A Sensitive Probe for Measuring Concentration Profiles in Water Vapor-Gaseous Mixtures

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Although the use of lithium chloride in measuring the amount of water vapor in air is not new, it is the simplicity of construction of such a probe, its ease of calibration, its accuracy and great utility in mass transfer studies that form the basis for this note. A small concentration probe, capable of measuring accurately the concentration of water vapor in air or other nonreactive gases at a point or at different radial positions in a flowing stream, can be constructed and effectively utilized. All measurements made with such a probe indicate that excellent concentration profiles may be obtained directly in a manner similar to that for obtaining velocity or temperature profiles. The principle involved is essentially one of equilibrium between water vapor and the lithium chloride on the probe under constant temperature conditions. In a flowing stream at steady state conditions equilibrium is established in about 2 min. and, in the case of a wetted-wall column, the varying concentrations of water vapor at the various radial positions affect the resistance of the lithium-chloride probe. Dunmore (*1*) developed devices using lithium chloride to measure relative humidity. Although devices similar to his are discussed throughout the literature (*2* to *10*) the adoption of this technique for measuring concentration profiles in mass transfer experiments has not been fully exploited. Such a probe easily may be constructed and calibrated and made applicable over wide ranges of water vapor concentrations.

The probe can be constructed from any thin glass tubing or other suitable material. Typical dimensions of the tube used by the authors were approximately 1 mm. in diam. and about 3 in. in length. A thin silver or platinum wire, about 0.1 mm. in diam., is fed through the inside of the glass tubing. Enough wire is fed through the tubing to provide sufficient length for wrapping the wire in a helix around the outside surface of the glass tube. The end of the wire, after forming the helix, may be cemented to the glass surface. A second wire or lead is cemented to the outside surface of the glass and also wrapped in a helix parallel to the first wire. The end of this wire may be

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A Note on the Prediction of Wall Shear Stress Distribution in the Eccentric Annulus

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In applying a generalized velocity correlation to the calculation of turbulent velocity fields, a knowledge of the wall stress is generally required. For example, in the Deissler-Taylor method (*1*) the wall stress must be found by a laborious iterative procedure for irregular passages such as eccentric annuli.

The interest in the flow and heat transfer characteristics of eccentric annuli stems from the utility of the eccentric annulus as a model of the misalignment of a tube in an otherwise symmetric tube or rod bundle with in-line flow. Experimental data taken on different rods in the same tube bundle indicate that the problem of tube misalignment may be a serious one with drastic changes resulting in the heat transfer rate (*2*). A calculation of the heat transfer coefficient for the eccentric annulus requires a knowledge of the velocity distribution. The purpose of the present note is to illustrate a simple method for predicting the variation of wall stress around the inner and outer surfaces of an eccentric annulus.

THE ANALYSIS

The geometry of the eccentric annulus is illustrated in Figure 1. The major assumption involved in the present analysis is that the local wall stress in the eccentric annulus may be determined by treating each local wall position as a position in an effective concentric annulus in a manner to be subsequently explained.

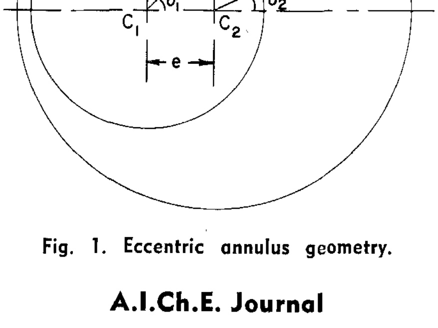

Fig. 1. Eccentric annulus geometry.

In a concentric annulus with inner and outer radii of r_1 and r_2 respectively, the locus of maximum velocity occurs at some radius r_m between r_1 and r_2. For laminar flow, the radius of maximum velocity is given by the equivalent expressions

$$(r_m/r_1)^2 = \frac{(r_2/r_1)^2 - 1}{2 \ln (r_2/r_1)} \qquad (1a)$$

and

$$(r_m/r_2)^2 = \frac{(r_1/r_2)^2 - 1}{2 \ln (r_1/r_2)} \qquad (1b)$$

It has been verified experimentally that Equation (1) is also valid for turbulent flow (*3*).

Because the radius r_m is a line of zero shear stress, a force balance on the

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secured at the end of the probe. The distance between the two wires in the helix is approximately 2 mm. and the overall length of the helix may be about 1 in. or less. Figure 1 is a schematic drawing of a typical probe. The two ends of the wire may be of sufficient length for connecting the probe to an electrical circuit. The entire probe may be constructed to fit any traversing mechanism to obtain concentration profile data.

The sensitive part of the probe is composed of a mixture of polyvinyl alcohol and lithium chloride and is applied directly on the glass and wires. Approximately 0.5 g. of polyvinyl alcohol and a range of concentrations from 0.01 to 0.1 g. of lithium chloride in 10 cc. of water comprise the mixture. The amount of lithium chloride used depends to a large extent upon the sensitivity desired, the range of partial pressure of water vapor to be measured, and the physical construction of the probe itself. The mixture may be heated slightly to make the polyvinyl alcohol and the resulting mixture less viscous. The helix end of the probe may then be dipped or immersed in the mixture and slowly rotated in a horizontal position until a uniform layer covers the glass and wires on the outside of the probe. Several hours are required for the layer to be sufficiently dry to take measurements. The layer after drying will be about 0.05 to 0.1 mm. thick and will be colorless and transparent. A layer composed of larger concentrations of lithium chloride will have an opalescent appearance. The resistance of the probe, when in equilibrium with air or gases containing water vapor at some known temperature, is a measure of the concentration of water vapor present and may be measured easily by a conductivity bridge since a.-c. current is used. The conductivity bridge used by the authors gave good resolution down to water vapor concentrations of approximately 8 mm. mercury partial pressure. Presumably this could be improved with special bridge equipment. As previously indicated, a change in sensitivity may also be accomplished by varying the amount of lithium chloride used in the construction of the probe.

Although the probe, with proper care and precautions, is capable of remaining in its state of original calibration for several weeks, it should be checked

Fig. 1. Schematic drawing of a typical probe.

INFORMATION RETRIEVAL

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A model building technique for chemical engineering kinetics, Hunter, W. G., and Reiji Mezaki, **A.I.Ch.E. Journal, 10,** No. 3, p. 315 (May, 1964).

Key Words: Reviewing-8, Forecasting-8, Reactions-9, Deriving-8, Experimental Design-10. Computers-10, Equations-10, Statistical Analysis-10, Methane-1, 6, Oxygen-1, 6, Nitrogen-1, 6, Air-1, 6, Carbon dioxide-1, 2, 6, Water-1, 2, 6, Palladium-4, 6, Oxidation-9.

Abstract: The application of statistical techniques to model building problems is discussed with reference to solid-catalyzed reactions. There is a need for procedures for iteratively improving models. One such method which is proposed here is illustrated by finding an adequate reaction model for the total catalytic oxidation of methane.

Laminar flow in the inlet section of parallel plates, Wang, Y. L., and P. A. Longwell, **A.I.Ch.E. Journal, 10,** No. 3, p. 323 (May, 1964).

Key Words: Fluid Flow-8, Laminar Flow-8, Parallel Plates-9, Channel-9, Inlet Section-9, Velocity Distribution-2, Pressure Drop-2, Finite-Difference Method-10, Numerical Solution-10, Vorticity Diffusion-8, Newtonian Fluid-9, Incompressible Flow-9, Convergence-7, Nonlinear-9, Computer-10.

Abstract: Numerical solutions of the exact momentum equations are presented for the steady isothermal laminar flow of an incompressible Newtonian fluid in the inlet section of parallel plates. Velocity distributions, pressure gradients, and overall pressure drop are presented for two cases at a Reynolds number of 300. For case I the velocity distribution was taken as flat at the entrance, and in case II the distribution was taken as flat far upstream. No boundary-layer assumptions were made, and it was verified that the usual boundary-layer assumptions are not valid near the leading edge.

Asymptotic solution for combined free and forced convection in vertical and horizontal conduits with uniform suction and blowing, Carter, Leo F., and William N. Gill, **A.I.Ch.E. Journal, 10,** No. 3, p. 330 (May, 1964).

Key Words: Ducts-5, Pipes-5, Brickman Number-6, Grashof Number-6, Prandtl Number-6, Rayleigh Number-6, Suction Rate-6, Injection Rate-6, Conduit Attitude-6, Conduit Geometry-6, Cross Flow-6, Dissipation-6, Nusselt Number-7, Friction Factor-7, Pressure Gradient-7, Temperature Profile-7, Velocity Profile-7, Laminar Flow-8, Heat Transfer-8, Forced Convection-8, Free Convection-8, Transition-9, Stability-9, Computer-10, Transpiration-.

Abstract: This study considers the nonlinear problem of laminar fully developed combined free and forced convection in vertical and horizontal two-dimensional conduits with finite transverse velocity. Similarity transformations are given which reduce the equations of change for pipes and ducts to nonlinear systems of two coupled ordinary differential equations. The effects of interfacial velocity on temperature profiles and heat transfer increase dramatically with N_{Pr}. Suction creates steeper transverse temperature gradients and accentuates buoyancy effects in vertical flows, whereas the reverse is true for blowing. Heat and momentum transfer are discussed in terms of relevant system parameters.

Free-radical yields in n-alcohols resulting from gamma irradiation, Zwiebel, Imre, and Randolph H. Bretton, **A.I.Ch.E. Journal, 10,** No. 3, p. 339 (May, 1964).

Key Words: Radiolysis-8, Gamma Radiation-4, Radiation-2, n-Alcohols-1, n-Methyl Alcohol-1, n-Ethyl Alcohol-1, n-Propyl Alcohol-1, n-Butyl Alcohol-1, n-Pentyl Alcohol-1, Diphenylpicrylhydrazyl-4, Free Radical-2, Scavengers-1, Photometry-10, Degassing-10, Cobalt-60-10, Isosbestic Point-10, Oxygen-3, G-values-7, Radiation Protection-9, Water-3, Radical Yields-7, Scavengers-8.

Abstract: The initial free-radical yields, resulting from gamma irradiation, have been measured in five normal alcohols. The scavenger technique was employed, using diphenylpicrylhydrazyl (DPPH) as the scavenger. It was found that thorough degassing and drying of the samples was necessary to obtain meaningful results. The radical yields have been reported as G-values, and these are in good agreement with results reported in the literature obtained through more complicated methods of determination. No effect of temperature was noted on the yields between —80° and 40°C. As expected, the effect of radiation intensity on the radical formation was linear. A kinetic model has been proposed for the scavenger system.

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periodically. After about one year, the hygroscopic layer should be removed with water, replaced, and recalibrated. The probe may be damaged to the extent of having to replace the sensitive layer and necessitating an earlier recalibration because of the following reasons: droplets of liquid water might come into actual contact with the probe; overexposure of the probe to saturated air for long periods of time; mechanical damage resulting in a short circuit; excessive electrical heating which might change the properties of the hygroscopic layer; contamination with foreign materials; and polyvinyl alcohol, being an organic compound, changes slightly over a period of time and causes the instrument to drift off calibration. When the probe is not in use, it is recommended that it be kept over a saturated solution of salt corresponding to a partial pressure of water vapor in the midrange of the measurements.

The calibration of a typical probe has been accomplished with air having a known partial pressure of water vapor resulting from contact with saturated solutions of various salts (*11, 12*) in closed flasks in which the probe is inserted. The flasks were maintained at constant temperature with an accuracy of ± 0.1°C. The calibration consisted of determining the resistance of the probe at known partial pressures of water vapor under conditions of constant temperature. When the resistance of the probe is determined and plotted against the partial pressure of the water vapor on log-log coordinates, the resulting curve is linear over a wide range of values for a given temperature. The range of water vapor concentrations that might be handled conveniently with a single typical probe was from 8 mm. mercury to about 28 mm. mercury. This corresponds to a relative humidity range of approximately 25 to 85%. Other probes may be constructed to shift these ranges somewhat. It was possible to detect changes in the partial pressure of water vapor in an air stream of 0.1 mm. mercury. Reproducibility for data obtained by the authors is of the order of ± 0.5 mm. mercury except at very high water vapor concentrations where it is approximately ± 1.0 mm. mercury. This difference in reproducibility is not entirely owing to the probe itself. Better reproducibility in this high range might be obtained by special bridge equipment, a change in lithium chloride concentration on the probe itself, and rigid temperature control. The probe is quite sensitive to temperature fluctuations and any calibration must take this into account. Figure 2 illustrates the utility of the probe and presents typical and actual concentration profile data

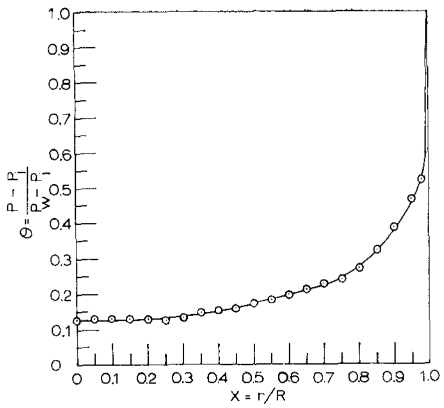

Fig. 2. Typical illustration of a concentration profile obtained in a wetted-wall column under isothermal and given turbulent flow conditions.

obtained in a 2¾ in. I.D. wetted-wall column. In this figure a dimensionless partial pressure term defined as

$$\theta = \frac{P - P_i}{P_w - P_i}$$

is plotted against a dimensionless radial position term defined as $X = r/R$. The probe might be constructed much smaller in size, but is is doubtful if the response time could be reduced to much less than 1 min. Although the probe is capable of sensing a small change in water vapor concentration,

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sizing of overall equipment, with emphasis on the air-water system in both portions. Numerical illustrations are liberally provided. The mathematical level of presentation has been kept elementary, with much of the theoretical background developed in intuitive or empirical fashion. However, it is intended that subsequent volumes will present a more solid theoretical foundation and extend the methods. Mass units are used for concentrations and rates; the notation employed differs frequently from that found in the chemical engineering literature, but is consistent and readily understood. The author writes with a personalized, effective style not often found in a technical presentation.

The nature of "Convective Mass Transfer" makes it difficult to specify precisely the place of this book from a chemical engineering viewpoint. Many of the common mass transfer problems in chemical engineering may be handled as or more readily by other approaches or treated more exactly by recent theoretical developments; and the extremely detailed presentation and general organization may well discourage a person already familiar with other techniques from perusing the book. These characteristics also limit its attractiveness as an introductory textbook, quite aside from the question almost certain to arise as to whether the model proposed is the most satisfactory way to introduce mass transfer concepts. This book, however, has many features to recommend it for consideration. Professor Spalding has brought an extensive and impressive knowledge of transport processes to the development of his methods, and examination of his concepts is a stimulating experience that may be very helpful in clarifying and extending the reader's basic ideas on mass transfer. The unified approach to mass transfer calculations which permits treating, in a relatively simple fashion, the complicated problems arising when high heat transfer and chemical reactions are coupled with mass transfer is of considerable interest because of the increasingly frequent occurrence of these types of problems in today's technology. Some very effective comparisons with experimental results have been provided for these more complex cases; however, more experimental substantiation of the general validity of the proposed methods for such complex situations appears desirable. Perhaps this will be included in the subsequent volumes.

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Lateral Solids Mixing in Fluidized-Packed Beds, Gabor, John D., **A.I.Ch.E. Journal, 10,** No. 3, p. 345 (May, 1964).

Key Words: Solids Mixing-7, Particles-6, Fluidization-8, Fluidized-Packed Bed-8, Gas-1, Nitrogen-1, Packing-6, Diffusion Coefficient-7, Copper Shot-1, Nickel Shot-1, Spheres-6, Cylinders-6, Packed Bed-5, Random-Walk-10.

Abstract: A study was made of the mixing of particulate solids fluidized with nitrogen in the voids of a packed bed of larger, nonfluidized bodies. A measure of the particle movement was achieved by the determination of diffusion coefficients for the rates of solids mixing in the lateral direction for copper-nickel shot fluidized in the voids of spherical and cylindrical packing. Experimental data showed that the particle mixing was related to the void structure of the packed bed by a random-walk model.

Some variables affecting the rate of crystal growth in aqueous solutions, Palermo, Joseph A., and C. S. Grove, Jr., **A.I.Ch.E. Journal, 10,** No. 3, p. 351 (May, 1964).

Key Words: Alum-1, 2, 5, 8, 10, Aluminum potassium sulfate-1, 2, 5, 8, 10, Crystallization-7, Crystallizer-10, Diffusion-7, 9, Equations-2, 8, 10, Experiments-2, 8, 10, Growing-7, 8, Kinetics-7, 9, Mass Transfer-7, 9, Orientation-7, 9, Rates-7, 9, Relationships-2, 8, 10, (Solution)-5, Supersaturation-6, Temperature-6, Theories-2, 8, 10, Viscosity-7, 9.

Abstract: Theoretical equations are derived and experimentally verified governing the growth of groups of crystals of uniform size in supersatured solutions. In a study of the growth of potassium alum crystals mass transfer coefficients are determined for low supersaturations at various temperatures. Data show that at low supersaturations diffusion controls the rate, while at high supersaturations integration controls. It is found that the change in size factor is constant for each size group of crystals grown under the same conditions in conformance with the McCabe ΔL law.

Experimental transient response of a pilot-plant distillation column: part IV. Response of ten-tray column, Luyben, William L., Vincent S. Verneuil, Jr., and J. A. Gerster, **A.I.Ch.E. Journal, 10,** No. 3, p. 357 (May, 1964).

Key Words: Disturbance-1, Perturbation-1, Step Change-1, Pulse Change-1, Transient Response-2, Feed Change-6, Reflux Change-6, Vapor-Rate Change-6, Transient Response-8, Distillation-8, Column-8, Control-9, Analog Computer-10.

Abstract: Experimental transient response data are presented for a ten-tray, 2-ft. diameter, bubble-cap distillation column when step or pulse changes are made in either feed rate, feed composition, reflux rate, or vapor rate to the tower. Simultaneous changes in feed rate, reflux rate, and vapor rate were also studied. The experimental results compare well with those predicted by a set of perturbation type of differential equations solved on an analog computer.

Activity coefficients at infinite dilution: 2-propanol-water system, Slocum, Edgar W., and Barnett F. Dodge, **A.I.Ch.E. Journal, 10,** No. 3, p. 364 (May, 1964).

Key Words: Water-9, 2-Propanol-9, Activity Coefficient-8, Vapor Pressure-8, Vapor-Liquid Equilibria-8, Constant Temperature-6, Constant Pressure-6.

Abstract: Activity coefficients at infinite dilution for the system 2-propanol-water have been calculated from measurements of the slopes at infinite dilution of the total vapor pressure vs. liquid composition curve at constant temperature and the vapor pressures of the pure components in the temperature range from 80° to 100°C. Utilization of the activity coefficients thus obtained as constants in the van Laar equation permits a prediction of isobaric vapor-liquid equilibrium values. The values are shown to compare favorably with values from the literature for the 1-atm. isobar.

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adequate time must be allowed to insure equilibrium.

The experimentally determined concentration profiles are considered to be very reliable. When the concentration or partial pressure values making up the profile are integrated over the column cross section by the following expression

$$\overline{P} = \frac{2}{\overline{v}} \int_0^1 P\, v\, X\, dX \qquad (1)$$

a mean partial pressure term may be obtained making use of velocity profile data. When this value from Equation (1) is compared with the average partial pressure value determined from the loss of liquid from the system by evaporation, the two values are found to agree to within 0.5 mm. mercury for Reynolds numbers ranging from approximately 4,000 to 50,000.

NOTATION

P = partial pressure of water vapor at a particular point
P_i = partial pressure of water vapor in inlet stream to the column
P_w = vapor pressure of water at the wall at some specified temperature
$\overline{P}$ = mean or average partial pressure of water vapor
R = radius of the wetted-wall column
r = radial distance measured from the center
v = point value of velocity
$\overline{v}$ = mean or average velocity of fluid flowing
X = dimensionless radial position term
θ = dimensionless partial pressure term

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