gravitational force is neglected and $J_m \simeq 0$ is taken

$$[p_{zL}]_R = \frac{J}{A} 1 + \frac{1}{2}\frac{d \ln k_1}{d \ln a} + \frac{k_1}{2}\sigma_1$$

where

$$k_1 = \left(\frac{J/A}{P_{RL}}\right)$$

Thus, if $[p_{Lz}]_R$ is a unique function of the velocity gradient $\left[\frac{dv_z}{dr}\right]_{r=R}$, that is, if it represents uniquely a material property, then one may conclude from Equations (20*a*) and (26) that $h = 0$. The reverse is also true. Also, the magnitude of the parameter h need not be known since P_{RL} is a measured quantity. Since in the tests of reference *6* P_{RL} was found to be much larger than J/A, it follows that $k_1 \simeq 0$ and $h \simeq 0$.

With regard to the assumption made in reference *6* that the fluid is completely relaxed at the point where $A = A_m$, if $F_m \neq 0$, then the magnitude of the material parameter σ_2 is simply larger than computed since P_{RL} is a measured quantity [see Equations (26) and (27) of reference *6*]. The accuracy with which the area ratio $\alpha = A_m/A$ is known in the tests of reference *6* is not important since the magnitude of the stress $[p_{zL}]_R$ relative to P_{RL} was determined as an upper limit; that is, for $J_m \rightarrow 0$ when α would be very large compared to unity.

NOTATION

A = cross-sectional area, sq. ft.
a = driving force per unit volume in the direction of flow, lb.-force/(sq. ft.)(ft.)
D = diameter, ft.
F = total tensile force, lb.-force
J = momentum flux, lb.-force
L = specified tube length, ft.
P = pressure measured by observer at tube wall, lb.-force/sq. ft.
p = stress component, lb.-force/sq. ft.
p'' = hydrostatic pressure, lb.-force/sq. ft.
R = radius, ft.
r = radial coordinate or radial distance from tube or jet axis, ft.
v_z = velocity component in z direction, ft./sec.
z = axial coordinate or axial distance, ft.
α = A_m/A, area ratio, dimensionless
ξ = dummy variable, appropriate units
σ_1 = material function, lb.-force/sq. ft.
σ_2 = material function, lb.-force/sq. ft.
τ = shear stress, lb.-force/sq. ft.

Subscripts

L = at tube exit
m = at position of maximum jet diameter
o = at tube or jet axis, or at origin of z coordinate
R = at tube wall
r = in the r direction, or at a radial distance, r
z = in the z direction, or at an axial distance, z

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Catalytic Effectiveness in Multicomponent and Variable Diffusivity Systems

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A method of evaluating catalytic effectiveness in systems of variable diffusivity is proposed. These systems are encountered when catalysts with bi-disperse pore-size distributions are employed or when multicomponent mixtures are involved. The diffusivity is taken to be a linear function of length, and an effectiveness factor is defined for this case. Application of the method is discussed and a numerical example is given.

The problem of diffusional retardation of reaction kinetics in catalytic systems originally studied by Thiele (*1*) has been extended by numerous workers. Some of the more important of these investigations have dealt with further study of isothermal and nonisothermal systems (*2, 3, 4, 5, 6*) and of the effects of catalyst geometry and pore-size distribution (*7, 8, 9, 10, 11*) on the combined diffusion-reaction process.

It has been shown in this prior work that the effectiveness of a catalyst in carrying out a reaction depends on the mechanism of diffusion which occurs, and that the structure of the catalyst is very important in determining this. In many supported catalysts of commercial importance one of the predominant characteristics of the structure is a dual or bi-disperse distribution of pore sizes within the solid. This distribution of pore sizes is often such that mass transport within the solid occurs by a combination of Knudsen and bulk diffusion which can be related to the distribution. A full discussion of this is given in a recent paper by Wakao and Smith (*9*).

A qualitative description of particle structure is suggested by the bi-disperse distribution of pore sizes in which the pore matrix is visualized as consisting predominantly of micropores branching off into individual particles of the catalytic solid (the agglomerate of which composes the pellet) from the macropore structure which exists between them. One expects the micropores to be of predominate importance in the diffusion-reaction process since the majority of the catalytically active surface exists within the micropore structure, but this is apparently not the case at all. The work of Smith et al. (*10*) on micropore effectiveness indicates that only when extremely fast reactions are carried out on catalysts pelleted from large individual particles does the micropore effectiveness factor differ from unity. The reason for this interesting result may be the fact that the diffusion lengths encountered in the micropore structure are very small.

The available evidence indicates that diffusion through the macropore structure is really what is important in most cases for determination of catalytic effectiveness. No restriction is made as to the type of diffusion which occurs within the macropores. The characteristic diameter of the macropores is dependent on the pelleting process and the resulting particle density, so diffusion in any range from bulk to Knudsen, or their combination, might occur. The term "macropore," thus, is used only with respect to micropore; its use does not presume that the controlling transport processes consist solely of a form of bulk diffusion.

DIFFUSION IN POROUS MEDIA UNDER NONREACTIVE CONDITIONS

Transport through solids occurs predominantly through the macropore structure. Since micropore effectiveness is normally unity, it would seem that a good estimate of the diffusivities involved in mass transport within porous solids may be obtained from relatively simple diffusion experiments in the absence of reaction.

The procedure suggested by Wicke and Kallenbach (*12*) has been used by a number of investigators to obtain data on the counterdiffusion of binary gas mixtures through porous solids. Interpretation of the results of such work is difficult because flux ratios for Knudsen and bulk diffusion are the same (*13*, *14*).

Scott and Dullien (*15*) and Rothfeld (*16*) have recently, however, presented essentially equivalent developments by which one may define an effective diffusion coefficient for the entire range from Knudsen to bulk diffusion for binary mixtures. The development is readily extended to the multicomponent case (*17*) in which

$$D_{im} = \frac{N_i - y_i \sum_{j=1}^{n} N_j}{\dfrac{N_i}{D_{Ki}} + \delta \sum_{\substack{j=1 \\ j \neq i}}^{n} \dfrac{y_j N_i - y_i N_j}{\mathfrak{D}_{ij}}} \tag{1}$$

The form of Equation (1) follows that of Rothfeld and is derived from consideration of combined diffusion in a cylindrical capillary. Theoretically, thus, Equation (1) does not describe the bi-disperse pore-size distribution but only the mixed mode of diffusion in a single pore. In an application of the equation to diffusion through a solid with bi-disperse pore-size distribution, however, the quantities D_{Ki} and δ may be treated as experimentally determined parameters and the expression used to describe the overall diffusion process.

The point important here is not to claim that Equation (1) affords the best representation of diffusion through porous media, but rather to note that this definition, as others which have been proposed involving mixed diffusion and bi-disperse distribution, is strongly concentration dependent. Treatment of the question of catalytic effectiveness when diffusivity is variable is the objective of the following development; mixed diffusion and multicomponent mixtures are considered since they are both involved in many reaction systems of interest.

DIFFUSION AND REACTION IN SYSTEMS OF VARIABLE DIFFUSIVITY

The reaction

$$aA + bB \rightarrow uU + vV$$

occurs irreversibly and under isothermal conditions within a porous catalytic solid. The flux relationships established by the reaction stoichiometry are

$$\begin{aligned} aN_u &= -\,uN_A \\ aN_v &= -\,vN_A \\ aN_B &= bN_A \end{aligned} \tag{2}$$

For the simple case of first-order kinetics

$$r = kc_A \tag{3}$$

and the equation of continuity may be written as

$$\nabla \cdot (D_{Am} \nabla c_A) = kc_A \tag{4}$$

This equation may be solved numerically, with D_{Am} evaluated at each point within the network and with the appropriate boundary conditions, as in the recent work of Smith and Wakao (*18*) on binary systems. Such methods are useful, but they are probably far more accurate than the data with which one must normally work, and the results cannot be expressed very conveniently in terms of catalytic effectiveness.

Bird and Hsu (*19*) have shown that the assumption of a linear variation of the diffusivity with either concentration or distance is a very effective technique to employ when variable diffusivities are involved. The method is not as accurate for defining concentration profiles as for determination of diffusional fluxes, but in the definition of catalytic effectiveness the profile will be used only to establish the flux at the point where the value of diffusivity is presumably most accurately known, the surface. The surface flux should then be given to a good degree of accuracy by this procedure.

The functional form of D_{Am} to be used with Equation (4) is accordingly defined as

$$D_{Am} \equiv \beta + \alpha\lambda \equiv D_{A\lambda} \tag{5}$$

in which D_{Am} at a given point, λ_1, may be computed by use of Equation (1) or any other effective diffusivity model which may be used. Effects of concentration dependence arising from both the bi-disperse distribution and the multicomponent system are thus included in α and β. Equation (4) is now

$$\nabla \cdot [(\beta + \alpha\lambda)\, \nabla c_A] = kc_A \tag{6}$$

and the usual boundary conditions may be employed:

$$c_A = c_{A\Lambda}; \quad \lambda = \Lambda \tag{7}$$

$$\frac{dc_A}{d\lambda} = 0; \quad \lambda = 0$$

When Equation (6) is expanded in rectangular coordinates

$$(\beta + \alpha\lambda)\frac{d^2c_A}{d\lambda^2} + \alpha\frac{dc_A}{d\lambda} - kc_A = 0 \tag{8}$$

which can be written as the following form of Bessel's equation

$$(D_{A\lambda})^2 \frac{d^2c_A}{d(D_{A\lambda})^2} + D_{A\lambda}\frac{dc_A}{d(D_{A\lambda})} - \frac{k}{\alpha^2}\, c_A\, D_{A\lambda} = 0 \tag{9}$$

The boundary conditions remain essentially as before:

(Continued on page 710)

INFORMATION RETRIEVAL*

Prediction of vapor-liquid equilibria with Benedict-Webb-Rubin equation of state, Lin, Min-Shuey, and Leonard M. Naphtali, **A.I.Ch.E. Journal, 9,** No. 5, p. 580 (September, 1963).

Key Words: Predicting-8, Estimating-8, Correlating-8, Vapor-Liquid-Equilibrium-9, Vaporization-9, Equation of State-10, Thermodynamics-10, NonLinear-Estimation-10, NonLinear-Regression-10, Least-Squares Method-10, Benedict-Webb-Rubin Equation of State-9, IBM-704 Computer-10, Vapor Pressure-9, Nitrogen-9, Methane-9, Carbon Dioxide-9, Propane-9, N-Butane-9.

Abstract: Application of the Benedict-Webb-Rubin equation to mixtures for prediction and correlation of vapor-liquid equilibria was reexamined with nonlinear estimation on a computer. It was necessary to improve the representation of pure component data by modifying the equation to improve the accuracy of prediction for mixtures. A modification of component interaction constants without altering the pure-component fit was ineffective. The modified equation gives satisfactory results with nitrogen-methane, methane-carbon dioxide, propane carbon dioxide, and n-butane carbon dioxide.

Problem of solidification with Newton's cooling at the surface, Hrycak, Peter, **A.I.Ch.E. Journal, 9,** No. 5, p. 585 (September, 1963).

Key Words: A. Semi-Infinite, Isotropic Slab-1, Cooling-6, Step Temperature Change-9, Surface Film Coefficients-8. B. Heat-Balance Integral-10, Depth of Solidification-7. C. Solution-2, Bounds-10, Neumann's Solution.

Abstract: Semi-infinite, isotropic slab initially at a constant temperature throughout is cooled by a step temperature change at the surface. Effect of finite surface film coefficients on depth of solidification is shown by the heat-balance integral method. Lower and upper bounds for the solution are given, showing that the approximate solution with finite film coefficients converges asymptotically to the exact Neumann's solution.

Heat and mass transfer in fixed and fluidized beds of large particles, Bradshaw, R. D., and J. E. Myers, **A.I.Ch.E. Journal, 9,** No. 5, p. 590 (September, 1963).

Key Words: Heat Transfer-8, Mass Transfer-8, Fluid Flow-8, Porous-, Spheres-9, Cylinders-9, Water-9, Beds-9, Fixed-, Fluidized-, Reynolds Number-6, j-factor-7, Correlations-10, Drying-8, Surface Temperature-7.

Abstract: Heat and mass transfer coefficients and friction factors were obtained for water evaporating into an air stream from fixed and fluidized beds of spheres and cylinders of diameters ranging from 0.160 to 0.335 in. Heat and mass transfer coefficients were independent of velocity for fluidized beds. Statistical analysis of the results indicated that correlations of the mass transfer factor vs. modified Reynolds number varied significantly for different sizes of particles; however, results for all runs for all particles in both fixed and fluidized beds had a standard deviation of only 22%.

The viscosity of dissociated and undissociated gases for temperatures up to 10,000°K., Mathur, G. P., and George Thodos, **A.I.Ch.E. Journal, 9,** No. 5, p. 596 (September, 1963).

Key Words: Viscosity-7, Dissociated Gases-5, Undissociated Gases-5, High Temperatures-6, Critical Constants-9, Viscosity Parameter-9, Quantum Effects-7, Force Constants-9, Generalized-8.

Abstract: A generalized method has been developed for the prediction of the viscosity of any substance in its molecular, atomic, or partially dissociated states for temperatures up to 10,000°K. A single curve was found to represent the dependence of the viscosity parameter $\mu^*\xi$ on reduced temperature for either the pure molecular or pure atomic species. Combining rules were developed which also enable the viscosity of a partially dissociated gas to be calculated from this curve.

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* For details on the use of these key words and the A.I.Ch.E. Information Retrieval Program, see **Chem. Eng. Progr.,** 57, No. 5, p. 55 (May, 1961), No. 6, p. 73 (June, 1961); **58,** No. 7, p. 9 (July, 1962).

NOTE: *Additional pages of information retrieval abstracts and key words in this issue are available on request.*

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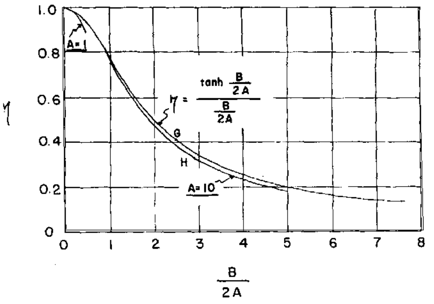

Fig. 1. Catalytic effectiveness in constant and variable diffusivity systems.

$$c_A = c_{A\Lambda};\quad D_{A\lambda} = D_{A\Lambda} = \beta + \alpha\Lambda \quad (10)$$

$$\frac{dc_A}{d(D_{A\lambda})} = 0;\quad D_{A\lambda} = \beta$$

The concentration distribution within the solid is given by the solution of Equations (9) and (10) as

$$c_A = F\,c_{A\Lambda}\,[F\,I_o(A) + K_o(A)]^{-1}\, I_o\left(\frac{2}{\alpha}\sqrt{k\,D_{A\lambda}}\right) + c_{A\Lambda}\,[F\,I_o(A) + K_o(A)]^{-1}\,K_o\left(\frac{2}{\alpha}\sqrt{k\,D_{A\lambda}}\right) \quad (11)$$

where

$$\mathrm{A} = \frac{2}{\alpha}\sqrt{k\,D_{A\Lambda}}$$

$$B = \frac{4\,k\,\Lambda}{\alpha} \quad (12)$$

$$F = \frac{K_1(\sqrt{A^2 - B})}{I_1(\sqrt{A^2 - B})}$$

The rate of transfer at the surface is

$$N_{A\Lambda} = -\frac{D_{A\Lambda}}{\Lambda}\left(\frac{dc_A}{d\lambda}\right)_{\lambda=\Lambda} \quad (13)$$

and the resulting effectiveness factor is

$$\eta = \frac{N_{A\Lambda}}{r_\Lambda} = \frac{2A}{B}\left[\frac{F\,I_1(A) - K_1(A)}{F\,I_o(A) + K_o(A)}\right] \quad (14)^*$$

This expression may be generalized with respect to geometry following the argument of Aris (7) if one defines Λ as the ratio of particle volume to surface. The parameter F implies that B cannot be larger than A^2 which corresponds to the plausible physical re-

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* This result assumes that α in $D_{Am} = \beta + \alpha\lambda$ is positive. If α is a negative number, that is if the form of the expression is

$$D_{Am} = \beta - \alpha\lambda$$

the result of Equation (14) may be applied if one defines

$$F = \frac{K_1(\sqrt{A^2 + B})}{I_1(\sqrt{A^2 + B})}$$

and $|\alpha|$ is used to compute A and B.

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INFORMATION RETRIEVAL

(Continued from page 710)

Filtration behavior of a mixture of two slurries, Shirato, Mompei, Masao Sambuichi, and Sakio Okamura, **A.I.Ch.E. Journal, 9,** No. 5, p. 599 (September, 1963).

Key Words: Filtration-8, Flow-8, Separation-8, Resistance-9, Efficiency-9, Physical Properties-9, Properties (Characteristics)-9, Porosity-9, Permeability-9, Void Fraction-9, Resistance-9, Mixtures-1, Slurries-1, Clays-1, Filtrate-2, Porous Media-5, Cakes-5, Physical Properties-6, Properties (Characteristics)-6, Porosity-6, Void Fraction-6, Pressure-7, Pressure Drop-7, Compression-Permeability Cell-10.

Abstract: For a study of the internal mechanism of flow through a compressible, porous cake, the liquid pressure in a filter bed is determined as a function of distance and time by using air-sealed manometers. The p_x distribution curves in combination with compression-permeability-cell data permit an indirect calculation of local, or point, values of the porosity ϵ_x. With many materials the filtration resistance α_F decreases substantially with increasing concentration of the solids in the prefilt. Failure to recognize this fact has contributed partially to the frequent lack of agreement of theory and experiment.

A method of analyzing and correlating the data is presented for the prediction of the filtration characteristics of a mixture of two clays the individual characteristics of which are known.

Numerical and experimental study of damped oscillating manometers: I. Newtonian fluids, Biery, John C., **A.I.Ch.E. Journal, 9,** No. 5, p. 606 (September, 1963).

Key Words: A. Manometers (Damped Oscillating)-9, Newtonian Fluids-9, Transient Behavior-8, Viscosity-6, Damping Factor-7, Frequencies-7. B. Simulation (Mathematical)-8 Numerical Integration-10, Equation of Motion-10, Velocity Profiles-7, Computer (Digital)-10, Digital Computer-10, Convergence-7. C. End Effects (Manometer)-8, Flow Reversal-8, Surface Tension-8. D. Fluids (Manometer)-9, Newtonian, Non-Newtonian, Sucrose-9, Glycerine-9, Water-9. E. Rheology-8, Viscosity-8, Newtonian Fluids-9, Non-Newtonian Fluids-9, Cone and Plate Viscometer-10.

Abstract: The time-dependent behavior of Newtonian oscillating manometers was studied experimentally and mathematically. The manometers were successfuly simulated by numerically integrating the axial component of the equation of motion in cylindrical coordinates. Modifications in the driving-force term were made to include end effects of surface tension and flow reversal. The integrations showed that the velocity profiles were not parabolic.

The dynamic behavior of a pulsed plate extraction column, Watjen, John W., and Robert M. Hubbard, **A.I.Ch.E. Journal, 9,** No. 5, p. 614 (September, 1963).

Key Words: Acetic Acid-1, Methyl Isobutyl Ketone-1, Pulse Rate-6, Extraction Dynamic Frequency-6, Stage Efficiency-7, Holdup-7, Eddy Diffusivity-7, Dynamic Response-7, Frequency Response-7, Extraction-8, Columns-10, Sieve Plates-10, Perforated Plates-10, Pulsed Column-10.

Abstract: The pulse method was used to determine the dynamics of liquid extraction for the methyl isobutyl ketone—acetic acid—water system in a ¾-in. perforated plate column. The results in the mixer-settler flow region of low column, pulse frequency were in good agreement with a linear model theory including a dead-time term.

The onset of different modes of instability for flow between rotating cylinders, Nissan, A. H., J. L. Nardacci, and C. Y. Ho, **A.I.Ch.E. Journal, 9,** No. 5, p. 620 (September, 1963).

Key Words: Hydrodynamic Instability-8, Taylor Vortices-8, Rotationally Symmetric- , Nonrotationally Symmetric- , Horizontal Concentric Cylinders-10, Vertical Concentric Cylinders-10, Critical Points-8, Stationary Outer Cylinder- , Both Cylinders Rotating- , Flow Patterns-8, Transition Region-

Abstract: The formation of nonrotationally symmetric Taylor vortices has been observed in a horizontal and vertical apparatus. With the outer cylinder stationary, the value of the second critical point averages about 20% higher than the first critical point.

For rotation in opposite directions, the rotation of the outer cylinder increases the tendency for the formation of nonrotationally symmetric vortices.

For rotation in the same direction, the rotation of the outer cylinder stabilizes the flow against the formation of nonrotationally symmetric vortices.

Between the first and second critical points, a transition region between steady square Taylor vortices and nonrotationally symmetric vortices was noticed.

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striction that $k\beta \geqq 0$. The form of the function defined by Equation (14) is compared with the normal Thiele function in Figure 1 by plotting vs. $\frac{B}{2A}$, which is identical to the modulus used by previous workers. It should be noted, however, that the difference in η between the two curves at a given value of $B/2A$ does not represent the effect of diffusivity variation on effectiveness. If one computes a value of η using the Thiele form (point G) and then uses this to estimate the values of A and B, the resulting η from Equation (14) will be displaced to a higher value of the abscissa (for example, at point H). Details of this are pointed out in the illustration.

For purposes of estimation, η from Equation (14) is more conveniently presented in Figure 2, with B as the abscissa. The lower envelope of these curves is defined by

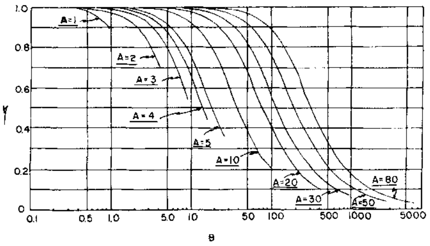

Fig. 2. Effectiveness factor for multicomponent and variable diffusivity systems.

$$\eta = \frac{2A}{B}\left[\frac{I_1(A)}{I_0(A)}\right]; \quad A^2 = B \quad (15)$$

since $F = \infty$ at this point. For D_{AA} and k which lead to conditions of reduced catalytic effectiveness, a very small value of α, which indicates small variation in the diffusivity, leads to large values of A and B, and the numerical result of Equation (14) approaches the Thiele value.

The possible effects of volume change on reaction are not included in the foregoing analysis. In ordinary bulk diffusion it is possible for convective transport to be established owing to total pressure variation and superimposed on the diffusion occurring. One can estimate beforehand whether or not this is of importance; for example, in the representation of Equation (1), the value of $(1/D_{Ki})$ as determined experimentally will be nearly zero when

(Continued on page 714)

INFORMATION RETRIEVAL

(*Continued from page 712*)

Experimental study of laminar flow heat transfer with prescribed wall heat flux, Akins, R. G., and J. S. Dranoff, **A.I.Ch.E. Journal, 9,** No. 5, p. 624 (September, 1963).

Key Words: Heat Transfer-8, Laminar Flow-8, Experimental-8, Water-5, Cylindrical Duct-10, Prescribed Flux-6, Electrical Heating-10, Wall Temperature-7, Vertical-10, Theoretical Predictions-9.

Abstract: Heat transfer to water in laminar flow through a vertical cylindrical tube was studied experimentally. Water was heated by an electrical resistance coil which provided a heat flux that varied with axial distance along the tube. Temperatures at the water-tube wall interface were measured to within 0.1°C. and compared with theoretically predicted wall temperatures. Good agreement was found between measured and predicted values, and thus validity of the theoretical analysis was indicated.

Interphase mass transfer for laminar concurrent flow of carbon dioxide and water between parallel plates, Tang, Y. P., and D. M. Himmelblau, **A.I.Ch.E. Journal, 9,** No. 5, p. 630 (September, 1963).

Key Words: Interphase Mass Transfer-8, Carbon Dioxide-1, Water-1, Gas-5, Laminar Flow-8, Transport Phenomena-9, Models-10, Boundary Layer-10, Penetration Theory-10, Diffusivity-8, Temperature-6.

Abstract: Interphase mass transfer has been studied between carbon dioxide and water in concurrent flow in a laminar rectangular channel. Three methods of solving the transport equations—the eigensolution method, the boundary layer theory, and the penetration theory—were used to compute the liquid-phase diffusion coefficients, which agreed within 5% of the literature values in the range of 20° to 30°C.

Mixing rates in stirred tanks, Biggs, R. D., **A.I.Ch.E. Journal 9,** No. 5, p. 636 (September, 1963).

Key Words: Agitation-8, Mixing-8, Rates-8, Time-8, Stirred Tanks-9, Tanks-9, Baffles-10, Impellers-10, Propellers-10, Turbines-10, Diameter-6, Impellers-6, Speed-6, Viscosity-6, Mixing-7, Time-7.

Abstract: Mixing rates in an agitated, baffled tank system are reported for a propeller and three types of turbine agitators. The mixing rate is related to the time required for the tank contents to approach a uniform concentration after a small quantity of tracer is introduced. Mixing times, called ***terminal mixing times,*** were measured and correlated as a function of impeller type, impeller diameter, impeller speed, and liquid kinematic viscosity. These data are compared with other terminal mixing time data reported in the literature. The mixing rate process is characterized further by two additional mixing times and the ratio of the maximum tracer concentration to the well-mixed tracer concentration. The significance of these quantities is shown by their relationship to the parameters of a stirred-tank model previously described in the literature.

Formation of moderate size bubbles, Mahoney, John F., Jr., and Leonard A. Wenzel, **A.I.Ch.E. Journal, 9,** No. 5, p. 641 (September, 1963).

Key Words: Bubbles-7, Flow-9, Air-5, Water-5, Orifice-9, Chambers-6, Frequency-7, Submergence-6, Forming-7, Wettability-6, Bubbling-8, Analogue-9, Weeping-7, Photography-9, Surface Tension-6, Photo Tubes-9, Depth-6.

Abstract: Bubble formation from a single submerged orifice was studied with the air-water system. Factors influencing the bubble frequency were gas flow rate, volume of gas chambers both above and below the orifice, orifice dimensions, and plate wettability. With fixed-system geometry bubble-formation time did not depend upon gas flow rate. A system model is developed, and from it two equations are written. One predicts the mathematical form of the frequency curve; the other indicates those system geometries which result in the same frequency curve.

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bulk diffusion predominates. From the experimental data which have been reported (*9, 16*), it appears that this is not the case except for very large macropores or high pressures; Knudsen diffusion is important in most commercial catalysts of moderately high densities and the effect of volume change on reaction will not be large unless there is a large difference between moles of reactants and products. Experimentation on this point would be most useful in determining such limits quantitatively.

For values of A and B not given in the representative range of Figure 2, η can be computed with Equation (14). A table of Bessel functions for large arguments (*20*) may be required for this purpose.

DIFFUSION AND REACTION—SECOND ORDER KINETICS

Under isothermal conditions the linearization of rate equations through use of Taylor series expansion is convenient. The validity of this procedure depends on the system under consideration, but the linear approximation is certainly less restrictive than the first-order case.

For the simple second-order case in which the rate expression is written as

$$r = k' c_A{}^2 \tag{16}$$

the series expansion of the rate about concentration $c_{A\Lambda}$ is

$$\Omega = Mc_A - N \tag{17}$$

where

$$M = \left(\frac{\partial r}{\partial c_A} \right)_{ci,T}$$

evaluated at $c_{A\Lambda}$.
Thus

$$\begin{aligned} M &= 2\,k' c_{A\Lambda} \\ N &= k' c^2{}_{A\Lambda} \end{aligned} \tag{18}$$

The form of Equation (10) may be recovered with Ω as the dependent variable and with the resulting effectiveness factor again defined as in (14) with the parameters A and B modified to

$$A = \frac{2}{\alpha} \sqrt{M\,D_{A\Lambda}} \tag{12a}$$

$$B = \frac{4\,M\,\Lambda}{\alpha}$$

For the more complex second-order reaction in which the rate equation is

$$r = k'' c_A c_B \tag{19}$$

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series expansion results in terms containing both c_A and c_B. Convenient analytical solution is not possible without restrictive assumptions, but there is one case of importance in which a solution is available. In this case, though the individual diffusivities such as D_{Am} may vary throughout the reaction zone, the ratios of these quantities will be much more insensitive to variation. Then a relationship between c_A and c_B is

$$\frac{dc_B}{dc_A} = \frac{D_{A\lambda}}{D_{B\lambda}}\left(\frac{b}{a}\right) \tag{20}$$

with the boundary condition

$$c_B = c_{B\Lambda} \text{ at } c_A = c_{A\Lambda} \tag{21}$$

The resulting linearized rate expression is

$$\Omega' = M' c_A - N' \tag{22}$$

and

$$M' = \frac{k''b}{a}\left(\frac{D_{A\lambda}}{D_{B\lambda}}\right) c_{A\Lambda} + k'' c_{B\Lambda}$$

$$N' = \frac{k''b}{a}\left(\frac{D_{A\lambda}}{D_{B\lambda}}\right) c^2{}_{A\Lambda} \tag{23}$$

Equations (12*a*) and (14) may be applied with M' used in determination of A and B. The requirement of constant diffusivity ratio applies best to systems in which Knudsen diffusion predominates.

APPLICATION OF THE METHOD

The variation in diffusivity which affects the diffusion-reaction process is determined, for a given catalyst, by the composition variations of the individual reactants and products through the porous matrix. In order to evaluate the quantities α and β of Equation (5) it is necessary to estimate internal compositions of all components at a given point within the pellet. An iteration procedure is required in which an initial approximation is refined until the solution has converged (as indicated by a constant value of η, or of A and B, on successive iterations). The procedure suggested may be applied easily to machine computation techniques, but the calculations are simple and convergence rapid so that it is doubtful that these methods are necessary.

The most direct way to begin is by estimation of compositions using the constant diffusivity development. For first-order reaction, thus

$$c_{A\lambda_1} = (c_{A\Lambda})\,\frac{\cosh\left(\sqrt{\dfrac{k}{D_{A\Lambda}}}\,\lambda_1\right)}{\cosh\left(\sqrt{\dfrac{k}{D_{A\Lambda}}}\,\Lambda\right)} \tag{24}$$

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INFORMATION RETRIEVAL

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Large-scale turbulence characteristics of a submerged water jet, Rosler, R. S., and S. G. Bankoff, **A.I.Ch.E. Journal, 9,** No. 5, p. 672 (September, 1963).

Key Words: Mean Velocity Profiles-7, Integral Scales-7, Water Jet-8, Large-Scale Characteristics-8, Turbulence-9, Hot-Film Anemometer-10, Free Surface-10.

Abstract: Measurements of mean velocity profiles, macroscales, and intensities of turbulence in a water jet emerging at the bottom of an open tank were made with a constant-temperature, hot-film anemometer and compared with air data in the same geometry (except for the absence of the free surface) and Reynolds number, as well as with previous air data. The effect of the free surface on the mean and root-mean-square velocities was small. Reynolds stress measurements agreed well with the predictions of a momentum integral balance. A form factor was derived to take into account mean profile and turbulent intensity at the jet exit. The similarity constant, C, calculated from the axial mean velocity distribution and from the radial mean velocity profiles, has averaged values of 6.49 and 6.83 for air and for water, respectively. The integral scale in water was considerably smaller than air, and thus increased intermittency due to the presence of the free surface is reflected.

Pulsation in a fixed-bed reactor, Biskis, E. G., and J. M. Smith, **A.I.Ch.E. Journal, 9,** No. 5, p. 677 (September, 1963).

Key Words: Styrene-1, α-MethylStyrene-1, Hydrogen-1, Cumene-2, Palladium-4, Pulsed Flow-4, Alumina-5, Liquid Phase-5 Pulsation-6, Diffusion-6, Reaction Rate-6, Amplitude-6, Frequency-6, Hydrogenation-8, Reactor-10, Fixed Bed- .

Abstract: Rates of reaction were measured for the liquid-phase hydrogenation of α-methylstyrene in a pulsed, fixed-bed reactor. Data obtained at 80 lb./sq.in.abs. and 55°C. with a catalyst of 0.5 wt. % palladium on ⅛-in. alumina spheres indicated that the mass transfer of dissolved hydrogen to the catalyst surface controlled the rate of conversion of styrene to cumene. Hence the data were employed to calculate mass transfer coefficients as a function of pulse frequency and amplitude.

Comparison with nonpulse data at the same Reynolds number showed that pulsation increased the mass transfer rate as much as 80%.

Numerical solution of convective transport problems, Stone, Herbert L., and P. L. T. Brian, **A.I.Ch.E. Journal, 9,** No. 5, p. 681 (September, 1963).

Key Words: Differential Equations-1, 8, Convective Transport-1, 8, Difference Methods-2, 6, Errors of Approximation-7, Mathematical Analysis-10, Computers-10, Linear Equations- , First Order- , Second Order- .

Abstract: The accuracy of finite-difference approximations to linear differential equations which characterize certain convective transport phenomena is analyzed. The method leads to improved difference approximations judged by criteria developed in the paper or by the quality of numerical solutions of a linear differential problem. Similar improvement should also be obtained for nonlinear problems; this hypothesis will be tested and the results reported in a later paper.

Microstructure of a low-pressure hydrogen-bromine flame, Frazier, George C., Jr., Robert M. Fristrom and J. Francis Wehner, **A.I.Ch.E. Journal, 9,** No. 5, p. 689 (September, 1963).

Key Words: Hydrogen-1, Bromine-1, Flame-8, Structure-9, Kinetics-9, Diffusion-9, Transport-9, Temperature-9, Composition-9, Experimental-10, Hydrogen Bromide-2, Atoms-2, Thermal-10.

Abstract: The structure of a low-pressure hydrogen-bromine flame was determined by thermocouple traversing and chemical analyses of samples withdrawn from the flame zone by fine quartz probes. The flame studied had an initial composition of 44.2 mole % bromine at 8.87 ± 0.02 cm mercury total pressure. The bromine atom profile was estimated with the steady state hypothesis of classical low temperature kinetics. The temperature profile and the composition profiles were used to derive a heat-release profile that was used to obtain a better estimate of the bromine atom concentration. The influence of diffusion and thermal diffusion is discussed.

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lustrative to recount the methods of synthesis mentioned in chapter titles. They are transfer and addition, chemical, radical and radiation, mechanico-chemical, condensation, and ionic. To the chemical engineer in industry it may be disappointing to note that the most extensive coverage, 32 pages, is devoted to mechanico-chemical syntheses, and only four pages are devoted to ionic syntheses. Only the most cursory recognition is given to the existence of stereo block polymers. An additional chapter entitled "Industrial Synthesis" actually consists of a tabulation of patents assigned to various industrial firms and gives no clue as to whether any of these have in fact been reduced to industrial practice.

From all points of view the chapter covering characterization of block copolymers is one of the most interesting and important in the book. The difficulties inherent in characterization are well illustrated by the fact that of the 1,200 polymer syntheses described in the book less than five per cent of the polymers have been isolated with any degree of purity and less than twenty completely characterized. The author perceptively states, "There is not, therefore, a universal procedure for isolating sequence copolymers from their associated homopolymers and each system has, in general, to be attacked in a different manner." But, he then assumes a severe and unnecessary limitation by restricting his coverage of characterization to techniques suitable for preparing sufficient material for subsequent physical or chemical analysis. While extensive treatment is given to several precipitation and elution techniques, no mention is made of the potential of double gradient chromatographic procedures. This is unfortunate, but it is no more so than the omission of various techniques which appear to offer promise of characterization without fractionation such as nuclear magnetic resonance, differential thermal analysis, and various other procedures for the elucidation of solid phase structure.

The final chapter which treats properties is brief and general but provides a valuable point of departure for the engineer interested in applications.

It is to be expected that this book will prove helpful to those seeking entree to the study of block and graft copolymers and a useful source book outside the specialty of those already at work in the field.

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It may be shown for the other components in the reaction mixture that according to Equation (24)

$$c_{i\lambda_1} = c_{i\Lambda} + c_{A\Lambda}\left(\frac{w_i}{a}\right) \frac{1}{\cosh\left(\sqrt{\frac{k}{D_{A\Lambda}}}\,\Lambda\right)} \left[\cosh\left(\sqrt{\frac{k}{D_{A\Lambda}}}\,\lambda_1\right) - \cosh\left(\sqrt{\frac{k}{D_{A\Lambda}}}\,\Lambda\right)\right] \tag{25}$$

The compositions and mole fractions at point λ_1, computed from (24) and (25), are used to determine a value of $D_{A\lambda_1}$; α and β corresponding are computed from (5), and F, A, and B are determined from (12). Center line values ($\lambda_1 = 0$) may be used for this procedure, although it is preferable in later application not to use them.

The concentration distribution of all components may now be estimated using the values of F, A, and B in Equation (11) (for component A) and in the following expression, similar to (25), for the other components:

$$c_{i\lambda_1} = c_{i\Lambda} + \left(\frac{w_i}{a}\right) \left[\frac{c_{A\Lambda}}{FI_o(A) + k_o(A)}\right] \int_{\Lambda}^{\lambda_1} \left(\frac{D_{A\lambda}}{D_{i\lambda}}\right) \{F(g_\lambda)[I_1(h_\lambda)] - (g_\lambda)[K_1(h_\lambda)]\}\,d\lambda \tag{26}$$

where

$$g_\lambda = \sqrt{\frac{k}{D_{A\lambda}}}$$

$$h_\lambda = \frac{2}{\alpha}\sqrt{k\,D_{A\lambda}}$$

The values of c_A, c_B, c_i determined from (11) and (25) at the point λ_1, are used to recompute $D_{A\lambda_1}$. All the parameters corresponding are determined, and the procedure is repeated until successive computations agree. Point λ_1 should be located close to the surface since it is the concentration gradient at that point which determines the catalytic effectiveness.

NUMERICAL EXAMPLE

The dehydration of ethanol to ethylene and water on pelleted alumina at 200°C. will be used to illustrate the method of computation.

The following conditions are typical:

Pressure = 1 atm.
Total concentration of gas phase

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$= 1.21 \times 10^{-3}$ lb. mole/cu.ft.
$k = 0.224$ sec.$^{-1}$ [computed from (*21*)]
Mole fractions in vapor phase:
y_A (alcohol) $= 0.60$;
y_u (ethylene) $= 0.20$;
y_v (water) $= 0.20$

The alumina catalyst used is commercially available and of moderately high density such as that reported by Rothfeld (*16*). Equation (1) is used in computing effective diffusivities for this illustration. The following data on catalyst and diffusivities are available:

D_{KA} (alcohol) $= 2.60 \times 10^{-2}$ sq. cm./sec. [computed from (*16*)]
D_{Ku} (ethylene) $= 3.33 \times 10^{-2}$ sq. cm./sec. [computed from (*16*)]
D_{Kv} (water) $= 4.15 \times 10^{-2}$ sq. cm./sec. [computed from (*16*)]
$\mathfrak{D}_{Au}$ (alcohol–ethylene) $= 0.210$ sq.cm./sec. [computed from (*22*)]
$\mathfrak{D}_{Av}$ (alcohol–water) $= 0.298$ sq. cm./sec. [computed from (*22*)]
$\mathfrak{D}_{uv}$ (ethylene–water) $= 0.478$ sq. cm./sec. [computed from (*22*)]
$\Lambda = 0.318$ cm.
$\delta = 15.9$ [from (*16*)]

Effective diffusivities at the surface are

$D_{A\Lambda}$ (alcohol) $= 0.0113$ sq.cm./sec.
$D_{u\Lambda}$ (ethylene) $= 0.0088$ sq.cm./sec.
$D_{v\Lambda}$ (water) $= 0.0120$ sq.cm./sec.

Estimation at the point $\lambda_1 = 0.308$ (0.01 cm. from the surface), by Equations (24) and (25) of the composition at that point gives

y_A (alcohol) $= 0.52$
y_u (ethylene) $= 0.25$
y_v (water) $= 0.23$
$D_{A\lambda_1}$ (alcohol) $= 0.0111$ sq.cm./sec.
$D_{u\lambda_1}$ (ethylene) $= 0.0092$ sq.cm./sec.
$D_{v\lambda_1}$ (water) $= 0.0110$ sq.cm./sec.
Total concentration $= 1.33 \times 10^{-3}$ lb. mole/cu.ft.
η (constant diffusivity) $= 0.63$

The parameters of the variable diffusivity analysis, computed from these results are

$$\alpha = 1.8 \times 10^{-2} \text{ cm./sec.} \qquad A = 5.6$$
$$\beta = 5.55 \times 10^{-3} \text{ sq.cm./sec.} \qquad B = 15.9$$
$$\eta = 0.55$$

These quantities are used to recompute, at $\lambda_1 = 0.308$, the composition by means of Equations (11) and (26). The results of this are

y_A (alcohol) $= 0.56$
y_u (ethylene) $= 0.23$
y_v (water) $= 0.22$,
$D_{A\lambda_1}$ (alcohol) $= 0.01115$ sq.cm./sec.
Total concentration $= 1.23 \times 10^{-3}$ lb. mole/cu.ft.

Parameters evaluated from this estimate are

$$\alpha = 1.3 \times 10^{-2} \text{ cm./sec.} \qquad A = 7.8$$
$$\beta = 7.14 \times 10^{-3} \text{ cm./sec.} \qquad B = 21.9$$
$$\eta = 0.58$$

Further computation again results in $\eta = 0.58$, compared with the constant diffusivity value of 0.63.

It is worthwhile noting that estimation of A and B using Equations (24) and (25) results in a value of η which may be used as a rough (and conservative) indication of the actual effectiveness. The diffusivity variation does not have a very large effect here (about 10%), since changes in composition affect the numerator and denominator of Equation (1) to almost the same extent in this case. The magnitude of maximum effects one might encounter is difficult to specify quantitatively, since they depend very much on the reaction system, and many factors are involved. Differences in η of $> 50\%$ are not unreasonable to expect; equimolal reactions under conditions such that the $\mathfrak{D}_{ij}$ are small would probably be most affected.

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The assistance of Mr. Peter Rasmussen in computer calculation of Figure 2 is gratefully acknowledged.

NOTATION

A, B, U, V = reactants and products
A, B, F = parameters of Equation (12)
a, b, u, v = stoichiometric coefficients
c_i = concentration of component i (Ml^{-3})
D_{Ki} = coefficient for Knudsen diffusion of i in porous material $(l^2 \theta^{-1})$
D_{im} = effective diffusivity of i in multicomponent mixture $(l^2\theta^{-1})$
$D_{i\lambda_1}$ = effective diffusivity of i in multicomponent mixture at point λ_1, $(l^2\theta^{-1})$
$\mathfrak{D}_{ij}$ = bulk diffusion coefficient for binary mixture of i and j $(l^2 \theta^{-1})$
g_λ = parameter of Equation (26) (l^{-1})
h_λ = parameter of Equation (26)
k = first-order rate constant (θ^{-1})
k' = second-order rate constant in $r = k' c_i^2$ $(l^3\theta^{-1}M^{-1})$
k'' = second-order rate constant in $r = k'' c_i c_j$ $(l^3\theta^{-1}M^{-1})$
M, M' = parameters of Equations (18) and (23)
N, N' = parameters of Equations (18) and (23)
N_i = flux of component i $(Ml^{-2}\theta^{-1})$
$N_{A\Lambda}$ = flux of component A at Λ $(Ml^{-3}\theta^{-1})$

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INFORMATION RETRIEVAL

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The effect of artificial surface roughness on heat and momentum transfer, Savage, D. W. and J. E. Myers, **A.I.Ch.E. Journal, 9,** No. 4, p. 694 (July, 1963).

Key Words: Fluid Flow-8, Heat Transfer-8, Water-5, Circular Duct-5, Transverse Internal Fins-5, Fin Height-6, Fin Spacing-6, Reynolds Number-6, Prandtl Number-6, Form Drag-7, Skin Friction-7, Friction Coefficients-7, Heat Transfer Coefficients-7.

Abstract: The effect of surface protuberances on heat transfer and drag forces was studied for water flowing through a pipe having transverse fins on the inside wall. The ratio of fin height to tube diameter e/D ranged from 0.041 to 0.165 and the relative spacing e/L from 0 to 1.5. The Prandtl number was varied from 2.8 to 8.0. Net skin friction was small for large fin spacings but represented the total resistance to flow for spacings of approximately e/L = 1. Skin friction coefficients were independent of fin height, but strongly dependent on spacing. The average heat transfer coefficient around a single heated fin was only slightly dependent on fin height and spacing.

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n = number of components
r = rate of reaction ($Ml^{-3}\theta^{-1}$)
w_i = stoichiometric coefficient of i, positive for reactants and negative for products
y_i = mole fraction of component i

Greek Letters

α = parameter of Equation (5) ($l\theta^{-1}$)
β = parameter of Equation (5) ($l^2\theta^{-1}$)
δ = bulk diffusion parameter of Equation (1)
η = effectiveness factor
λ = distance from center of catalyst particle (l)
Λ = distance from center to surface of particle, computed as ratio of volume to surface (l)
Ω, Ω' = linearized rate, Equations (17) and (22) ($Ml^{-3}\theta^{-1}$)

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