COMMUNICATIONS TO THE EDITOR

Intraparticle Pressure Gradients in Porous Catalysts

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The effectiveness of the intrapellet surface in porous catalysts has been shown (*4*) to depend only upon pore-diffusion and surface-reaction resistances for reactions with no change in number of moles. For the general gaseous reaction an additional factor may be significant—the change in total pressure with position within the pellet. For example, for an increase in number of moles, the steady state pressure will increase from the outer surface of a spherical pellet toward the center. Previous studies on reaction rates in pores have been limited to cases for which there is no change in number of moles, regardless of the order of the rate equation used for the reaction. However, the existence of pressure gradients was noted by Hoogschagen (*3*) and Wheeler (*6*), and the influence of a pressure gradient upon diffusion, without reaction, has been studied by Evans and co-workers (*2*) and by Wicke and Hugo (*7*).

The purpose of this paper is to consider the effect of a change in number of moles on the pressure within the pore for a simple case, an irreversible first-order reaction, at isothermal and steady state conditions.
The reaction may be written

$$A \rightarrow nB \qquad (1)$$

where the rate per unit of pore surface is

$$r_A = k_S C_A \qquad (2)$$

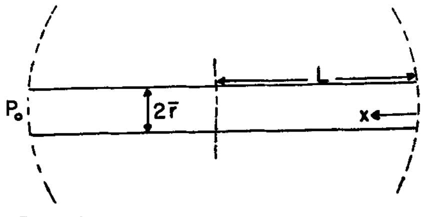

Fig 1. Single-pore model of catalyst pellet.

Equations are presented for the general case in which diffusion occurs by both Knudsen and bulk processes, and hence the diffusion rates are functions of pressure and composition within the pellet. The magnitude of the pressure gradient and its influence on the effectiveness factor can be determined simply when the diffusion is solely of

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Generalized Peak Heat Flux for Dilute Binary Mixtures

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Boiling of binary mixtures is of particular importance in the chemical process industries. It is also of interest for possible applications to boiling nuclear reactors, where a second component might be added to the primary fluid for metallurgical purposes, and in aerospace engineering for cooling of space probe components during reentry. In these applications it is often only knowledge of the peak heat flux in nucleate boiling q_p'', that is desired by the designer since errors of 50° to 100°F. can be accepted in prediction of the surface temperature.

Experiments by van Wijk, Vos, and von Stralen with small diameter wires yielded peak heat fluxes in excess of that found for either pure component, making the use of binary mixtures seem even more attractive (*1*). The work of Bonilla and Perry (*2*) with a flat heating surface showed comparable results, but the increase was not as striking as in the extreme case noted by van Wijk et al. To date no generalized treatment has been proposed which would adequately predict the variation of q_p'' with respect to mixture composition; the engineer may only use single component correlations evaluated with average properties. In the present paper the author considers a physical analogy between the boiling of binary mixtures and subcooled single component boiling. A correlation is obtained for the significant case of the peak heat flux for dilute binary mixtures.

First, visualize the process physically. For a large volume the liquid depth and transverse dimensions may be considered infinite. As the liquid vaporizes, the mixture in the vicinity of a bubble tends toward being denuded of the component with the lower boiling point. The turbulent mixing action of the bubbles and the effects of mass diffusion act to alleviate this situation; but it is expected that, on a time-averaged basis, a concentration gradient will be produced perpendicular to the surface. This gradient determines the saturation temperature gradient in the liquid, which, in turn, approximates the liquid temperature variation except in close proximity to the heated surface, where it is slightly superheated. For a mixture which is dilute in *B*, the volatile component, it is expected that only component *A* will be present at the heater surface, except at very low heat fluxes. As a bubble rises, with vapor temperature corresponding to the bubble composition, it transfers heat to the cooler surrounding liquid, condensing vapor, until thermal equilibrium is approached. In addition, the concentration difference between vapor and liquid at any height above the heater induces some degree of mass transfer. A steady state is set

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The adsorption of nitrogen-methane on molecular sieves, Lederman, Peter B., and Brymer Williams, **A.I.Ch.E. Journal, 10,** No. 1, p. 30 (January, 1964).

Key Words: A. Adsorption-8, Separation-8, Cryogenics-5, High Pressure-6, Isothermal-2. B. Gases-1, Mixtures-1, Methane-1, Nitrogen-1, Helium-1, Mixtures-1, Molecular Sieve-1,

Abstract: Adsorption isotherms for the system methane-nitrogen molecular sieves were made for temperatures between 123° and 295°K. and pressures up to 85 atm. Constants for the Langmuir equation were obtained for the pure components. For the mixtures, constants for a modified Langmuir equation are presented. The results indicate that for this system selectivity is based only on adsorptivity of the components. Adsorption increases with decreasing temperature and approaches a maximum of about 5 mg. moles of nitrogen or methane at 123° and 175° respectively. This is equivalent to approximately 95% monolayer coverage.

Transient absorption at small contact times: moving-band absorber, Govidan, T. S., and J. A. Quinn, **A.I.Ch.E. Journal, 10,** No. 1, p. 35 (January, 1964).

Key Words: Absorption-8, Mass Transfer-8, Carbon Dioxide-9, Water-5, Penetration Theory-8, Interfacial Resistance-8, Diffusion-6, Liquid Films-10, Rotating Band-10, Contact Time-8.

Abstract: A new technique has been developed for measuring the rate of absorption of a gas into a liquid. The technique involves the formation of a liquid film on a thin metal ribbon, running as an endless belt. The absorption of carbon dioxide into water in the range of contact times 0.8 to 50 msec. was investigated with 1, 3, and 10 cm. nominal contact lengths and film thicknesses of 10 to 50 μ. The experimental results, which are slightly lower than those predicted from penetration theory, indicate that any resistance at the carbon dioxide-water interface is negligibly small.

Frictional pressure drop in two-phase flow: A. a comparison of existing correlations for pressure loss and holdup, Dukler, A. E., Moye Wicks III, and R. G. Cleveland, **A.I.Ch.E. Journal, 10,** No. 1, p. 38 (January, 1964).

Key Words: Horizontal Two-Phase Pressure Drop Data-1, Holdup Correlations-1, Mean Deviation-2, Standard Deviation-2, Statistics-5, Regression Analysis-5, Data Bank-5, Liquid and Gas Rates of Flow-6, Liquid Viscosity-6, Pipe Size-6, Pressure Drop-7, Holdup-7,Testing-8, Correlations of Pressure Drop and Holdup-9, IBM 650 Computer-10.

Abstract: An experimental data evaluation procedure has been devised, and an expandable data bank has been developed. With carefully evaluated data from this bank validity tests are made of five well-known pressure drop correlations and three holdup correlations. Correlations are statistically compared with the data. Based on the results of over three thousand observations covering a wide range of experimental conditions, the pressure drop correlation of Lockhart and Martinelli and the holdup correlation developed by Hughmark, are the best of those tested.

Frictional pressure drop in two-phase flow: B. an approach via similarity analysis, Dukler, A. E., Moye Wicks, III, and R. G. Cleveland, **A.I.Ch.E. Journal, 10,** No. 1, p. 44 (January, 1964)).

Key Words: Two-Phase Flow-8, Frictional Pressure Drop-7, Acceleration Pressure Drop-7, Friction Factor-7, Reynolds Number-6, Model Theory-10, Similarity Principle-10, Euler Number-7, Correlation-9, Liquid and Gas Rates-6, Fluid Properties-6, Conduit Diameter-6, Comparison with Data-8.

Abstract: Model theory and similarity analyses are used to develop the variable groupings by which two-phase frictional pressure drop can be correlated. Expressions are developed for the Reynolds numbers and Euler number (twice the friction factor) for two-phase flow in which the correct mixture properties and the velocity are shown to be defined by the conditions of similarity which are imposed.

The proposed correlations are compared on a statistical basis with test data over a wide range of flow conditions, fluid properties, and line sizes, and are shown to give better agreement than other existing correlations.

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the Knudsen type. For other cases numerical solution of the equations is necessary.

DIFFUSION AND FLOW EQUATIONS

Suppose the reaction occurs in a straight cylindrical pore of radius $\bar{r}$ and length $2L$ as shown in Figure 1. The total mass flux N [moles/(sec.)(sq.cm.)] will include a diffusion contribution and a flow contribution due to the total pressure gradient. An overall mass balance on an element of pore length gives

$$\frac{dN}{dx} = \frac{2}{\bar{r}}(-r_A + r_B) = \frac{2}{\bar{r}}(n-1)k_s C_A \qquad (3)$$

where Equation (2) has been employed to express the rate of disappearance of A.

Before a mass balance for component A is written, it is desirable to formulate the rate of diffusion under the influence of a pressure gradient. Evans, Watson, and Mason (*2*) have considered this problem in terms of their dusty-gas model (*1*). It is convenient to express their result in terms of an effective diffusivity, D_e, according to the equations

$$N_A = -D_e \frac{dC_A}{dx} \qquad (4)$$

where

$$D_e = \frac{1}{\dfrac{1 - wy_A}{D_{AB}} + \dfrac{1}{D_k}} \qquad (5)$$

$$w = \frac{N}{N_A} = 1 + \frac{N_B}{N_A} \qquad (6)$$

These equations are the same in form as those for constant total pressure as given by Wakao and Smith (*5*). However, when the total pressure is not constant D_e is a function of x, because y_A varies with x and the bulk diffusivity, D_{AB}, depends upon the pressure.

A mass balance of reactant A on an element of pore length gives

$$\frac{d}{dx}(N_A) + \frac{2k_s C_A}{\bar{r}} = 0 \qquad (7)$$

This may be expressed in terms of C_A by employing Equation (4) for the flux of A:

$$\frac{d}{dx}\left(D_e \frac{dC_A}{dx}\right) - \frac{2k_s C_A}{\bar{r}} = 0 \qquad (8)$$

Equations (5) and (8) determine the relationship between C_A and x along the pore length. If bulk diffusion is important the integration of Equation (8) is difficult because D_e is a func-

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tion of pressure and composition. The flux-ratio function w is a constant, as seen when Equations (3) and (7) are divided:

$$\frac{dN}{dx} \bigg/ \frac{dN_A}{dx} = \frac{dN}{dN_A} = 1 - n$$

When they are integrated one obtains

$$\frac{N}{N_A} = w = 1 - n \qquad (9)$$

or

$$\frac{N_B}{N_A} = -n \qquad (10)$$

This result is a consequence of the stoichiometry of the reaction. Equation (9) permits the effective diffusivity to be expressed in a somewhat simpler way:

$$D_e = \frac{1}{\dfrac{1-(1-n)y_A}{D_{AB}} + \dfrac{1}{D_k}} \qquad (11)$$

To complete the description of the problem an expression is needed which relates the flux N to the pressure gradient and the properties of the porous solid and reaction gases. An exact equation in terms of measureable physical properties has not been obtained but there are available useful expressions which contain one or more constants. For example, Evans and colleagues (2) presented two relationships: one the result of momentum balance and the other from the dusty-gas model. Both give the flux as the sum of a flow at constant pressure and a contribution due to the pressure gradient. The second form, which is more suitable for our problem, can be written as

$$N - \left[1 - \left(\frac{M_A}{M_B}\right)^{1/2}\right] N_A = -\frac{C}{RT}\frac{dP}{dx} \qquad (12)$$

where C is a flow coefficient.

The second term on the left side of Equation (12) is the diffusive slip contribution to the flow; that is, the diffusion at constant pressure. For example, if the pressure gradient is zero Equation (12) reduces to the form

$$N = N_A + N_B = \left[1 - \left(\frac{M_A}{M_B}\right)^{1/2}\right] N_A \qquad (13)$$

$$\text{or} \quad \left.\begin{aligned} \frac{N_B}{N_A} &= -\left(\frac{M_A}{M_B}\right)^{1/2} \\ \frac{N_B}{N_A} &= -n^{1/2} \end{aligned}\right\} \qquad (14)$$

where M_A and M_B are the molecular weights of the two components. Equa-

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which are used in the solvent treatment of lubricating oils. But this association also leads him to develop in some detail the difficulties which may arise when the complex systems of that industry are simplified for the sake of expediency to "equivalent" ternaries, as is so often done in the practice of solvent refining. Systems of interest in metallurgy are not specifically mentioned nor are the complex equilibriums found in the distribution of metal compounds between aqueous and organic liquids discussed.

There is an excellent short chapter on experimental techniques, over a hundred pages of tables listing published systems which form two liquid phases(not including some 1,500 systems studied by Francis in unpublished work), a long supplement to the author's earlier book on critical solution temperatures, and a bibliography of over 900 entries. The detailed table of contents and a good glossary of terms substitute for an index.

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Design of Equilibrium Stage Processes, Buford D. Smith, McGraw-Hill, New York (1963). 647 pages. $17.50.

This is a well-written book and fills a very real need. The theoretical equilibrium stage presentation is an excellent method for both teaching and carrying out the calculations involved in separation processes. The concept of a theoretical mixer-separator is an easy one to grasp and generalizations can be extended to cover distillation, extraction, and adsorption. In some chemical engineering curricula a simplified staged operations' course follows the usual mass and energy balances that are the student's introduction to chemical engineering. Frequently, advanced courses in the various separation processes are offered at the graduate level. This book is intended to offer a single approach, and presumably a single course, that would make both students and practicing chemical engineers proficient in the stage calculations of the separation processes.

To a certain extent, the author encounters difficulties in trying to adapt the book for both students and practicing engineers. However, the contradictions involved are recognized by the author in the preface. The first sentences of each of the first three paragraphs of the preface are quoted: "This text was prepared primarily for the plant engineers. . . . Although it is anticipated that the major use of this book will be by practicing engineers, a strong attempt was made to make it suitable also for classroom use. . . . It is, unfortunately, impossible to satisfy both the practicing engineer and the engineering professor with one book." The author also notes that the reader is assumed to have the equivalent of an undergraduate education in chemical engineering. Actually, certain parts of the book assume a familiarity and working knowledge of thermodynamics and calculation methods not necessarily possessed by the average graduate. These factors might indicate that a more unified approach aimed at teaching an engineer or an undergraduate student the subject matter, or additional references to other texts for more detailed presentation of some subjects, would have produced a book that would be easier to use.

The chapter on design variables and the application of this subject matter in all succeeding chapters is an outstanding feature of the book. Beyond its use in phase-rule applications, this subject has been ignored in other texts. The general application of this method of determining variance to design calculations is fully as important as its use in the phase rule.

The author employs difference equations indicating constant net flows in the chapters on enthalpy-composition diagrams and extraction but uses the operating line form of the same equations in x-y diagram methods. This reviewer would prefer that true phase diagram calculations using enthalpy- or temperature-composition diagrams be used to introduce separation calculations for binary systems rather than the McCabe and Thiele method. In this way the importance of constant net flows, discontinuities, and ratios of phases could be emphasized. The use of the x-y-diagram could then be introduced as a shortcut or sufficiently accurate approximation.

Shortcut methods are presented prior to the rigorous methods for multicomponent separations. Here again the conflict between using the book for teaching or practice arises. Presumably the practicing engineer would want to use shortcut methods and might investigate them first. For a complete understanding of the subject matter and adaptation to computer calculations, the reverse approach might be more rewarding.

It should be emphasized that the comments contained in this review represent little more than an expression of a difference in point of view. The book should prove to be extremely useful, and it is hoped that more and more chemical engineers will be exposed to this approach to separation processes.

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INFORMATION RETRIEVAL

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Momentum and heat transfer correlations for a reacting gas in turbulent pipe flow, Callaghan, Michael J., and David M. Mason, **A.I.Ch.E. Journal, 10,** No. 1, p. 52 (January, 1964).

Key Words: A. Heat transfer-8, Momentum Transfer-8, Reacting Gas-1, Flow-6, Heat Flux-6, Temperature-7, Velocity-7; B. Nitrogen dioxide-1, Nitrogen Tetroxide-1, Deissler's Analogy-9, Sieder-Tate Correlation-9, Friction Factor Correlation-9, Pipe Flow-6.

Abstract: Experimental values of radial temperature and velocity in the gaseous equilibrium type of system $N_2O_4 \rightleftharpoons 2NO_2$ in fully developed turbulent flow in a tubular heat exchanger have been found to follow correlations applicable to nonreacting systems. Deissler's analogy for constant fluid properties is found to be applicable if a dimensionless specific enthalpy H^+ is used in place of t^+ in plotting vs. y^+. The Sieder-Tate heat transfer correlation is applicable if specific enthalpy is used as a driving force in the Nusselt number. The ordinary u^+ vs. y^+ correlation and the friction factor—Reynolds number correlation are valid.

Non-Newtonian viscosity of polybutadiene solutions, Seely, Gilbert R., **A.I.Ch.E. Journal, 10,** No. 1, p. 56 (January, 1964).

Key Words: A. Solution-5, Benzene-5, Hydrocarbon-5, Shear Stress-6, Concentration-6, Intrinsic Viscosity-6, Viscosity-7, Flow-8, Polybutadiene-9, Polyisoprene-9, Polyisobutylene-9, Viscometer-10, Non-Newtonian-. B. Shear Stress-6, Viscosity-7, Flow-8, Curve Fitting-10, Capillary-, Apparent-, Non-Newtonian-, Graphical-.

Abstract: The viscosity of cis-polybutadiene solutions decays exponentially with stress toward a limiting value. The parameters describing the stress dependence may be so chosen that they are independent of concentration for polybutadiene of intrinsic viscosity less than 4 dl./g.

A set of curves is derived to relate apparent capillary viscosity to wall shear stress for fluids whose viscosity decays exponentially. With their aid parameters appropriate to a given fluid are found by curve fitting.

This procedure applies to polyisoprene solutions, but with only limited success to literature data for polyisobutylene.

The role of porosity in filtration: Part VI. new definition of filtration resistance, Tiller, F. M., and Mompei Shirato, **A.I.Ch.E. Journal, 10,** No. 1, p. 61 (January, 1964).

Key Words: Filtration-8, Filtration Resistance-7, Porosity-7, Variable Flow Rate-7, Slurry Concentration-6, Pressure-6, Clay-1, Kaolin-1, Hydraulic Pressure-7, Definition of Filtration Resistance-9.

Abstract: A new definition of filtration resistance is presented which depends upon the variation of flow rate within a cake. Filtration resistance is shown to decrease with increasing slurry concentration. Equations are derived for calculating internal flow rate variation with distance when the hydraulic gradient is known. Filtration resistances are presented for clay and kaolin in the form of equations with applied pressure and slurry concentration as variables.

A flow method for measuring transport properties at flame temperatures, Ember, George, J. R. Ferron, and Kurt Wohl, **A.I.Ch.E. Journal, 10,** No. 1, p. 68 (January, 1964).

Key Words. Transport Property-7, Diffusion-8, Self-Diffusivity-7, Tracer diffusivity-7, Binary Diffusivity-7, Temperature-6, Flame-10, Flow Method-10, Radioisotope-10, Carbon Dioxide-5, Methane-5, Water-5, Flat-Flame Burner-10, Combustion-10, Carbon Monoxide-1, Hydrogen-1, Porous Burner-10, Radioactivity Detection-8, Tritium-1, Carbon 14-1, Kinetic Theory-8, Polarity-6, Nonsphericity-6, Thermal Conductivity-7.

Abstract: An apparatus for use at room temperature and at 1,000° to 1,700°K. for measuring self-diffusivities and binary diffusivities of certain gases is described. The technique involves observing the spread of radioactive tracer gas released from a simulated point source into a vertical, laminar gas stream. Hot gases are produced by a flat flame which burns at the base of the apparatus. Data for the system carbon dioxide-methane at 297°K. and for the system carbon dioxide-water at 975° to 1,616°K. demonstrate use of the apparatus. The data also illustrate the need for modifications of current kinetic theory methods for predicting high-temperature transport properties.

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tion (14) gives the well-established expression for the flux ratio for constant-pressure diffusion. When constant pressure is postulated for a reacting system, it is also required that there be no change in moles; that is $n = 1$. Then Equation (13) shows that $N = 0$ or $N_B = -N_A$, as required by the stoichiometry of Equation (1) with $n = 1$.

Equations (7), (8), (9), (11), (12) determine the fluxes, N and N_A, and C_A and P as a function of x. The fluxes can be eliminated from Equation (7) and (12) to reduce this set to two equations involving only P and C_A. First, note that $M_A/M_B = n$ and then combine Equations (9) and (12) to give

$$(1-n)\,N_A - (1-n^{1/2})\,N_A = -\frac{C}{RT}\frac{dP}{dx}$$

or

$$N_A\,(n-n^{1/2}) = \frac{C}{RT}\frac{dP}{dx} \qquad (15)$$

This expression can be differentiated, by regarding C as a constant, and combined with Equation (7) to yield the first of the two equations:

$$-\frac{2\,k_sC_A}{\bar{r}}\,(n-n^{1/2}) = \frac{C}{RT}\frac{d^2P}{dx^2} \qquad (16)$$

The second relationship is obtained by using Equation (11) for D_e in Equation (8), with the result

$$\frac{d}{dx}\left[\frac{1}{\dfrac{1-(1-n)RTC_A/P}{D_{AB}}+\dfrac{1}{D_k}}\;\frac{dC_A}{dx}\right]-\frac{2\,k_sC_A}{\bar{r}}=0 \qquad (17)$$

Equations (16) and (17) are general for the single-pore system in that they apply for the complete range of diffusion processes from Knudsen to bulk. Analysis of the dimensionless forms of the equations indicates that the pertinent groups of variables, in addition to y_{A_0} and n, are

D_{AB_0}/D_k — diffusivity ratio where D_{AB_0} is the bulk diffusivity evaluated at the pressure at the pore mouth

h_b — Thiele modulus in terms of the bulk diffusivity, D_{AB_0}

D_{AB_0}/C — ratio of diffusivity to flow coefficient.

The present state of uncertainty of the value of C reduces the usefulness of the general solution. For very small pores C will approach D_k, as shown in the following section. For very large pores C will be analogous to the permeability and be a function of the viscosity of the gas and the square of the radius of the pore. Except for the small-pore case, flow data are necessary to evaluate C. For example, Evans, et al. (2) have found $C = 0.96$ sq. cm./(sec.) for helium-argon diffusing in a porous graphite with a most probable pore radius of 2.5 μ.

SOLUTION FOR KNUDSEN DIFFUSION

For a catalyst like silica gel most of the pores have a size less than 100 Å. Therefore diffusion is of the Knudsen type up to several atmospheres pressure. Even in bidisperse porous catalysts, such as alumina pellets, Knudsen diffusion may predominate at atmospheric pressure. In such cases $D_{AB} >> D_k$ and Equation (5) reduces to the form

$$D_e = D_k \qquad (18)$$

The important simplification here is that D_e is no longer a function of pressure and thus of pore length. Hence Equation (17) becomes

$$\frac{d^2 C_A}{dx^2} - \left(\frac{2 k_s}{\bar{r} D_k}\right) C_A = 0 \qquad (19)$$

This is identical with the expression obtained by Thiele (4) for constant pressure. Accordingly, the concentration along the pore length will be the same for constant or variable total pressure, and hence the same for all first-order reactions regardless of the change in number of moles. In terms of the Thiele modulus h_k, the result is given by the expression

$$C_A = C_{A_o} \frac{\cosh h_k \left(\frac{x}{L} - 1\right)}{\cosh h_k} \qquad (20)$$

Here C_{A_o} is the concentration at the entrance to the pore where $x = 0$.

The effectiveness factor is the actual rate of reaction over the pore surface divided by the rate if all the surface had been exposed to a concentration C_{A_o}. Thus

$$E = \frac{\int_o^L k_s C_A \, (2\pi\bar{r})\, dx}{k_s \, C_{A_o} \, 2\, \bar{r}\, L} = \frac{\tanh h_k}{h_k} \qquad (21)$$

The equality on the right is obtained by using Equation (20) to evaluate the integral, that is, by assuming Knudsen diffusion. This equation shows that E depends only upon the relation between C_A and x. Since this relation is the same whether or not the total pressure is constant, one may conclude that the Thiele relationship between E and h_k is also true for reactions involving a change in moles.

Using Equation (20) for C_A, Equation (16) can now be solved for the

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An engineering study of the rotary drum crystallizer, Chaty, John C., and Harold A. O'Hern, **A.I.Ch.E. Journal, 10,** No. 1, p. 74 (January, 1964).

Key Words: A. Crystallization-8, Drum-10, Cooling-8, Heating-8, Agitation-8. B. Separation-10, Melt Temperature-6, Coolant Temperature-6, Melt Agitation-6, Melt Impurity-6, Drum Speed-6, Product Quality-7. C. Separation-10, Naphthalene-1, 2, Benzoic Acid-1, Beta Naphthol-1, *p*-xylene-1, 2, *m*-xylene-1, Water-1, 2, Sodium Chloride-1, D. Heat Transfer-8, Water-5, Wilson Plot-8, Agitator Geometry-6, Agitator Speed-6, Density-6, Viscosity-6, Thermal Conductivity-6, Specific Heat-6, Local Coefficients-7, Mass Transfer-8, Chilton-Colburn Analogy-8, Crystallization Rate-8, Colburn-Drew Analogy-8, Heat Transfer for Coefficients-6, Thermal Driving Force-6,Physical Properties-6, Cake Thickness-7, Contact Time-7.

Abstract: A rotary drum crystallization device has been studied in terms of its effectiveness of separation of binary mixtures over a range of melt and coolant temperature, drum rotational rate, melt impurity concentration, and agitation of the melt. Results show that separation improved with increasing agitation and coolant temperature and decreasing drum speed and melt impurity. The study was carried out with the systems naphthalene-benzoic acid, beta-naphthol-naphthalene, *p*-xylene-*m*-xylene, and water-sodium chloride.

Properties of nickel fume generated in a plasma jet, Selover, Theodore B., Jr., **A.I.Ch.E. Journal, 10,** No. 1, p. 79 (January, 1964).

Key Words: A. Argon-1, 5, 6, Nickel Carbonyl-1, 6, Oxygen-1, 5, 6, Fume-2, 7, 9, Gas Ionization-2, Nickel-2, 7, 9, Nickel Oxide-2, 7, 9, Non-Stoichiometry 2, 7, Temperature-2, 6, Carbon-3, 7, Tungsten-3, 7, Direct Current Arc-4, 10, Plasma Jet-4, 8, 10, Electrodes-6, 10, Enthalpy-6, Quenching-6, Particle Size-7, Surface Area-7, 9, Condensation-8, Plasma Chemistry-8, Sintering-8, Thermal Decomposition-8, Electron Microscope-10.

Abstract: Decomposition of nickel carbonyl in a plasma jet has been investigated as a means for producing ultrafine nickel oxide powder. The effects of arc operating parameters have been characterized in relationship to particle size, surface area, stoichiometry, and sintering. Particles range in size from 50 to 300Å. with surface areas as high as 167 sq. meter/g.

Backflows in rotating fluids moving axially through expanding cross sections, Gore, R. W., and W. E. Ranz, **A.I.Ch.E. Journal, 10,** No. 1, p. 83 (January, 1964).

Key Words: Vortical Flow-8, Swirling Flow-8, Rotating Flow-8, Secondary Flow-7, Backflow-7, Reversed Flow-7, Toroidal Vortex-7.

Abstract: Swirled or rotated fluids moving axially through expanding cross sections developed, under certain conditions, an axisymmetric, toroidal vortex having axial backflow. Theoretically, this vortex is an interesting example of a large-scale secondary flow not associated with a boundary. It is basically an inviscid flow phenomenon and can be generated in a highly turbulent fluid. Practically, this vortex controls air flow in liquid fuel burners.

Size, shape, and velocity field were measured for a number of vortices. Conditions for existence and characteristics of the backflow are described.

The constant-volume heat capacity of gaseous tetrafluoromethane, Hwang, Yu-Tang, and Joseph J. Martin, **A.I.Ch.E. Journal, 10,** No. 1, p. 89 (January, 1964).

Key Words: Heat Capacity-7, Constant-Volume Calorimeter-10, Tetrafluoromethane-10, Thermodynamic Properties-7, Spectroscopic Frequencies-7, Statistical Heat Capacity-7, Anharmonicity-7, Dichlorodifluoromethane-10.

Abstract: The constant-volume heat capacity of tetrafluoromethane was measured in a thin-wall large-volume adiabatic calorimeter at densities ranging from 0.0364 to 0.0929 g./cc. and temperatures from 30° to 200°C. Calorimeter calibration was made with the same gas tetrafluoromethane, and calorimeter performance was checked by determining heat capacity of dichlorodifluoromethane. Results on tetrafluoromethane were compared with statistical heat capacity based on fundamental vibrational frequencies, corrected approximately for anharmonicity.

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pressure at any point in the pore. The differential equation and boundary conditions are as follows:

$$\frac{d^2P}{dx^2} = -\frac{2\,k_s\,C_{A_o}\,RT\,(n - n^{1/2})}{\overline{r}\,C\cosh h_k} \cosh h_k\left(\frac{x}{L} - 1\right) \quad (22)$$

$$\left.\begin{array}{ll} \dfrac{dP}{dx} = 0 & x = L \\ P = P_o & x = 0 \end{array}\right\} \quad (23)$$

The solution may be written

$$P_x - P_o = \frac{RTC_{A_o}D_k(n - n^{1/2})}{C} \left[1 - \frac{\cosh h_k\left(\dfrac{x}{L} - 1\right)}{\cosh h_k}\right] \quad (24)$$

Before proceeding further, the coefficient C should be evaluated. Since we have assumed diffusion to be solely by impingement with the pore walls (Knudsen diffusion) the flow rates of A and B will be by the same process. Therefore, the flow rates are given by Equation (4), with D_e replaced by the appropriate Knudsen diffusivities:

$$N_A = -D_{kA}\frac{dC_A}{dx} \quad (25)$$

$$N_B = -D_{kB}\frac{dC_B}{dx} \quad (26)$$

Summing these equations to obtain the total flow rate N and noting that the total concentration, $C_t = C_A + C_B$

$$N = N_A + N_B = (D_{kB} - D_{kA})\frac{dC_A}{dx} - D_{kB}\frac{dC_t}{dx} \quad (27)$$

The Knudsen diffusivities are inversely proportional to the square root of the molecular weight. Hence,

$$\frac{D_{kB}}{D_{kA}} = \left(\frac{M_A}{M_B}\right)^{1/2} = n^{1/2} \quad (28)$$

Substituting Equation (25) for dC_A/dx, and simplifying with Equation (28), reduces Equation (27) to the form

$$N - \left[1 - \left(\frac{M_A}{M_B}\right)^{1/2}\right] N_A = -D_{kB}\frac{dC_t}{dx} = -\frac{D_{kB}}{RT}\frac{dP}{dx} \quad (29)$$

The last equality in this expression assumes that the ideal gas law is applicable.

A comparison of Equation (12) with Equation (29) shows that

$$C = D_{kB} = D_{kA}\ n^{1/2} \qquad (30)$$

Using this value for C, and noting that $C_{Ao} = P_o\ y_{Ao}/(RT)$, Equation (24) becomes

$$P_x - P_o = P_o\ y_{Ao}\ (n^{1/2} - 1) \left[1 - \frac{\cosh\ h_k \left(\frac{x}{L} - 1 \right)}{\cosh\ h_k} \right] \qquad (31)$$

where y_{Ao} is the mole fraction of A at the pore mouth.

The pressure difference between the midpoint of the pore and the pore mouth expressed as the fraction of the external pressure P_o, is obtained by substituting $x = L$ in Equation (31):

$$P_L^* = \frac{P_L - P_o}{P_o} = y_{Ao}\ (n^{1/2} - 1) \left(1 - \frac{1}{\cosh\ h_k} \right) \qquad (32)$$

The following special applications of Equation (32) are of interest:

1. If $n = 1$ (no change in moles accompanying reaction), $P_L = P_o$.
2. For a very slow reaction (k_s small) the Thiele modulus h_k approaches zero, and again $P_L = P_o$.
3. For a very fast reaction, or very low diffusivity (catalyst with small pores) h_k becomes large and

$$P_L^* = y_{Ao}\ (n^{1/2} - 1) \qquad (33)$$

This is the maximum pressure difference between center and mouth of the pore. Wheeler (*6*) derived an expression, in terms of total concentration, equivalent to Equation (33).

Figure 2 shows the pressure difference P_L^* as a function of y_{Ao}, n, and h_k as determined from Equation (32). If k_s, D_k, and $\bar{r}$ are known, Figure 2 can be used to determine the pressure drop between the center and surface of a catalyst where the average pore length is $2L$. In Table 1 three illustrative examples are shown. The parameters for case 1 were chosen to

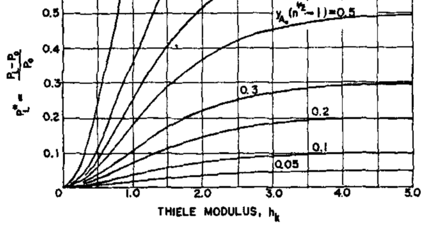

Fig. 2. Pressure drop in a catalyst pore.

INFORMATION RETRIEVAL

(Continued from page 140)

Idealized theory for turbulent mixing in vessel, Rosensweig, R. E., **A.I.Ch.E. Journal, 10,** No. 1, p. 91 (January, 1964).

Key Words: Turbulence-8, Mixing-8, Statistical Theory-10, Kolmogoroff-, Spectrum-1, Cascade-6, Wave Number-1, Stirred Tank-8, Fluctuations-8, Inertial Subrange-1, Scale-6, Residence Time-6, Universal Equilibrium-6.

Abstract: The unmixedness of a fluid stream flowing from a continuous-flow stirred tank fed with separate streams is quantitatively described. Theoretical treatment is by the statistical description of turbulence and draws on the concept of universal equilibrium. Numerical examples illustrate application to mechanically-agitated and fluid-stirred systems. The performance of all real systems will deviate from the predictions of this model to a greater or lesser extent. The model is offered as a framework from which deviations of real mixers can be compared and as a stimulus for further work on the turbulent-mixing problem.

Transient characteristics of continuous extraction with agitation, Staffin, H. K., and Ju Chin Chu, **A.I.Ch.E. Journal, 10,** No. 1, p. 98 (January, 1964).

Key Words: Concentration Response-2, Convolution Integral-10, Concentration Time Constants-7, Dynamic Analysis-10, Fourier Integral-6, Impulse Function-10, Impulse Response Function-10, Interfacial Area-9, Interphase Mass Transport-9, Residence Time Distribution-9, Liquid-Liquid Systems-5, Step Function-2, Transfer Function-8, Mass Transfer-8, Extraction-8, Mass Transfer Coefficient-8, Extractor-9.

Abstract: Interphase mass transport, in the case of a continuous agitated extractor, has been studied with a systems approach. The systems and concentrations studied permitted use of a linearized model for the interphase diffusion resistances as well as the solubility equilibrium data. The resistance elements were determined as system time constants which were related to the mass transfer coefficients. An attempt was made to correlate the results with a correlation suggested for mass transfer coefficients. The time constants obtained with a linear mathematical model assumed did not correlate well with the mass transfer correlation.

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give a relatively large value of P_L^*. The small-pore radius combined with a total pressure of 1 atm. ensures that the restriction of Knudsen flow and diffusion is met. The reaction rate constant k_w is comparatively large but not unrealistic. The relations used for evaluating D_k and k_s (from k_w) are given at the bottom of the table. The average pore length ($2L = 1.0$ cm.) corresponds to a large catalyst pellet. The diffusivity is also large ($M_A = 2$). In this case the fractional pressure drop is estimated to be 32% of the external pressure. Hence the pressure at the center of the pore is 1.32 atm. In case 2 several parameters were changed in the direction of decreasing the pressure drop; that is, n reduced to 2, lower reaction rate, lower diffusivity. As a result the change in pressure from center to pore mouth is found to be but 1.3% of the external pressure. Case 3, compared with case 1, shows the effect of increasing the pore radius. The surface area, S_g, and k_w for the two cases were adjusted to be approximately consistent with each other. Note that rate constant per unit surface area, k_s, is about the same. The result is a decrease in pressure drop to 10% of P_o.

Equation (32) shows that the pressure drop will tend to be the largest during the initial stage of a reaction because y_{Ao} will be the largest. Hence, in a fixed-bed reactor the pressure difference within the catalyst pellet could be significant at the entrance to the catalyst bed and negligible at the exit.

While for Knudsen diffusion it is seen that the effectiveness factor is not

TABLE 1

Design parameters	Case 1	Case 2	Case 3
y_{Ao}	0.5	0.5	0.5
M_A	2	30	2
n	3	2	3
k_w—g. moles/(sec.)(g.)	10^{-5}	2×10^{-7}	3×10^{-6}
T—°K.	373	673	373
P_o—atm.	1	2	1
S_g—sq. cm./g.	400×10^4	400×10^4	150×10^4
$\bar{r}$—cm.	20×10^{-8}	20×10^{-8}	60×10^{-8}
L—cm.	0.5	0.25	0.50
Computed results			
k_s—cm./sec.	7.6×10^{-8}	1.38×10^{-9}	6.12×10^{-8}
D_k—sq. cm./sec.	0.027	0.0092	0.079
h_k	2.66	0.30	0.80
E	0.37	0.96	0.83
P_L^*	0.32	0.013	0.10
$P_L - P_o$—atm.	0.32	0.026	0.10

$$D_k = 9.7 \times 10^3 \, \bar{r} \sqrt{\frac{T}{M_A}}$$

$$k_s = \frac{k_w}{S_g}\left(\frac{RT}{P_o}\right)$$

affected by a change in moles during reaction, this would not be the case for other conditions. To evaluate the magnitude of the effect on E it is necessary to know the flow coefficient C. Then Equations (16) and (17) could be solved for $C_A = f(x)$ and used in Equation (21) to evaluate E.

ACKNOWLEDGMENT

The support of the United States Army Research Office (Durham), through Grant #DA-ARO (D)-31-124-G191, is gratefully acknowledged.

NOTATION

A, B = gaseous reactant and product
C = flow coefficient defined by flow equation [Equation (12)], sq. cm./sec.
C_A = concentration of reactant A, g. moles/cc.
C_t = total concentration, g. moles/cc.
D_{AB} = binary diffusivity (bulk) for gas system of A and B, sq. cm./sec.
D_e = effective diffusivity, defined by Equations (5) and (6), sq. cm./sec.
D_{kA} = Knudsen diffusivity of A, sq. cm./sec.
E = effectiveness factor
h = Thiele modulus;

$$h_b = L\left(\frac{2\,k_s}{\bar{r}\,D_{AB_0}}\right)^{1/2};$$

$$h_k = L\left(\frac{2\,k_s}{\bar{r}\,D_k}\right)^{1/2}$$

k = first-order specific reaction rate; k_w refers to a unit mass of catalyst, g. moles/(sec.)(g.); k_s refers to a unit surface of catalyst, cm./sec.
L = pore length, cm.
M_A, M_B = molecular weights of A and B
N = total flux, g. moles/(sq. cm.)(sec.)
N_A = flux of A
N_B = flux of B
n = stoichiometric ratio, moles of B formed per mole of A reacted
P = total pressure, atm.
P_o = pressure at pore mouth
R = gas constant cc. (atm.)/(g. mole) °K.
$\bar{r}$ = pore radius, cm.
r_A = rate of reaction, g. moles of A reacted/(sq. cm.) sec.
r_B = g. moles of B formed/(sq. cm.)(sec.)
T = temperature, °K.
S_g = surface area of catalyst, sq. cm./g.
w = ratio of fluxes, N/N_A
x = axial distance along pore, cm.
y_A = mole fraction of component A
y_{A_0} = pore mouth conditions

INFORMATION RETRIEVAL

(Continued from page 142)

The effect of applied voltage on boiling heat transfer, Markels, Michael, Jr., and Robert L. Durfee, **A.I.Ch.E. Journal, 10,** No. 1, p. 106 (January, 1964).

Key Words: A. Boiling-2, 7, 8, Heat Transfer-2, 7, 8, Isopropanol-5, 9, Water-5, 9, Peak Heat Flux-1, Electric Field-4, 6, Horizontal Tube-1. B. Film Boiling-1, Transitional Boiling-1, Nucleate Boiling-2, Destabilized Film Boiling-2, Surface Wetting-2, Electrical Forces-4, 6, Coulomb Attraction-4, Dielectrophoresis-4, Heat Flux-7.

Abstract: Boiling heat transfer to isopropanol from a horizontal, steam-heated, chrome-plated, copper tube 0.375 in. in diameter was increased as much as eight times the normal peak heat flux by the application of up to 10,000 v. d.c. between the liquid and the tube. Heat transfer coefficients observed in the normal film region ranged up to 3,120 B.t.u./hr.-sq. ft.-°F. The process completely eliminated film and transitional boiling above 500 v., and the boiling is nucleate over the entire range of overall temperature difference covered (40° to 260°F.). Similar results were obtained with distilled water. The electricially generated force which destabilizes the film boiling appears to arise from the sum of the condenser effect (coulomb attraction) and dielectrophoresis in a nonuniform electrical field. The results obtained substantiate the theories of surface wetting during transitional boiling.

Simplification of the mathematical description of boundary and initial value problems, Hellums, J. D., and S. W. Churchill, **A.I.Ch.E. Journal, 10,** No. 1, p. 110 (January, 1964).

Key Words: Applied Mathematics-10, Asymptotic Solution-10, Boundary-Layer Theory-8, Boundary Value Problem-8, Condensation-8, Convection-8, Conduction-8, Differential Equations-8, Diffusion-8, Dimensional Analysis-10, Fluid Mechanics-8, Forced Convection-8, Free Convection-8, Group Theory-10, Heat Transfer-8, Laminar Flow-8, Momentum Transfer-8, Natural Convection-8, Partial Differential Equations-10, Scale Up-10, Similar Solutions-10, Similarity Transformations-10, Transformations-10, Transport Phenomena-10.

Abstract: A technique is described which not only yields the least set of parameters which can be used to describe a mathematical model, but also indicates transformations of variables which will reduce the number of variables. The method is particularly useful in choosing and investigating approximations and for finding asymptotic solutions. It should prove applicable in teaching and as a guide to both theoretical and experimental research. The method is first illustrated for several familiar problems in conduction, forced convection, and free convection. Then it is used to produce new results for condensation in the presence of noncondensables.

Vapor condensation in the mixing zone of a jet, Hidy, George M., and S. K. Friedlander, **A.I.Ch.E. Journal, 10,** No. 1, p. 115 (January, 1964).

Key Words: Condensation-8, Vapor-1, Jet-10, Mixing-10, Glycerine-1, Fog-2, Diffusion-6, Nucleation-6, Supersaturation-8, Turbulence-8, Aerosol-2.

Abstract: Experimental studies were made of fog formation in free jets containing condensable vapors. Condensation took place near the nozzle in the mixing between the jet and the ambient air. Measurements of condensation and temperature distributions revealed several new effects and gave information on the condensation mechanism.

Scale of mixing in a stirred vessel, Rice, A. W., H. L. Toor, and F. S. Manning, **A.I.Ch.E. Journal, 10,** No. 1, p. 125 (January, 1964).

Key Words: Mixing-8, Reaction-8, Stirred Tanks-8, Turbine Impeller-8, Baffles-8, Acid-5, Base-5, Water-5, Phenolphthalein-4, Speed-6, Diameter-6, Reaction Time-9, Mixing Scale-9.

Abstract: The scale of subdivision achieved by a flat-bladed turbine impeller is estimated by introducing a basic solution below the impeller and measuring the resulting disk-shaped zone of reaction with the bulk acid solution. Phenolphthalein indicator renders the reaction zone visible. Reaction times are computed with estimated velocity profiles. The base tracer solution is assumed to be sheared into small elements, and the appropriate element size that would react by molecular diffusion in the observed reaction times is calculated. These computed sizes, which are about 10^{-3} to 10^{-5} cm., are compared with the previous work of Manning and Wilhelm.

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ERRATA

Equation (25) of the article "Catalytic Effectiveness in Multicomponent and Variable Diffusivity Systems" by John B. Butt, which appeared on page 707 of the September, 1963, issue of the *A.I.Ch.E. Journal*, should read

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

Equations (16), (20), (21), and (24) of the article "The Laminar-Turbulent Transition in Nonisothermal Flow of Pseudoplastic Fluids in Tubes" by R. W. Hanks and E. B. Christiansen, which appeared on page 467 of the September, 1962, issue of the *A.I.Ch.E. Journal*, should read

$$X_{ch} = \left[\frac{f(n)}{1 + 2f(n)}\right]^{\frac{1}{1+f(n)}} \qquad (16)$$

$$r(n) = 1 + 2f(n) \qquad (20)$$

$$R(n, \Delta\Phi, \lambda) = f(n)\left\{(\lambda)^{\frac{1+3n}{n}} + \frac{\frac{1+3n}{n}\exp(\Delta\Phi)}{3 + f(n)}\left[1 - \lambda^{3+f(n)}\right]\right\}^2 \qquad (21)$$

$$\zeta_f^2 = \frac{R(n, \Delta\Phi, \lambda)}{f(n)} \qquad (24)$$