Tubular Reactor Sensitivity

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The empty lumped constant tubular reactor is considered for an incompressible fluid in which an arbitrary number of chemical reactions is occurring. It is assumed that the reactor influents are steady with time on the average but have superimposed upon them random fluctuations. If the random perturbations are infinitesimally small, the unsteady state equations are linear, the linearity following from the fact that any transient may be considered as a perturbation from the steady state. Thus the effluents are random functions whose mean and variance may be calculated with ease. Reactor sensitivity is defined as the ratio of the standard deviation of an output to the standard deviation of an input. The general theory is developed and two examples are worked to illustrate the method.

It is now recognized that the problem of designing a piece of equipment for steady state operation is bigger than it was once thought. No apparatus operates in a mathematical steady state, and it has been amply demonstrated that small variations in some parameters of a system may cause instabilities of very large variations in yield or quality. The well agitated continuous reactor has been treated in some detail (*1, 2, 3, 4*), while the tubular reactor has been treated by Barkelew (*5*) and others (*6*). The well agitated continuous reactor is more amenable to treatment since the mathematical background is well developed. The tubular reactor is more difficult and does not lend itself as readily to the kind of computation necessary for the solution of the problem.

In this paper the empty tubular reactor will be treated to determine the sensitivity of the outputs to certain inputs to the system. The sensitivity of the reactor is defined as the ratio of the standard deviation of an output to a standard deviation of an input when that input is subjected to a small random perturbation superimposed upon its steady state value. If the perturbations are small enough the unsteady state behavior resulting may be described by linear partial differential equations, where this statement is rigorously true for infinitesimal perturbations. The linear equations are obtained by linearizing the original nonlinear equations about the steady state solution for the problem. It is then shown how the variances or standard deviation, of the outputs may be related to the variances of the inputs and a sensitivity parameter defined therefore. An essential feature of this definition is that it puts on a qualitative basis what has been previously considered only on a qualitative basis.

In particular the lumped constant tubular reactor will be examined. This implies that there are no distributed parameters, the velocity profile is flat, heat transfer is lumped at the wall, diffusion is negligible, etc. It would be interesting to solve the problem with these assumptions relaxed, but so far this has not been possible.

MATHEMATICAL DEVELOPMENT

Consider a lumped constant reactor in which chemical transformations are carried out in a fluid which is essentially incompressible. Let f_{ij} be the reaction rate in moles per unit volume of component i formed in the j^{th} reaction per unit time.
where

$$\sum_{i=1}^{n} a_{ij} A_i = 0 \quad , \quad j = 1, 2, \ldots, m \quad (1)$$

are the m reactions. The a_{ij} are stoichiometric coefficients, where a_{ij} is taken positive for a product. It is assumed that the velocity profile is flat. Under these circumstances the conservation equation for component i is

$$u \frac{\partial c_i}{\partial x} + \frac{\partial c_i}{\partial \theta} = \sum_{j=1}^{m} f_{ij} \ ,$$
$$\mathrm{i} = 1, 2, 3, \ldots n \qquad (2)$$

In the j^{th} reaction

$$\frac{f_{ij}}{a_{ij}} = \frac{f_{kj}}{a_{kj}} = f_j$$

so that

$$\frac{Dc_i}{D\theta} = u \frac{\partial c_i}{\partial x} + \frac{\partial c_i}{\partial \theta}$$
$$= \sum_{j=1}^{m} a_{ij} f_j \ , \ \mathrm{i} = 1, 2, 3, \ldots n \quad (3)$$

In this equation f_j may be a function of all n concentrations c_i and the temperature. While Equation (3) is really n equations, these are not all independent. In fact the number of independent equations is equal to the rank of the matrix:

$$\begin{bmatrix} a_{11} & a_{12} \ldots\ldots a_{1m} \\ a_{21} & a_{22} \ldots\ldots a_{2m} \\ \vdots & \\ a_{n1} & a_{n2} \ldots\ldots a_{nm} \end{bmatrix} = \overline{\overline{\mathrm{A}}}$$

If the rank of this matrix is r, then there are r independent equations. Suppose, for the sake of convenience, that the r^{th} order determinant which is not zero is in the upper left-hand corner of $\overline{\overline{\mathrm{A}}}$. (If it is not, the component species may be renumbered so that this is the

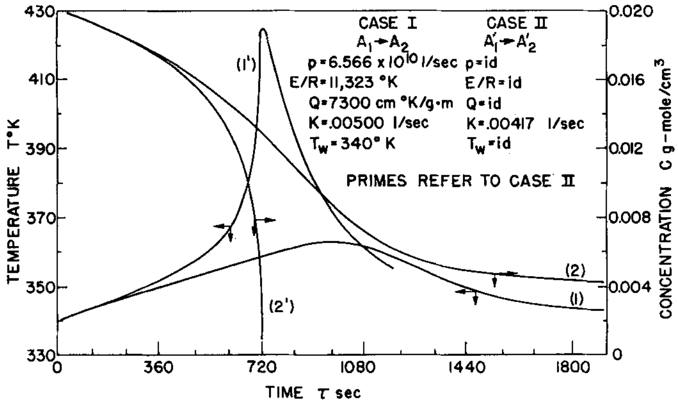

Fig. 1. Steady state profiles, first-order reaction K = 0.00500 and K = 0.00417 (number one refers to temperature and number two to concentration, primes refer to Case II).

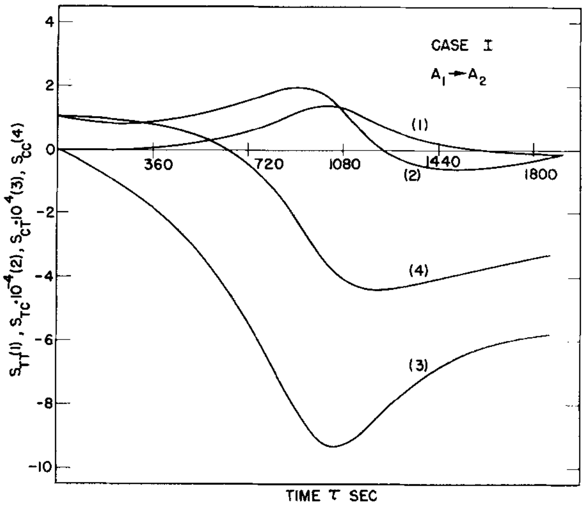

Fig. 2. Sensitivities of the temperature and concentration on input temperature and concentration (numbers of this curve and those to follow refer to the proper ordinate to be read).

case.) Then there exists $n-r$ sets of constants $E_i^{(k)}$, i = 1 to r, $k = n+1$ to n such that

$$\frac{Dc_k}{D\theta} = \sum_{i=1}^{r} \frac{Dc_i}{D\theta} E_i^{(k)} ,$$

$$k = r+1, r+2, \ldots, n \qquad (4)$$

This may be integrated to give

$$c_k - c_{ko} = \sum_{i=1}^{r} E_i^{(k)} (c_i - c_{io}) \qquad (5)$$

and thus there are r independent concentrations.

The energy equation, with the usual simplifying assumptions, may be written

$$\frac{DT}{D\theta} = \frac{hP}{Ac_p}(T_w - T) + \frac{1}{c_p}\sum_{j=1}^{m} f_j(-\Delta H_{Tj}) \qquad (6)$$

where $c_p = \sum_{i=1}^{n} c_i\, c_{pi}$, c_{pi} being the heat capacity per mole of component i and c_p is assumed constant.

The analytic solution of Equations (3) and (6), $r+1$ in number, is not possible. However an approximation may be made which will be shown later to be not an approximation at all for the result desired here. The authors' interest in this paper is in unsteady state solutions near steady state solutions. Steady state solutions will follow from the set of equations

$$u\frac{dc_{is}}{dx} = \sum_{j=1}^{m} a_{ij} f_j$$

$$u\frac{dT_s}{dx} = \frac{hP}{Ac_p}(T_w - T_s) + \frac{1}{c_p}\sum_{j=1}^{m} f_j(-\Delta H_{Tj})$$

$$c_{is} = c_{io} , \quad x=0$$

$$T_s = T_o , \quad x=0$$

These form an ordinary set of differential equations $r+1$ in number whose numerical solutions may be found by any of the standard techniques. Call these solutions

$$c_{is} = F_i\left(\frac{x}{u}, c_{10}, c_{20}, \ldots, c_{n0}\right) \qquad (7)$$

$$T_s = G\left(\frac{x}{u}, c_{10}, c_{20}, \ldots, c_{n0}\right) \qquad (7)$$

Consider now unsteady state solutions in the neighborhood of these steady state solutions. That is, let

$$c_i(x,\theta) = c_{is}(x) + \gamma_i(x,\theta) , i = 1 \text{ to } r$$

$$T(x,\theta) = T_s(x) + \gamma_{r+1}(x,\theta)$$

where γ_j is assumed to be small.

The right-hand side of Equations (3) and (6) may now be expanded into their Taylor series expansions about the local steady state with only the linear terms retained. Under these circumstances

$$\frac{D\gamma_i}{D\theta} = \sum_{j=1}^{r+1} \alpha_{ij}\gamma_j , \text{i} = 1 \text{ to } r+1 \qquad (9)$$

where the α_{ij} are functions of x, calculated from the steady state solutions. Note that the $\gamma_i(x, t)$ are the unsteady state perturbations superimposed upon steady state solutions and that the above set of equations is valid only for infinitesimal perturbations. Let the perturbations be introduced through the influent condition so that

$$\gamma_i = \gamma_{jo}(\theta) \quad , \; x = o \; ,$$

$$j = 1, 2, \ldots r+1 \qquad (10)$$

The set of Equations (9) have characteristics $u\theta - x$ = constant and the differential equations along these characteristics are, written in vector form

$$\frac{d\overline{\gamma}}{d\tau} = \overline{\overline{M}}\,\overline{\gamma}$$

$$\overline{\gamma} = \overline{\gamma_o} \; , \; \tau = o \qquad (11)$$

where $\overline{\overline{M}}$ is the matrix $[\alpha_{ij}]$. This set of equations may be solved by the following useful artifice. Define a matrix $\overline{\overline{Y}}$ as the solution of the system

$$\frac{d\overline{\overline{Y}}}{d\tau} = \overline{\overline{M}}\,\overline{\overline{Y}}$$

$$\overline{\overline{Y}} = \overline{\overline{I}} \; , \; \tau = o \qquad (12)$$

where $\overline{\overline{I}}$ is the idem matrix of order $r+1$. Then the solution of Equation (11) is

$$\overline{\gamma} = \overline{\overline{Y}}\,\overline{\gamma_o}$$

as may be shown by direct substitution. In terms of the variables in Equation (9) the solution is

$$\overline{\gamma} = \overline{\overline{Y}}(\tau)\,\overline{\gamma_o}(t-\tau) \quad , \; \text{t} > \tau \quad (13)$$

where τ is interpreted as x/u in the reactor. For a fixed value of τ Equation (13) would then give a fixed point in the reactor the perturbation γ as a function of the time.

The inlet perturbations will now be considered as stationary random fluctuations with zero mean and specified variance. Although the variance should be calculated over an ensemble of functions, the ergodic hypothesis will be invoked so that time averages may be used. The operator is defined (7) as

$$E[\;] = \lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}[\;]\,dt$$

It follows that $E[\gamma_o(t)] = 0$ and $E[\gamma(t)] = 0$ if $\gamma_o(t)$ is a stationary process. The correlation function for two random functions $z(t)$ and $y\ (t)$ is defined as

$$\phi_{zy}(s) = E\,[z(t)\ y(t+s)]$$

where $\phi_{zy}(0)$ is the covariance and $\phi_{yy}(0)$ is the variance.

A correlation matrix $\overline{\overline{\phi}}(s)$ may be defined by the following procedure. Form the product $\overline{\gamma}\,\overline{\gamma}^T$ and form

$$E\,[\overline{\gamma}(t)\ \overline{\gamma}^T(t+s)] = \overline{\overline{\phi}}(s) \qquad (14)$$

Then the elements on the main diagonal of $\overline{\overline{\phi}}(s)$ are the auto correlation functions

$$\phi_{\gamma_i \gamma_i}(s)$$

while the elements off the diagonal are the cross correlation functions

$$\phi_{\gamma_i \gamma_j}(s)\quad,\ i \neq j$$

and, for $s=o$, are the variances and covariances, respectively.

Application of (14) to (13) gives

$$\overline{\overline{\phi}}(s) =$$

$$E\,[\overline{\overline{Y}}(\tau)\ \overline{\gamma}_o(t-\tau)\ \overline{\gamma}_o^T(t-\tau+s)\ \overline{\overline{Y}}^T(\tau)]$$

$$= \overline{\overline{Y}}(\tau)\ \overline{\overline{\phi}}_o(s)\ \overline{\overline{Y}}^T(\tau) \qquad (15)$$

Note that $\overline{\overline{\phi}}(s)$ also depends upon the choice of τ, although $\overline{\overline{\phi}}_o(s)$ does not because of the stationary nature of the process. $\overline{\overline{\phi}}_o(s)$ is a square matrix, the off-diagonal terms representing the correlation of the inputs. If there is no input coupling, $\overline{\overline{\phi}}_o(s)$ is diagonal. The variances and covariances may be computed from

$$\overline{\overline{\phi}}(o) = \overline{\overline{Y}}(\tau)\ \overline{\overline{\phi}}_o(o)\ \overline{\overline{Y}}^T(\tau)$$

For the sake of convenience let $\phi_{\gamma_i \gamma_j}(o) = \phi_{ij}$, and $\phi_{\gamma_{io} \gamma_{jo}}(o) = \phi_{ijo}$; then

$$\phi_{ij}(s) = \sum_{k=1}^{r+1} Y_{ij} \sum_{p=1}^{r+1} \phi_{kpo}(s)\ Y_{jp}$$

and

$$\sigma^2_{ij} = \phi_{ij}(o) = \sum_{k=1}^{r+1} Y_{ij} \sum_{p=1}^{r+1} \phi_{kpo}(o)\ Y_{jp}$$

In the special case where there is no input coupling, $\phi_{ijo}(o) = 0,\ i \neq j$

$$\sigma^2_{ij} = \sum_{k=1}^{r+1} Y_{ik}\, Y_{jk}\, \phi_{kko}(o)$$

$$\sigma^2_{ii} = \sum_{k=1}^{r+1} Y^2_{ik}\, \sigma^2_{kko}$$

If only one input has a random perturbation, say the k^{th}, then

$$\frac{\sigma^2_{ii}}{\sigma^2_{kko}} = Y^2_{ik}$$

and

$$\frac{\sigma_{ii}}{\sigma_{kko}} = Y_{ik}$$

Now in the limit for very small perturbations this formula is exact, since in this case the approximation made to linearize the nonlinear transient equation is not an approximation at all. Therefore a parameter S_{ik}, the sensitivity

$$S_{ik} = \frac{\sigma_{ii}}{\sigma_{kko}} = Y_{ik} \qquad (16)$$

may be defined and its physical significance is apparent. S_{ik}, or Y_{ik}, gives the standard deviation of the i^{th} output caused by a prescribed standard deviation in k^{th} input. One sees immediately that the artifice used to solve Equation (11) gives a matrix $\overline{\overline{Y}}$, the elements of which have an immediate physical significance. Further it should be stressed that the sensitivity parameter depends upon steady state calculations only. For example if C is an effluent concentration and T is an inlet temperature, then S_{CT} is the sensitivity of the concentration on the temperature.

EXAMPLE I

Consider the irreversible reaction $A_1 \rightarrow A_2$, or $A_2 - A_1 = 0$, first order on A_1; Then

$$\frac{\partial c_1}{\partial \tau} + \frac{\partial c_1}{\partial \theta} = -\,kc_1$$

$$\frac{\partial T}{\partial \tau} + \frac{\partial T}{\partial \theta} = K(T_w - T) + kc_1\left(\frac{-\Delta H}{c_p}\right)$$

Let c_{1s} and T_s satisfy

$$u\,\frac{dc_{1s}}{dx} = -\,kc_{1s}$$

$$(17)$$

$$n\,\frac{dT_s}{dx} = K(T_w - T_s) + kc_{1s}\left(-\frac{\Delta H}{c_p}\right)$$

$$c_{1s} = c_{1so}\ ,\ x = o$$

$$T_s = T_{so}\ ,\ x = o$$

and let

$$\gamma_1 = c_1(x, \theta) - c_{1s}(x)$$

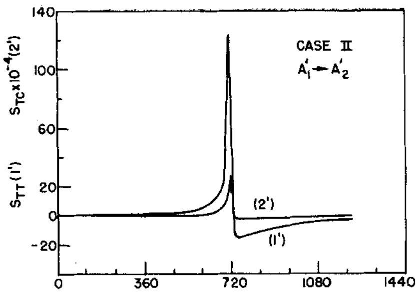

Fig. 3. Sensitivities of the temperature, first-order reaction K = 0.0041667.

$$\gamma_2 = T(x, \theta) = T_s(x)$$

Then

$$\frac{d\gamma_1}{d\tau} = \alpha_{11}\,\gamma_1 + \alpha_{12}\,\gamma_2$$

$$;\ \frac{d\overline{\gamma}}{d\tau} = \overline{\overline{M}}\,\overline{\gamma}$$

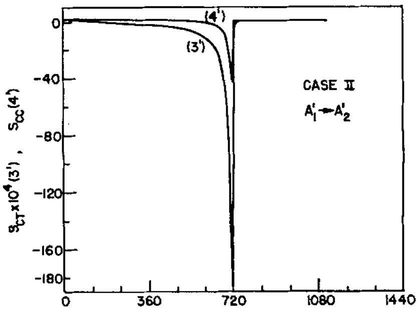

Fig. 4. Sensitivities of the reactant, first-order reaction K = 0.0041667.

$$\frac{d\gamma_2}{d\tau} = \alpha_{21}\,\gamma_1 + \alpha_{22}\,\gamma_2$$

where

$$\overline{\overline{M}} = \begin{pmatrix} -\,k_s & \dfrac{-\,k_s\,c_{1s}\,E}{RT_s^{\,2}} \\ \dfrac{-\Delta H\,k_s}{c_p} & \dfrac{-\Delta H\,k_s\,c_{1s}\,E}{c_p\,R\,T_s^{\,2}} - K \end{pmatrix}$$

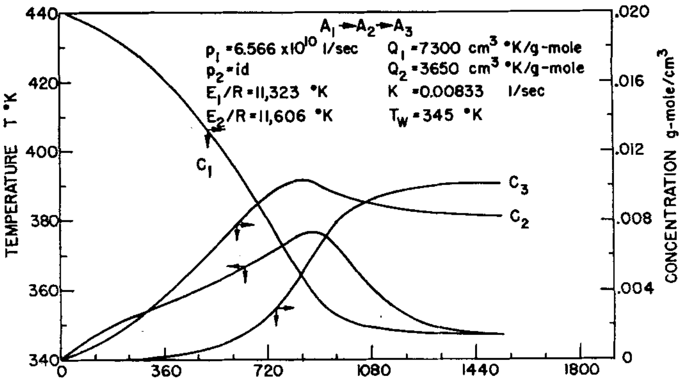

Fig. 5. Steady state profiles, two first-order consecutive exothermic reactions.

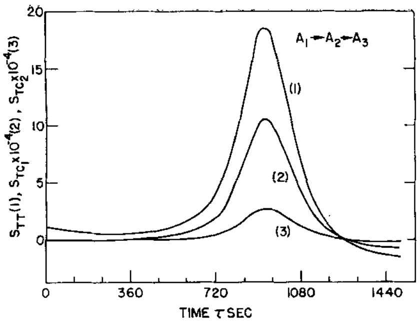

Fig. 6. Sensitivities of the temperature, two first-order consecutive exothermic reactions.

In this case

$$\overline{\overline{Y}} = \begin{bmatrix} Y_{11} & Y_{12} \\ Y_{21} & Y_{22} \end{bmatrix}$$

$$\overline{\overline{Y}} = \overline{\overline{I}}, \ \tau = 0$$

and

$$\frac{dY_{11}}{d\tau} = -k_s Y_{11} - \frac{k_s c_{1s} E}{RT_s^2} Y_{21}$$

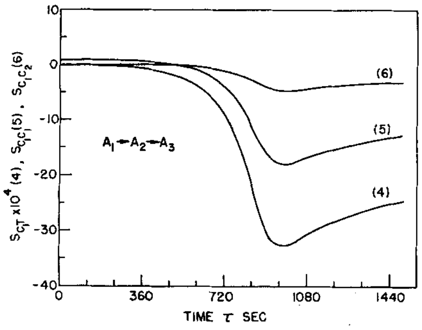

Fig. 7. Sensitivities of the reactant, two first-order consecutive exothermic reactions.

$$\frac{dY_{21}}{d\tau} = \frac{(-\Delta H)\ k_s}{c_p} Y_{11}$$

$$+ \left[\frac{(-\Delta H)\ k_s c_{1s} E}{c_p RT_s^2} - K \right] Y_{21}$$

$$Y_{11} = 1 \ , \ Y_{21} = 0 \ , \ \tau = 0$$

$$\frac{dY_{12}}{d\tau} = -k_s Y_{12} - \frac{k_s c_{1s} E}{RT_s^2} Y_{22}$$

$$\frac{dY_{22}}{d\tau} = \frac{(-\Delta H)\ k_s}{c_p} Y_{12}$$

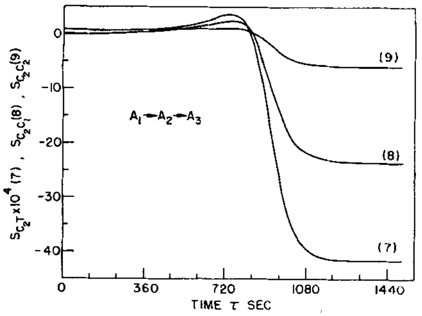

Fig. 8. Sensitivities of the intermediate product, two first-order consecutive exothermic reactions.

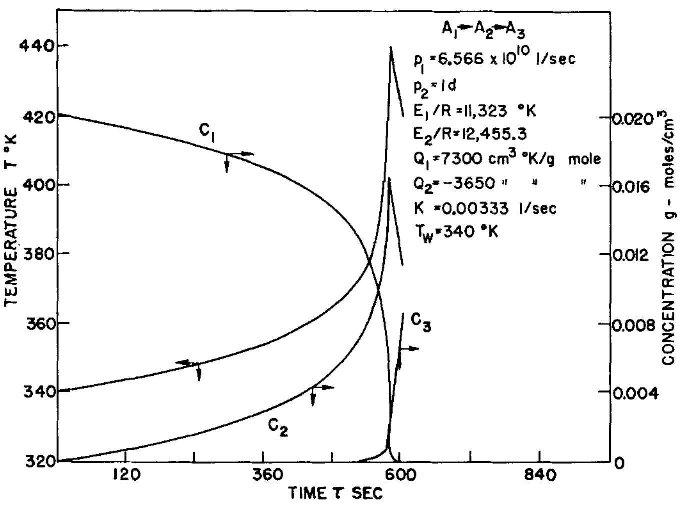

Fig. 9. Steady state profiles, two first-order consecutive exothermic and endothermic reactions.

$$+ \left[\frac{(-\Delta H)\ k_s c_{1s} E}{c_p RT_s^2} - K \right] Y_{22}$$

$$Y_{12} = 0 \ , \ Y_{22} = 1 \ , \ \tau = 0$$

These equations are the same in pairs and indeed are the same save for initial conditions. The equations for solution are six. The steady state equations need solution; then two sets of two each are solved, where the coefficients in the latter are obtained only after the steady state solutions are calculated. With no input coupling

$$\sigma^2_{\gamma_1} = Y^2_{11}\, \sigma^2_{\gamma_{10}} + Y^2_{21}\, \sigma^2_{\gamma_{20}}$$

$$\sigma^2_{\gamma_2} = Y^2_{12}\, \sigma^2_{\gamma_{10}} + Y^2_{22}\, \sigma^2_{\gamma_{20}}$$

The numerical data are given on Figure 1 which is a plot of steady state temperature and concentration profiles for two different values of K. Figures 2, 3, and 4 give the four sensitivities for the two steady state cases computed above. These curves are calculated for a standard deviation in the inlet temperature and concentration of 1°C. and 10^{-4} g. mole/cc., respectively. The interesting point in these calculations is that the system is extremely sensitive to the parameter K.

EXAMPLE II

As a second example the reaction $A_1 \rightarrow A_2 \rightarrow A_3$ will be considered. It will be assumed here that the reactions are first order on A_1 and first order on A_2 so that the steady state solutions are

$$u \frac{dc_{1s}}{dx} = k_{1s}\, c_{1s}$$

$$u \frac{dc_{2s}}{dx} = k_{1s}\, c_{1s} - k_{2s}\, c_{2s}$$

$$u \frac{dc_{3s}}{dx} = k_{2s}\, c_{2s}$$

$$u \frac{dT_s}{dx} = k_{1s}\, c_{1s} \left(-\frac{\Delta H_2}{c_p} \right)$$

$$+ k_{2s}\, c_{2s} \left(-\frac{\Delta H_2}{c_p} \right) + K\,(T_w - T_s)$$

with appropriate initial conditions. The third equation is obviously superfluous, and it may be shown that the rank of the stoichiometric matrix is two. The $\overline{\overline{M}}$ matrix for this case is

$$\overline{\overline{M}} = \begin{bmatrix} -k_{1s} & 0 & \dfrac{-k_{1s}\, c_{1s}\, E_1}{RT_s^2} \\ k_{1s} & -k_{2s} & \left[\dfrac{k_{1s}\, c_{1s}\, E_1}{RT_s^2} - \dfrac{k_{2s}\, c_{2s}\, E_2}{RT_s^2} \right] \\ -\dfrac{k_{1s}\, c_{1s}\, \Delta H_1}{c_p} & -\dfrac{k_{2s}\, c_{2s}\, \Delta H_2}{c_p} & \left[\dfrac{-\Delta H_1}{c_p} k_{1s} \dfrac{E_1\, c_{1s}}{RT_s^2} + \dfrac{-\Delta H_2}{c_p} k_{2s} \dfrac{E_2\, c_{2s}}{RT_s^2} - K \right] \end{bmatrix}$$

In this instance there will be three steady state differential equations and three sets of three each of differential equations. The equations in the three sets are identical but must be calculated from different initial conditions. The numerical data for this case are given on the graphs, Figure 5 representing a calculation for two successive exothermic reactions. Figure 6 gives the sensitivity of the temperature on itself, on A_1, and on A_2; Figure 7 gives sensitivities of A_1 on each of the three pertinent quantities, T, A_1, and A_2, and Figure 8 repeats the same calculation for A_2. Figure 9 considers two successive reactions with the first exothermic and the second endothermic, and Figures 10, 11, and 12 give the corresponding sensitivities. The same standard deviations were used in these problems as in the first calculation. Actually plots of this kind are not rigorously correct, since the technique developed above holds only for infinitesimal standard deviations. Plots which would be rigorous are those of Y_{ij} vs. τ.

In the first example the sensitivity analysis shows that a change in the value of K of 16% changes the sensitivities by more than 10,000%. From a computational point of view the quantity which is needed is the matrix $\overline{\overline{Y}}$. The elements of this matrix are the sensitivities, and their value gives the pertinent information except for coupling.

CONCLUSIONS

The calculations were performed on a computer. The Runge-Kutta-Gill routine was used for the solution of the differential equations, and considerable effort was expended to determine the proper interval of integration. The interval was chosen in an optimal way largely by trial and error; it was decreased in size until essentially the result of the calculation was unchanged by further reduction. In actual fact this may never be achieved, since a further reduction in interval size may lead to a point beyond which round-off error increases the errors. It was wound in these calculations that an interval between 0.1 and 1 sec. was satisfactory. Some effort was made to devise a routine whereby the computer could choose the interval size, but a suitable criterion for choice which was general enough was never achieved.

It is felt that this technique, that of characterizing input perturbations by means of a random process, should have other applications, and the use of the linearizing procedure, valid for infinitesimal perturbations, should enable one to characterize sensitivities for a wide variety of processes where the nonlinear transient equations cannot be solved at all. While one might argue that results equivalent to those derived here could be derived from a frequency-response method with infinitesimal input amplitudes, it is difficult to see how the effect of input coupling could be measured by such a technique.

NOTATION

a = radius of reactor
a_{ij} = stoichiometric coefficient of i^{th} component in the j^{th} reaction
A_i = chemical component
$\overline{\overline{A}}$ = stoichiometric matrix
A = cross-sectional area of reactor

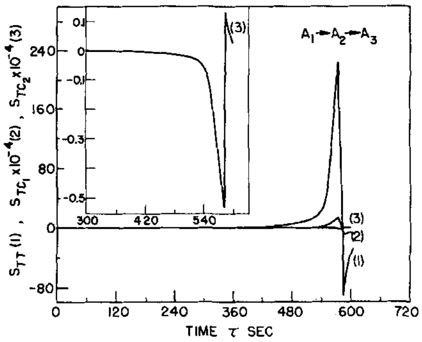

Fig. 10. Sensitivities of the temperature, two first-order consecutive exothermic and endothermic reactions.

c_i = concentration of component i (moles/unit volume)
c_{io} = inlet concentration of component i
c_p = molar heat capacity of reaction mixture
c_{pi} = molar heat capacity of component i

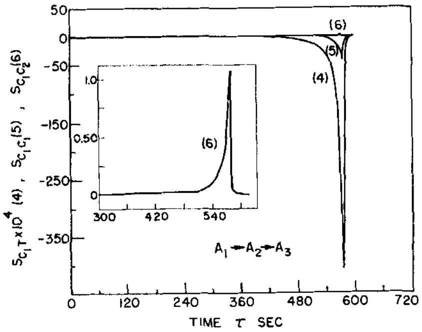

Fig. 11. Sensitivities of the reactant, two first-order consecutive exothermic and endothermic reactions.

c_{is} = steady state concentration of component i
D = substantial operator
E = averaging operator (also used as an activation energy)
$E_i^{(k)}$ = constant defined in text
E_1, E_2 = activation energies
f_{ij} = reaction rate, moles of i formed in the j^{th} reaction (moles/unit volume/time)

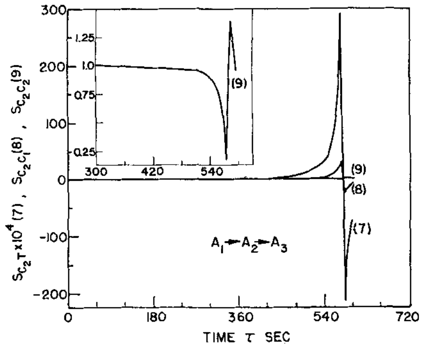

Fig. 12. Sensitivities of the intermediate product, two first-order consecutive exothermic and endothermic reactions.

f_j = intrinsic rate of j^{th} reaction
h = wall heat transfer coefficient
ΔH_{Tj} = heat of reaction of j^{th} reaction at temperature T
$\overline{\overline{I}}$ = idem matrix
K = $2h/ac_p$
k_s = reaction velocity constant computed from a steady state temperature profile (k_{1s} and k_{2s} have the same significance)
$\overline{\overline{M}}$ = matrix defined in text
p = frequency factor in $k = p \exp\left(-\frac{E}{RT}\right)$
P = reactor-tube perimeter
Q = $\Delta H/c_p$
S_{ij} = sensitivity parameter
T = temperature of reaction mixture
T_w = wall temperature
T_s = steady state reaction mixture temperature
T_o = inlet reaction mixture temperature
u = axial velocity of reaction mixture
x = axial variable
$\overline{\overline{Y}}$ = matrix defined in text
Y_{ij} = element of matrix $\overline{\overline{Y}}$

Greek Letters

α_{ij} = element of matrix $\overline{\overline{M}}$
γ_i = perturbation in concentration
$\underline{\gamma}$ = vector of γ_i
$\underline{\gamma}_o$ = vector of inlet perturbations
ϕ_{zy} = correlation function between z and y (ϕ_{yy} is an autocorrelation function)
$\phi_{\gamma_i\gamma_j}^{(s)}$ = correlation function between γ_i and γ_j ($= \phi_{ij}$)
$\overline{\overline{\phi}}(s)$ = matrix of ϕ_{ij}
$\overline{\overline{\phi}}_o(s)$ = matrix of inlet correlation functions
σ = standard deviation
σ^2_{ij} = covariance between γ_i and γ_j
$\sigma^2_{\gamma_i}$ = variance in γ_i
$\sigma^2_{\gamma_{io}}$ = variance in γ_{io}, an input
θ = time
τ = residence time

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