition for the existence of this solution is $\alpha > n$. This result is consistent with the general case, noting that $\lim_{\gamma \to \infty} \theta_{l_2} = \infty$.

Considering now only the case $\theta'_o > 0$ at $x = 0$, which happens when Eq. 7 is violated, the following possibilities can arise:

i) $\alpha > n$, $\theta^i < \theta_{l_1}$: $\theta''_o < 0$ at $x = 0$; runaway may occur depending on the values of the parameters involved.

ii) $\alpha > n$, $\theta^i \geq \theta_{l_1}$: $\theta''_o \geq 0$ at $x = 0$; runaway occurs soon at the reactor entrance.

iii) $\alpha \leq n$: the locus curve for $\theta > 1$ is restricted in the $x \leq 0$ region; runaway cannot occur.

As in the general case, only the first possibility needs to be considered further in the following. The second derivative of the isocline is obtained by differentiating Eq. A6:

$$\theta''_{iso} = -n\left[\frac{(\alpha - \theta_x)}{\beta\theta \exp(-\theta)}\right]^{2/n} \frac{\theta[n - (\theta - 1)^2]}{(\theta - 1)^3} \quad \text{(A10)}$$

θ''_{iso} vanishes for two values of the temperature, $\theta = 1 \pm \sqrt{n}$, where only the larger one is in the range $\theta > 1$ for all values of n. This result, which was obtained by Adler and Enig (1964) in a different way, coincides with the solution, $\bar{\theta}$ of Eq. 17 in the limit $\gamma \to \infty$. The uniqueness of the value $\bar{\theta}$ in the range $\theta \in [\theta_-, \theta_+]$, already recognized in the general case, is therefore confirmed for all reaction orders and $\gamma \to \infty$ as well.

LITERATURE CITED

Adler, J., and J. W. Enig, "The Critical Conditions in Thermal Explosion Theory with Reactant Consumption," *Comb. and Flame*, **8**, 97 (1964).

Aris, R., *Introduction to the Analysis of Chemical Reactors*, Prentice-Hall, Englewood Cliffs, NJ (1965).

Barkelew, C. H., "Stability of Chemical Reactors," *Chem. Eng. Prog. Symp. Ser.*, **25** (55), 37 (1959).

Bilous, O., and N. R. Amundson, "Chemical Reactor Stability and Sensitivity. II," *AIChE J.*, **2**, 117 (1956).

Chambré, P. L., "On the Characteristics of a Nonisothermal Chemical Reactor," *Chem. Eng. Sci.*, **5**, 209 (1956).

Dente, M., A. Cappelli, G. Buzzi Ferraris, and A. Collina, "La sensitivitá del regime dei reattori chimici a flusso longitudinale—I", *Ing. Chim. Ital.*, **2**, 5 (1966).

Dente, M., and A. Collina, "Il comportamento dei reattori chimici a flusso longitudinale nei riguardi della sensitivitá," *Chim. e Industria*, **46**, 752 (1964).

Hlaváček, V., M. Marek, and T. M. John, "Modelling of Chemical Reactors, XII," *Coll. Czechoslov. Chem. Comm.*, **34**, 3868 (1969).

Kimura, S., and O. Levenspiel, "Temperature Excursions in Adiabatic Packed Bed Reactors," *Ind. Eng. Chem. Proc. Des. Dev.*, **16**, 145 (1977).

Oroskar, A., and S. A. Stern, "Stability of Chemical Reactors," *AIChE J.*, **25**, 903 (1979).

Tsotsis, T. T., and R. A. Schmitz, "Exact Uniqueness and Multiplicity Criteria for a positive-order Arrehnius Reaction in a Lumped System," *Chem. Eng. Sci.*, **34**, 135 (1979).

Van den Bosch, B., and D. Luss, "Uniqueness and Multiplicity Criteria for an n-th order Chemical Reaction," *Chem. Eng. Sci.*, **32**, 203 (1977).

Van Welsenaere, R. J., and G. F. Froment, "Parametric Sensitivity and Runaway in Fixed Bed Catalytic Reactors," *Chem. Eng. Sci.*, **25**, 1503 (1970).

Varma, A., and N. R. Amundson, "Some Problems Concerning the Non-Adiabatic Tubular Reactor," *Can. J. Chem. Eng.*, **50**, 470 (1972).

Manuscript received February 19, 1980; revision received August 6, 1981, and accepted August 24, 1981.