COMMUNICATIONS TO THE EDITOR

Fins in Series

T. R. BUMP
Argonne National Laboratory, Argonne, Illinois

For the purposes of this discussion, a fin is defined as a body of thermal interest in which the temperature differences in the cross section are unimportant compared with those in the

(*Continued on page 177*)

A Note on Mixing Rates in Stirred Tanks

PAUL SYKES and ALBERT GOMEZPLATA
University of Maryland, College Park, Maryland

The purpose of this note is to present a comparison of the recent data of Biggs (*4*) with the mixing time correlation of Landau and Prochazka (*8*) and to indicate a distinction between the terminal mixing time of Biggs and of Norwood and Metzner (*10*).

Landau and Prochazka presented a model of the homogenation process in a batch baffled turbulent stirred tank. The model left unresolved three parameters. These parameters were determined by following the rate of batch homogenation of miscible liquids in baffled stirred tanks in the turbulent region ($N_{Re} > 10^4$) with conductometric, thermometric, and colorimetric probes (*7*). Mixing time correlations were developed for three blade square pitch propellers, six blade fan disk turbines, and four blade 45 deg. inclined paddles. Their correlations are:

Propeller
$$nt = 3.48\ (D/d)^{2.02} \log (2.0/X) \qquad (1)$$

45-deg. paddle
$$nt = 2.02\ (D/d)^{2.20} \log (2.0/X) \qquad (2)$$

Fan disk turbine
$$nt = 0.905(D/d)^{2.57} \log (2.0/X) \qquad (3)$$

The quantity X is the approach of the entire tank contents to homogeneity. At any time X is the integral mean value throughout the tank of the local degree of homogeneity which is defined as

$$x = \frac{|C(t) - C(f)|}{C(f) - C(i)} \qquad (4)$$

Landau and Prochazka found the mean value of X at time zero to be 2.0.

Biggs introduced a salt pulse into the feed stream of a flow stirred tank and measured several time quantities of the exit stream response curve. The time for the exit stream to settle to ±5% of its quasi steady value (Biggs-t_3) will be considered here and will be designated $t(0.05)$.

Certain differences exist between the test conditions of the two studies; they are presented in Table 1.

In both systems the liquid depth was equal to the tank diameter, and the mixing tank contained four wall baf-

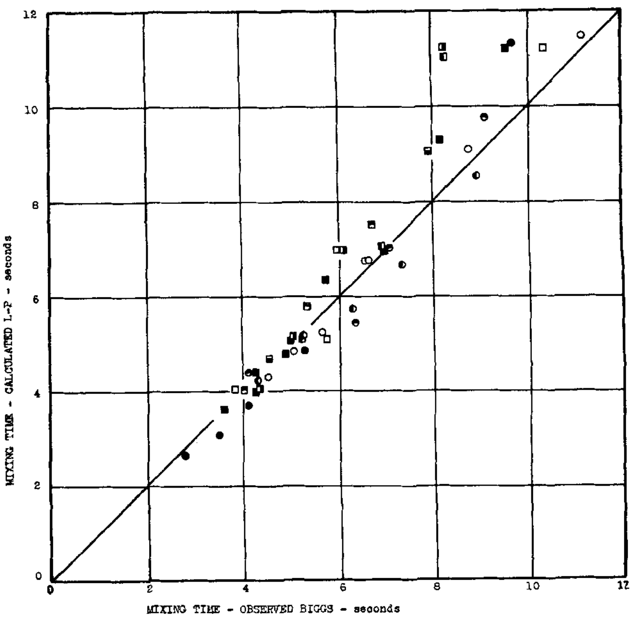

Fig. 1. Overall comparison of Biggs' data with Landau-Prochazka correlations.

TABLE 1. COMPARISON OF TEST CONDITIONS

	Biggs	L-P
Type of system	Flow	Batch
Position studied	Exit stream	Total tank contents
Impeller clearance	Impeller diameter	Tank mid height
$\frac{\text{Tank diameter}}{\text{Impeller diameter}}$	2.4 to 3.9	3.0 to 10.0
$\frac{\text{Baffle width}}{\text{Tank diameter}}$	$\frac{1}{10}$	$\frac{1}{12}$
Tank diameter (in.)	9.62	8.25, 13.0, 21.6

fles. The exact method or position of tracer addition by Landau and Prochazka was not indicated for all tests, but it was noted by them that a variety of positions of addition as well as different volumes and concentrations of tracer seemed to have little effect on their mixing times.

An overall comparison of the mixing times as calculated by the *L-P* correlation with $X = 0.05$ and the observed $t(0.05)$ data of Biggs is presented in Figure 1. Included in Figure 1 are the data points and the calculated values of the *L-P* correlation for three blade square pitch propeller (Biggs did not present a correlation for the propeller data in his article); the *L-P* values are in agreement with the limited data of Biggs. The Biggs data for feed stream passing through the tank in upflow and for the six blade 45 deg. inclined paddle are not included in Figure 1 since they did not match any of the *L-P* correlation lines. It should be mentioned that the six blade 45-deg. paddle data fell about midway between the four blade 45-deg. paddle and six blade fan disk turbine correlations of

(Continued on page 182)

Suitability of the Nernst-Planck Equations for Describing Electrokinetic Phenomena

E. N. LIGHTFOOT and E. M. SCATTERGOOD

University of Wisconsin, Madison, Wisconsin

The quantitative description of electrokinetic phenomena requires the use of reliable rate expressions to relate mass fluxes and the concentration, electrical, and pressure driving forces tending to cause mass movement. Present indications are that (*7*), at least for systems of simple ionic constituents, the linear flux relations of irreversible thermodynamics (5) are adequate for this purpose. There appear, however, to be very few cases in which the full set of phenomenological coefficients required by these relations has been determined. This is because of the large amount of information required for such a description: $n(n - 1)/2$ diffusivities and associated activity data for a system of n diffusing species.* The most complete available treatments appear to be those of Spiegler (*13*) and Mackay and Meares (*11*).

In practice, most experimental investigations have been interpreted on the basis of the much simpler pseudo-binary Nernst-Planck equations (6), even though these are known to be incapable of providing a complete description of the systems concerned, and even though their use has often led to poor agreement between prediction and experiment (*1*). They are known to be useful only for correlation of data taken for individual electrokinetic processes, for example ion exchange (*9*) or electrodialysis (*1*).

Tests of the usefulness of the Nernst-Planck equations are as yet inconclusive, and no generally sound method has been suggested for making such tests. The purpose of this paper is to provide such a method and to demonstrate the need for tests. This is done by rewriting the complete set of linear flux expressions in the form of the Nernst-Planck equations so that the differences between the two sets of flux expressions may be seen clearly. Procedures for testing the Nernst-Planck equations are then developed and some examples are given. The approach is similar to that used for estimating pseudo-binary diffusivities in ideal gases.

The Nernst-Planck equations are presented in such a wide variety of forms that the use of a single name for all is misleading. In this paper the

TABLE 1†

Friction coefficients $\left(\frac{\text{Joule sec.}}{\text{sq. cm}\cdot\text{mole}}\right)$

$^*F_{M^+W} = 4.93 \times 10^8$
$^*F_{A^-W} = 3.32 \times 10^8$
$^*F_{WR^-} = 4.65 \times 10^6$
$^*F_{M^+R^-} = 2.13 \times 10^8$
$^*F_{A^-R^-} = 2.0 \times 10^6$
$F_{M^{*+}M^+} = 2.0 \times 10^6$ (estimated)

Diffusivities $\left(\frac{\text{sq. cm.}}{\text{sec.}}\right)$

$\overline{D}_{M^+W} = 4.92 \times 10^{-6}$
$\overline{D}_{A^-W} = 7.30 \times 10^{-6}$
$\overline{D}_{WR^-} = 5.86 \times 10^{-6}$
$\overline{D}_{M^+R^-} = 1.28 \times 10^{-7}$
$\overline{D}_{A^-R^-} = 1.35 \times 10^{-5}$
$\overline{D}_{M^{*+}M^+} = 1.35 \times 10^{-5}$ (estimated)

Concentration in membrane $\left(\times 10^{-3}\,\frac{\text{mole}}{\text{liter}}\right)$

$^*c_{M^+} = 0.468$
$^*c_{A^-} = 0.0124$
$^*c_W = 40.7$
$^*c_{R^-} = 0.4556$

Equivalent fraction in membrane

With A^-	Without A^- (estimated)
$x_{M^+} = 0.0113$	$x_{M^+} = 0.011$
$x_{A^-} = 0.0003$	$x_{A^-} = 0$
$x_w = 0.9775$	$x_w = 0.978$
$x_{R^-} = 0.0109$	$x_{R^-} = 0.011$

† Values of the F_{ij} and the c_i are those of Mackay and Meares except $F_{M^{*+}M^+}$. This was estimated to be equal to $F_{A^-R^-}$ because of lack of specific information. All $\overline{D}_{ij}$ except $\overline{D}_{A^-W}$ and $\overline{D}_{A^-R^-}$ are calculated on the basis of the A^--free compositions. A^- = anion, M^+ = cation, M^{*+} = cation isotope, R^- = resin.

---

[*] In this paper the membrane is considered to be one of the diffusing species.

(*Continued from page 180*)

Some molecular transport characteristics in binary homogeneous systems, Longwell, P. A., and B. H. Sage, **A.I.Ch.E. Journal, 11,** No. 1, p. 46 (January, 1965).

Key Words: Methane-5, *n*-Butane-5, Hydrocarbons-5, Binary Systems-5, Composition-6, Diffusion Coefficients-7, Diffusion-8, Mass Transport-8, Fick-, Chapman and Cowling-.

Abstract: The behaviors of several diffusion coefficients are shown for the methane-*n*-butane system under conditions such that solutions are very nonideal and the concentrations of both components are significant. The coefficient proposed by Chapman and Cowling shows the least variation with state and is recommended for use under such conditions in hydrocarbon systems. Several other coefficients commonly used show large variations with state, and coefficients with concentration as a potential are even negative in certain regions.

Effective binary diffusion coefficients in mixed solvents, Tang, Y. P., and D. M. Himmelblau, **A.I.Ch.E. Journal, 11,** No. 1, p. 54 (January, 1965).

Key Words: Mass Transfer-8, Transport-8, Diffusion-8, Multicomponent-8, Liquids-8, Mixtures-9, Absolute Rate Theory-10, Liquid Jet-10, Carbon Dioxide-5, Water-5, Ethanol-5, Benzene-5, Toluene-5, Carbon Tetrachloride-5.

Abstract: The diffusion of carbon dioxide through ethanol-water, benzene-toluene, and carbon tetrachloride benzene was studied over the entire range of compositions for the solvent pairs. The results were interpreted in terms of an effective binary diffusion coefficient. Two semiempirical correlations were derived with the aid of absolute reaction rate theory to predict the effective binary diffusion coefficient from the binary diffusion coefficients of the solute in the individual pure solvents. These equations, although only crude approximations, reproduced the experimental data for six diffusion systems fairly well, including the highly nonideal solvent mixture ethanol-water.

Film boiling of nitrogen with suction on an electrically heated porous plate, Wayner, P. C., Jr., and S. G. Bankoff, **A.I.Ch.E. Journal, 11,** No. 1, p. 59 (January, 1965).

Key Words: Nitrogen-5, Vapor Flow Rate-6, Heat Transfer Coefficient-7, Temperature Driving Force-6, Heat Flux-6, Film Boiling with Vapor Suction-8, Porous Heater-10.

Abstract: Experimental equipment to study the film boiling of liquid nitrogen on a porous heat source with vapor suction was developed. The electrically heated element was a 3.69 in. sintered stainless steel screen, which was also used as a resistance thermometer in conjunction with an a.c. potentiometric circuit. In preliminary work, this mode of heat transfer was unstable, but stability was achieved by placing a porous flow control element on the liquid side of the heater. It was found that the Nusselt number was a function of only the Reynolds number; the heat transfer coefficient was increased by a factor of as much as 2.5 over the heat transfer coefficient in normal film boiling; it was possible to vary independently any two of the three variables, heat flux, flow rate through the plate, and temperature difference; and the generated vapor was considerably superheated. Fluctuations in the local surface temperature were measured in film boiling from both porous and nonporous flat plates, indicating that momentary solid-liquid contacts can occur, for all practical purposes, in film boiling.

Film boiling of nitrogen with suction on an electrically heated horizontal porous plate: effect of flow control element porosity and thickness, Pai, V. K., and S. G. Bankoff, **A.I.Ch.E. Journal, 11,** No. 1, p. 65 (January, 1965).

Key Words: Nitrogen-5, Vapor Flow Rate-6, Heat Transfer Coefficient-7, Temperature Driving Force-6, Heat Flux-6, Film Boiling With Vapor Suction-8, Porous Heater-10.

Abstract: The study of film boiling of liquid nitrogen with vapor suction on an electrically heated porous plate, initiated by Wayner and Bankoff, is continued here. The stability and the heat transfer rate were not affected by a considerable reduction in the thickness of the flow control element, providing that the flow resistivity (determined by the porosity and average pore diameter) was correspondingly increased. The superheat of the exhaust vapor was appreciable and seemed to be independent of the nature of the flow control element. Similarly the Nusselt number appeared to be a function of only the Reynolds number in the range used in the study.

(*Continued on page 184*)

(*Continued from page 175*)

L-P; the data were consistently 10% greater than the time predicted by the fan disk turbine correlation of Biggs.

The overall agreement is seen to be satisfactory with the exception of times greater than 10 sec. (which corresponds to impeller Reynolds number less than 2 × 10^4). The amount of scatter is not unexpected since there are several differences between the test conditions and since in the Biggs' correlation for the fan disk turbine the exponent of rotational speed is −0.84 and the *L-P* value is −1.0.

Biggs indicates that the time $t(0.05)$ is the batch terminal mixing time and also the first step in the three step mixing sequence suggested by Beek and Miller (*3*). It can be argued that the volume which the probe sees will determine how many of the time steps are included in the mixing time measurement; that is a probe which sees a smaller volume than Biggs' would require a longer time to settle down to ± 5% concentration fluctuation than $t(0.05)$. This argument leads to the possibility that the relatively small volume probe of Biggs may measure both the dispersion time and the time to generate additional contact area but not the final time step of degradation of the tracer blobs by diffusion. If this is true, then the time $t(0.05)$ differs from the acid base terminal mixing time of Fox and Gex (*5*) or Norwood and Metzner by the time step of diffusion of the last drop of base to be neutralized. This is supported by the comparison made by Biggs of $t(0.05)$ with the terminal mixing time correlation of Norwood and Metzner. Most of the data points are less than the correlation group; that is the time $t(0.05)$ is less than the terminal mixing time.

The time step for diffusion can be estimated by the relation of Hughes (*6*):

$$t(m) = l_s^2/2D_v \qquad (5)$$

$$l_s = \nu^{3/4}/\epsilon^{1/4} \qquad (6)$$

$$\epsilon = Pg_c/\rho V \qquad (7)$$

$$P = N_p\, \rho n^3 d^5/g_c \qquad (8)$$

where N_p is the power group and it is approximately constant at Reynolds numbers above 10^4 (*2, 13*). Combination of these terms gives

$$t(m) = (Vd)^{1/2}/2N_p^{1/2}(N_{Re})^{3/2}D_v \qquad (9)$$

The assumptions made in obtaining this expression for $t(m)$ are:

1. The energy is dissipated uniformly in the entire liquid volume rather than only in the volume swept out by the impeller (*4, 14*).
2. All the energy supplied to the

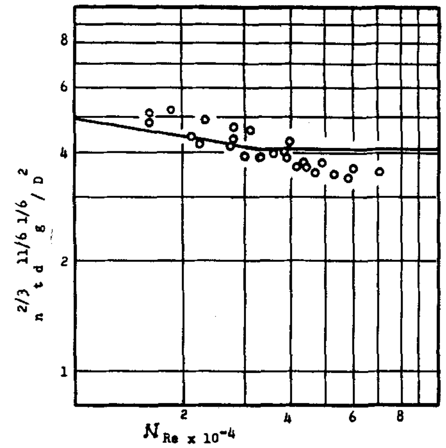

Fig. 2. Comparison of modified Biggs' terminal mixing time with the acid-base mixing time correlation of Norwood.

impeller is dissipated in turbulent processes in contrast with Rosensweig's estimate (*12*) of 50%.

3. The length scale (l_s) expression, Equation (6), can be taken as an equality rather than only as an order of magnitude estimate (9).

Values of $t(m)$ were computed for the fan disk turbine (2.5, 3, and 4 in.) and straight blade turbine (3 in.) with a diffusivity of 2×10^{-5} sq.cm./sec. and the power group constants of Bates (2). These time values were added to the time values of Biggs' correlation at Biggs test speeds, and comparison of this sum with the Norwood and Metzner correlation (modified for tank diameter equal to liquid depth) of terminal mixing time is presented in Figure 2. The terminal mixing times of Biggs after inclusion of the diffusion time step is in slightly better agreement with the correlation line of Norwood than the data of Biggs. The modified values are within ± 20% reproducibility of the Norwood correlation (*10*).

The scale expression, Equation (6), when applied to the test conditions of Rice et al (*11*) predicts length scale values which are larger by a factor of about 30 than estimated by their experiments. However, it may be noted that scale values of the same order of magnitude as those of Rice can be obtained by Equation (6) if the volume swept out by the impeller is used as the volume term in Equation (7). It may also be noted that the concentration scale suggested by Batchelor (*1*)

$$l_c = \left(\frac{\nu D_v^2}{\epsilon}\right)^{1/4} \qquad (10)$$

predicts scale values of the same order of magnitude as those of Rice. Both Equations (6) and (10) predict that the scale varies as $n^{-3/4}$ rather than n^{-1} as reported by Rice. The differences

INFORMATION RETRIEVAL

(*Continued from page 182*)

Liquid atomization in a high intensity sound field, Wilcox, R. L., and R. W. Tate, **A.I.Ch.E. Journal, 11,** No. 1, p. 69 (January, 1965).

Key Words: Air-6, Atomization-8, Atomizer-10, Cavity-10, Droplet Size-7, Droplets-2, Liquid-1, Nozzle-10, Sonic Generator-10, Sonic Whistle-10, Sound-6, Spray-2, Streams-10.

Abstract: High intensity sound was investigated as a means for liquid breakup Sonic generators provided energy to atomize liquid introduced near the sound source. Droplet size was measured at several conditions of air and liquid flow for sound intensities ranging up to 160 decibels.

Atomization was good at low liquid flows but became rather coarse as flow rate increased. The droplet size distributions were not uniform. No improvement in breakup could be attributed directly to the sonic compressions and rarefactions beyond that normally produced by the tearing action of air in conventional two-fluid atomizers at comparable air/liquid ratios.

Mass transfer in a sparged contactor: Part I. Physical mechanisms and controlling parameters, Braulick, W. J., J. R. Fair, and B. J. Lerner, **A.I.Ch.E. Journal, 11,** No. 1, p. 73, (January, 1965).

Key Words: A. Absorption-8, Mass Transfer-8, Sparged Contactor-10, Bubble Contactor-10, Air-1, Water-5, Aqueous Sodium Sulfite-5, Copper Sulfate-4, Gas Rate-6, Submergence-6, Mass Transfer Coefficient-7. B. Aeration-9, Agitation-9, Bubbling-9, Sparged Contactor-10, Bubble Contactor-10, Air-1, Water-5, Aqueous Sodium Sulfite-5, Gas Rate-6, Submergence-6, Gas Holdup-7.

Abstract: Studies of the air oxidation of aqueous sodium sulfite solutions were made in simple bubble contacting columns of 3-, 4-, and 6-in. diameter. Superficial gas rates up to 300 lb./hr.-sq.ft. were used. Contacting action is described in detail, and comparisons with air-water data show the marked influence of small, ionic bubbles. Mass transfer and dynamic gas holdup data are presented, and the former are compared with mass transfer data for bubble-cap trays.

Kinetics of the heterogeneous decomposition of iron pentacarbonyl, Carlton, H. E., and J. H. Oxley, **A.I.Ch.E. Journal, 11,** No. 1, p. 79, (January, 1965).

Key Words: Metal Carbonyl-1, Iron Pentacarbonyl-1, Metal Coating-2, Carbonyl Iron-2, Carbon Monoxide-3, Temperature-6, Pressure-6, Flow Rate-6, Deposition Rate-7, Kinetics-8, Chemical Kinetics-8, Reaction Kinetics-8, Heterogeneous Decomposition-8, Thermal Decomposition-8, Pyrolysis-8, Vapor Plating-8, Vapor Deposition-8, Coating-8, Adsorption-9, Order of Reaction-9, Heat of Adsorption-9, Activation Energy-9, Reactor-10, Filament-10, Differential Reactor-10.

Abstract: The decomposition of iron pentacarbonyl at pressures between one and 400 Torr was studied from 120° to 300°C. Up to about 200°C. the rate was primarily limited by surface kinetics of adsorbed carbonyl. Gas phase diffusional resistances were controlling at higher temperatures. In the kinetically controlled region the deposition rate was correlated by a Langmuir type of equation. Corrections for diffusion resistances in the kinetic region and kinetic resistances in the diffusion region were found to be appreciable.

On the stability of a detailed packed-bed reactor, McGuire, M. L. and Leon Lapidus, **A.I.Ch.E. Journal, 11,** No. 1, p. 85 (January, 1965).

Key Words: Packed-Bed Reactor-1, Porous Particles-1, Steady State Response-2, Transient Response-2, Stability-2, Axial and Radial Gradients-6, Internal Particle Gradients-6, Digital Computer-10

Abstract: An analysis of the stability of a packed-bed reactor is presented subject to a model including axial and radial gradients in the interparticle field and gradients plus reaction in the intraparticle field. The stability of the entire reactor is characterized in terms of various stable and unstable conditions inside the porous particles. Simplifications in the mathematical model are shown to be invalid in many situations.

(*Continued on page 186*)

between the scales that have been suggested in this paper, and those found experimentally by Rice are not yet completely understood. Therefore, the suggested time step of diffusion, Equation (9), must be considered as tentative until the differences are resolved.

Notation

$C()$ = concentration, (t) at time t, (f) final, (i) initial
d = impeller diameter (L)
D = tank diameter (L)
D_v = diffusivity (L^2/θ)
g_c = conversion constant $(ML/F\theta^2)$
l_s, l_c = viscous scale, concentration scale (L)
n = rotational speed θ^{-1}
N_p = power group $Pg_c/n^3d^5\rho$ (dimensionless)
P = power (LF/θ)
N_{Re} = Reynolds group nd^2/ν (dimensionless)
$t, t(m)$ = mixing time, diffusion time step (θ)
V = tank holdup (L^3)
x = local degree of homogeneity
X = total tank degree of homogeneity
ϵ = energy dissipated/mass time (L^2/θ^3)
ρ = density (M/L^3)
ν = kinematic viscosity (L^2/θ)

Measurements

F = force
M = mass
L = length
θ = time

LITERATURE CITED

1. Batchelor, G. K., *J. Fluid Mech.*, **5**, 113 (1959).
2. Bates, R. L., P. L. Fondy, and R. R. Corpstein, *I and E C Process Design and Development*, **2**, 311 (1963).
3. Beek, J., and R. S. Miller, *Chem. Eng. Progr. Symposium Ser. No. 25*, **55**, 23 (1959).
4. Biggs, R. D., *A.I.Ch.E. Journal*, **9**, 636 (1963).
5. Fox, E. A., and V. E. Gex, *ibid.*, **2**, 539 (1956).
6. Hughes, R. R., *Ind. Eng. Chem.*, **49**, 947 (1957).
7. Landau, J., and J. Prochazka, *Collection of Czechoslavak Chemical Communications*, **26**, 1976 (1961).
8. *Ibid.*, p. 2961.
9. Levich, V. G., "Physicochemical Hydrodynamics," p. 24, Prentice Hall, Englewood Cliffs, N. J. (1962).
10. Norwood, K. W., and A. B. Metzner, *A.I.Ch.E. Journal*, **6**, 432 (1960).
11. Rice, A. W., H. L. Toor, and F. S. Manning, *ibid.*, **10**, 125 (1964).
12. Rosensweig, R. E., *ibid.*, p. 91.
13. Rushton, J. H., E. W. Costich, and H. J. Everett, *Chem. Eng. Progr.*, **46**, 395, 467 (1950).
14. Shinnar, R., *J. Fluid Mech.*, **10**, 259 (1961).