II. Behavior away from Equilibrium

An analysis is made of diffusion and chemical reaction in an isothermal multicomponent fluid. Transient gas-phase reaction in a one-dimensional nonflow system and steady state gas-phase or surface reaction in a tubular reactor are considered. The equations are linearized around some state away from equilibrium. Multicomponent and binary diffusivity expressions are used and a series of reactions of varying complexity is considered. The possibility of oscillations increases as the complexity of the reactions is increased. These oscillations occur with time in the nonflow system and with space-time in the tubular reactor, and it appears that any reacting mixture which oscillates in one of these two systems will also oscillate in the other.

In Part I the linearized equations governing diffusion and reaction in a multicomponent mixture in a tubular reactor were solved (*21*); it was assumed that the reacting mixture was near chemical equilibrium. In this work nonequilibrium behavior is treated. The concentration profiles and reaction rates for several reactions are determined as functions of time in a one-dimensional diffusion tube and as functions of space-time for a flow reactor. A series of reactions of varying complexity is treated.

Toor has considered the linearized equations of diffusion and reaction in multicomponent systems (*23*). One-dimensional bounded and semi-infinite geometries without flow were treated. Toor showed that oscillations in time are not possible in ideal fluids near equilibrium.

Oscillations can occur in a system which is away from equilibrium. Gmitro and Scriven (*7*) and Othmer and Scriven (*14*) have analyzed transient diffusion and reaction in nonflow systems. Several geometries are discussed and mass exchange with the surroundings is allowed. Regions of oscillatory and unstable behavior are delineated.

Further discussion of multicomponent reaction and diffusion is presented in this work. The occurrence of oscillations is considered in nonflow and in flow systems. Nonautocatalytic reactions which cannot oscillate if not coupled with diffusion are studied.

If the chemical reactions are autocatalytic, oscillations and instabilities can occur in a homogeneous system (*1, 6, 9 to 13, 15*). The catalytic decomposition of hydrogen peroxide is often cited as an example of such an oscillating reaction (*4, 5*), although recently it has been suggested that it does not occur homogeneously (*19*). Oscillations have been observed in the thermal decomposition of sodium dithionite (*18*) and a subsequent analysis of this system has been made (*2*). Oscillating reactions in biological systems have been observed and analyzed (*8*). The coupling of autocatalytic reactions and diffusion yields some interesting phenomena. Spatially dependent perturbations can be unstable and thus initially homogeneous systems can become inhomogeneous (*7, 14, 16, 17, 24*). This can lead to inhomogeneous steady states in open systems.

FORMULATION—NO FLOW

Consider a tube of length $2L$ joining two large reservoirs at $z^* = \pm L$. The system is initially at steady state with different concentrations in each of the two reservoirs. The concentrations of the reservoirs are held away from equilibrium by exchange of mass with the surroundings. At time zero the concentration of one reservoir is instantaneously made equal to that of the second and the system is allowed to approach a new steady state. It is assumed that there is no volume change on reaction, that there is no flow, and that the system is isothermal. The reaction rate expression is linearized about the concentration of the reservoirs at the final steady state. It is necessary to linearize about the concentration in the reservoirs rather than about the concentration in the diffusion tube since the latter is a function of position. Linearized expressions will also be used for the diffusional flux and the constant diffusivities are evaluated at the final steady state composition of the reservoirs.

The dimensionless equations describing the system are

$$\frac{\partial (y)}{\partial \theta} = [D] \frac{\partial^2 (y)}{\partial z^2} - [K]\,(y) \tag{1}$$

with boundary conditions $(y) = (0)$ at $z = \pm 1$. Let (x^-) and (x^+) be the vectors of mole fractions in the reservoirs at $z = -1$ and $z = +1$, respectively, at $t < 0$; furthermore, let (x_{ss}) be the steady state solution to the mass balance equations having those boundary conditions. Then the initial condition for Equation (1) is $(y) = (x_{ss}) - (x^+)$ at $t = 0$. The matrices are $n \times n$ where there are $n + 1$ species in the mixture.

Two types of diffusivity matrices are considered. The first is a general multicomponent diffusivity matrix D_{MC} for which all the elements are nonzero. In some of the examples in ternary mixtures discussed below numerical values are needed; expressions relating the elements to the binary diffusivities $\mathcal{D}_{12}$, $\mathcal{D}_{13}$, and $\mathcal{D}_{23}$ of an ideal gas are used (*21*). This method of evaluating the elements of $[D]_{MC}$ is strictly valid only at equilibrium but will be used here for nonequilibrium mixtures for lack of a better alternative. The second diffusivity matrix used is designated $[D]_B$ which is diagonal but for which the elements on the diagonal are unequal. The matrix $[D]_B$ is thus applicable to a system of dilute reactants and products in an inert. It is also used here as an approximation to $[D]_{MC}$.

A solution to Equation (1) which is symmetric in z has been given by Toor (*23*). With very slight modification of his result the solution of Equation (1), with the initial condition and boundary conditions considered here, is

$$(y) = \sum_{p=1}^{\infty} \sin\{A_p^{1/2}\,(z+1)\}\,\exp\{-[L_p]\,\theta\}\,(b_p) \tag{2}$$

where

$$A_p = p^2\,\pi^2/4 \qquad p = 1, 2, \ldots \tag{3a}$$

$$[L_p] = A_p\,[D] + [K] \tag{3b}$$

The nature of the solution thus depends on the eigenvalues λ of $[L_p]$. Toor has shown that for an ideal system near equilibrium with $[D] = [D]_{MC}$ that the λ are all real and non-negative and therefore that the system is nonoscillatory and stable (*23*). If $[D]$ and $[K]$ are evaluated away from equilibrium, complex λ can arise. For ternary systems the matrices are 2×2. Simple criteria for the occurrence of oscillations or instabilities can then be developed. Oscillations result for $\Omega_p < 0$ where

$$\Omega_p = \{A_p\,(D_{11} - D_{22}) + (K_{11} - K_{22})\}^2 + 4\,(A_p\,D_{12} + K_{12})\,(A_p\,D_{21} + K_{21}) \tag{4a}$$

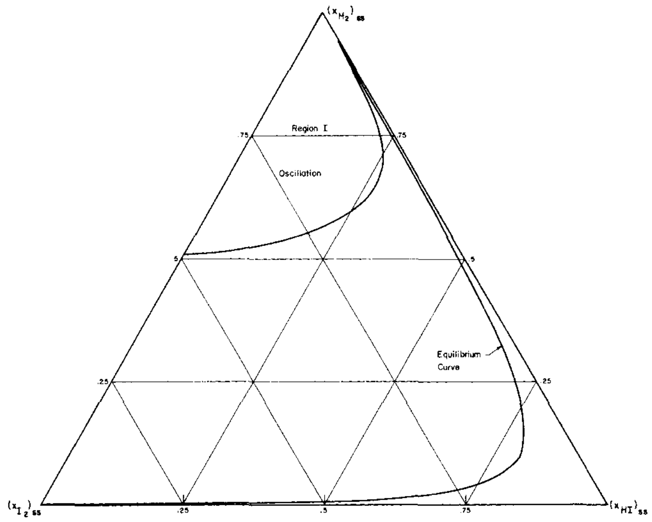

Fig. 1. Region of oscillation for the reaction $H_2 + I_2 \rightleftarrows 2HI$ at $T = 680°K.$, $P = 4.9$ atm., $L = 20$ cm.

If the cross terms of the diffusivity matrix are zero or are neglected, then oscillations occur for $\omega_p < 0$ where

$$\omega_p = \{A_p\ (D_1 - D_2) + (K_{11} + K_{22})\}^2 + 4K_{12}\ K_{21} \tag{4b}$$

where D_1 and D_2 are the diagonal elements of the diffusivity matrix. The oscillations are damped if Γ_p and γ_p are negative where

$$\Gamma_p = -\ A_p\ D_{11} - A_p\ D_{22} - K_{11} - K_{22} \tag{5a}$$

$$\gamma_p = -\ A_p\ D_1 - A_p\ D_2 - K_{11} - K_{22} \tag{5b}$$

Nonoscillatory solutions ($\Omega_p > 0$) are damped if Γ_p or γ_p is negative and Δ_p or δ_p is positive where

$$\Delta_p = (A_p\ D_{11} + K_{11})\ (A_p\ D_{22} + K_{22}) - (A_p\ D_{21} + K_{21})\ (A_p\ D_{12} + K_{12}) \tag{6a}$$

$$\delta_p = (A_p\ D_1 + K_{11})\ (A_p\ D_2 + K_{22}) - A_p^2\ K_{21}\ K_{12} \tag{6b}$$

DISCUSSION—NO FLOW

As an example the reaction $H_2 + I_2 \rightleftarrows 2HI$ has been considered. The kinetic expression of Sullivan (*22*) is used to calculate [*K*], although at the temperatures considered (around 700°K.) the value of [*K*] is very close to that calculated using the older kinetic expression of Bodenstein (*3*). The dimensionless matrices [*D*] and [*K*] depend on the temperature, pressure, tube length, and the final vector of steady state mole fractions in the reservoirs; these are denoted by *T, P, L*, and (x^+), respectively. The results will be discussed in terms of *T, P, L*, and (x^+) rather than in terms of [*D*] and [*K*].

If the multicomponent diffusivity matrix $[D]_{MC}$ is used, oscillations are predicted for certain values of the parameters. In order to determine under what conditions complex λ arise, *P, T*, and *L* are fixed and the Ω_p are calculated for a range of (x^+). In order for oscillations to occur, at least one of the Ω_p must be negative. Results are presented in reference *20* for several cases.

The results for a typical case are presented graphically in Figure 1 for $T = 680°K.$, $P = 4.9$ atm., and $L = 20$ cm. Oscillations are found for every (x^+) in region I; no oscillations occur for any (x^+) outside of region I. The equilibrium curve is also shown. As shown by previous workers (*15, 23*) oscillations are not possible near equilibrium, and this is substantiated by Figure 1. However, it is also seen that the statement that oscillations are not possible near equilibrium must be interpreted cautiously. For low hydrogen concentrations region I, in which oscillations occur, is far from the equilibrium curve. However, for large hydrogen concentrations region I approaches very close to (but does not touch) the equilibrium curve. Thus although oscillations are not possible at equilibrium, they do occur if the steady state mole fraction is taken to be slightly to the left of the equilibrium curve in the upper part of Figure 1.

The scanning of the system parameters may also be done by choosing *T, P*, and (x^+) and by finding values of the tube length *L* such that oscillations occur. A pair of eigenvalues λ arises from Equation (*3b*) for each A_p. If a complex eigenvalue is predicted for a given A_p, this complex eigenvalue will occur only over a finite range of tube lengths *L*. The tube lengths in which complex λ are predicted for the A_p may or may not overlap. For example consider $T = 650°K.$, $P = 5$ atm., and a steady state mole fraction of 55% hydrogen and 30% iodine. The first two eigenvalues found from A_1 are complex for a tube length between 38 and 62 cm. The second two eigenvalues found from A_2 are complex for tube lengths between 77 and 124 cm. and those predicted from A_3 are complex for tube lengths between 116 and 186 cm., etc. Thus oscillatory behavior occurs for tube lengths between 38 and 62 cm. and any length greater than 77 cm.

The transient behavior of the hydrogen iodide reaction is always damped. It is of interest to determine whether or not the oscillations could be detected in a laboratory experiment. The period of oscillation ranges from 400 sec. to one day, while the time required for a disturbance to fall to $1/e$ of its value ranged from 1 to 3,000 sec. The ratio of the former to the latter was never less than about 20,

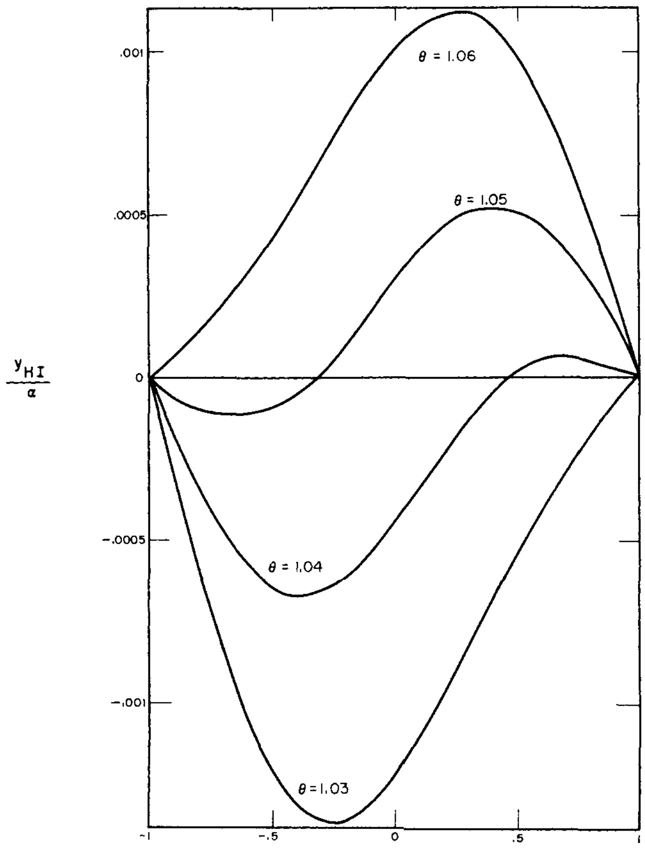

Fig. 2. HI mole fraction versus distance for $H_2 + I_2 \rightleftarrows 2HI$; $T = 680°K.$, $P = 4.9$ atm., $L = 20$ cm. $x^+_{H_2} = 0.85$, $x^+_{I_2} = 0.05$.

so that the oscillations would be extremely difficult to observe.

The nature of the oscillations is shown in Figures 2 and 3 for a case within region I of Figure 1, namely, $T = 680°K.$, $P = 4.9$ atm., $L = 20$ cm. and 85% hydrogen, 5% iodine. In Figure 2 the deviation of the mole fraction of hydrogen iodide from the final steady state is shown as a function of position with time as a parameter. The steady states are taken to be linear with position even though the dependency is actually more complicated. The difference between the mole fractions of hydrogen and iodine in the two reservoirs is taken to be α at time zero where α is arbitrary, that is, $x^- - x^+ = \alpha$; the corresponding difference for hydrogen iodide is thus -2α. The deviation of the mole fraction of iodine and hydrogen iodide from their final steady values integrated over the tube length are shown in Figure 3; this figure is not to scale since the rapid damping would make it impossible to see the oscillations on a figure drawn to scale.

If the above calculations are repeated using a diagonal diffusivity matrix, no oscillations occur. It can be shown in general for a reaction of the form $A + B \rightleftarrows 2C$ that oscillations can arise if a multicomponent diffusivity matrix is used, but that only nonoscillatory behavior is predicted with a diagonal diffusivity matrix.

More complicated reactions are now considered. The proofs or numerical examples are relatively straightforward and are given in reference *20*. Only the results are presented here.

Consider next the two coupled reversible reactions $A \rightleftarrows B \rightleftarrows C$. Oscillations are predicted with either the multicomponent diffusivity matrix or with a diagonal matrix. The predictions of oscillations using a diagonal diffusion matrix can be contrasted to the results found for $A + B \rightleftarrows 2C$. The increased coupling with two reversible reactions is enough to introduce oscillatory behavior even though the diffusional fluxes are not coupled by multicomponent diffusion. Of course if the elements of the diffusivity matrix are equal, oscillations are no longer possible; as shown by Toor (*23*) the reactions in this latter case can be uncoupled by a suitable transformation.

If the reactions are irreversible, that is $A \rightarrow B \rightarrow C$, oscillations cannot occur with a diagonal diffusivity matrix since there is no feedback present; however, multicomponent diffusion does give enough coupling to produce oscillations. It may be further shown that any set of irreversible reactions with any number of species cannot oscillate if the diffusivity matrix is diagonal.

Four-component systems will now be considered in order to determine the effect of increasing the number of species. For four-component mixtures the behavior still depends on the eigenvalues of $[L_p]$ given in (3*b*). Since that matrix is now 3 × 3, no simple expression such as (4*a*) or (4*b*) can be found. The behavior is therefore investigated by numerical evaluation of the eigenvalues. Only diagonal diffusivity matrices are considered. Consider first the addition of a fourth but inert component to the reaction $A + B \rightleftarrows 2C$. The addition of the inert is not sufficient to produce oscillatory behavior. However, if the fourth component is allowed to take part in the reaction, complex eigenvalues occur. Thus the reaction $A + B \rightleftarrows 2C$ in an inert cannot oscillate while the reaction $A + B \rightleftarrows C + D$ (with no inert) can oscillate. Two reversible reactions involving four species also yield complex eigenvalues, that is, the reaction $D \rightleftarrows A + B \rightleftarrows 2C$ can oscillate.

The reactions considered here are nonautocatalytic and could not oscillate in a homogeneous system. Oscillations are thus caused by a coupling between diffusion and chemical reaction. Autocatalytic reactions can oscillate without diffusional effects as noted in the introduction.

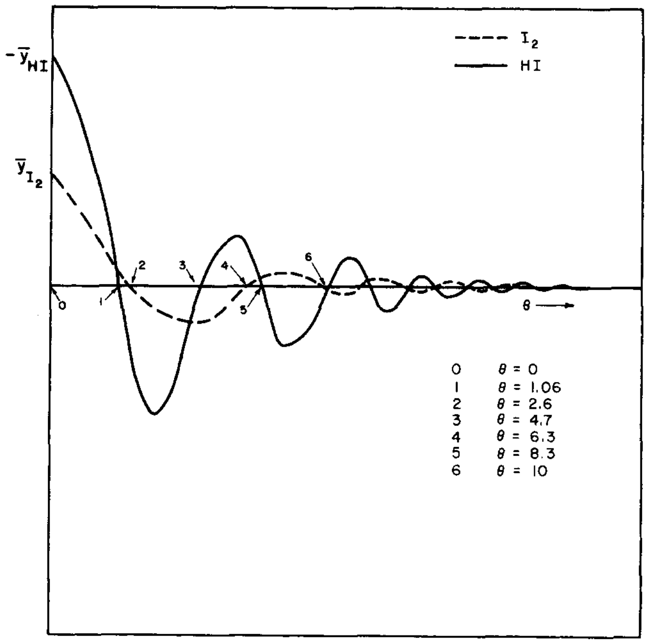

Fig. 3. Damped oscillatory behavior near the steady state; integrated mole fraction versus time; $H_2 + I_2 \rightleftarrows 2HI$; $T = 680°K.$, $P = 4.9$ atm., $L = 20$ cm.; $x^+_{H_2} = 0.85$, $x^+_{I_2} = 0.05$.

THE FLOW REACTOR

Consideration is now given to chemical reaction and diffusion in a multicomponent isothermal ideal gas which is in fully developed laminar flow in a tubular reactor. The behavior of the system away from equilibrium is investigated. As in the nonflow systems comparisons are made between results predicted using multicomponent and binary diffusivity expressions. Concentration profiles and reaction rates are calculated. The system is at steady state and the oscillations which sometimes arise are functions of axial position or space-time rather than time.

A mixture, which is away from chemical equilibrium, is introduced into the reactor. Far downstream equilibrium will be attained. The behavior near equilibrium has been discussed in Part I (*21*). Consideration is given here to the behavior near the inlet. In order to be able to analyze the problem easily, the equations are linearized. This linearization is made about (x^0), where the inlet mole fraction vector is equal to or close to (x^0). All properties are evaluated at (x^0). This linearization about (x^0) cannot be rigorously justified since the mole fractions in the reactor change as the mixture flows downstream, that is, (x) is a function of space-time. The approximation is valid at best only near the reactor inlet and the results are viewed as more qualitative than quantitative. The linearized equation is

$$\{1 - \eta^2\} \frac{\partial (y)}{\partial z} = [D] \nabla_\eta^2 (y) + [K] (y) + (R^0) \tag{7}$$

with boundary conditions

$$[D] \frac{\partial (y)}{\partial \eta} + [F] (y) + (R_s^0) \qquad \eta = 1$$

$$(y) = (y^0) \qquad z = 0$$

with symmetry at $\eta = 0$. The vector (y) is the deviation from (x^0) or $(y) = (x) - (x^0)$. The constant vectors (R^0) and (R_s^0) are the rates of reaction evaluated at (x^0). Equation (7) is similar to that solved in Part I (*21*), except for the presence of the nonhomogeneous term (R^0). The method of solution is similar to that presented in Part I (*21*). The Galerkin method is used and the behavior of the system is seen to depend on the eigenvalues of a nonsymmetric matrix. These eigenvalues were calculated but the concentration profiles were not found. Details are given in reference *20*.

Consider the reaction $H_2 + I_2 \rightleftarrows 2HI$ with no inerts present. The inlet molar composition is equal to or is a small stoichiometric perturbation from 70% H_2, 20% I_2, and 10% HI; $T = 794$°K., $P = 10$ atm. Far downstream an equilibrium of 51.06% H_2, 1.06% I_2, and 47.88% HI will be attained; the behavior near this equilibrium has been discussed in Part I and some mole fraction profiles are presented in Figure 6 of that study (*21*). Near equilibrium the first four eigenvalues are −5.3, −11.3, −23.3, −31.9, and −6.4, −29.9, −34.5, −89.0, using the multicomponent and binary diffusivities, respectively. Near the composition (x^0), the respective eigenvalues are −8.4, $-23.1 \pm 5.0i$, −37.3 and −10.0, −28.3, −40.4, −88.5. Oscillations are thus predicted by the linear analysis when the multicomponent diffusivity matrix is used but not if the diagonal diffusivity matrix is used.

Consider now an inlet state of 27% H_2, 27% I_2, and 46% HI at $T = 978$°K. and $P = 2.77$ atm. Far downstream this would decay to an equilibrium composition of 13.5% H_2, 13.5% I_2, and 73% HI. The behavior near equilibrium is discussed in Part I and is shown in Figure 2 of that work (*21*); near equilibrium the first four eigenvalues are −5.2, −8.9, −13.4, −21.6, and −4.7, −8.4, −12.0, and −19.1, using the multicomponent and binary diffusivity matrices, respectively. Near (x^0) the first four eigenvalues are −8.2, −13.2, −18.3, −26.9, and −6.1, −11.3, −15.7, −21.4, using the multicomponent and binary diffusivity matrices, respectively.

These calculations were repeated for several inlet compositions for the hydrogen iodide reaction. The differences in the eigenvalues calculated using the two diffusivity matrices were larger away from equilibrium than they were near equilibrium; it is not known if this would be true in general since only a limited number of cases was considered. Use of the diagonal diffusivity always gave real eigenvalues; this is consistent with the nonoscillatory behavior predicted using a diagonal diffusivity for the diffusion tube which was discussed above. Use of the multicomponent diffusivity resulted in complex eigenvalues for conditions sufficiently far from equilibrium. A diagram qualitatively similar to Figure 1 could be drawn for the flow reactor.

The reaction $A \rightleftarrows B \rightleftarrows C$ was also considered in the flow reactor (*20*). Calculations using a diagonal diffusivity resulted in complex eigenvalues in some cases. An irreversible reaction, namely, the gas-phase decomposition of cyclopropane to propylene in inert helium was also considered. No oscillations in space-time were found using either diffusivity matrix.

Thus in each of the cases considered the behavior with space-time in the steady state tubular reaction is qualitatively similar to the behavior with time in a nonflow diffusion tube; reactions which oscillate in one system also oscillate in the other. It is expected that this similarity is general.

Consider next a reaction taking place on the tube wall, namely, the decomposition of hydrogen peroxide at $P =$ 1 atm., $T = 550$° or 450°C., and an (x^0) of 20% H_2O_2, 25% O_2, and 55% H_2O. This has no analogy in the diffusion tube studies described above since only gas-phase reactions were studied there. This is far from equilibrium since the reaction is irreversible. This reaction can take place on a catalytic tube wall. The reaction is often taken to be first order in H_2O_2. A large range of rate constants can be obtained by varying the surface material. A range between 5 and 1,000 cm./sec. is considered. At 550°C. a gas-phase reaction also takes place but it can be neglected at 450°C. The eigenvalues are always real if a diagonal diffusivity matrix is used. With a multicomponent diffusivity matrix the following results were found. At the temperature where the gas-phase reactions can be neglected, the tendency for oscillations in space-time to occur increases as the surface reaction rate constant increases. For example, the first five nonzero eigenvalues are −6.3, −32.4, −39.3, −102, −105, and −6.6, −32.4, −40.7, $-105 \pm 0.37i$ and −6.7, −32.4, −41.1, $-105 \pm 8.1i$ for surface reaction rate constants 25, 100, and 1,000 cm./sec., respectively. At the higher temperature where a gas-phase reaction also occurs, no oscillations in space-time occur for the same three surface rate constants. Details and a figure showing the mole fraction distribution for simultaneous gas-phase and surface reactions can be found in reference *20*.

An isothermal multicomponent mixture of ideal gases which reacts nonautocatalytically will reach equilibrium far downstream in a tubular reactor. Oscillations in space-time are not possible near equilibrium; this is shown by linearizing the governing equations around equilibrium. If the equations are linearized about the inlet composition to the reactor complex eigenvalues arise in some cases. This linearization is approximate and the results are not conclusive as noted above. However, it is possible that the species concentrations oscillate in space-time near the inlet of the reactor and that these oscillations die out as the fluid travels downstream so that equilibrium is approached in a nonoscillating manner. Conclusive evidence of this could only be obtained from a solution of the full nonlinear equations.

NOTATION

A_p = defined by Equation (*3a*)
D_R = reference diffusivity, sq.cm./sec.
D_i = i^{th} element of a diagonal diffusivity matrix, dimensionless
D_{ij} = element of $[D]$, dimensionless
$\mathcal{D}_{ij}$ = binary diffusivity, sq.cm./sec.
$[D]$ = $[D]^*/D_R$, dimensionless
$[D^*]$ = general diffusivity matrix, sq.cm./sec.
$[D]_B$ = diagonal diffusivity matrix, dimensionless
$[D]_{MC}$ = multicomponent diffusivity matrix, dimensionless
$[F^*]$ = linearized surface reaction rate constant matrix, cm./sec.
$[F]$ = $[F^*]R/D_R$, dimensionless
$[I]$ = identity matrix
K_{ij} = element of $[K]$
$[K]$ = $[K^*]R^2/D_R$ (tubular reactor) or $[K^*]L^2/D_R$ (nonflow), dimensionless
$[K^*]$ = linearized gas-phase reaction rate constant matrix, sec.$^{-1}$
L = length of diffusion tube, cm.
$[L_p]$ = defined in Equation (*3b*)
P = pressure, atm.
R = tube radius, cm.
(R^0) = rate of production by gas-phase reaction at inlet to tubular reactor, dimensionless
$(R_s{}^0)$ = rate of production by surface reaction at inlet to tubular reactor, dimensionless
t = time, sec.
T = temperature, °K.
V_m = maximum of Poiseuille velocity profile, cm./sec.
(x) = vector of mole fractions
(x^0) = vector of mole fractions at the inlet to the tubular reactor
(x^+) = vector of mole fractions in the reservoir at $z =$

$+1$ for $\theta < 0$

(x^-) = vector of mole fractions in the reservoir at $z = -1$ for $\theta < 0$

(y) = $(x) - (x^+)$ for the nonflow diffusion tube or $(x) - (x^0)$ for the tubular reactor

$\bar{y}$ = mole fraction integrated over tube length

z = z^*/L (nonflow) or $z^* D_R/V_m R^2$ (tubular reactor) = axial coordinate, dimensionless

z^* = axial coordinate, cm.

Greek Letters

α = $x^- - x^+$

η = radial position in tubular reactor, dimensionless

θ = $t\, D_R/L^2$ = time, dimensionless

λ = eigenvalue

ω_p = defined by Equation (4*b*)

Ω_p = defined by Equation (4*a*)

LITERATURE CITED

1. Bak, Thor A., "Contributions to the Theory of Chemical Kinetics," W. A. Benjamin, New York (1963).
2. Bischoff, Jerry R., and David M. Mason, *Chem. Eng. Sci.*, **23**, 447 (1968).
3. Bodenstein, Max, *Z. Phys. Chem.*, **29**, 295 (1899).
4. Bray, William C., *J. Am. Chem. Soc.*, **43**, 1262 (1921).
5. Bray, William C., and Kerman A. Liebhafsky, *ibid.*, **53**, 38 (1931).
6. Christiansen, J. A., *Z. Elektrochemie*, **62**, 225 (1958).
7. Gmitro, John I., and L. E. Scriven, "Symposium of the International Society for Cell Biology," Vol. V, p. 221, Academic Press, New York (1966).
8. Higgins, Joseph, *Ind. Eng. Chem.*, **59**, 18 (1967).
9. Kim, Young Gul, *Chem. Eng. Sci.*, **23**, 687 (1968).
10. Lefever, R., G. Nicolis, and I. Prigogine, *J. Chem. Phys.*, **47**, 1045 (1967).
11. Lotka, Alfred J., *J. Phys. Chem.*, **14**, 271 (1910).
12. ———, *J. Am. Chem. Soc.*, **42**, 1595 (1920).
13. Moore, Margaret J., *Trans. Faraday Soc.*, **45**, 1098 (1949).
14. Othmer, H. G., and L. E. Scriven, paper presented at 35th Ann. Chem. Eng. Symp., A.C.S., Illinois Inst. Tech., Chicago (Dec. 1968).
15. Prigogine, I., "Introduction to the Thermodynamics of Irreversible Processes," 3rd edit., Interscience, New York (1967).
16. ———, and R. Lefever, *J. Chem. Phys.*, **48**, 1695 (1968).
17. Prigogine, I., and G. Nicolis, *ibid.*, **46**, 3542 (1967).
18. Rinker, Robert G., Scott Lynn, David M. Mason, and William H. Corcoran, *Ind. Eng. Chem. Fundamentals*, **4**, 282 (1965).
19. Shaw, D. H., and H. O. Pritchard, *J. Phys. Chem.*, **72**, 1403 (1968).
20. Solomon, Robert Lee, Ph.D. thesis, Univ. Illinois, Urbana (1969).
21. ———, and J. L. Hudson, *AIChE J.*, **17**, 371 (1971).
22. Sullivan, John H., *J. Chem. Phys.*, **46**, 73 (1967).
23. Toor, H. L., *Chem. Eng. Sci.*, **20**, 941 (1965).
24. Turing, A. M., *Phil. Trans. Roy. Soc.*, **237**, 37 (1952).

Manuscript received April 24, 1969; revision received February 24, 1970; paper accepted March 2, 1970.

Analysis of Flow Choking of Two-Phase, One-Component Mixtures

W. J. KLINGEBIEL and R. W. MOULTON

University of Washington, Seattle, Washington

The nature of flow choking has been studied as steam-water mixtures are passed through a tube with ever increasing pressure gradient. Choked flow for two-phase, one-component mixtures has been characterized with a separated flow model as resulting from maximization of the ratio of gas to liquid velocities, or slip ratio. Slip ratios at choking were measured and found to increase from 1.2 to 5.0 at 30 lb./sq.in. exit plane pressure with decrease in quality from 0.95 to 0.02. Separated models predict either 9.3 or 28.4 with no quality dependence. The difference is attributed to liquid entrainment. Flow regimes were observed to vary from purely entrained to annular entrained to slug entrained as quality decreased. Normal shock waves were observed in the free jet at qualities above 0.25. Choking flow rates were predicted with an average error of less than 2% with a stagnation energy balance model using an empirically developed slip ratio relation corrected for entrainment.

High-velocity flow of vapor-liquid mixtures through ducts is characterized by ill-defined interfaces between phases and momentum and thermal relaxation times sufficiently long to result in nonequilibrium flow. Improved characterization of such a complex flow system has been the goal of researchers working in such diverse fields as oil reservoir recovery, rocket engine design, and nuclear reactor cooling. Of particular interest has been the prediction of choking conditions under which further increases in flow rate through a duct cannot be produced by decreasing downstream pressure.

Historically, choking, or critical flow, in a two-phase system was first analyzed by assuming that the two phases

---

W. J. Klingebiel is with Union Carbide, Bound Brook, New Jersey.