These films as resistance thermometers may displace conventional devices lacking versatility and reliability.

The technique for evaporation by electron bombardment permitted the evaluation of the electrical properties of thick films of the refractories, molybdenum, tungsten, and tantalum.

The performance of films has been evaluated in three typical hot liquids, organic, weakly ionic, and strongly ionic in nature, to permit predictions of their behavior in other media. These and tests of their abrasion resistance indicate that suitable selected films should be rugged enough for service in most liquids, in gentle contact with solids, and in contact with gases and vapors.

Chemical behavior against mineral acids likewise has been compared with the behavior of the bulk metal. Generally films have been found to be moderately to markedly superior.

Data have been collected concerning the resistivities and temperature coefficients of resistivity of these films. The important variables causing behavior unique to the film state have been outlined. Deposition of metal on a substrate at 200°C. proved strikingly effective in producing films of superior adherence with greater stability and electrical properties closer to those of the bulk metal. The temperature coefficients of thick films show an interesting correlation with their atomic number.

Techniques and recommendations for the practical use of evaporated films have been outlined.

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Chemical Reactor Stability and Sensitivity

II. Effect of Parameters on Sensitivity of Empty Tubular Reactors

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In this paper extensive calculations on the quasi isothermal tubular reactor are presented. Temperature and concentration profiles were obtained on an analogue computer (R.E.A.C.). The calculations tend to show that there are regions of operation in which the reactor effluent is very sensitive to operating conditions. For example, it is shown that in some regions of operation a small change in the heat transfer coefficient at the reactor wall or a small dilution of the feed will produce large changes in the effluent. In such cases the reactor is said to exhibit *parametric sensitivity*. It is shown analytically that this sensitivity may be predicted by analyzing the frequency response or transient response of the reactor approximated by a local linearization. This linearization requires complete solutions of the steady state problem. Semiquantitative results are then obtained for the regulation required from a given specification of product limits. The frequency-response analysis should be useful in connection with the control problem.

If the reactor is fed partially with a recycle stream, then experience with electrical systems indicates that the possibility of instability exists. It is shown that at least theoretically these instabilities do exist, and a method based on the transfer function is developed for derivation of criteria of stability or instability.

In Part I of this paper the stability of the well-agitated reactor was examined in detail and criteria were developed based on the steady state values so that reactor behavior after perturbations, either small or large, might be predicted. This problem was not difficult because the transient behavior is described by ordinary differential equations. The treatment of stability problems for chemical systems exactly parallels the treatment of problems in nonlinear mechanics. This is fortunate as the theory therefore must only be restated in terms of the parameters of the chemical system. When one considers the tubular reactor, however, the problem is considerably more difficult, because transient reactor behavior is described by partial-differential equations which are nonlinear, and no adequate method of solution or estimate of the error in their linearization is available. Thus the treatment given in the following must be considered unsatisfactory from a rigorous point of view although it will be shown that machine solutions of the rigorous equations agree in a semiquantitative way with the solutions of the approximated equations. This may be

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considered as a partial confirmation of the mathematical theory by the engineer.

The solutions to problems for the quasiisothermal tubular reactor have not been carried out in detail in the literature, although one recent paper (*4*) illustrated in a qualitative way some aspects of the problem. In general, in the past reaction systems have been assumed to be adiabatic or isothermal, the calculations for which are not difficult. In the quasiisothermal case there are two differential equations for the steady state, an energy balance and a mass balance. Even at the steady state these will be nonlinear and so calculation is not a simple task. As there seemed to be no general discussion of reactor behavior as the parameters of the system were varied, it was decided to make an extensive series of calculations in order to investigate anomalous behavior, if any. It should be stressed that the physical model used is a very simple one, all complicating factors having been neglected. This may seem rash, but the purpose of this paper is to show that complications may arise in very simple systems and to illustrate how such complications might be handled Additional factors may be easily taken into consideration. It is generally true that if the basic problem has been well set, marginal corrections result from adding to the problem such factors as variation in velocity, heat capacities, heat transfer coefficients, pressure drop, and radial and longitudinal mixing The addition of packing in the reactor, however, will increase the complications tremendously.

COMPUTER SOLUTIONS

The simple reaction $A \longrightarrow B$, which is first order and irreversible, with heat of reaction ΔH, may be carried out in an unpacked tubular reactor whose ambient temperature is constant at T_W. The concentration of A at any point along the reactor may be x and the temperature y. Then a simple mass and heat balance will be

$$\frac{Dx}{D\theta} = \frac{\partial x}{\partial \theta} + v\frac{\partial x}{\partial \tau} = -pe^{-a/y}x \quad (1)$$

$$\frac{Dy}{D\theta} = \frac{\partial y}{\partial \theta} + v\frac{\partial y}{\partial \tau} = K(T_w - y) + Qpe^{-a/y}x \quad (2)$$

where

$$k = p \exp\left(-\frac{a}{y}\right), \qquad a = \frac{E}{R}$$

$$K = \frac{2h}{rc\rho}$$

$$Q = \frac{-\Delta H}{c\rho}$$

with reactor radius r, wall heat transfer coefficient (over-all) h, c the specific heat, and ρ the density. Equations (1) and (2) describe the transient behavior of the system. The steady state is described by

$$v\frac{dx_s}{d\tau} = -k_s x_s \quad (3)$$

$$v\frac{dy_s}{d\tau} = K(T_w - y_s) + Qk_s x_s \quad (4)$$

where the subscript s denotes the steady state value. k_s still depends upon the exponential variation of the temperature. Solutions to these equations may be found with the aid of the analogue computer (R.E.A.C.). Families of curves for different values of the parameters may be obtained without difficulty once the equations have been programmed for the machine, and these have been secured.

In Figure 1*a* is shown the effect of changes in the ambient temperature on the temperature profile, all other parameters being fixed. Over a small range of wall temperature the character of the profile changes appreciably. Figure 1*b* is the corresponding concentration profile. These two sets of plots were made with an activation energy of 11,250 cal./mole. The reaction is exothermic. In Figure 2*a* and *b* the same plots are made with doubled activation energy and frequency factor and with the other parameters changed somewhat. These changes have made the reactor behavior more pronounced. There is a critical change in the temperature and concentration profile as one moves from 335° to 337.5°K.

Figure 3*a* and *b* shows that the endothermic reaction displays no such unusual behavior when graphs with similar coordinates are prepared.

Figure 4*a* and *b* shows the effect of dilution of the feed on temperature and concentration profiles, and once again there is a critical value of the feed concentration above and below which reactor profiles are appreciably different. Figure 5 repeats the same graphs for an endothermic reaction but no unusual condition seems to exist.

Figure 6*a* and *b* shows the effect of small changes of the reactor-wall heat transfer coefficient. Small changes in the coefficients produce a marked change in the conversion. This effect is accentuated as the activation energy increases.

Thus from this rather extensive series of profiles one can see that certain conditions may occur under which reactor operation, without being unstable in the literal sense, will be extremely sensitive to small changes in the operating characteristics of the system. Changes such as gradual fouling of heat transfer surfaces or reactor surfaces or poor control of temperatures or concentrations might make continuous operation extremely difficult. Since these computations have shown that operation is very sensitive to the parameters of the system in some regions, this phenomenon will be referred to as *parametric sensitivity.*

To make a more formal study of the situation one can calculate the derivative of the temperature or concentration with respect to one of the parameters; for example,

$$v\frac{d}{d\tau}\left(\frac{dx_s}{dT_w}\right) = -k_s\frac{dx_s}{dT_w} - \frac{a}{y_s^2}k_s x_s\frac{dy_s}{dT_w}$$

$$v\frac{d}{d\tau}\left(\frac{dy_s}{dT_w}\right) = K - \left(K - Qk_s\frac{ax_s}{y_s^2}\right)\frac{dy_s}{dT_w} + Qk_s\frac{dx_s}{dT_w}$$

where these are differential equations in the derivatives with respect to the ambient temperature These derivatives may be generated on the R.E.A.C. and this has been done in Figure 7 This plot corresponds to the temperature and concentration profiles given in Figure 2*a* and *b* and shows, quite naturally, that the dependence on wall temperature is most strong near the hot point.

In order to show that parametric sensitivity is not due to a mathematical change in the nature of the solution of the steady state equations, a phase space representation (*6*) of the temperature profiles was made for the case of feed dilution. This phase space representation was obtained by plotting the temperature gradient against the temperature. If there is a change in the nature of the solution a separatrix should exist between the two families of solutions if such exist. Figure 8*a* and *b* shows phase space trajectories which form a continuous family and there seems to be no evidence for a separatrix.

Parametric sensitivity in an industrial reactor might manifest itself in many ways. If a reactor is designed for a high conversion near a region of sensitivity, reactor-product quality might be difficult to control. On the other hand a side reaction to the one of interest might exhibit such a character, in which case yields of desired products would fall off. In a reaction such as a controlled oxidation it may be necessary to operate at a low temperature to produce a partially oxidized product. Sensitivity in this case might produce an overoxidized product.

ANALYTICAL TREATMENT OF PARAMETRIC SENSITIVITY

It is clear that it would be desirable to have methods for the prediction of parametric sensitivity without the necessity of plotting many reaction paths. The task of hand calculating reaction paths for the quasiisothermal reactor is not an easy one although on the analogue or digital computor it is not difficult. A numerical scheme, either by hand or on a digital computer, inevitably involves a step-by-step integration down the reactor. This would not be difficult in the insensitive region but in the region of sensitivity the size of the steps would of necessity be small as by the very nature of parametric sensitivity the future course of the calculation depends strongly on small inaccuracies occurring during the course of the computation. Because of this difficulty in reproducing a multitude of reaction paths the problem will now be considered from an analytical point of view. The general method of attack is to calculate the response of the reactor to a sinusoidal input or to a step-function input. If this response can be calculated easily, then sensitivity may be predicted. It is the purpose of this section to show that such a computation is not difficult. From the different point of view of system engineering it is useful to know the harmonic response of a reactor. This has been investigated by Deisler and Wilhelm (*2*) and by Kramers and Alberda (*5*) but with a slightly different end in view.

If a first-order reaction is carried out isothermally in a tubular reactor, then

$$\frac{\partial x}{\partial \theta} + v\frac{\partial x}{\partial \tau} = -kx$$

If $\bar{x}$ is the Laplace transform of x and if the initial condition of the reactor is taken as zero,

$$\frac{d\bar{x}}{d\tau} = -(k + s)\frac{\bar{x}}{v}$$

where s is the transform variable.

If the input is sinosoidal and given by

$$x_i = A' \sin \omega\theta$$

then

$$\bar{x}_i = A'\mathcal{L}(\sin \omega\theta) = A'S$$

and so

$$\bar{x} = e^{-kL/v}e^{-sL/v}A'S$$

It is clear from the property of inverse transforms that the amplitude ratio of input and output signals is

$$e^{-kL/v}$$

and that there is a phase lag in the sinusoidal output equal to

$$\frac{\omega L}{v}$$

The output may be written

$$x_0 = Ae^{-kL/v}\sin\left(\omega\theta - \frac{\omega L}{v}\right)$$

On the other hand if the input is a step function

$$x_i = \begin{cases} 0 & \theta < 0 \\ \epsilon & \theta > 0 \end{cases}$$

then

$$\bar{x} = e^{-kL/v}\frac{e^{-sL/v}}{s}\epsilon$$

and the reactor output is

$$x_0 = e^{-kL/v}\epsilon, \qquad \theta > \frac{L}{v}$$

In the language of control theory the function

$$\Omega(s) = e^{-(k+s/v)L}$$

is called the *transfer function.*

The generalization to more complicated isothermal systems is obvious and may be carried out by the matrix method (*1*). Instead, however, the quasiisothermal system considered in the earlier part of this paper will be treated. In Equations (1) and (2)

$$x = x_s(\tau) + X(\tau, \theta)$$

$$y = y_s(\tau) + Y(\tau, \theta)$$

where X and Y are the transient parts of x and y and satisfy, after the first-order linearization is taken about the steady state, the equation

$$\frac{\partial X}{\partial \theta} + v\frac{\partial X}{\partial \tau} = -k_s X - k_s\frac{ax_s}{y_s^2}Y \quad (5)$$

$$\frac{\partial Y}{\partial \theta} + v\frac{\partial Y}{\partial \tau} = Qk_s X + \left(Qk_s\frac{ax_s}{y_s^2} - K\right)Y \quad (6)$$

These equations are somewhat more complicated than might appear at first sight, as the coefficients of X and Y on the right-hand side are not constants but are complicated functions of the distance along the reactor as given by the steady state solutions. Thus on *a priori* grounds a simple solution might not be expected. Note also that the type of linearization used to derive Equations (5) and (6) does not involve a single linearization throughout the whole reactor but is a local linearization in which a new linearization is taken at each point along the reactor.

If the matrix $F(s, \tau)$ is defined by

$$\mathbf{F}(s, \tau) = -\begin{bmatrix} \dfrac{k_s + s}{v} & \dfrac{k_s a x_s}{v y_s^2} \\ \dfrac{-Qk_s}{v} & \dfrac{1}{v}\left[K - Qk_s\left(\dfrac{ax_s}{y_s^2}\right) + s\right] \end{bmatrix} \quad (7)$$

and if

$$\mathbf{M} = \ln \mathbf{\Omega}(s) = \int_0^L \mathbf{F}(s, \tau)\, d\tau$$

from which

$$\mathbf{M} = -\begin{bmatrix} \displaystyle\int_0^L \frac{k_s + s}{v}\, d\tau & \displaystyle\int_0^L \frac{k_s a x_s}{v y_s^2}\, d\tau \\ \displaystyle -\int_0^L \frac{Qk_s}{v}\, d\tau & \displaystyle\frac{1}{v}\int_0^L \left(K - Qk_s\frac{ax_s}{y_s^2} + s\right) d\tau \end{bmatrix} \quad (8)$$

then let it be assumed that the solution may be expressed in the form

$$\overline{\mathbf{V}}_o = \mathbf{\Omega}(s)\overline{\mathbf{V}}_i$$

$$= e^{\mathbf{M}}\overline{\mathbf{V}}_i$$

where $\mathbf{V}_o$ and $\mathbf{V}_i$ are the matrices of the output and input, respectively, and $\bar{\mathbf{V}}_o$ and $\bar{\mathbf{V}}_i$ are their respective Laplace transforms. Thus

$$\mathbf{V}_0 = \begin{pmatrix} X_o \\ Y_o \end{pmatrix}, \qquad \mathbf{V}_i = \begin{pmatrix} X_i \\ Y_i \end{pmatrix}$$

In these formulas $\bar{\mathbf{V}}_o$ is the transform of the output for an arbitrary input.

From transfer function theory the output signal caused by a sinusoidal input signal is given in complex form by

$$\mathbf{V}_o = \mathbf{\Omega}(j\omega)\mathbf{V}_i$$

and X_i and Y_i are complex sinusoidal inputs on the concentration and temperature of the same frequency but of different or the same amplitudes.

Because of the structure of the matrix M it can be separated into the sum of two matrices as

$$\mathbf{M} = \frac{-sL}{v}\mathbf{I} + \mathbf{N} \quad (9)$$

where **I** is the unitary matrix and

$$\mathbf{N} = -\begin{bmatrix} \displaystyle\int_0^L \frac{k_s}{v}\, d\tau & \displaystyle\int_0^L \frac{k_s a x_s}{v y_s^2}\, d\tau \\ \displaystyle -\int_0^L \frac{Qk_s}{v}\, d\tau & \displaystyle\frac{1}{v}\int_0^L \left(K - Q\frac{k_s a x_s}{y_s^2}\right) d\tau \end{bmatrix} \quad (10)$$

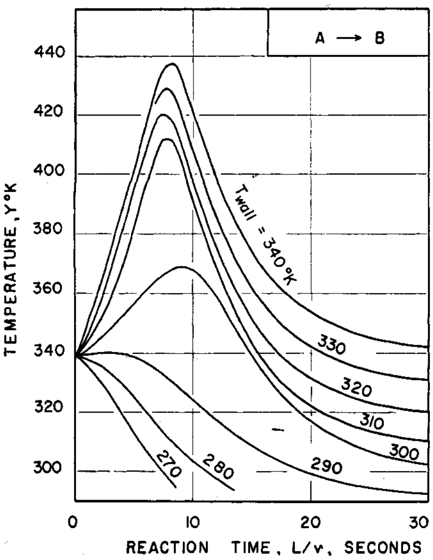


Fig. 1*a*. Temperature profiles in a tubular reactor; effect of wall temperature. $E = 11{,}250$, $p = 1.59 \times 10^{13}$, $x_i = 0.020$, $Q = 10{,}000$, $K = 0.20$, $T_i = 340°\text{K}$.

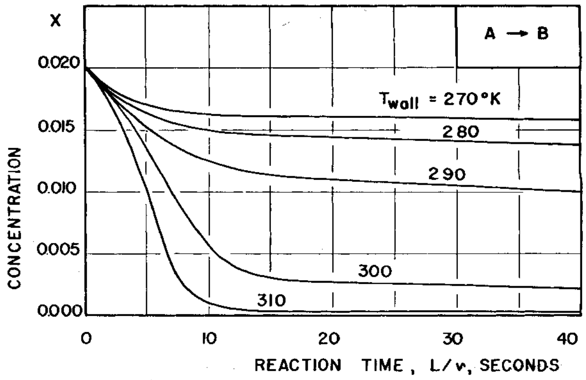


Fig. 1*b*. Concentration profiles in a tubular reactor; effect of wall temperature. Data are same as in Figure 1*a*.

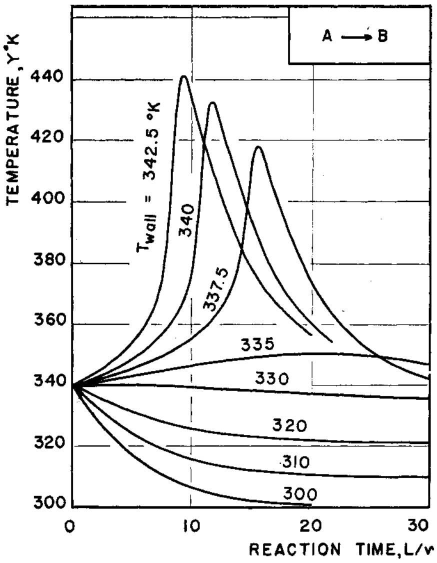


Fig. 2*a*. Temperature profiles in a tubular reactor; effect of wall temperature. $E = 22{,}500$, $p = 3.94 \times 10^{12}$, $x_i = 0.20$, $Q = 7{,}300$, $K = 0.20$, $T_i = 340°\text{K}$.

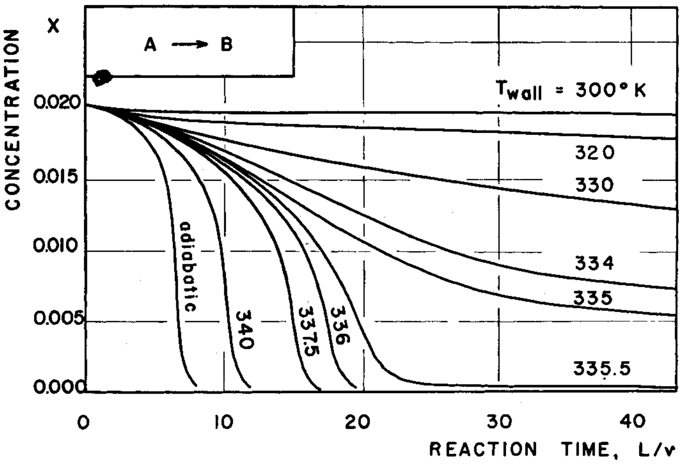


Fig. 2*b*. Concentration profiles in a tubular reactor; effect of wall temperature. Data are the same as in Figure 2*a*.

Now the matrix

$$\exp\left[\alpha\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\right] \tag{11}$$

may always be written

$$e^{\alpha}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \tag{12}$$

and by Sylvester's theorem (*1, 3*) a second-order square matrix may be decomposed as

$$e^{\begin{pmatrix}A & B\\ C & D\end{pmatrix}} = e^{\frac{A+D}{2}}\frac{\sinh\Delta}{\Delta}\begin{bmatrix}\dfrac{A-D}{2}+\dfrac{\Delta}{\tanh\Delta} & B\\ C & \dfrac{D-A}{2}+\dfrac{\Delta}{\tanh\Delta}\end{bmatrix} \tag{13}$$

where

$$2\Delta = \sqrt{(A-D)^2+4BC}$$

Thus the function $\mathbf{\Omega}(s)$ may be written in the form

$$\mathbf{\Omega}(s) = e^{-sL/v}\begin{pmatrix}\alpha & \beta\\ \gamma & \delta\end{pmatrix} = e^{-sL/v}\mathbf{R}$$

where $\alpha, \beta, \gamma, \delta$ are implicitly defined by Equation (13). Therefore

$$X_0 = (\alpha X_i + \beta Y_i)e^{-i\omega L/v}$$

$$Y_0 = (\gamma X_i + \delta Y_i)e^{-i\omega L/v}$$

These are the complex responses X_o, Y_o to complex feed excitations X_i, Y_i of the feed concentration and temperature respectively. The phase angle is still $\omega L/v$, which is a lag behind the input signal. If the amplitudes of the input signals are θ and η, respectively, on concentration and temperature, then the amplitudes of the output signals are $\alpha\epsilon + \beta\eta$ and $\alpha\epsilon + \delta\eta$, respectively, and hence there is an interaction between the two signals. In complex form these are written

$$X_o = (\alpha\epsilon + \beta\eta)e^{-i\omega(\theta - L/v)}$$

$$Y_o = (\gamma\epsilon + \delta\eta)e^{-i\omega(\theta - L/v)}$$

Case A: 335°K.

L/v	0	5.04	12.60	21.50	30.20	35.20	40.50
x	0.0200	0.0190	0.0151	0.0107	0.0070	0.0065	0.0057
y	340	343	346	351	347	343	340

Case B: 337.5°K.

L/v	0	2.50	5.04	7.55	10.10	12.60	13.82	15.10	15.90
x	0.0200	0.0195	0.0190	0.0175	0.0158	0.0130	0.0105	0.0050	0.0012
y	340	342	346	350	355	365	377	410	418

If one supposes that the input is not sinusoidal but a step function, then

$$\bar{\mathbf{V}}_o = \frac{\mathbf{\Omega}(s)}{s}\mathbf{V}_i$$

in which $\mathbf{V}_i$ is the matrix of the two input steps. Then it follows that

$$\bar{\mathbf{V}}_o = \frac{e^{-sL/v}}{s}\begin{pmatrix}\alpha & \beta \\ \gamma & \delta\end{pmatrix}\mathbf{V}_i$$

and so

$$X_o = \alpha\epsilon + \beta\eta, \qquad \theta > \frac{L}{v}$$

$$Y_o = \gamma\epsilon + \delta\eta, \qquad \theta > \frac{L}{v}$$

with ϵ and η as steps in the influent.

Thus it is clear that there is no essential difference in the two methods; response to a sinusoidal or step input leads to the same conclusion.

Two integrals enter the expression for $\mathbf{\Omega}(s)$:

$$I = \frac{1}{v}\int_0^L k_s\,d\tau$$

$$= -\frac{1}{v}\int_0^L \frac{v}{x_s}\,dx_s = \ln\frac{x_{initial}}{x_{final}}$$

$$J = \frac{1}{v}\int_0^L \frac{k_s a x_s}{y_s^2}\,d\tau = \int_{x_{final}}^{x_{initial}} \frac{a\,dx_s}{y_s^2}$$

With these definitions

$$\begin{bmatrix} A & B \\ C & D\end{bmatrix} = \begin{bmatrix} -I & -J \\ QI & -\dfrac{KL}{v} + QJ\end{bmatrix}$$

From the foregoing data

	Case A	*Case* B
I	1.253	2.820
J	0.00135	0.001486

Case A

$$\Omega(j\omega) = e^{-40.50j\omega}\begin{bmatrix} -1.267 & 0.000021 \\ -142 & -1.308\end{bmatrix}$$

Case B

$$\Omega(j\omega) = e^{-15.90j\omega}\begin{bmatrix} -35.0 & -.00924 \\ 128{,}000 & 30.4\end{bmatrix}$$

In order to determine whether there is a basic difference between temperature profiles or concentration profiles at different parametric values two steady states will be treated, those at 335° and 337.5° in Figure 2*a* and *b*. The pertinent numerical data are

E = 22,500 cal./g. mole
p = 3.94 × 10^{12} min.$^{-1}$
Q = 7,300 (cu. cm.)(°C.)/mole
K = 0.200 min.$^{-1}$
T_i = 340°K. (feed temperature)
x_i = 0.020 mole/liter (feed concentration)

With a wall temperature of 337.5°K. the temperature of the reactant stream rises rapidly to 418°K., and at this point conversion is fairly complete. For a wall temperature of 335° there is only a moderate rise in temperature and the reaction proceeds slowly. From Figure 2*a* and *b* the data of cases *A* and *B* may be read:

In order to illustrate better the meaning of the quantities thus obtained, the amplitudes of the output signals or, alternatively, the steady state value resulting from step inputs, caused by an input signal of 1% of the steady state values applied on either feed temperature or feed concentrations, was calculated. For simplicity the notation (Y_o, X_i) will designate the amplitude of the outlet temperature variation due to a 1% sinusoidal change in the feed concentration. The amplitudes are independent of the excitation frequency. (*See* Table 1.)

From an inspection of these values it is apparent that operation under Case *B* is highly sensitive to small variations in the operating conditions and that Case *A* has no unusual features. This was expected once the whole series of steady state profiles had been calculated. It seems therefore that sensitivity can be predicted from the calculation of a single profile. It should be remarked that the method presented here is a linearization and results are valid only for infinitesimal signal amplitudes on the steady state values. Thus the results in Case *B*, while they indicate correctly the amplification of an infinitesimally small input signal, should not be considered correct when applied to a 1% signal. However, the prediction of sensitivity even in a qualitative way, if one is not prepared to accept the quantitative result, is of some value.

Table 1

	Case *A*		Case *B*	
	Absolute value	%	Absolute value	%
(X_o, X_i)	2.53 × 10^{-4}	4.4	70.0 × 10^{-4}	580
(X_o, Y_i)	7 × 10^{-5}	1.2	0.0317	2,600
(Y_o, X_i)	0.028°K.	0.0	25.6°K.	6.1
(Y_o, Y_i)	4.45°K.	1.3	103°K.	25

In this illustration the output signals on temperature and feed reactant concentration resulting from a given input signal were found. From a design point of view it is much more interesting to determine the effect of temperature and feed concentration signals on the product concentration signal. Although the method described below is not needed on the example used, the method is needed on more complicated systems. If $Z(\tau, t)$ is the product signal, then the linearized equation for Z is

$$\frac{\partial Z}{\partial \theta} + v\frac{\partial Z}{\partial \tau} = k_s X + \frac{k_s a x_s}{y_s^2}Y \qquad (14)$$

The matrix $\mathbf{M}$ for this problem when Equations (5), (6), and (14) are combined is

$$\mathbf{M}_s = -\begin{bmatrix} \displaystyle\int_0^L \frac{k_s + s}{v}\,d\tau & \displaystyle\int_0^L \frac{k_s a x_s}{v y_s^2}\,d\tau & 0 \\ \displaystyle\int_0^L -\frac{Qk_s}{v}\,d\tau & \displaystyle\frac{1}{v}\int_0^\tau \left(K - Q\frac{k_s a x_s}{y_s^2} + s\right)d\tau & 0 \\ \displaystyle -\int_0^L \frac{k_s}{v}\,d\tau & \displaystyle\int_0^L \frac{k_s a x_s}{v y_s}\,d\tau & \displaystyle\int_0^\tau \frac{s}{v}\,d\tau \end{bmatrix} \qquad (15)$$

and

$$\mathbf{\Omega}(s) = e^{-sL/v}\begin{bmatrix} \alpha & \beta & 0 \\ \gamma & \delta & 0 \\ I\alpha + J\gamma & I\beta + J\delta & 1\end{bmatrix} \qquad (16)$$

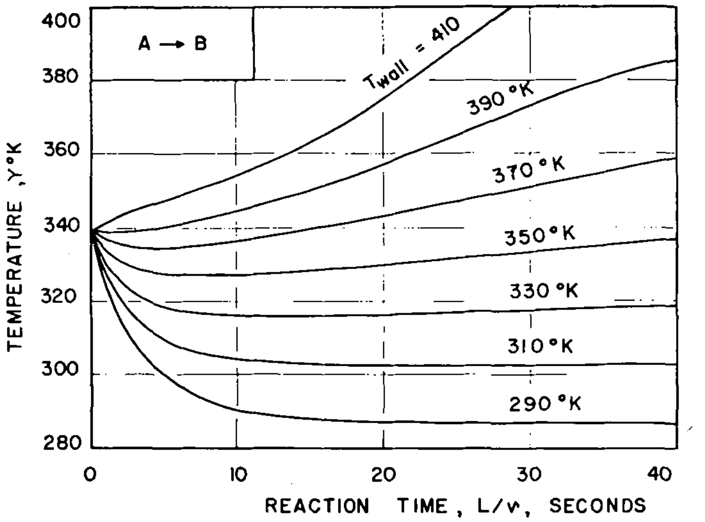


Fig. 3a. Temperature profiles in a tubular reactor; effect of wall temperature on an endothermic reaction. $E = 11{,}250$, $p = 1.59 \times 10^{13}$, $x_i = 0.20$, $Q = -10{,}000$, $T_i = 340°K.$, $K = 0.20$.

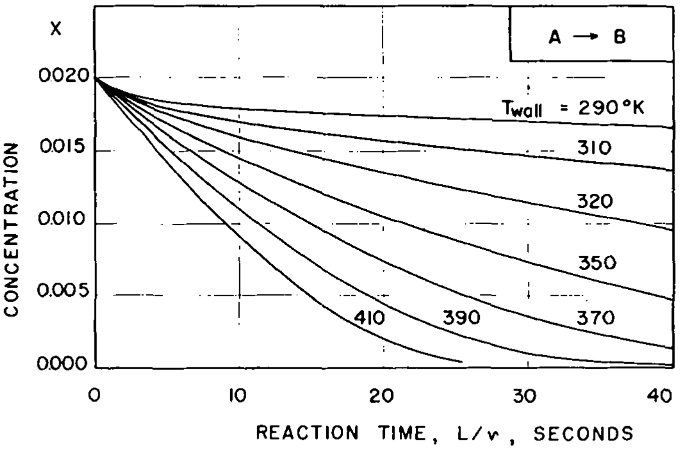


Fig. 3b. Concentration profiles in a tubular reactor; effect of wall temperature on an endothermic reaction. Data are the same as in Figure 3a.

where $\alpha, \beta, \gamma, \delta, I$, and J are as previously defined.

Thus the amplitude of the output signal on product concentration resulting from an input signal on feed concentration only or feed temperature only is given, respectively, by

$$|Z_0| = |I\alpha + J\gamma|\ |X_i|$$

$$|Z_0| = |I\beta + J\delta|\ |Y_i|$$

and with the data of the illustration

	Case A	Case B
$I\alpha + J\gamma$	1.776	91.4
$I\beta + J\delta$	0.00174	0.0218

Suppose now that it is required to keep the product stream quality within 5% of its steady state value. Assuming that this deviation is caused either by a variation in feed concentration alone or feed temperature alone, one may calculate the necessary percentage of regulation on the feed concentration or temperature; thus

	Case A	Case B
Feed concentration	2.02%	0.05%
Feed temperature	0.121% (0.4°)	0.013% (.04°)

It appears therefore that very stringent requirements on feed characteristics may be necessary under some operating conditions. The foregoing calculations are simple to carry out once the complete steady state profiles have been computed. Calculations such as these should give first approximations to the severity of the required process control and should give information in connection with the choice of control equipment.

A Complicated Example

The same example will be considered as was treated in Part I.

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + F, \qquad \Delta H_{12}$$

$$C \xrightarrow{k_3} E, \qquad \Delta H_3$$

A, B, C, F, and E may be the unsteady state concentrations and A_s, B_s, C_s, F_s, and E_s the corresponding steady state concentrations. a, b, c, f, and e may be the unsteady state parts of the concentration and t the unsteady part of the temperature; then

$$A = A_s + a \qquad C = C_s + c$$

$$B = B_s + b \qquad F = F_s + f$$

$$T = T_s + t$$

If the kinetics are second and first order, respectively, the equations of the unsteady state are

$$\frac{DA}{D\theta} = -k_1AB + k_2CF \tag{17}$$

$$\frac{DB}{D\theta} = -k_1AB + k_2CF \tag{18}$$

$$\frac{DF}{D\theta} = k_1AB - k_2CF \tag{19}$$

$$\frac{DC}{D\theta} = k_1AB - k_2CF - k_3C \tag{20}$$

$$\frac{DT}{D\theta} = K(T_w - T) + Q_{12}(k_1AB - k_2CF) + Q_3k_3C \tag{21}$$

In order to obtain the steady state solution only Equations (17), (20), and (21) need be used, as there are some simple relations among the concentrations. If the column matrices

$$\mathbf{V} = \begin{bmatrix} a \\ b \\ c \\ f \\ t \end{bmatrix}; \quad \mathbf{V}_o = \begin{bmatrix} a_o \\ b_o \\ c_o \\ f_o \\ t_o \end{bmatrix}; \quad \mathbf{V}_i = \begin{bmatrix} a_i \\ b_i \\ c_i \\ f_i \\ t_i \end{bmatrix}$$

and the matrix

$$\mathbf{F}(s, \tau) = \mathbf{P} - \frac{s}{v}\mathbf{I}$$

are defined where I is the unitary matrix and

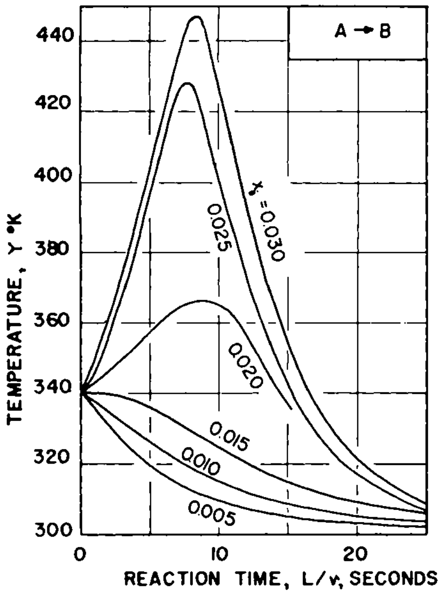


Fig. 4*a*. Temperature profiles in a tubular reactor; effect of feed dilution. $E = 11{,}250$, $p = 1.59 \times 10^{13}$, $Q = 10{,}000$, $K = 0.20$, $T_i = 340°\text{K.}$, $T_w = 300°\text{K.}$

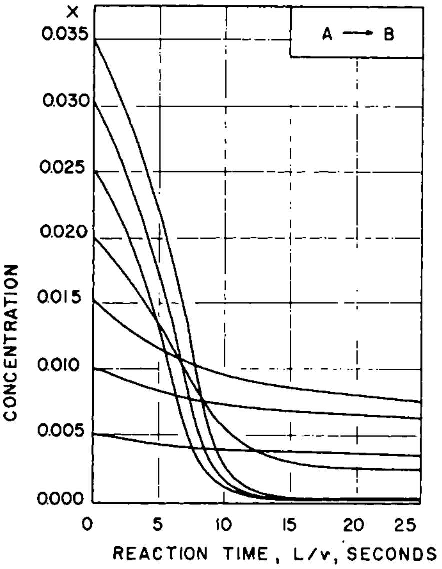


Fig. 4*b*. Concentration profiles in a tubular reactor; effect of feed dilution. Data are the same as in Figure 4*a*.

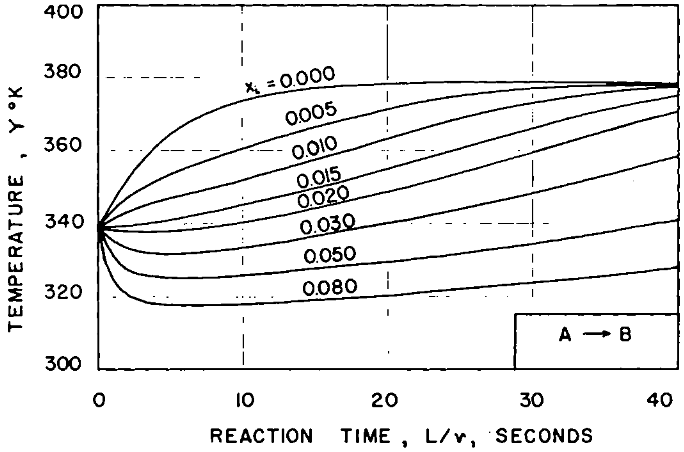


Fig. 5. Temperature profiles in a tubular reactor; effect of food dilution on an endothermic reaction. $E = 11{,}250$, $Q = -10{,}000$, $p = 1.59 \times 10^{13}$, $T_i = 340°\text{K.}$, $T_w = 380°\text{K.}$, $K = 0.200$.

$$\mathbf{P} = \frac{1}{v}\begin{bmatrix} -k_{1s}B_s & -k_{1s}A_s & k_{2s}F_s & k_{2s}C_s & -X_s \\ -k_{1s}B_s & -k_{1s}A_s & k_{2s}F_s & k_{2s}C_s & -X_s \\ k_{1s}B_s & k_{1s}A_s & -k_{2s}F_s - k_{3s} & -k_{2s}C_s & -Y_s \\ k_{1s}B_s & k_{1s}A_s & -k_{2s}F_s & -k_{2s}C_s & X_s \\ -k_{1s}B_s\dfrac{\Delta H_{12}}{c\rho} & -k_{1s}A_s\dfrac{\Delta H_{12}}{c\rho} & W_s & k_{2s}C_s\dfrac{\Delta H_{12}}{c\rho} & -Z_s \end{bmatrix} \quad (22)$$

where

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

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

$$W_s = k_{2s}F_s\,\frac{\Delta H_{12}}{c\rho} - k_{3s}\,\frac{\Delta H_3}{c\rho}$$

$$Z_s = -X_s\,\frac{\Delta H_{12}}{c\rho} - K - k_{3s}\,\frac{E_3}{RT_s^{\,2}}\,C_s\,\frac{\Delta H_3}{c\rho}$$

then

$$\mathbf{M} = \ln \mathbf{\Omega}(s) = \int_0^L \mathbf{F}(s, \tau)\,d\tau = \int_0^L \left(\mathbf{P} - \frac{s}{v}\,\mathbf{I}\right) d\tau = \frac{-sL}{v}\,\mathbf{I} + \int_0^L \mathbf{P}\,d\tau$$

Note that $\int_0^L \mathbf{P}\,d\tau$ is the analogue of Equation (10) and that Equation (22) is identical with the matrix which appeared in Part I for the same chemical system. In order to evaluate the integrated matrix in numerical terms eight calculations based on the steady state must be made. Therefore it will be assumed that the solution may be expressed in the form

$$\overline{\mathbf{V}}_o = \mathbf{\Omega}(s)\overline{\mathbf{V}}_i$$

where $\overline{\mathbf{V}}_o$ is the Laplace transform of $\mathbf{V}_o$ and $\overline{\mathbf{V}}_i$ is the Laplace transform of $\mathbf{V}_i$. If $\mathbf{V}_i$ represents the matrix of a sinusoidal input, then the output in complex form is

$$\mathbf{V}_o = \mathbf{\Omega}(j\omega)\mathbf{V}_i$$

$$\mathbf{V}_o = \mathbf{R}\mathbf{V}_i e^{-j\omega L/v}$$

where **R** is a matrix derived from

$$\exp \int_0^L \mathbf{P}\,d\tau = \mathbf{R}$$

by Sylvester's theorem in the same manner as Equation (13) was derived. **R** will be a matrix of the form

$$\mathbf{R} = [a_{ij}] \qquad i, j = 1, 2, 3, 4, 5$$

and so

$$a_o = (a_{11}a_i + a_{12}b_i + a_{13}c_i + a_{14}f_i + a_{15}t_i)e^{-j\omega(\theta - L/v)}$$

$$c_o = (a_{31}a_i + a_{32}b_i + a_{33}c_i + a_{34}f_i + a_{35}t_i)e^{-j\omega(\theta - L/v)}$$

$$t_o = (a_{51}a_i + a_{52}b_i + a_{53}c_i + a_{54}f_i + a_{55}t_i)e^{-j\omega(\theta - L/v)}$$

where in this set of formulas a_i, b_i, c_i, f_i, and t_i are the amplitudes of the input signals and the a_o, b_o, c_o, f_o, and t_o are the output sinusoidal responses. The gain can be simply calculated from these formulas. If the input had been a step function rather than a sinusoid, the

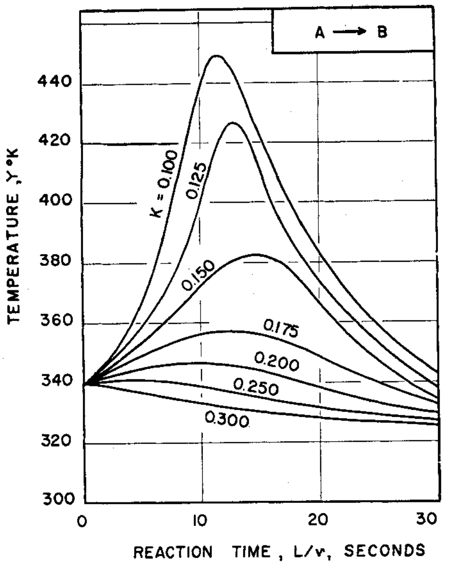


Fig. 6a. Temperature profiles in a tubular reactor; effect of heat transfer coefficient K. $E = 11{,}250$, $p = 7.89 \times 10^{12}$, $x_i = 0.020$, $T_i = 340$, $T_w = 320$.

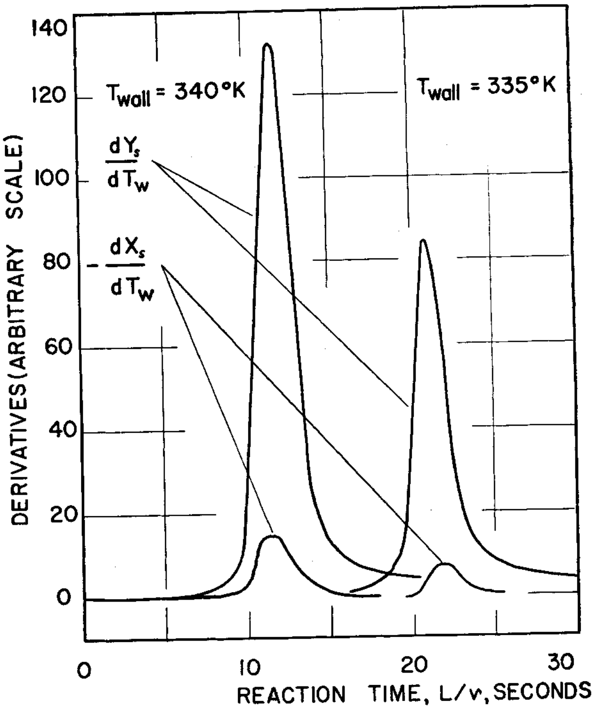


Fig. 7. Plot of derivatives of concentration and temperature with respect to the wall temperature against position in the reactor; effect of wall temperature. $E = 22{,}500$, $p = 3.94 \times 10^{12}$, $Q = 8{,}400$, $T_i = 340$°K., $K = 0.200$.

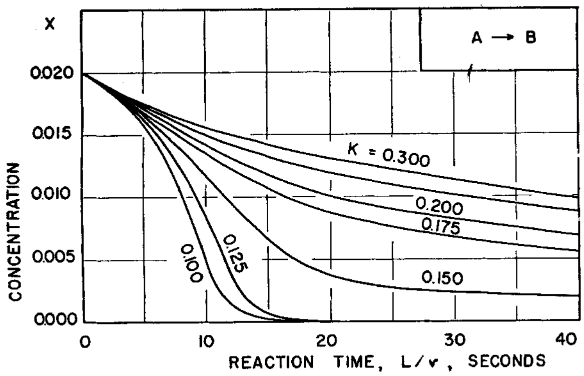


Fig. 6b. Concentration profiles in a tubular reactor; effect of heat transfer coefficient K. Data are the same as in Figure 6a.

exponential factors in these formulas would be missing, as if a_i, b_i, c_i, f_i, and t_i are steps in the input (small steps to be sure), then

$$\bar{\mathbf{V}}_o = \frac{\mathbf{\Omega}(s)}{s}\mathbf{V}_i$$

and the inverse of this is given by

$$a_o = (a_{11}a_i + a_{12}b_i + a_{13}c_i + a_{14}f_i + a_{15}t_i), \qquad \theta > \frac{L}{v}$$

with analogous formulas for b_o, c_o, f_o, and t_o. The quantity e_o may be computed as in the previous example and will not be repeated here.

STABILITY OF A TUBULAR REACTOR WITH A RECYCLE LOOP

Recycling is often used in industrial practice as a means of temperature control or to improve the yield if the yield per pass is low. The external feed and drawoff may be assumed to be q and the amount of recycle Q. The total internal flow is then $q + Q$. λ is defined as the recycle parameter

$$\lambda = q/Q$$

If by $\mathbf{V}_i$ the total feed matrix to the reactor is denoted, then

$$\bar{\mathbf{V}}_o = \mathbf{\Omega}(s)\bar{\mathbf{V}}_i$$

Also if $\mathbf{v}_i$ is the external feed (exclusive of recycle) and if differences in heat capacities are neglected, then

$$(Q + q)\bar{\mathbf{V}}_i = Q\bar{\mathbf{V}}_o + q\bar{\mathbf{v}}_i$$

where this is a combination energy and mass balance in matrix form.
Then

$$\bar{\mathbf{V}}_i = \frac{1}{1+\lambda}\bar{\mathbf{V}}_o + \frac{\lambda}{1+\lambda}\bar{\mathbf{v}}_i$$

and

$$\bar{\mathbf{V}}_o = \frac{1}{1+\lambda}\mathbf{\Omega}\bar{\mathbf{V}}_o + \frac{\lambda}{1+\lambda}\mathbf{\Omega}\bar{\mathbf{v}}_i$$

$$[(1+\lambda)\mathbf{I} - \mathbf{\Omega}]\bar{\mathbf{V}}_o = \lambda\mathbf{\Omega}\bar{\mathbf{v}}_i$$

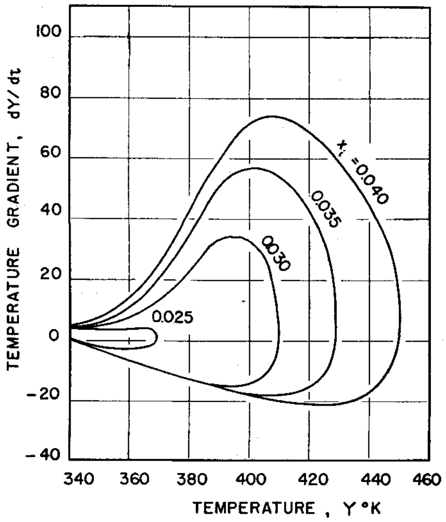
with the result

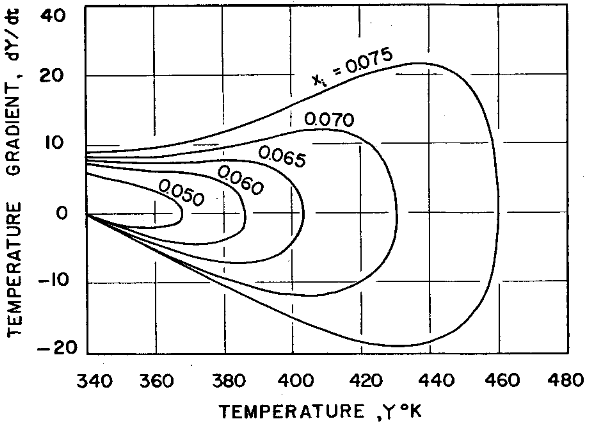
$$\bar{\mathbf{V}}_o = \lambda[(1+\lambda)\mathbf{I} - \mathbf{\Omega}]^{-1}\mathbf{\Omega}\bar{\mathbf{v}}_i \qquad (23)$$

where this is a matrix equation in which the order must be preserved and in which the exponent, -1, is standard notation for the inverse matrix. In Equation (23) the matrix

$$\mathbf{\Omega}_R = \lambda[(1+\lambda)\mathbf{I} - \mathbf{\Omega}]^{-1}\mathbf{\Omega}$$

is the transfer matrix for the recycle system. If $\mathbf{\Omega}$ is a matrix of the nth order, then it is clear that the transfer matrix is of the nth order each of whose terms consists of a quotient of sums of products of terms from $\mathbf{\Omega}$ and the adjoint of $[(1+\lambda)\mathbf{I} - \mathbf{\Omega}]$. Each of these sums of products will be divided by the determinant of $[(1+\lambda)\mathbf{I} - \mathbf{\Omega}]$.





←Fig. 8*a*. Phase diagram of a tubular-reactor temperature profile. $E = 33{,}750$, $p = 7.89 \times 10^{12}$, $Q = 4{,}370$, $K = 0.300$

↑ Fig. 8*b*. Phase diagram of a tubular-reactor temperature profile. $E = 13{,}100$, $p = 7.89 \times 10^{12}$, $Q = 4{,}370$, $K = 0.300$, $T_i = T_w = 340°\mathrm{K}$.

The details of a simple problem will now be carried out. Equation (16) gives the transfer function for the output product signal in terms of the input feed signals for the problem $A \longrightarrow B$. Then

$$[(1+\lambda)\mathbf{I} - \mathbf{\Omega}(s)] = e^{-sL/v} \begin{bmatrix} (1+\lambda)e^{Ls/v} - \alpha & -\beta & 0 \\ -\gamma & (1+\lambda)e^{Ls/v} - \delta & 0 \\ -(I\alpha + J\gamma) & -(I\beta + J\delta) & (1+\lambda)e^{(L/v)s} - 1 \end{bmatrix}$$

Then

$$\mathbf{\Omega}_R(s) = \lambda \begin{bmatrix} (1+\lambda)e^{Ls/v} - \alpha & -\beta & 0 \\ -\gamma & (1+\lambda)e^{Ls/v} - \delta & 0 \\ -(I\alpha + J\gamma) & -(I\beta + J\delta) & (1+\lambda)e^{(L/v)s} - 1 \end{bmatrix}^{-1} \begin{bmatrix} \alpha & \beta & 0 \\ \gamma & \delta & 0 \\ I\alpha + J\gamma & I\beta + \delta J & 1 \end{bmatrix} \tag{24}$$

When one takes the inverse Laplace transform of $\bar{\mathbf{V}}_o$, he is concerned with the poles of the transform and their location. If there are poles in the right half of the s plane, then there is no finite steady state solution and the system is said to be unstable. It is clear from the analysis thus far that poles can enter only at the zeros of the denominator of terms in $\mathbf{\Omega}_R(s)$ or at the zeros of the determinant of $[(1 + \lambda)\mathbf{I} - \mathbf{\Omega}]$, i.e., at the zeros of

$$[(1+\lambda)e^{(L/v)s} - 1][(1+\lambda)^2 e^{2Ls/v} - (\alpha + \delta)(1+\lambda)e^{Ls/v} + \delta\alpha - \beta\gamma] = 0$$

The determinant will always be a product of

$$(1+\lambda)e^{(L/v)s} - 1$$

and a polynomial in $(1 + \lambda)e^{Ls/v}$. With this in mind one finds that the remaining analysis will follow a general procedure rather than one which holds for the quadratic term only.

Since $\lambda > 0$

$$e^{Ls/v} = \frac{1}{1+\lambda}$$

can have a root in s only with negative real part. If σ_1 and σ_2 are the roots of the characteristic equation of the matrix $\mathbf{\Omega}$, in which

$$\sigma = (1+\lambda)e^{Ls/v}$$

then the system will be stable if the absolute values of the roots σ_1 and σ_2 are less than $1 + \lambda$; i.e.,

$$|\sigma_1| < 1 + \lambda$$

$$|\sigma_2| < 1 + \lambda$$

or if the roots in σ of the equation

$$(1+\lambda)^2\sigma^2 - (1+\lambda)(\alpha+\delta)\sigma + \alpha\delta - \beta\gamma = 0$$

lie inside the unit circle.

The transformation

$$\sigma = \frac{1+\xi}{1-\xi}$$

maps the inside of the unit circle on the left hand of the ξ plane. Hence if the equation

$$[(1+\lambda)^2 + (1+\lambda)(\alpha+\delta) + \alpha\delta - \beta\gamma]\xi^2 + 2\xi[(1+\lambda)^2 - \alpha\delta + \beta\gamma] + [(1+\lambda)^2 - (1+\lambda)(\alpha+\delta) + \alpha\delta - \beta\gamma] = 0$$

has no roots in the right half of the ξ plane, the solution is stable. This will always be a polynomial in ξ to which the Routh-Hurwitz criterion (*see* Part I) may be applied. If

$$C_1 = [(1+\lambda)^2 - \alpha\delta + \beta\gamma][(1+\lambda)^2 + (1+\lambda)(\alpha+\delta) + \alpha\delta - \beta\gamma] > 0$$

$$C_2 = [(1+\lambda)^2 - \alpha\delta + \beta\gamma][(1+\lambda)^2 - (1+\lambda)(\alpha+\delta) + \alpha\delta - \beta\gamma] > 0$$

then by the Routh-Hurwitz criterion the system is stable. In the physical problem considered here the stability condition may be obtained more simply from the characteristic equation of $\mathbf{\Omega}(s)$

$$\sigma^2 - (\alpha + \delta)\sigma + \alpha\delta - \beta\gamma = 0$$

by writing that $\pm(1 + \lambda)$ be exterior to the root interval and that the product of the roots lies inside the circle of radius $(1 + \lambda)^2$ centered at the origin. The treatment which has been given above is more general and would apply to a characteristic equation of any degree.

If the same analysis is applied to an isothermal system it may be shown without difficulty that it is always stable in this sense. It may be noted that the aforementioned restrictions are lifted if λ becomes infinite; i.e., there is no recycle.

If the details of Equation (24) are carried out, it may be shown that

$$Z_o = \frac{\lambda(1 + \lambda)e^{Li\omega/v}}{(1 + \lambda)^2 e^{2Li\omega/v} - (\alpha + \delta)(1 + \lambda)e^{Li\omega/v} + \alpha\delta - \beta\gamma}[UX_i + VY_i] \quad (25)$$

where X_i and Y_i are the complex feed signals on concentration and temperature and Z_o is the complex signal of the outlet product with

$$U = \frac{(I\alpha + J\gamma)(1+\lambda)e^{Li\omega/v} + (\beta\gamma - \alpha\delta)I}{(1+\lambda)e^{Li\omega/v} - 1}$$

$$V = \frac{(I\beta + J\delta)(1+\lambda)e^{Li\omega/v} + (\beta\gamma - \alpha\delta)J}{(1+\lambda)e^{Li\omega/v} - 1}$$

Example. A tubular reactor is assumed, with temperature and concentration profiles as in case A of the numerical example. The values of the elements for the matrix $\mathbf{\Omega}$ have also been calculated. For a recycle parameter $\lambda = 0.70$ the expressions in the stability conditions C_1 and C_2 may be calculated and are

$$C_1 = 0.197 > 0$$

$$C_2 = 11.0 > 0$$

This loop system with this recycle ratio is therefore stable. Such a loop would require an external feed concentration $x_i = 0.0404$ and would give a product concentration $z_0 = 0.0347$. The advantage of using a recycle loop in this case is that temperatures remain low, control is easy, and the ratio of concentrations B/A in the effluent has been increased by a factor of 2.43.

A discussion of the sign of the expressions C_1, C_2 shows in the present case that the loop is unstable for values of the recycle parameter $0 < \lambda < 0.308$ and stable if $\lambda > 0.308$.

The response of the system may be calculated on the assumption that an input signal frequency of $\omega = 0.01$. Equation (25) may be shown to reduce to

$$Z_o = (-0.606 + 0.500j)X_i + (-0.000623 + 0.000522j)Y_i$$

From this result the amplitude ratio and phase lag of output to input signal for an input signal on external feed concentration alone or feed temperature alone may be computed.

	Amplitude ratio	Phase lag
Z_o/X_i	0.785	130°
Z_o/Y_i	0.000814	130°

If the heat capacities of feed and product are markedly different, these quantities should be corrected.

Two or three calculations of this sort covering an adequate range of frequencies would usually give an idea of the control requirements. If more detailed information is required, Bode and Nyquist diagrams may be plotted in the usual way.

SUMMARY

In this paper an attempt has been made to analyze the quasiisothermal tubular reactor. This has been done by making extensive computations on the R.E.A.C., an analogue computer, for a simple mathematical model. These calculations reveal that regions of sensitivity exist in which slight changes in the operating conditions produce large changes in the yields. A method based on a local linearization was developed for the prediction of such sensitivity. This linearization requires for its use the calculation of the steady state temperature and concentration profiles. Small changes in the feed concentration or temperature may be transmitted through the reactor with accentuation or attenuation depending upon the region of operation. Numerical and theoretical examples were posed.

By analogy to electrical systems chemical systems with recycle or feedback should exhibit instability for some values of the parameters. These are shown to exist theoretically, and methods for prediction of the unstable regions are presented.

It should be pointed out clearly that the form of the solution is not exact for matrices. The quantity $\bar{\mathbf{V}}_0 = e^{\mathbf{M}}\bar{\mathbf{V}}_i$ after Equation (8) must be treated as an approximation of the true solution. The quantity appears to have the correct form but has not, because of the noncommutativity of some of the matrices involved.

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NOTATION

A, B, C, F, E, etc. = chemical species and concentrations of species
a, b, c, d, e, etc. = perturbations from steady state concentrations
c = specific heat of reactant stream
E = activation energy
h = over-all heat transfer coefficient
I, J = two calculated quantities defined in text
$\mathbf{I}$ = unitary matrix
j = $\sqrt{-1}$
K = $2rh/c\rho$
k = reaction velocity constant, also k_1, k_2, k_3
L = reactor length
$\mathbf{M}$ = matrix defined in text, Equation (8)
$\mathbf{N}$ = matrix defined in text, Equation (10)
p = frequency factor in velocity constant
Q = $-\Delta H/c\rho$
q = feed rate in recycle problems
Q = recycle rate in recycle problems
r = reactor radius
T_W = reactor ambient temperature
v = velocity in reactor
$\mathbf{V}_0$ = reactor output signal
$\mathbf{V}_i$ = reactor input signal
x = concentration of feed in first problem
y = temperature in first problem
X, Y, Z = perturbations on x, y, z
z = concentration of product in first problem

Greek Letters

$\alpha, \beta, \gamma, \delta$ = matrix elements in first problem
ϵ, η = amplitudes or steps in concentration and temperature, respectively
λ = recycle parameter = q/Q
σ = $(1 + \lambda)e^{Ls/v}$
ΔH = heat of reaction
θ = time
ρ = density
τ = reactor-length variable
$\mathbf{\Omega}(s)$ = open-loop transfer function
$\mathbf{\Omega}_R(s)$ = recycle-loop transfer function

Sub- and Superscripts

s = steady state value
—(over symbols) = Laplace transform

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