k = thermal conductivity of fluid, (B.t.u.)(ft.)/(hr.)(sq. ft.)(°F.)
L = length of pipe, ft.
n = constant in Equation (7) = slope of j_h vs. Re_f curves in Figure 9 = 1 − slope of curves in Figure 10, dimensionless
p = *absolute pressure*, lb.-force/sq. ft.
Δp_{fr} = frictional pressure drop, lb. force /sq. ft.
Pr = Prandtl number = $C_p\mu/k$, dimensionless
Re = Reynolds number = $DV\rho/\mu$, dimensionless
t = temperature of fluid, °F.
t_b = average bulk temperature of fluid = $(t_1 + t_2)/2$, °F.
t_f = film temperature = $(t_b + t_s)/2$, °F.
t_s = inside surface temperature of pipe, °F.
Δt_{max} = temperature difference between inside surface of pipe and axis of pipe, °F.
Δt_{mean} = temperature difference between inside surface of pipe and bulk of fluid, °F.
T = absolute temperature, °R.
V = velocity of fluid, ft./hr.
V_b = velocity of fluid defined by G/ρ_{avg}
v = specific volume of fluid, cu. ft./lb.
w = weight rate of air flow, lb./hr.
α = ratio of total diffusivity of heat to total diffusivity of momentum, dimensionless
μ = viscosity of fluid, lb./(ft.)(hr.)
ρ = density of fluid, lb./cu. ft.
ρ_{avg} = density of fluid evaluated at $(p_1 + p_2)/2$ and t_b, lb./cu. ft.
ρ_f = density of fluid evaluated at $(p_1 + p_2)/2$ and t_f, lb./cu. ft.

Subscripts

1 = test pipe entrance (slightly different for pressure drop than for heat transfer)
2 = test pipe exit (slightly different for pressure drop than for heat transfer)
b = bulk, evaluated at temperature t_b
f = film, fluid properties evaluated at temperature t_f

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Control of Continuous-flow Chemical Reactors

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I. Frequency-response Relations for a Continuously Stirred Tank Reactor

Although applications of frequency-response techniques to the control of processes are well known in electrical engineering and in the instrumentation field, relatively little has been done to develop in a quantitative manner the employment of these techniques in the control of chemical reactions. As a result the control characteristics of chemical reactors are today being come upon either in the pilot plant or in the field. This study was motivated by the fact that processes designed on the basis of steady state operation may sometimes prove inadequate for automatic control.

It is the purpose of this paper then to show how frequency-response analysis may be used to develop the theory of control of continuous-flow chemical reactors. The response equations are developed for simple and complex reactions of any order, and, for clarity, their applications are illustrated with selected numerical examples and by the use of polar plots.

The effects on the reactor-product stream which are considered in the equations include variations in feed-stream composition and temperature, the heat input or cooling of the reactor by coils, and the effect of temperature level on the rates of reaction and of heat release. How automatic-control requirements may influence proper reactor design is also illustrated. Only single-stage reactors are considered here. Chains of reactors will be treated in Part II.

The transient behavior of continuous reactor systems has been considered by Mason and Piret (*7*) and the self-regulation properties of chains of reactors by Devyatov and Bogshev (*3*); Kramers and Alberda (*6*) have applied the method of complex amplitudes to the study of mixing and residence times in reactors. These investigations are all limited to first-order processes with no temperature effects. Transient equations for second-order processes in continuous reactors with no temperature effects were recently treated by Acton and Lapidus (*1*). The

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general theory of frequency-response analysis has, of course, long been developed.

THE PROBLEM

In the continuous operation of a stirred tank reactor the product obtained must be of uniform quality. Thus composition of the outlet stream from the reactor should be maintained within given limits around the steady state value, the width of the permissible band being determined by the severity of specifications. As the product composition depends on many variables, such as feed concentration and reactor temperature, one part of the problem is to find the effect of variations in these upon the product composition. When this effect is known, one can calculate the limits which should be imposed upon feed concentration and reactor temperature to hold the subsequent variation in outlet-stream composition within the allowable range.

In practice the fluctuations externally imposed on the reactor are likely to be highly irregular. For analytical purposes however sinusoidal variations are usually assumed. Thus results remain general and the mathematics is more tractable. The results are general because in a linear system an arbitrary fluctuation can, at least theoretically, be resolved into its harmonic components and the response functions of these integrated to find the total effect.

A second problem concerns more specifically the design of the control system. Process characteristics being known from the first part of the study, the control characteristics best suited to the problem are examined, especially the effects of the different types of control on the behavior of the continuous process. A specific question which arises at this point is the effect of dead time in the control loop on the cycling tendencies of the process. This question is briefly examined in Part II for the limiting case of a tubular reactor.

THEORY

The first problem may be restated as follows. Given a small periodic variation in the parameters defining reactor operation, find the resulting periodic variation in composition of the effluent stream from the reactor.

The Basic Equations

As is usually done in the theory of continuously stirred tank reactors, uniformity of conditions will be assumed throughout the reactor space. The steady state performance is then readily predictable for either simple or complex reactions, as shown in reference *2* and reference *4*. Two chemical components, A in the feed and B in the product, will be considered, component B representing the product of interest. The theory could of course be developed in general for any number of components, but consideration of only two components of interest is sufficient for most of the actual applications. For simplicity, developments presented here are for the case where

$$\frac{dB}{dt} = -\frac{1}{\alpha}\frac{dA}{dt} = R(x, T)$$

The reaction rate $R(x, T)$ is a function of x, the concentration of A, and the temperature T. The stoichiometric coefficient is α. No assumption is made about the order of the reaction, and so the case examined remains quite general. The mass balances across the reactor give the basic transient equations

[accumulation] = [input] − [output] − [reacted]

$$\theta\frac{dx}{dt} = x_0 - x - \alpha\theta R(x, T) \qquad (1)$$

$$\theta\frac{dy}{dt} = y_0 - y + \theta R(x, T) \qquad (2)$$

and from the heat balance

$$\theta\frac{dT}{dt} = T_0 - T + \theta h(T) + Q\alpha\theta R(x, T) + \theta H(t) \qquad (3)$$

where

$\theta = V/F$ = reactor holding time, hr.

T, T_0 = temperature in the reactor and in the feed stream, °K.

$Q = -\Delta H_R/c\rho$ = change in temperature caused by adiabatic reaction per mole of component A reacted in a unit volume of reacting mixture, (°K.)(liter)/mole. Q is positive for an exothermic reaction. The specific heat per unit volume, $c\rho$, is taken constant and the same for the feed and product

$h(T)$ = heat input to the reactor volume expressed as change in temperature, °K./hr., due to heat input from sources which depend on T only. $h(T)$ is equal to the rate of heat input to the whole reactor due to temperature-dependent sources, divided by the total reactor heat capacity, $Vc\rho$.

$H(t)$ = heat input, °K./hr., from independent time-varying sources such as would be caused by the manipulation of a steam valve

The notations of this section are illustrated in Figure 1. For convenience Q has been assumed to be a constant independent of concentration and temperature. All other factors are considered either negligible or remaining constant in this analysis. The heat input $h(T)$ covers heat losses by the reactor surface and heat inputs (due to heat transfer from heating or cooling coils or jackets operating at constant temperatures for example). The equations will first be linearized and then solved by methods commonly used in the analysis of electrical networks.

Linearization

The three equations [(1), (2), (3)] where the derivatives are set equal to zero define the steady state conditions

$$x_s, \quad y_s, \quad T_s$$

related by

$$x_0 - x_s - \alpha\theta R(x_s, T_s) = 0 \qquad (4)$$

$$y_0 - y_s + \theta R(x_s, T_s) = 0 \qquad (5)$$

$$T_0 - T_s + \theta h(T_s) + \theta H_s + Q\alpha\theta R(x_s, T_s) = 0 \qquad (6)$$

For nonsteady operations the variables X, Y, Z defined by

$$x = x_s + X \qquad (7)$$

$$y = y_s + Y \qquad (8)$$

$$T = T_s + Z \qquad (9)$$

are introduced. They represent variations around the steady state. This study will be concerned with small variations only; that is, second-order terms in X, Y, Z will be assumed negligible. Under this assumption the reaction rate $R(x, T)$ may be written as follows:

$$R(x, T) = R(x_s, T_s) + R_x'(x_s, T_s)X + R_T'(x_s, T_s)Z \qquad (10)$$

$R_x'(x_s, T_s)$ and $R_T'(x_s, T_s)$ being the partial derivatives of the rate with respect to concentration of A and temperature.

In order to simplify the problem, the derivative $h_T'(T_s)$ of the heat-input function will be neglected. Thus instead of $h(T) = h(T_s) + h_T'(T_s)Z$ one may write

$$h(T) = h(T_s) \qquad (11)$$

Also $H(t) \equiv H_s + \Delta H(t)$. Replacing (x_0, y_0, T_0) by $(X_0 + x_0, Y_0 + y_0, Z_0 + T_0)$ and introducing (7), (8), (9) and (10), (11) in the three transient equations (1), (2), (3) gives

$$\theta\frac{dX}{dt} + (1 + \alpha\theta R_x')X + \alpha\theta R_T'Z = X_0 \qquad (12)$$

$$\theta\frac{dY}{dt} - \theta R_x'X + Y - \theta R_T'Z = Y_0 \qquad (13)$$

$$\theta \frac{dZ}{dt} - Q\alpha\theta R_x'X + (1 - Q\alpha\theta R_T')Z = \theta\Delta H + Z_0 \qquad (14)$$

These are now linear first-order differential equations. The forcing functions X_0, Y_0 and $\theta\Delta H + Z_0$, where X_0, Y_0 and Z_0 are the varying parts of the feed concentrations in A and B and of the feed temperature, will be later assumed to be periodic functions.

Method of Complex Amplitudes

The method of complex amplitudes is rigorously based on Fourier transforms, but the simple presentation given below is sufficient here. A more detailed treatment may be found in reference *5*.

In all this section the existence of a steady state response of the system to the periodic forcing functions is assumed. Thus the calculated response will have no physical significance if the system is unstable. System stability may be discussed by consideration of the roots of its characteristic equation.

The periodic functions used in this treatment will be represented by the form

$$\chi(t) \equiv Xe^{j\omega t} \qquad (15)$$

where $\chi(t)$ is the periodic function, for instance a variation in concentration or temperature, X is a complex number, and $e^{j\omega t} = \cos \omega t + j \sin \omega t$. The frequency of oscillation in radians/hour is represented by ω and j stands for $\sqrt{-1}$. The derivative of $\chi(t)$ is

$$\frac{d\chi(t)}{dt} = X \frac{d}{dt} e^{j\omega t} = j\omega Xe^{j\omega t} = j\omega\chi(t) \qquad (16)$$

and therefore in this case, that is to say for periodic functions of Form (15), the operation of taking the time derivative is equivalent to the operation of multiplication by $j\omega$.

Since the solutions will therefore be of the same form as the forcing functions, the system of linear differential equations (12), (13), and (14) may be written as follows:

$$(1 + j\omega\theta + \theta\alpha R_x')X + \theta\alpha R_T'Z = X_0 \qquad (17)$$

$$- \theta R_x'X + (1 + j\omega\theta)Y - \theta R_T'Z = Y_0 \qquad (18)$$

$$- Q\alpha\theta R_x'X + (1 + j\omega\theta - Q\alpha\theta R_T')Z = \theta\Delta H + Z_0 \qquad (19)$$

The applications below are based on these three equations. For present purposes the feed concentration of B and the inlet-feed temperature will usually be held constant and thus in the forms above Y_0 and Z_0 become zero.

In the first case, discussed below, temperature effects will for clarity be considered negligible so that only the variations in concentration of the feed will affect the concentration of the products. One way in which this can come about is the case where the temperature of the reactor is maintained steady; i.e., Z equals zero when heat input balances output, $-\alpha QR_x'X = \Delta H$, in particular if the heat of reaction Q is zero and there is no heat input. Another way occurs if the rate of reaction is not strongly temperature dependent over the control range and so $R_T' = 0$.

In the second case the internal reactor temperature will be allowed to vary with the heat of the reaction. Finally, the third case will concern variations in product concentrations and reactor temperature caused by heat input alone when the feed concentration is constant, that is to say, with $X_0 \equiv 0$.

First Case: Variations in Concentration Alone

For the case where there is no temperature effect,

$$(1 + j\omega\theta + \alpha\theta R_x')X = X_0$$

$$- \theta R_x'X + (1 + j\omega\theta)Y = 0$$

from which is found

$$Y = \frac{\theta R_x'}{(1 + j\omega\theta)(1 + j\omega\theta + \alpha\theta R_x')} X_0 \qquad (20)$$

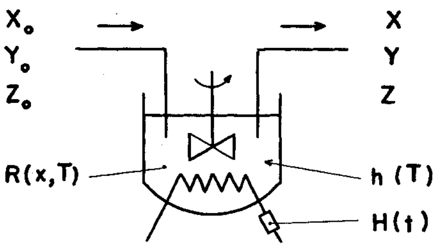

Fig. 1. Illustration of nomenclature.

This may be written as follows, by putting the complex number Y/X_0 in the polar form (15):

$$Y = \frac{\theta R_x'}{\sqrt{(1 + \alpha\theta R_x' - \omega^2\theta^2)^2 + \omega^2\theta^2(2 + \theta\alpha R_x')^2}} e^{j\phi}X_0 \qquad (21)$$

with the angle ϕ defined by

$$\tan \phi = \frac{-\omega\theta(2 + \alpha\theta R_x')}{1 + \theta\alpha R_x' - \omega^2\theta^2} \qquad (22)$$

Therefore, the ratio of the magnitude of the variation in product concentration $|Y|$ to the magnitude of the variation in feed concentration $|X_0|$ is

$$\left| \frac{Y}{X_0} \right| = \frac{| \theta R_x' |}{\sqrt{(1 + \theta\alpha R_x' - \omega^2\theta^2)^2 + \omega^2\theta^2(2 + \alpha\theta R_x')^2}} \qquad (23)$$

and this result is valid whatever the order of the reaction, provided that the amplitudes of the variations are small.

Inspection of (23) shows that the reactor is stable in all cases, because the denominator of the transfer function cannot be zero for real values of ω. Furthermore the homogeneous system has the solution $Y = Ce^{-t/\theta}$.

Illustration I

The second-order reaction is

$$2A \rightarrow B + D$$

with a rate expressed by

$$\frac{dB}{dt} = -\frac{1}{2}\frac{dA}{dt} = k[A]^2$$

The kinetic rate constant k is

$$k = 1.165\ 10^{14}e^{-10,000/T} \text{ mole}^{-1} \text{ hr.}^{-1}$$

The reactor is operated with a holding time

$$\theta = 20 \text{ min.}$$

and a feed containing 1.75 moles/liter of A. The reactor temperature is 80°C. The effect of variations in the concentration of A in the feed upon the concentration of product B in the effluent are calculated. At 80°C. the value of the rate constant is $k = 1.165\ (10^{14})\ e^{-10,000/T} = 58.10$ mole^{-1} hour^{-1} and the steady state composition of the reacting mixture is given by the following mass balances:

on component A

$$x_s - 1.75 + 2\left(\frac{20}{60}\right)(58.1)x_s^2 = 0$$

on component B

$$y_s - \left(\frac{20}{60}\right)(58.1)x_s^2 = 0$$

The solutions are

$x_s = 0.20$ mole/liter,
$y_s = 0.775$ mole/liter

The equations, similar to (20), (21), (22), which must be used in this case to determine the effect of variations in the concentration of A in the feed upon the concentration of product B in the effluent are

$$Y = \frac{\theta R_x'}{(1 + j\omega\theta)(1 + j\omega\theta + 2\theta R_x')} X_0$$

$$Y = \frac{\theta R_x'}{\sqrt{(1 + 2\theta R_x' - \omega^2\theta^2)^2 + 4\omega^2\theta^2(1 + \theta R_x')^2}} e^{j\phi} X_0$$

with the angle ϕ defined by

$$\tan \phi = -\frac{2\omega\theta(1 + \theta R_x')}{1 + 2\theta R_x' - \omega^2\theta^2}$$

where

$$R(x) = kx^2$$

and therefore

$$\theta R_x' = 2k\theta x = 2 \times 58.10 \times \tfrac{1}{3} \times 0.20 = 7.750$$

For the numerical data of the illustration the following values of the variation $|Y/X_0|$ and the phase angle ϕ are obtained for different values of frequency.

$\omega\theta$	0.01	0.10	0.50	1.00	2.00	10.0	100
ω	0.03	0.30	1.50	3.00	6.00	30.00	300
$\lvert Y/X_0\rvert$	0.470	0.467	0.419	0.331	0.203	0.040	0.001
ϕ	−0.6	−6	−28	−49	−70	−115	−170

The frequency ω is expressed in radians per hour and the phase angle ϕ in degrees.

Second Case: Variations in Concentration and Temperature

In the derivation of (20) it has been assumed that the temperature effects on the process could be neglected. In the case where there is an appreciable temperature effect the variations in product concentration due to variation in feed concentration of component A alone are related through the equations

$$(1 + j\omega\theta + \alpha\theta R_x')X + \alpha\theta R_T'Z = X_0$$

$$-\theta R_x'X + (1 + j\omega\theta)Y - \theta R_T'Z = 0$$

$$-\alpha Q\theta R_x'X + (1 + j\omega\theta - \alpha Q\theta R_T')Z = 0$$

which are a special case of Equations (17), (18), (19) with no independent time-varying heat input, $\Delta H = 0$.

The expression corresponding to (20) for the present use is

$$Y = \frac{\theta R_x'}{(1 + j\omega\theta)(1 + j\omega\theta + \theta\alpha R_x' - Q\alpha\theta R_T')} X_0 \qquad (24)$$

which may be written, similarly to (21):

$$Y = \frac{\theta R_x' e^{i\phi}}{\sqrt{(1 + \theta\alpha R_x' - \alpha Q\theta R_T' - \omega^2\theta^2)^2 + \omega^2\theta^2(2 + \alpha\theta R_x' - \alpha Q\theta R_T')^2}} X_0 \qquad (25)$$

where the phase angle ϕ is given by

$$\tan \phi = -\frac{\omega\theta(2+\alpha\theta R_x' - \alpha Q\theta R_T')}{1+\alpha\theta R_x' - \alpha Q\theta R_T' - \omega^2\theta^2} \qquad (26)$$

The stability and the relative sensitivity of reaction systems may be more readily evaluated by factoring out a nonfrequency term from the response equations. For instance, Equation (24) may be rewritten as

$$\frac{Y}{X_0} = \frac{\theta R_x'}{1 + \alpha\theta R_x' - Q\alpha\theta R_T'} \cdot \frac{1}{(1 + j\omega\theta)\left(1 + j\omega \dfrac{\theta}{1 + \theta\alpha R_x' - Q\alpha\theta R_T'}\right)}$$

The first or amplification factor describes the response of the system to a steady perturbation, whereas the second factor indicates its dynamic behavior and thus the controllability.

It is seen that the condition of stability is

$$1 + \theta\alpha R_x' - Q\alpha\theta R_T' > 0$$

hence in terms of the heat of reaction the system is unstable when

$$Q > \frac{1 + \theta\alpha R_x'}{\alpha\theta R_T'}$$

Since R_T', the temperature coefficient of the reaction rate, is usually positive, this means that instability may occur for exothermic reactions with a sufficiently high value of the heat of reaction. Expressed in terms of the holding time the condition of stability yields

$$\theta < \frac{1}{(QR_T' - R_x')\alpha}$$

where

$$Q > \frac{R_x'}{R_T'}$$

Thus, when a reaction is sufficiently exothermic ($Q > R_x'/R_T'$), reactor operation as described by the linearized model will be stable only when the holding time θ does not exceed a certain value. There is no limitation on the holding time for the case of an endothermic reaction.

This discussion is an example of a case when control requirements may place limitations on reactor design.

Illustration 2

In order to give an idea of the magnitude of the temperature effect the variation in product concentration due to a variation in feed concentration will be calculated, the temperature effect being taken into account with the data used in Illustration 1.

With the introduction of the stoichiometric coefficient $\alpha = 2$, Expression (25) for the present case becomes

$$Y = \frac{\theta R_x' e^{i\phi}}{\sqrt{(1 + 2\theta R_x' - 2Q\theta R_T' - \omega^2\theta^2)^2 + 4\omega^2\theta^2(1 + \theta R_x' - Q\theta R_T')^2}} X_0$$

with

$$\tan \phi = -\frac{2\omega\theta(1+\theta R_x' - Q\theta R_T')}{1+2\theta R_x' - 2Q\theta R_T' - \omega^2\theta^2}$$

The data of Illustration 1 gives

$$k = 1.165\ 10^{14} e^{-10,000/T_s}$$

$$x_s = 0.200 \text{ mole/liter,}$$

$$T_s = 80°\text{C.}$$

$$\theta = 20 \text{ min.}$$

Assuming that the reacting mixture has the density and heat capacity of water and that the heat of reaction is

$$\Delta H_R = -50{,}000 \text{ cal./mole of } A$$

yields

$$Q = 50\ (°\text{K.})(\text{liter})/\text{mole}$$

Then

$$\theta R_x' = 7.750$$

$$Q\theta R_T' = 3.112$$

Reactor operation is stable since

$$1 + 2\theta R_x' - 2Q\theta R_T' = 10.28 > 0$$

The values of the variation amplitude ratio $|Y/X_0|$ and the phase angle ϕ have been calculated for different values of the variation frequency ω and are presented below:

Second-order exothermic reaction: $Q = 50°$K.

$\omega\theta$	0.01	0.10	0.50	1.00	2.00	10.0	100
ω	0.03	0.30	1.50	3.00	6.00	30.0	300
$\lvert Y/X_0\rvert$	0.755	0.751	0.673	0.531	0.331	0.054	0.0008
ϕ	−0.6	−6	−29	−51	−74	−128.	−174.

The calculations have also been made for the case of an endothermic second-order reaction, with $Q = -75°K.$, for the data used in Illustration 1.

Second-order endothermic reaction: $Q = -75°K.$

$\omega\theta$	0.01	0.10	0.50	1.00	2.00	10.0	100
ω	0.03	0.30	1.50	3.00	6.00	30.0	300
$\lvert Y/X_0 \rvert$	0.300	0.298	0.268	0.211	0.1334	0.0278	0.001
ϕ	−0.6	−6	−28.	−47.	−68.	−105.	−165.

The values resulting from the calculations of Illustrations 1 and 2 are represented in Figure 2, which is called a Nyquist polar plot. If M is a point of the plot which represents a particular operating condition for the reactor, the length of the vector joining the origin to M is $|Y/X_0|$ and the angle of the vector with the positive direction of the horizontal axis is the phase angle ϕ. The lower half of the curve corresponds to positive frequencies, the upper half being a reflection of those on the real axis.

On the polar plot of Figure 2 are represented the values of Illustration 1, where the reaction is assumed to have a negligible temperature dependence, by the locus $Q = 0$. The data of Illustration 2, where the reaction considered is exothermic, are shown by the locus $Q = 50$(°K.)(liter)/mole. Also presented is the case of an endothermic reaction, with $Q = -75$(°K.)(liter)/mole. Several values of $\omega\theta$ are shown in Figure 2 to indicate how the curves are prepared from the foregoing tables.

It is apparent from the polar plots of Figure 2 that the outgoing concentrations of endothermic reactions and temperature-insensitive reactions are less sensitive toward variations in feed composition than are those of exothermic reactions.

This fact is easily understood in a qualitative way, as a concentration increase in the feed reactant for the case of an endothermic reaction brings about a temperature decrease which counteracts the effect of increased feed concentration on the reaction rate. An endothermic reaction thus possesses a certain degree of self-regulation. On the countrary, an exothermic reaction is autocatalyzed through its heat output: an increase in feed concentration increases the reaction rate and the heat of reaction only serves further to increase the rate. Thus exothermic reactions may be expected to present some instability; however, an increased rate burns out the excess reactant and the process tends to normal. The equation developed here of course take these simultaneous effects into account.

It appears from Figure 2 that the Nyquist plots for variations in concentration are nearly circular and may be approximated by a family of circles. A system with a single time lag, called a first-order system, has a circular Nyquist plot. The approximation is usually possible because of the preponderance of the holding-time lag over the other lags in the system.

As a final result of the Nyquist plots for Illustrations 1 and 2, it may be observed that the maximum amplitude ratio of the concentration variations is given by

$$\left|\frac{Y}{X_0}\right|_{max} = \left|\frac{\theta R_x'}{1 + 2\theta R_x' - 2Q\theta R_T'}\right| \tag{27}$$

Expression (27) shows that the maximum amplitude ratio is infinite when

$$Q = \frac{1 + 2\theta R_x'}{2\theta R_T'} = 132.7(°K.)(\text{liter})/\text{mole}.$$

This represents a limiting case of stability in the example. Reactions with $Q \geq 132.7$ (°K.)(liter)/mole would be unstable under the conditions of Illustration 2.

Third Case: Heat-input Variations

Coming back to the more general case chosen for the exposition of the theory, one may now examine the nature of the influence of independent variations in heat input to the reactor H upon product concentration and reactor temperature. A constant feed composition and temperature will be assumed in order to isolate clearly the results of interest. Knowledge of the effect of heat-input variations on reactor temperature is necessary in order to determine later the sensitivity, rate of response, and other characteristics of the instruments and elements in a reactor heat-control loop which will provide an adequate degree of control.

Equations (17), (18), and (19) will be used, with the assumption that $X_0 \equiv 0$, which corresponds to a constant feed composition

$$(1 + j\omega\theta + \alpha\theta R_x')X + \alpha\theta R_T'Z = 0 \tag{17'}$$

$$-\theta R_x'X + (1 + j\omega\theta)Y - \theta R_T'Z = 0 \tag{18'}$$

$$-\alpha Q\theta R_x'X + (1 + j\omega\theta - \alpha Q\theta R_T')Z = \theta\Delta H \tag{19'}$$

The solutions are

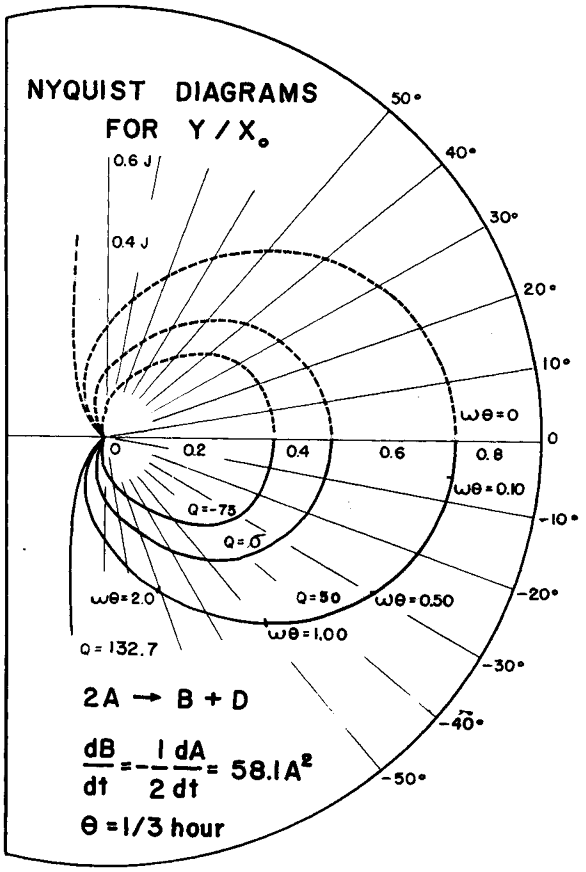

Fig. 2. Nyquist-type diagrams for concentration variations in a C.S.T.R. Data of illustrations 1 and 2 for the second-order reaction $2A \rightarrow B + D$.

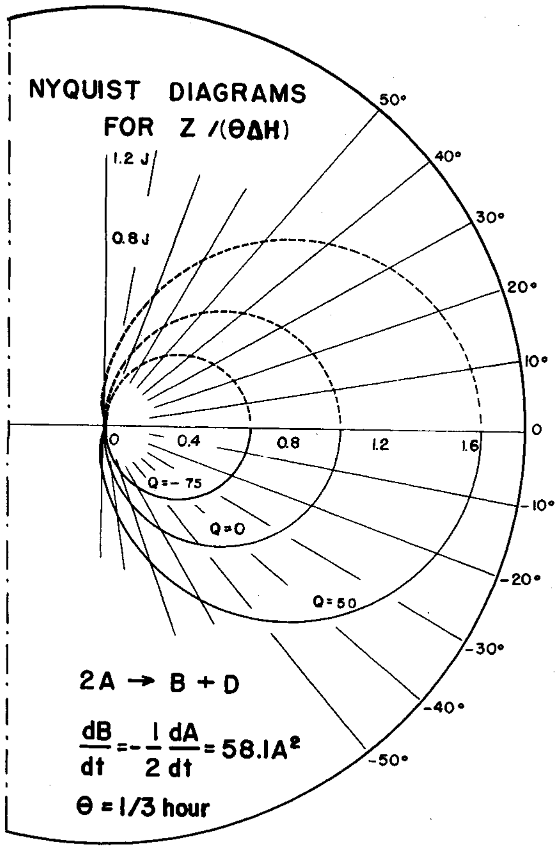

Fig. 3. Nyquist diagrams for temperature variations in a C.S.T.R. Data of illustration 3 for the second-order reaction $2A \rightarrow B + D$.

$$\frac{Z}{\theta \Delta H} = \frac{(1 + \alpha\theta R_x' + j\omega\theta)}{(1 + j\omega\theta)(1 + \alpha\theta R_x' - \alpha Q\theta R_T' + j\omega\theta)} \tag{28}$$

for the relation between reactor temperature variations Z and heat-input variations ΔH and

$$\frac{Y}{\theta \Delta H} = \frac{\theta R_T'}{(1 + j\omega\theta)(1 + \alpha\theta R_x' - \alpha Q\theta R_T' + j\omega\theta)} \tag{29}$$

for the relation between variations in product concentration Y and heat-input variations. It is seen that Expression (29), giving the relationship $Y/(\theta\Delta H)$, has the same structure as (24), which gives Y/X_0. The polar plots corresponding to these expressions will therefore have the same shape, and the discussion of system stability made in the second case will apply.

Illustration 3

The plots of $Z/(\theta\Delta H)$, which express the dependence of reactor temperature on reactor heat input, are presented in Figure 3, for the data of the preceding illustration. The plots representing $Y/(\theta\Delta H)$ are similar to those of Figure 2, differing only by the scale factor R_T'/R_x', and therefore have not been redrawn. The values used for Figure 3, which represents $Z/(\theta\Delta H)$, are tabulated below.

In the case of the second-order reaction, which we assume, Expressions (28) and (29) take the form

$$\frac{Z}{\theta \Delta H} = \frac{(1 + 2\theta R_x' + j\omega\theta)}{(1 + j\omega\theta)(1 + 2\theta R_x' - 2Q\theta R_T' + j\omega\theta)}$$

$$\frac{Y}{\theta \Delta H} = \frac{\theta R_T'}{(1 + j\omega\theta)(1 + 2\theta R_x' - 2Q\theta R_T' + j\omega\theta)}$$

Results of the calculation of the absolute value and phase angle of $Z/(\theta\Delta H)$ are presented below for different values of the heat of reaction parameter Q.

$Q = 50$(°K.)(liter)/mole (exothermic reaction)

$\omega\theta$	0.01	0.10	0.50	1.00	2.00	10.0	100.
ω	0.03	0.30	1.50	3.00	6.00	30.0	300.
$\lvert Z/(\theta\Delta H)\rvert$	1.608	1.600	1.436	1.132	0.710	0.1338	0.0101
ϕ	−0.6	−6.	−28.	−47.	−68.	−97.	−93.

$Q = -75$(°K.)(liter)/mole (endothermic reaction)

$\omega\theta$	0.01	0.10	0.50	1.00	2.00	10.0	100.
ω	0.03	0.30	1.50	3.00	6.00	30.0	300.
$\lvert Z/(\theta\Delta H)\rvert$	0.638	0.635	0.571	0.452	0.286	0.0692	0.0098
ϕ	−0.6	−6.	−26.	−44.	−61.	−74.	−84.

In this case too the diagrams appear as nearly circular. Indeed, for $Q = 0$ the Nyquist diagram for $Z/(\theta\Delta H)$ is a circle.

It should be remarked that variations in reactor concentration or temperature caused by variations in feed temperature are exactly the same as those examined above, the quantity $\theta\Delta H$ being replaced by Z_0, variation in feed temperature.

GENERALIZATION

For simplicity the previous theory was developed on the basis of a reaction involving a feed reactant A and a product B with rate dependent on the concentration of A and the temperature. If several reactants determine the rate, then an additional material-balance equation appears for each of these reactants. The resulting set of simultaneous differential equations is then most conveniently expressed by the use of matrices. The form of the solution for reactions where several components affect the rate will now be shown. A tabulation will also be presented of the specific frequency-response functions for typical complex reaction systems. It should be kept in mind that, since linearization has been used, the frequency-response functions obtained are valid for only small variation amplitudes, such as are usually present under automatic control.

Considered first is the case of m reactants: $A_1, A_2, \cdots, A_m$. It is assumed that the effect of temperature variations can be ignored*, and so the rate of increase of x_i, the concentration of A_i, can be written as $R_i(x_1, \cdots, x_m)$. Proceeding just as before, one finds that the frequency-response functions $X_1, X_2, \cdots, X_m$ to perturbations $X_1°, X_2°, \cdots, X_m°$, of frequency ω, in the feed concentrations satisfy the equations

$$[(1 + j\omega\theta)I - \theta\mathcal{R}] \begin{bmatrix} X_1 \\ \vdots \\ X_m \end{bmatrix} = \begin{bmatrix} X_1° \\ \vdots \\ X_m° \end{bmatrix}$$

where I is the identity matrix and $\mathcal{R}$ is a matrix whose element in the ith row and jth column is $\partial R_i/\partial x_j$ evaluated at the steady state values. The equations may then be solved by the usual Cramers' rule. The solutions appear as the quotient of two determinants, the denominator being det $[(1 + j\omega\theta)I - \theta\mathcal{R}]$ and the numerator being the same but with the appropriate column being replaced by

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*When temperature effects are included, the results are very similar to those shown here, but for the sake of brevity they are not presented.

TABLE 1. CLASSIFICATION OF REACTIONS ACCORDING TO THEIR RATE DEPENDENCE

Group	Example	Rate functions	General rate-function type
Single Irreversible Reactions	(1) $A \rightarrow B$	$R_1 = -R_2 = -kx,\ R_3 = R_4 = 0$	$R_2 = -R_1 = R(x),\ R_3 = R_4 = 0$
	(2) $2A \rightarrow 2B$	$R_1 = -R_2 = -kx^2,\ R_3 = R_4 = 0$	$R_2 = -R_1 = R(x),\ R_3 = R_4 = 0$
	(3) $A + C \rightarrow B$	$R_1 = R_3 = -R_2 = -kxu,\ R_4 = 0$	$R_2 = -R_1 = -R_3 = R(x, u),\ R_4 = 0$
Single Reversible Reactions	(4) $A \rightleftarrows B$	$R_1 = -R_2 = k_1y - k_2x,\ R_3 = R_4 = 0$	$R_2 = -R_1 = R(x, y),\ R_3 = R_4 = 0$
	(5) $2A \rightleftarrows 2B + C$	$R_1 = k_1uy - k_2x^2 = -R_2 = -2R_3,\ R_4 = 0$	$R_2 = -R_1 = 2R_3 = R(x, y, u),\ R_4 = 0$
	(6) $A + C \rightleftarrows B + D$	$R_1 = R_3 = -R_2 = -R_4 = k_1vy - k_2ux$	$R_2 = R_4 = -R_1 = -R_3 = R(x, y, u, v)$
Consecutive reactions	(7) $A \rightarrow B \rightarrow C$	$R_1 = -k_1x,\ R_2 = k_1x - k_2y,\ R_3 = k_2y,\ R_4 = 0$	$R_2 = R_2(x, y),\ R_1 = R_1(x),$ $R_3 = R_3(y),\ R_4 = 0$
Competing Reactions	(8) $\begin{cases} 2A \rightarrow B + D \\ B + C \rightarrow E \end{cases}$	$R_1 = -2k_1x^2,\ R_2 = k_1x^2 - k_2uy$ $R_3 = -k_2uy,\ R_4 = k_1x^2$	$R_2 = R_2(x, y, u),\ R_1 = R_1(x)$ $R_3 = R_3(y, u),\ R_4 = R_4(x).$
Consecutive and reversible Reactions	(9) $\begin{cases} 2A \rightleftarrows B + C \\ B \rightarrow D \end{cases}$	$R_1 = 2k_1uy - 2k_2x^2,$ $R_2 = k_2x^2 - k_1uy - k_3y$ $R_3 = k_2x^2 - k_1uy,\ R_4 = k_3y$	$R_1 = R_1(x, y, u),\ R_2 = R_2(x, y, u)$ $R_3 = R_3(x, y, u),\ R_4 = R_4(y)$
Competing Reactions	(10) $\begin{cases} A \rightleftarrows B + C \\ B + A \rightarrow D \end{cases}$	$R_1 = k_1uy - k_2x - k_3xy$ $R_2 = k_2x - k_1uy - k_3xy$ $R_3 = k_2x - k_1uy,\ R_4 = k_3xy$	$R_1 = R_1(x, y, u)$ $R_2 = R_2(x, y, u)$ $R_3 = R_3(x, y, u)$ $R_4 = R_4(x, y)$

NOTE: Letters x, y, u, v stand for the concentrations of A, B, C, D. The k's are rate constants.

$$\begin{bmatrix} X_1^\circ \\ \vdots \\ X_m^\circ \end{bmatrix}.$$

For example, there are four reactants $A_1 = A$, $A_2 = B$, $A_3 = C$, $A_4 = D$ with concentrations $x_1 = x$, $x_2 = y$, $x_3 = u$, $x_4 = v$. The frequency response Y of the variations in the concentration of B due to a perturbation X_0 in the feed concentration of A is given by

$$Y = \frac{\theta \begin{vmatrix} R_{2x}' & R_{2u}' & R_{2v}' \\ -\theta R_{3x}' & 1 + j\omega\theta - \theta R_{3u}' & -\theta R_{3v}' \\ -\theta R_{4x}' & -\theta R_{4u}' & 1 + j\omega\theta - \theta R_{4v}' \end{vmatrix} X_0}{\begin{vmatrix} 1 + j\omega\theta - \theta R_{1x}' & -\theta R_{1y}' & -\theta R_{1u}' & -\theta R_{1v}' \\ -\theta R_{2x}' & 1 + j\omega\theta - \theta R_{2y}' & -\theta R_{2u}' & -\theta R_{2v}' \\ -\theta R_{3x}' & -\theta R_{3y}' & 1 + j\omega\theta - \theta R_{3u}' & -\theta R_{3v}' \\ -\theta R_{4x}' & -\theta R_{4y}' & -\theta R_{4u}' & 1 + j\omega\theta - \theta R_{4v}' \end{vmatrix}}$$

where R_{1x}' denotes $\partial R_1/\partial x$ at the steady state value, etc.

If only the reactants A, B, C affect the rates of reaction, then $\partial R_1/\partial v = \partial R_2/\partial v = \partial R_3/\partial v = \partial R_4/\partial v = 0$ and the frequency response takes the form

$$Y = \frac{\theta \begin{vmatrix} R_{2x}' & R_{2u}' \\ -\theta R_{3x}' & 1 + j\omega\theta - \theta R_{3u}' \end{vmatrix} X_0}{\begin{vmatrix} 1 + j\omega\theta - \theta R_{1x}' & -\theta R_{1y}' & -\theta R_{1u}' \\ -\theta R_{2x}' & 1 + j\omega\theta - \theta R_{2y}' & -\theta R_{2u}' \\ -\theta R_{3x}' & -\theta R_{3y}' & 1 + j\omega\theta - \theta R_{3u}' \end{vmatrix}}.$$

For the cases where the reaction rates depend on neither C nor D one has

$$Y = \frac{\theta R_{2x}' X_0}{1 - \theta(R_{2y}' + R_{1x}') + \theta^2(R_{1x}'R_{2y}' - R_{1y}'R_{2x}' - \omega^2) + j\omega\theta[2 - \theta(R_{2y}' + R_{1x}')]}$$

In Table 1 are listed ten types of reactions, giving the specific rate functions for each case and also the general type to which the example belongs. In Table 2 various general types are listed and the frequency-response function is given for each of these. The material in these tables is by no means exhaustive and is offered only for convenience and as an indication of the general nature of the results. In Table 2 the notation $R_4 = R(x, y)$ denotes, as is customary, that R_4 does not depend on u and v and includes, for example, the case $R_4 = R(x)$ or $R_4 = 0$.

NONLINEARITY OF REACTOR EQUATIONS

Chemical rate equations which occur in industrial practice are usually nonlinear. In this work they have been treated by the method of linearization, which was justified by the fact that the deviations from the steady state which are considered are small. Nonlinear-system response for large deviations from equilibrium is usually treated by approximation methods, and the results are obtained in the form of series. As a test of the degree of approximation obtained by linearization, the case of the second-order reaction chosen in Illustration 1, has been treated below, any temperature effect being neglected. The reaction is

$$2A \rightarrow B + D$$

with the rate

$$\frac{dB}{dt} = -\frac{1}{2}\frac{dA}{dt} = kx^2$$

The equations, similar to (12) and (13) which give the variations in composition X and Y, are

$$\theta\frac{dX}{dt} + (1 + 4k\theta x_s)X + 2\theta kX^2 = X_0 \qquad (30)$$

$$\theta\frac{dY}{dt} + Y = 2k\theta x_s X + k\theta X^2 \qquad (31)$$

Here, however, the second-order terms have not been neglected.

For simplicity, in the first equation

$$A = 1 + 4k\theta x_s$$

$$\lambda = \omega\theta$$

TABLE 2. FREQUENCY-RESPONSE FUNCTIONS Y/X_0, FOR ISOTHERMAL CONCENTRATION VARIATIONS IN A CONTINUOUS STIRRED TANK REACTOR

Rate-function type	Frequency-response function Y/X_0
$R_2 = -R_1 = R(x),\quad R_3 = R_3(x, y),$ $R_4 = R_4(x, y, u)$	$\dfrac{\theta R_x'}{1 + \theta R_x' - \omega^2\theta^2 + j\omega\theta(2 + \theta R_x')}$
$R_2 = -R_1 = -R_3 = R(x, u),$ $R_4 = R_4(x, y, u)$	$\dfrac{\theta R_x'}{(1 + j\omega\theta)(1 + j\omega\theta + \theta[R_u' + R_x'])}$
$R_2 = -R_1 = R(x, y),\quad R_3 = R_3(x, y),$ $R_4 = R_4(x, y, u)$	$\dfrac{\theta R_x'}{(1 + j\omega\theta)(1 + j\omega\theta + \theta[R_x' - R_y'])}$
$R_2 = -R_1 = -R_3 = R_4 = R(x, y, u, v)$	$\dfrac{\theta R_x'}{(1 + j\omega\theta)(1 + j\omega\theta + \theta[R_x' + R_u' - R_y' - R_v'])}$
$R_1 = R_1(x, y),\quad R_2 = R_2(x, y)$ $R_3 = R_3(x, y),\quad R_4 = R_4(x, y, u)$	$\dfrac{\theta R_{2x}'}{1 - \theta(R_{2y}' + R_{1x}') + \theta^2(R_{1x}'R_{2y}' - R_{1y}'R_{2x}' - \omega^2) + j\omega\theta[2 - \theta(R_{2y}' + R_{1x}')]}$
$R_1 = R_1(x),\quad R_2 = R_2(x, y, u)$ $R_3 = R_3(y, u),\quad R_4 = R_4(x, y, u)$	$\dfrac{\theta R_{2x}'(1 + j\omega\theta - \theta R_{3u}')}{[1 + j\omega\theta - \theta R_{1x}'][1 - \theta(R_{2y}' + R_{3u}') + \theta^2(R_{2y}'R_{3u}' - R_{3y}'R_{2u}' - \omega^2) + j\omega\theta(2 - \theta[R_{2y}' + R_{3u}'])]}$

Its steady state solution in the first-order approximation is, as before,

$$X_1 = \frac{X_0}{A + j\lambda}$$

X_0 being a cyclic quantity of frequency ω.

To obtain a series expansion in powers of X_0 one writes

$$X = X_1 + X_2$$

Substituting into (30) gives

$$\theta \frac{dX_2}{dt} + AX_2 = \left(X_0 - \theta \frac{dX_1}{dt} - AX_1\right) - (2\theta k X_2^2 + 4\theta k X_1 X_2) - 2\theta k X_1^2$$

The first bracket on the right vanishes from the definition of X_1. The second contains second-order terms, which are neglected. The final equation for X_2 is therefore

$$\theta \frac{dX_2}{dt} + AX_2 = -\frac{2\theta k}{(A + j\lambda)^2} X_0^2$$

where X_0^2 is a cyclic quantity of frequency 2ω.

The steady-response term X_2 therefore is

$$X_2 = \frac{-2\theta k}{(A + j\lambda)^2(A + 2j\lambda)} X_0^2 \qquad (32)$$

In the same way

$$X_3 = \frac{8\theta^2 k^2 X_0^3}{(A + \lambda j)^3(A + 2\lambda j)(A + 3\lambda j)} \qquad (33)$$

The general term may be easily found, but for the present purposes the second-order approximation will be sufficient.

$$X = \frac{X_0}{A + j\lambda} \cdot \left[1 - \frac{2\theta k X_0}{(A + j\lambda)(A + 2j\lambda)}\right] \qquad (34)$$

Similarly, as $Y = Y_1 + Y_2$ in (31),

$$Y = \frac{2k\theta x_s X_0}{(A + j\lambda)(1 + j\lambda)} \cdot \left[1 + \frac{(1 + j\lambda)X_0}{2x_s(A + j\lambda)(A + 2j\lambda)}\right] \qquad (35)$$

The corrective factors depend on the input signal X_0. This dependence may be illustrated graphically by drawing a series of Nyquist polar diagrams of Y/X_0 for different values of the input signal amplitude X_0. However, since the correction factors are usually small, only the amplitude of the correction factor for Y/X_0 has been calculated as an example,

$$\epsilon = \frac{(1 + j\lambda)X_0}{2x_s(A + j\lambda)(A + 2j\lambda)} \qquad (36)$$

at vanishing frequency $\omega = 0$ for the data of Illustration 1. In the results presented below, the variation amplitude $|X_0|$ has been expressed in percentage of the feed concentration x_0.

$$A = 1 + 4k\theta x_s = 1 + 4 \times \tfrac{1}{3} \times 58.10 \times 0.20 = 16.49$$

and

$$\epsilon_{\omega=0} = \frac{1.75}{200 \times 0.20 \times 16.49^2} |X_0| \%$$

$$\epsilon_{\omega=0} = 0.000161 |X_0| \%$$

A few values are given below

$\lvert X_0\rvert$	0%	10%	20%	40%
$\epsilon_{w=0}$	0.0000	0.0016	0.0032	0.0064

Thus for an input signal amplitude of 10% of the steady state value of the feed concentration, the error in outlet amplitude Y at vanishing frequency, calculated from Equation (36), will be only 0.16%. The correction is therefore small.

COMMENT

The equations developed herein are mathematical consequences of the theories of continuously stirred tank reactors and of frequency-response analysis. Each theory can be verified separately by the proper means. Hence it is felt that an attempt to verify experimentally the response equations obtained would amount largely to a study of the approach to ideal performance of the entire system, including control valves, sensing elements, signal transmission lines, and degree of mixing and of the chemical reaction, etc., which might be chosen to make up the experimental system.

An alternate procedure, advantageous in selected cases, is to use frequency-response experiments, with the specific purpose of studying the transient behavior of the particular reaction, of the stirred reactor itself, of concentration sensing elements, or of other components used in the control-loop system. For such purposes the continuous-chemical-reactor-control theory presented in this paper, which allows for complex reactions and temperature effects, would prove useful in the analysis of the experimental results.

The relations describing the characteristics of several typical loop systems including the control elements will be presented in Part II. The use of analogue computers to solve the equations will also be considered as well as the response functions for reactor chains and for a tubular reactor.

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NOTATION

A = a chemical compound or its concentration (mole/liter)
B = same
c = specific heat of the reacting mixture, calories/g.
C = concentration, mole/liter
e = volumetric C.S.T.R. (continuously stirred tank reactor) to batch efficiency ratio
F = flow rate, liters/hr.
h = reactor heat input, °K./hr.
H = reactor heat input, °K./hr.
ΔH_R = heat of reaction, calories/mole of A
I = control quality
j = pure imaginary, $\sqrt{-1}$
k = reaction-rate constant, different units.
K = proportionality constant for a proportional controller
M = a matrix
n = mole fraction, or number of reactors in a chain or reaction order
Q = modified heat of reaction, (°K.)(mole)/liter of A
R = general reaction rate
t = time, hr.
T = temperature, °K., or controller time constant
V = reactor volume, liters or variation vector
x = concentration of feed component, mole/liter
X = variation in concentration of feed component, mole/liter
y = concentration of product component, mole/liter
Y = variation in concentration of product component, mole/liter
Z = variation in reactor temperature, °K.
α, β, γ = stoichiometric coefficients
Δ = fractional control quality
θ = C.S.T.R. holding time, hr.
ρ = density of reacting mixture, g./liter
τ = reaction time for a tubular reactor, hr.
ω = signal frequency, radians/hr.

Subscripts

0, 1 = C.S.T.R. feed and product streams
D = derivative controller
I = integral controller
n = reactor number in a chain
P = proportional controller
s = steady state

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II. Frequency-response Relations for Reactor Chains, Tubular Reactors, and Unit Reactor Control Loops

REACTOR CHAINS

The results which were obtained in Part I for a single reactor can be used to calculate step by step the response of a chain of reactors. Interest in these calculations is twofold. First the safe operation of the whole chain may put upon a reactor in the chain more stringent control requirements than would individual operation, especially in the case of reactions highly sensitive to temperature. Second, these calculations can be used to determine simpler modes of control for the whole chain. In some cases, for instance, the feed flow is controlled by inlet sampling and the whole heating system by a sampling of the final product, the individual heat-control loop on each reactor thus being eliminated. The calculations are straightforward and the theory is easily developed with the introduction of matrices. It will be developed here on the basis of the example used previously, of a reaction involving components A and B, with a rate $R(x, T)$.

First Case: Variations in Concentration Only

Equations (17) and (18) of Part I are used with the feed concentration variations X_0 and Y_0

$$(1 + \alpha\theta R_x' + j\omega\theta)X = X_0 \qquad (1)$$

$$-\theta R_x'X + (1 + j\omega\theta)Y = Y_0 \qquad (2)$$

These may be written in matrix form, the variation vector V_i representing the variations in the composition of the feed to reactor $i + 1$:

$$V_i = \begin{vmatrix} X_i \\ Y_i \end{vmatrix}$$

and the matrix M_i of the variation coefficients being introduced.

In matrix notation Equations (1) and (2) may be written

$$\begin{vmatrix} 1 + \alpha\theta R_x' + j\omega\theta, & 0 \\ -\theta R_x', & 1 + j\omega\theta \end{vmatrix} \cdot \begin{vmatrix} X \\ Y \end{vmatrix} = \begin{vmatrix} X_0 \\ Y_0 \end{vmatrix}$$

and for the reactor i in a chain

$$\begin{vmatrix} 1 + \alpha\theta_i R_{xi}' + j\omega\theta_i, & 0 \\ -\theta_i R_{xi}', & 1 + j\omega\theta_i \end{vmatrix} \cdot \begin{vmatrix} X_i \\ Y_i \end{vmatrix} = \begin{vmatrix} X_{i-1} \\ Y_{i-1} \end{vmatrix}$$

or

$$V_{i-1} = M_i V_i \qquad (3)$$

with

$$M_i = \begin{vmatrix} 1+\alpha\theta_i R_{xi}'+j\omega\theta_i, & 0 \\ -\theta_i R_{xi}', & 1+j\omega\theta_i \end{vmatrix} \qquad (4)$$

Therefore, the relation between product and feed variations in composition is

$$V_n = (M_1 M_2 \cdots M_i \cdots M_n)^{-1} V_0 \qquad (5)$$

This formula gives the desired result, namely that the product composition varies as a function of feed-composition variations.