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COMMUNICATIONS TO THE EDITOR

A Novel Technique for Determining Mass Transfer Coefficients in Agitated Solid-Liquid Systems

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In a recent paper Harriott (*4*) has pointed out the marked disagreement in the literature regarding mass transfer coefficients in agitated solid-liquid systems. Widely conflicting claims have been made as to the dependence of particle-fluid mass transfer coefficients upon various operating parameters (impeller speed, particle-fluid density difference, etc.). In part this may be owing to difficulties in obtaining reliable data suggesting the need for an improved experimental method, designed to overcome shortcomings of some of the earlier studies.

METAL-SOLUTION CHEMICAL REACTIONS FOR MASS TRANSFER STUDIES

It has been established that under proper circumstances certain metals will dissolve chemically in aqueous solutions at diffusion-controlled rates. This fact does not appear to be generally appreciated, and the potentialities for studying mass transfer using metal-solution reactions have not been fully exploited. In the application of this idea to studies on mass transfer in agitated solid-liquid systems, the use of a metal as the solid has several obvious advantages. First, the problem of particle attrition should be greatly minimized as compared with studies on crystalline solids, such as salt or boric acid. Second, particle geometry may be more precisely defined, at least under some circumstances. A number of metals and alloys are available as spheres in a wide range of sizes (ball bearings, Linde microspheres), and spherical shapes are also available for a number of other inert, nonmetallic materials (glass beads, plastics). The latter materials may be given a metal surface by various metallizing procedures. By appropriate choice of the substrate particle and regulation of the thickness of applied metal surface, a wide range of effective particle densities may be fabricated. This would make possible a systematic examination of the effect of particle-fluid density difference on the mass transfer coefficient without changing other properties of the solid-liquid system. This has not been possible in prior studies.

It should be noted that some of the advantages of metal-solution systems have been achieved in a different way in other studies. Harriott (*4*) claims to have circumvented the attrition problem, together with good definition of particle geometry, in studies on the neutralization of suspensions of small ion-exchange beads. The proposed metal-solution system, however, offers the additional advantage of a systematic study of the density-difference effect.

EVALUATION OF THE TECHNIQUE

Initial exploratory studies on the use of metal-solution reactions for studies in mass transfer were based upon the work of Gregory and Riddiford (*2*). Their study demonstrated that rotating copper and brass disks dissolve in aqueous potassium dichromate—sulfuric acid solutions at rates which are entirely diffusion-controlled, provided that the acidity is sufficiently high. Dissolution rates in their studies varied as the square root of the rotational speed of the disks, as required by the ex-

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tended Levich equation (*1*). The rapid chemical reaction occurring at the solid-liquid interface is

$$3\,(\mathrm{Cu, Zn}) + \mathrm{Cr_2O_7^{=}} + 14\mathrm{H^+} \rightarrow 2\mathrm{Cr^{+++}} + 3\,(\mathrm{Cu^{++}, Zn^{++}}) + 7\,\mathrm{H_2O}$$

At high acidities, the rate of metal dissolution is governed by the rate of transport of dichromate ions to the metal surface.

The first experiments in applying this to a study of mass transfer coefficients in agitated solid-liquid systems were conducted using 1/16-in. diam. brass ball bearings suspended by mechanical agitation in acid-dichromate solution. Agitation was provided by a flat-blade, turbine type of impeller operating at a constant speed in a baffled, cylindrical vessel. Samples of solution were withdrawn periodically and titrated with ferrous ammonium sulfate to determine the concentration of dichromate as a function of time.

The rate of disappearance of dichromate ion is given by

$$-V_s \frac{dc}{dt} = k\,A\,c \qquad (1)$$

or, upon rearrangement

$$\frac{d \ln c}{dt} = -\frac{kA}{V_s} \qquad (2)$$

Thus if concentration-time data and A and V_s are known, the mass transfer coefficient, k, may be evaluated. Proper choice of the initial dichromate concentration can minimize changes in the particle size and area (A). For a fixed impeller speed, good reproducibility of results was obtained and, in addition, the same values were obtained for k when the initial dichromate concentration was varied.

A few pertinent observations should be pointed out. It was found that a certain minimum impeller speed was necessary in order to completely suspend the charge of brass balls. Zwietering (*8*) has shown that the minimum impeller speed required for full suspension of particles in a system of this type depends upon system geometry and particle and fluid properties. For the case studied, an impeller speed of around 600 rev./min. was found to be necessary for full suspension. The value of k (at 25°C.) determined experimentally at 650 rev./min. was 0.0108 cm./sec. A question naturally arises as to whether or not the experimental value is, indeed, reasonable. Harriott (*4*) has suggested that the minimum value of the mass transfer coefficient to be expected when the particles are just completely suspended should be predictable. At this point the slip velocity of

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An experimental investigation of boiling heat transfer and pressure-drop characteristics of freon 11 and freon 113 refrigerants, Blatt, T. A., and R. R. Adt, Jr., **A.I.Ch.E. Journal, 10,** No. 3, p. 369 (May, 1964).

Key Words: Boiling-9, Boiling Refrigerants-9, Evaporation-9, Freon 11-9, Freon 113-9, Heat Transfer-9, Refrigerant Properties-9, Two-Phase Pressure Drops-9.

Abstract: This paper presents the results of an experimental investigation in which boiling heat transfer data for Freon 11 and Freon 113 refrigerants were obtained. The experimental apparatus used for the investigation is described. Forced convection boiling heat fluxes, heat transfer coefficients, and pressure drops were determined. The effects of mass flow rate, evaporation pressure, liquid film superheat, and exit vapor Reynolds number are presented. The coefficient C_{SF}, appearing in Rohsenow's correlation for nucleate boiling, is determined for both fluids in stainless steel and copper tubes. Two-phase flow pressure drops are presented for both refrigerants as a function of mass flow rate and exit quality.

Mixing on valve trays and in downcomers of a distillation column, Welch, N. E., L. D. Durbin, and C. D. Holland, **A.I.Ch.E. Journal, 10,** No. 3, p. 373 (May, 1964).

Key Words: Mixing-8, Plate Efficiency-7, Distillation-2, Eddy Diffusivity-7, Valve Trays-8, Viscosity-6, Surface Tension-6, Density-6, Vapor Rate-6, Liquid Rate-6, Peclet Number-6.

Abstract: The mixing characteristics for combinations of plates and downcomers for Glitsch V-1 ballast trays were determined with a three-plate column that was 27 in. in diameter. The mixing could be described by an eddy diffusion model. For combinations of plates and downcomers, the eddy diffusivity was found to be a function of the mean-linear velocity of the liquid and independent of the physical properties of the liquid as well as the gas flow rate throughout the range of liquid and gas flow rates employed in the investigation. A variety of liquids were used and the Peclet numbers ranged from 4.4 to 27.

Enthalpy values for hypothetical fluids from vapor-liquid equilibrium data, Welker, J. Reed, S. Dean Larson, and Dwight S. Hoffman, and James H. Weber, **A.I.Ch.E. Journal, 10,** No. 3, p. 380 (May, 1964).

Key Words: Vapor-Liquid Equilibrium Constants-1, Standard State Fugacities-1, Methane-9, Ethane-9, Hypothetical Fluids-9, Enthalpy Values-2, Thermodynamic Relationships-10.

Abstract: In previous papers fugacities for hypothetical fluids have been presented. These fugacity values, in turn, permitted the evaluation of vaporization equilibrium constants (so-called ideal K's) for substances at conditions above and below their respective critical temperature. In this work the vaporization equilibrium constants previously developed are used to evaluate enthalpy differences between the liquid and vapor states. By this method enthalpy values for pure substances in the hypothetical liquid state (for example at supercritical temperatures) and the hypothetical vapor state (for example when the total pressure of the system is greater than the vapor pressure of the pure substance) can be determined.

Upper and lower bounds on the drag coefficient of a sphere in a power-model fluid, Wasserman, Melvin L., and John C. Slattery, **A.I.Ch.E. Journal, 10,** No. 3, p. 383 (May, 1964).

Key Words: Sphere-5, Carboxymethylcellulose-5, Drag Force-8, Drag Coefficient-8, Variational-10, Non-Newtonian-, Ostwald-de Waele-, Power Law-, Rheology-.

Abstract: Upper and lower bounds to the drag force on a sphere moving slowly through a power-model fluid are obtained using variational methods. Available experimental data are compared with the average of the upper and lower bounds.

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the fluid relative to the particle should at least equal the terminal falling velocity of the particle. Harriott suggests that the semitheoretical equation of Ranz and Marshall (6) for mass transfer coefficients for single spheres to fluids in motion

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

be used to calculate the minimum value of $k(k_{min})$ to be expected. The Reynolds number (N_{Re}) in Equation (3) is to be evaluated using the terminal falling velocity of the particle. On the basis of Equation (3), k_{min} for 1/16-in. brass balls in acid-dichromate solution ($N_{Re} = 845$, $N_{Sc} = 1{,}100$) was found to be 0.0105 cm./sec., in good agreement with the experimental value of 0.0108 cm./sec. found at 650 rev./min. It is interesting to note that when the impeller speed was increased substantially (to 1,250 rev./min.), only a very small increase in k (to 0.0123 cm./sec.) was found experimentally. It should be noted, however, that for the case of brass bearings a very high density difference existed between solid and fluid ($\Delta\rho = 7.43$ g./cc.).

The situation was quite different when the particle-fluid density difference was decreased to approximately 0.6 g./cc. This case was studied using 1/16-in. diam. cellulose acetate spheres as substrate particles, silvering the surface by Brashear's process (3) to make it conductive, and then barrel electroplating to produce a copper surface. These lower density spheres were fully suspended at a much lower impeller speed (250 rev./min.), as predicted by Zwietering (8). Measured values of the mass transfer coefficient, k (at 25°C.), varied from 0.0055 cm./sec. at 300 rev./min. to 0.0080 cm./sec. at 800 rev./min. The predicted minimum value of k from Equation (3) ($N_{Re} = 187$) is 0.0050 cm./sec. again establishing that the magnitude of results is quite reasonable. These data indicate a stronger dependence of k upon impeller speed as the particle-fluid density difference is lowered, the particle size being essentially the same. This suggests that the effect of impeller speed on k may be closely coupled with the solid-fluid density difference. No such coupling effect has been suggested in prior studies and further work is planned to study this in detail.

It is clear that the copper (brass)—acid dichromate reaction system is limited effectively to a fixed set of solution properties (density, viscosity, diffusivity, Schmidt number). To permit further generalizations other diffusion-controlled metal-solution reaction systems with different physical properties may be found useful. Riddiford and

Bircumshaw (7) have shown that a number of metals (zinc, copper, brass, lead, nickel) dissolve in aqueous iodine-potassium iodide solutions at diffusion-controlled rates. Newson and Riddiford (5) recently reported on the physical properties of aqueous iodine-potassium iodide solutions, and, in addition, aqueous iodine-potassium iodide-sucrose solutions. The latter system involves subsivity of the tri-iodide ion, making possible a Schmidt number range from 350 to 33,000.

The discussion presented here has dealt primarily with applications to agitated solid-liquid systems. However, the basic technique may prove to be a powerful tool in other mass transfer studies as well.

ACKNOWLEDGMENT

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NOTATION

A = total solids area, sq. cm.

c = concentration of dichromate ion, g. moles/cc.

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Graphite oxidation at low temperature, Effron, Edward, and H. E. Hoelscher, **A.I.Ch.E. Journal, 10,** No. 3, p. 388 (May, 1964).

Key Words: A. Graphite-1, Carbon-1, Temperature-9, Oxidation-9, Combustion-9, Kinetics-9, Activation Energy-9, Reaction Order-9, Boudouard Reaction-9, B. Oxygen-1, Surface Complex-2, Partial Pressure-6, Pore Diffusion-9, Chemisorption-9. C. Carbon Monoxide-2, Carbon Dioxide-2, Production-7.

Abstract: Graphite oxidation studies have been carried out in oxygen and in air between 400° and 530°C. An analytical system capable of detecting product carbon dioxide and carbon monoxide at concentrations less than 10 parts/million was developed and used during the work. Kinetic results are compared with literature data obtained under similar conditions. The effect of bulk and surface properties of the graphite on oxidation rate and product distribution is considered. A reaction mechanism is proposed which reconciles much of the published data and the results reported herein.

The roles of capillary wicking and surface deposits in the attainment of high pool boiling burnout heat fluxes, Costello, C. P., and W. J. Frea, **A.I.Ch.E. Journal, 10,** No. 3, p. 393 (May, 1964).

Key Words: Boiling Burnout-6, Surface Coatings-6, Capillary Wicking-6, Heater Size-7, Burnout Heat Flux-8, Saturated Pool Boiling-5, Tap Water-5, Distilled Water-3, Surface Deposit-3, Silica-4, Fiberglas Wicking-6, Wetability-7, Critical Heat Flux-.

Abstract: Data are presented to show how the burnout heat flux varies with the presence of capillary wicking, surface deposits, and heater size. Cylindrical and semicylindrical heaters 1/16- to ½-in. diameter were tested, and some data are presented for larger flat plate heaters. It is shown that surface deposits which improve wetability can produce two to threefold increases in burnout heat flux and that smaller heaters give higher burnout heat fluxes. Fiberglas wicking provides a surface deposit which improves wetability. The wicking, when properly arranged, also constrains the vapor columns arising from a heater so that it behaves as a heater of smaller diameter. Heat fluxes of over 1,200,000 B.t.u./hr. sq. ft. were obtained with saturated pool boiling in the presence of wicking.

Gas absorption accompanied by a large heat effect and volume change of the liquid phase, Chiang, S. H., and H. L. Toor, **A.I.Ch.E. Journal, 10,** No. 3, p. 398 (May, 1964).

Key Words: A. Gas Absorption-8, Heat Effect-6, Volume Change-6, Diffusion Equation-1, Energy Equation-1, Mathematic Solution-2, Semi-Infinite Liquid Phase-5. B. Absorption-8, Ammonia-1, Water-1, Rate-9, Experimental -10.

Abstract: A solution is obtained to the equations of diffusion and energy for the absorption of a gas into a semi-infinite liquid accompanied by a large heat effect and a large volume change of the liquid phase.

Experimental data for the absorption of ammonia into water at short contact times are in agreement with the solution which indicates that in this system the effects of the heat generation and volume change on the rate of mass transfer almost cancel.

Measurement and correlation of turbulent friction factors of thoria suspensions at elevated temperatures, Eissenberg, D. M., **A.I.Ch.E. Journal, 10,** No. 3, p. 403 (May, 1964).

Key Words: Turbulence-, Pressure Drop-7, Pumping-10, Non-Newtonian-, Flocculated-, Thoria-1, Suspension-1, Temperature-6, Concentration-6, Velocity-6, Correlation-9, Extrapolation-9, Reynolds Number-10, Dispersed-10, Viscosity-10.

Abstract: Turbulent friction factors of non-Newtonian flocculate thoria suspensions were measured at elevated temperatures and correlated with a Reynolds number based on the measured Newtonian friction factor vs. Reynolds number relationship. A decrease in friction factor at high concentrations of thoria was ascribed to a change in the velocity profile.

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D = diffusion coefficient of dichromate ion, sq. cm./sec.
d_p = particle diameter, cm.
k = mass transfer coefficient, cm./sec.
N_{Re} = Reynolds number based on relative fluid-particle velocity, d_pU/ν, dimensionless
N_{Sc} = Schmidt number, ν/D, dimensionless
N_{Sh} = Sherwood number, kd_p/D, dimensionless
t = time, seconds
U = relative fluid-particle velocity, cm./sec.
V_s = solution volume, cc.

Greek Letters

ν = kinematic viscosity, sq. cm./sec.
$\Delta\rho$ = density difference between particle and fluid, g./cc.

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ERRATUM

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* was printed incorrectly both in the original article and on page 144 of the January, 1964, issue of the *A.I.Ch.E. Journal*. This equation should read

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