TABLE 1

Turbulent velocity

$u = V_z/V_{z\,\max}$

$\int_0^1 u\theta d\theta = 2\langle u\rangle$		
$u(0) = 1$	$u(1) = 0$	
$\frac{du}{d\theta}(0) = 0$	$\frac{du}{d\theta}(1) = -\chi$	$\frac{du}{d\theta}(\theta_c) = \theta_c \frac{d^2u}{d\theta^2}(u_c)$
$\frac{d^2u}{d\theta^2}(0) = \frac{-\chi}{\epsilon(0)}$	$\frac{d^2u}{d\theta^2}(1) = \chi\left[\frac{d\epsilon}{d\theta}(1) - 1\right]$	
$\frac{d^3u}{d\theta^3}(0) = 0$		$\frac{d^3u}{d\theta^3}(\theta_c) = \frac{\frac{d^2\epsilon}{d\theta^2}(\theta_c)\frac{du}{d\theta}(\theta_c)^2}{\chi\theta_c}$
$\frac{d^4u}{d\theta^4}(0) = \frac{\epsilon''(0)\chi}{\epsilon(0)^2}$		

Eddy viscosity

$\epsilon = \frac{\epsilon_{TOT}}{v}$

$\epsilon(0) = \frac{-\chi}{\frac{d^2u}{d\theta^2}(0)}$	$\epsilon = \frac{-x\theta}{\frac{du}{d\theta}}$	$\int_0^1 \epsilon du = \frac{\chi}{2}$
$\epsilon(0) = \frac{-\chi}{2\frac{du}{d\theta^2}(0)}$	$\frac{d\epsilon}{d\theta}(1) = 1 + \frac{\frac{d^2u}{d\theta^2}(1)}{\chi}$	$\frac{d\epsilon}{d\theta}(\theta_c) = 0$
$\frac{d\epsilon}{d\theta}(0) = 0$	$\frac{d^2\epsilon}{d\theta^2}(\theta_c) = \frac{\chi\theta_c\frac{d^3u}{d\theta^3}(\theta_c)}{\left[\frac{du}{d\theta}(\theta_c)\right]^2}$	
$\frac{d^2\epsilon}{d\theta^2}(0) = \frac{\frac{d^4u}{d\theta^4}(0)\chi}{\left[\frac{d^2u}{d\theta^2}(0)\right]^2}$		

Experimental evidence from many investigators shows that ϵ decreases near the center line. This, of course, implies that if $\frac{d\epsilon}{d\theta}(0) = 0$, then $\frac{d^2\epsilon}{d\theta^2}$ is necessarily positive at the center. Differentiating (6), applying L'hospital's rule, breaking up the limit into two parts, employing (11), the following is obtained.

$$\frac{d^2\epsilon}{d\theta^2}(0) = \chi \frac{\frac{d^4u}{d\theta^4}(0)}{\left[\frac{d^2u}{d\theta^2}(0)\right]^2} \quad (13)$$

Substituting from (10*b*),

$$\frac{d^2\epsilon}{d\theta^2}(0) = \frac{d^4u}{d\theta^4}(0)\frac{\epsilon(0)^2}{\chi} \quad (14)$$

This implies that $\frac{d^4u}{d\theta^4}(0)$ must be positive if ϵ reaches a minimum at $\theta = 0$.

$0 < \theta < 1$

If ϵ reaches a minimum at the center, then, as has been shown by many investigators, it reaches a maximum at a value of θ away from the center, denoted by θ_c. From (6), an expression at θ_c may then be written.

$$\frac{du}{d\theta}(\theta_c) = \theta_c \frac{d^2u}{d\theta^2}(\theta_c) \quad (15)$$

At θ_c, ϵ reaches a maximum, $\frac{d\epsilon}{d\theta} = 0$, and $\frac{d^2\epsilon}{d\theta^2}$ must be negative. Differentiating, taking the limit, and employing (15), the following is obtained.

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Chemical Reactor Stability by Liapunov's Direct Method

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In two recent articles (*1*, *2*), Berger and Perlmutter discuss the use of Liapunov functions to determine the stability range of a chemical reactor. Two points, however, require some additional comment. First, the conditions presented to determine the region of asymptotic stability are overly conservative. Second, a less restrictive definition of Krasovskii's theorem for the generation of Liapunov functions allows a search for a broader stable region.

CONDITIONS FOR STABILITY

In Liapunov's direct method, asymptotic stability of a system is assured in a region of the phase space enclosed by an analytic positive definite function, V, provided that its time derivative, $\dot{V}$, is negative throughout this region (except for the trivial solution at the focus). After constructing a quadratic function of the time derivatives of the state variables, the authors (*1*) use Sylvester's conditions to determine the sign of the derivative of the Liapunov function, $\dot{V}$. However, the Sylvester conditions are necessary only for positive definiteness throughout the phase space; they do not delineate the region in which the quadratic form is positive. For example, the Sylvester conditions are not fulfilled at any point for the function $F = x^2 + 3\,xy + y^2$; yet F is positive throughout a considerable part of the xy plane. Thus, the derivative of the Liapunov function as defined in reference *1* is negative in a region larger than that defined by the separatrices shown there.

In Figure 1 the cross-hatched region is bounded by the Liapunov function tangent to the separatrix. This is the region of asymptotic stability reported in reference *1*. The unshaded region is bounded by the smallest Liapunov function touching a contour of zero $\dot{V}$. The latter region is considerably larger that the former. Note that a portion of this extended region of asymptotic stability lies above the separatrix given in reference *1*.

The extent of the stable range could be of great interest; it could be used as a measure of merit in control system design.

KRASOVSKII'S THEOREM

Krasovskii's method to find a Liapunov function has more scope than reported in references *1* or *3*. Briefly, the theorem as given in references *4* or *5* is as follows.

Given the following system having an isolated solution at the origin

$$\dot{x} = f(x), \text{ where } x \text{ and } f \text{ are vectors} \quad (1)$$

Define the Jacobian matrix

$$J = (J_{ij}) = \left(\frac{\partial f_i}{\partial x_j} \right) \quad (2)$$

Define a positive definitive constant matrix $A = A^T$, where A^T is the transpose of A.
Then

$$f(x)^T A f(x) = V \quad (4)$$

is a Liapunov function proving asymptotic stability of (1) if

$$J^T A + AJ < -Q \quad (5)$$

where Q is a positive definite symmetric matrix. [Note that (5) requires

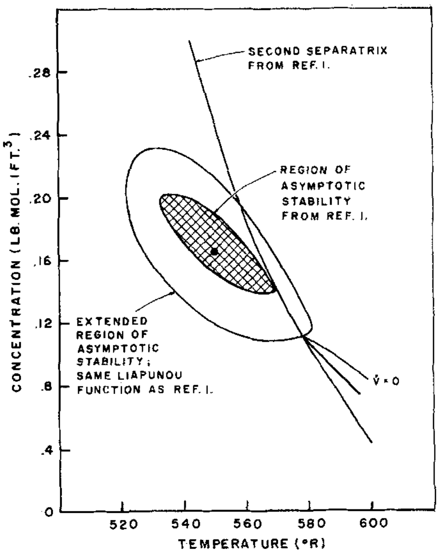

Fig. 1. Region of asymptotic stability for a chemical reactor.

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Mass Transfer from Particles in Agitated Systems: Application of the Kolmogoroff Theory

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Many industrially important fluid-particle transfer operations are carried out in agitated systems. An analytical description of such turbulent transport phenomena is virtually impossible. While some data exist on the detailed flow field in an agitated baffled vessel (*7*), no experimental study of the *relative* flow field experienced by a particle free to move with the fluid has been carried out. Of course, transport rates are governed by the flow relative to the particle, and hence might be different for two different particles in the same agitated vessel.

The usual approach to predicting the behavior of such a complex system is to assume, as a framework for a theory, a simple model for which an analytical or semi-empirical description exists, and to modify certain elements of the model in order to account for known experimental results. For example, in describing mass transfer by forced convection from spherical particles, one often starts with the well-known Frössling equation (*4, 10*)

$$N_{Sh} = 2 + 0.6\,(N_{Re})^{1/2}(N_{Sc})^{1/3} \quad (1)$$

which holds for transfer from single spheres in the absence of natural convection.

A fundamental objection to the use of Equation (1) lies in the fact that the Frössling equation is established for *steady state* flows, whereas a particle in an agitated vessel experiences varying mean relative velocities which depend upon the path of the particle through the vessel. Hence, transient effects might be of some importance in such a process, and might lead to transport laws of a form different from that of the Frössling equation. Even if Equation (1) is applicable to a particle in an agitated system, one must still estimate an appropriate velocity to use in the Reynolds number.

In what follows it is implied that steady state correlation such as the Frössling equation form a suitable framework for a theory applicable to agitated systems. The purpose of this note is to discuss rational methods of predicting the manner in which macroscopic agitation parameters enter such a correlation. It is proposed that the Kolmogoroff theory of universal equilibrium leads to useful results. The test of this approach is made with some data previously published by Harriott.

The Frössling equation is obtained from a boundary layer development which is most appropriate at high Reynolds numbers, when the flow relative to the sphere is turbulent. For small enough particles in an agitated tank it might happen that the Reyn-

Table 1. Mass Transfer Correlations

$kD_P/\mathcal{D} - 2 = K\,D_P^{2/3}D^{1/3}N^{1/2}\nu^{-1/6}\mathcal{D}^{-1/3}$	$D_P >> \eta$	(1)/(6)
$kD_P/\mathcal{D} - 2 = K\,D_P^{1/2}D^{1/4}N^{3/8}\nu^{-1/24}\mathcal{D}^{-1/3}$	$D_P << \eta$	(1)/(7)
$kD_P/\mathcal{D} - 2 = K\,D_P D^{1/2}N^{3/4}\nu^{-5/12}\mathcal{D}^{-1/3}$	$D_P << \eta$	(1)/(8)
$kD_P/\mathcal{D} - 2 = K\,D_P^{4/9}D^{2/9}N^{1/3}\mathcal{D}^{-1/3}$	$D_P >> \eta$	(2)/(6)
$kD_P/\mathcal{D} - 2 = K\,D_P^{1/3}D^{1/6}N^{1/4}\nu^{1/12}\mathcal{D}^{-1/3}$	$D_P << \eta$	(2)/(7)
$kD_P/\mathcal{D} - 2 = K\,D_P^{2/3}D^{1/3}N^{1/2}\nu^{-1/6}\mathcal{D}^{-1/3}$	$D_P << \eta$	(2)/(8)
$kD_P/\mathcal{D} - 2 = K\,D_P^{4/3}D^{2/3}N\,\mathcal{D}^{-1}$	$D_P >> \eta$	(3)/(6)
$kD_P/\mathcal{D} - 2 = K\,D_P D^{1/2}N^{3/4}\nu^{1/4}\mathcal{D}^{-1}$	$D_P << \eta$	(3)/(7)
$kD_P/\mathcal{D} - 2 = K\,D_P^{2}D\,N^{3/2}\nu^{-1/2}\mathcal{D}^{-1}$	$D_P << \eta$	(3)/(8)

(Continued from page 760)

Thermal conductivity measurements for nitrogen in the dense gaseous state, Misic, Dragoslav, and George Thodos, **A.I.Ch.E. Journal, 11,** No. 4, p. 650 (July, 1965).

Key Words: A. Thermal Conductivity-8, 9, Nitrogen-9, Gases-9, Coaxial Cylindrical Cell-10, Measurement-8, High Pressure-0, Transport Properties-8, 9, Physical Properties-8, 9, Thermal Properties-8, 9.

Abstract: A coaxial cylindrical type of cell was designed and constructed for the measurement of the thermal conductivity of gases at high pressures and moderate temperatures. This cell was used to establish the thermal conductivity of nitrogen for pressures up to 4,625 lb./sq.in.abs. and for temperature of 22.2° and 50.5°C. The resulting thermal conductivity values were found to be in agreement with values reported in the literature for nitrogen at these elevated pressures. These experimental measurements indicate that the cell developed for this investigation is capable of producing reliable thermal conductivities for gases at high pressures.

The effect of concentration level on the gas phase absorption coefficient, Vivian, J. Edward, and William C. Behrmann, **A.I.Ch.E. Journal, 11,** No. 4, p. 656 (July, 1965).

Key Words: A. Concentration-6, Mass Transfer-7, Gas-9, Inert-0, Solute-9, Turbulent Flow-9, Theoretical-0. B. Concentration-6, Mass Transfer-7, Absorption-8, Ammonia-1, Nitrogen-5, Water-5, Wetted-Wall Column-10, Experimental-0.

Abstract: A theoretical and experimental investigation of the effect of the concentration level on the rate of mass transfer shows the product of the gas phase coefficient and the mean inert gas concentration $k_y\ y_{BM}$ to be a constant in turbulent flow. Experimental data were obtained from a study of the adsorption of ammonia from mixtures with nitrogen into distilled water and aqueous ammonia solutions in a short wetted-wall column.

Deposits formed beneath bubbles during nucleate boiling of radioactive calcium sulfate solutions, Hospeti, Narayan B., and Russell B. Mesler, **A.I.Ch.E. Journal, 11,** No. 4, p. 662 (July, 1965).

Key Words. A. Nucleate Boiling-8, Calcium Sulfate-1, Bubbles-2, 9, Deposits-2, Thickness-8, 9, Sulfur-35-1, High-Speed Photogaphy-10, Autoradiographs-10, Counting-10, Estimation-8.

Abstract: A method was devised to estimate the microlayer thickness from the deposit formed by a series of bubbles during nucleate boiling of saturated calcium sulfate solution containing radioactive sulfur-35. The results support the microlayer evaporation hypothesis postulated by Moore and Mesler, which explains the sudden temperature drops observed by them during nucleate boiling of water.

Second-order chemical reactions in a nonhomogeneous turbulent fluid, Vassilatos, George, and H. L. Toor, **A.I.Ch.E. Journal, 11,** No. 4, p. 666 (July, 1965).

Key Words: A. Chemical Reactions-8, 9, Second Order-0, Reactor-10, Isothermal-0, Turbulent Flow-10, Mixtures-9, Nonhomogeneous-0, Chemical Kinetics-8, Mean Rate-8.

Abstract: Very rapid, rapid, and slow second-order reactions were studied in an isothermal turbulent flow reactor. The two aqueous reactant solutions were separately introduced through many alternate jets and the reaction took place in the resulting non-homogeneous mixture. Very rapid reactions were diffusion controlled and were in agreement with earlier theory. All reactions followed second-order rate laws based on time-average quantities. The apparent reaction velocity constant was controlled by the mixing for very rapid reactions, by the chemical kinetics for slow reactions, and by both mechanisms for rapid reactions.

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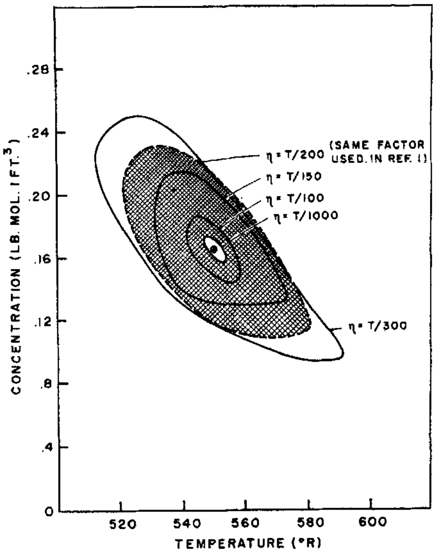

Fig. 2. Regions of asymptotic stability with parameters of normalized factor for temperature.

Sylvester conditions and that the region of asymptotic stability may be extended for nonlinear systems as described above.]

In reference *1* this theorem is actually used, since normalizing T in the problem amounts to dividing T and $\dot{T}$ by 200. Thus the A matrix is

$$A = \begin{bmatrix} \frac{1}{200^2} & 0 \\ 0 & 1 \end{bmatrix} \tag{6}$$

It is interesting that the non-normalized variables fail to provide a useful Liapunov function if the identity matrix is used for the A matrix as recommended in reference 3. In Figure 2 some regions of asymptotic stability are shown with parameters of normalization factors. Although the region enclosed for $\eta = T/200$ (used in reference *1*) is relatively large, it is almost completely contained in the larger region with $\eta = T/300$. Further area and shape changes are possible by manipulation of $a_{12} (= a_{21})$ of the A matrix.

ACKNOWLEDGMENT

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NOTATION

A = weighting matrix used in Krasovskii's theorem defined by Equation (4)

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a_{ij} = elements of A matrix
J = Jacobian matrix, defined by Equation (2)
Q = matrix defined by Equation (5)
T = temperature
V = Liapunov function
η = normalized temperature

Subscripts and Superscripts

= total time derivative
T = transpose
i, j = indices

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