
COMMUNICATIONS TO THE EDITOR

Observation of Binary Interdiffusion Coefficients in Constant-Volume Systems

FRIEDRICH HELFFERICH
Shell Development Company, Emeryville, California

PROBLEM

Isothermal interdiffusion of two liquids, *A* and *B*, across an inert porous disk separating two well-stirred reservoirs of constant volume is considered. The following assumptions are made: (1) the liquids are ideal and completely miscible, and mixing is not accompanied by changes in pressure or volume; (2) the disk is sufficiently porous so that any pressure differences arising between the reservoirs are instantaneously levelled out by convective flow in the disk; (3) agitation in the reservoirs is sufficient to restrict concentration gradients entirely to the disk; (4) the reservoirs are sufficiently large so that interdiffusion is quasi-stationary and the disk volume is negligible compared to the reservoir volumes; (5) the individual (or intrinsic) diffusion coefficients D_A and D_B are independent of liquid-phase composition.

The assumptions, in particular (5), are essentially those of the Hartley-Crank model (*1*) to which the derivation up to Equation (3) is equivalent. The purpose of the present note is not to enter into the controversy about this model (*2*) but, rather, to show that experimental results may fail to reflect the dependence of the interdiffusion coefficient on liquid-phase composition. According to the model, this dependence is pronounced; however, the system may behave as though the coefficients were constant.

DERIVATION

The fluxes of the components *A* and *B* relative to the disk are composed of transfer by diffusion relative to the

(*Continued on page 982*)

(*Continued from page 980*)

Optimization of multistage cyclic and branching systems by serial procedures, Aris, Rutherford, George L. Nemhauser, and Douglass J. Wilde, **A.I.Ch.E. Journal, 10,** No. 6, p. 913 (November, 1964).

Key Words: A. Optimization-6, Design-9, Operations-9, Recycle Systems-9, Branching Systems-9, Dynamic Programing-10, Calculus of Variations-10, Maximum Principle-10. B. Decision-1, Input State-1, Output State-2, Return Function-2, Objective Function-2, Transition Function-10, Optimum Seeking Methods-10.

Abstract: It is shown how to optimize cyclic and branching systems by extending techniques such as dynamic programing, calculus of variations, and the maximum principle, all employed originally for serial systems alone. Several new concepts, choice state, cut state, functional diagram, state inversion, and decision inversion, are introduced, and much of existing terminology is given precise definition. Optimum seeking methods can often be used to reduce the effects of cut state dimensionality.

Stability of droplets suddenly exposed to a high velocity gas stream, Haas, Frederick C., **A.I.Ch.E. Journal, 10,** No. 6, p. 920 (November, 1964).

Key Words: Drop-1, Sphere-1, Deformation-2, Disintegration-2, Air-5, Constant Velocity-5, Weber Number-6, Pressure Distribution-6, Deformation Ratio-7, Deformation Time-7, Disintegration Time-7, Deformation-8, Breakup-8, Orifice-10, Motion Pictures-10, Mercury-10, High Speed-0.

Abstract: The breakup of liquid globules exposed suddenly to a high velocity gas stream has been studied. When experimental measurements of the critical Weber number are utilized as a base, the predicted degree of deformation and time required for deformation show agreement with experimentally measured values for the formation of a thin wafer globule.

The mechanism of droplet breakup is described, and experimental measurements of time required for various stages of drop deformation are presented. Breakup of mercury drops suddenly exposed to an air stream with velocity between 100 and 400 ft./sec. was measured.

Solids mixing in straight and tapered fluidized beds, Littman, Howard, **A.I.Ch.E. Journal, 10,** No. 6, p. 924 (November, 1964).

Key Words: Solids Mixing-2, 8, Fluidized Bed-9, Radioactive Tracer-10, Copper Particles-10, Air-10, Gas Velocity-6, Bed Height-6.

Abstract: Batch solids mixing experiments are reported for —140 +200 mesh copper particles in straight and tapered fluidized beds of rectangular cross section with a 2-in. sq. inlet. Gas velocities up to 110% above the minimum and bed height to diameter ratios of 8 and 16 to 1 were employed in this study. The mixing was followed by radioactive tracer techniques.

Tapering was found to reduce solids mixing at gas velocities close to the minimum, particularly in the lower part of the bed. Tapering a bed that slugs increases the rate at which particles are uniformly dispersed in it principally by increasing the dispersion rate in the top of the bed. Otherwise, differences in solids mixing rates between tapered and untapered beds are small.

Kinetics of sulfochlorination of cyclohexane in carbon tetrachloride induced by gamma radiation, Schneider, A., and Ju Chin Chu, **A.I.Ch.E. Journal, 10,** No. 6, p. 930 (November, 1964).

Key Words: A. Gamma Radiation-10, Carbon Tetrachloride-5, Kinetics-8, Cyclohexane-1, Sulfur Dioxide-1, Chlorine-1, Cyclohexanesulfonyl Chloride-2, Hydrochloric Acid-2, Concentration-6, Radiation Itensity-6, Reaction Rate-7, Reaction Mechanism-9, Gamma Irradiation Facility-10, Free Radicals-9, Chain Reaction-9.

Abstract: Reaction rates were determined for the production of cyclohexanesulfonyl chloride, and a chain mechanism was derived.

(*Continued on page 984*)

(*Continued from page 967*)

liquid in the disk and of convective flow of this liquid:

$$J_A = -D_A \frac{\partial C_A}{\partial x} + C_A u,$$

$$J_B = -D_B \frac{\partial C_B}{\partial x} + C_B u \qquad (1)$$

The restriction of constant volume and pressure requires that

$$J_A + J_B = 0 \qquad (2)$$

Since, by definition, $C_A + C_B = 1$ one obtains from Equations (1) and (2)

$$J_A = -[(1 - C_A)D_A + C_A D_B] \frac{\partial C_A}{\partial x} \qquad (3)$$

The quantity in square brackets is the interdiffusion coefficient and depends strongly on liquid-phase composition.

In the quasi-stationary state, J_A is a function of t only, that is, it is independent of x for any given t. Integration of Equation (3) for any arbitrary t with the boundary conditions $C_A = C_A'(t)$ at $x = 0$ and $C_A = C_A''(t)$ at $x = d$ gives

$$J_A(t) = \frac{1}{d} \{D_A[C_A'(t) - C_A''(t)] - \frac{1}{2}(D_A - D_B)[C_A'^2(t) - C_A''^2(t)]\} \qquad (4)$$

Further discussion will remain restricted to reservoirs of equal volume and to the initial condition

$$t = 0, \quad C_A' = 1, \quad C_A'' = 0 \quad (5)$$

With negligible disk volume the material balance then is $-dC_A' = dC_A''$, and one obtains with condition (5)

$$t \geqq 0, \quad C_A''(t) = 1 - C_A'(t) \quad (6)$$

Equation (4) then reduces to

$$J_A(t) = \frac{D_A + D_B}{2d} [C_A'(t) - C_A''(t)] \qquad (7)$$

The reservoir concentrations and the flux as a function of time are now readily obtained by integration of the continuity condition

$$-V \frac{dC_A'}{dt} = S\ J_A(t) \qquad (8)$$

using Equations (6) and (7):

$$C_A'(t) = \frac{1}{2}[1 + \exp(-\alpha t)],$$

$$C_A''(t) = \frac{1}{2}[1 - \exp(-\alpha t)] \qquad (9)$$

$$J_A(t) = \frac{D_A + D_B}{2d} \exp(-\alpha t) \tag{10}$$

where

$$\alpha \equiv \frac{S(D_A + D_B)}{Vd}$$

DISCUSSION

The usual and most convenient experimental procedure for measuring interdiffusion is to observe the concentrations in the reservoirs as a function of time and to calculate the flux by Equation (8). Such measurements, however, do not lead to the interdiffusion coefficient as it appears in Equation (3) and which varies with liquid-phase composition and thus with location within the disk. Rather, the observed flux and concentration changes depend upon the respective average value of the coefficient over the whole disk. With reservoirs of equal volume and with one component in each reservoir initially [condition (5)], this average remains constant as the boundary concentrations change; the concentrations and the flux [Equations (9) and (10)] behave in exactly the same manner as one would observe in a system in which the actual interdiffusion coefficient was independent of composition and equal to the constant value $(D_A + D_B)/2$. This is apparent from Equations (7), (9), and (10). Measurements of the described type thus fail to reveal the dependence of the interdiffusion coefficient on composition.

Incidentally, similar situations are encountered in interdiffusion of two dissolved electrolytes with one common ion across an inert porous disk and in interdiffusion of counterions across ion-exchange membranes. The equations are somewhat different because, here, the restriction is conservation of electroneutrality, and the mechanism of conservation is electric transference of ions. Nevertheless, with reservoirs of equal volume and initial conditions analogous to condition (5), the average value of the interdiffusion coefficient over the whole disk is here, too, almost constant even if the actual coefficient depends strongly on composition. This explains why Gilliland (3) was able to fit experimental results on ionic interdiffusion to a theory based on the premise of a constant interdiffusion coefficient, an assumption which he recognized to be untenable.

The same argument could be advanced for interdiffusion of gases. Here, however, the underlying Hartley-Crank model appears to be unrealistic (4).

INFORMATION RETRIEVAL

(*Continued from page 982*)

Optimization of initial composition in adiabatic equilibrium gas-phase reactions, Pings, C. J., **A.I.Ch.E. Journal, 10,** No. 6, p. 934 (November, 1964).

Key Words: Optimization-8, Maximization-8, Initial Composition-9, Feed Composition-9, *Yield*-7, Reaction Temperature-7, Chemical Equilibrium-9, Thermodynamics-10, Homogeneous Reaction-8.

Abstract: Expressions are derived for the initial distribution of mole fractions of reactants required to obtain maximum yield in gas-phase reactions proceeding adiabatically to equilibrium. The initial composition necessary to attain the maximum equilibrium adiabatic temperature is also identified. The small but nontrivial corrections to the classic distribution of stoichiometric ratios involve heat capacities and the enthalpy of reaction.

The heterogeneous phase behavior of the helium-nitrogen system, Rodewald, *N. C., J. A. Davis,* and Fred Kurata, **A.I.Ch.E. Journal, 10,** No. 6, p. 937 (November, 1964).

Key Words: Phase Behavior-8, Solid-Vapor-8, Liquid-Vapor-8, Solid-Liquid-8, Solid-Liquid-Vapor-8, Densities (Saturated)-8, Helium-1, Nitrogen-1, Cryostat-5, Dew-and Bubble-Point Method-10, Thermodynamic Consistency Check-9, Thermodynamic Correlation-9, Solubility-8.

Abstract: The heterogeneous phase behavior of the helium-nitrogen system has been experimentally investigated from 50° to 77°K. The following experimental data are reported: P-X diagrams and saturated volumetric plots for isotherms of 77.2°, 69.3°, nd 64.9°K. to 1,000 lb./sq. in. abs., the P-T relationship of the S-L-V locus to 2,000 lb./sq. in. abs. (The corresponding three-phase L-V compositions were determined by several methods.), and the solid-vapor behavior for mixtures of 70.4, 90.4, 96.1, 98.30, 99.00, and 99.500 mole % helium.

Throughout the discussion of the data, an extensive comparison with the published data was undertaken, and significant deviations are pointed out.

Dynamic optimization of a two-stage reactor system, Thibodeau, Robert D., and William F. Stevens, **A.I.Ch.E. Journal, 10,** No. 6, p. 944 (November, 1964).

Key Words: Computer-10, Constrained-0, Control-8, Dynamic-0, Maximum-0, Multi-stage-10, Optimality-8, Optimization-8, Performance-7, Reactor-10, Sampled-0, Stochastic-0, System-10.

Abstract: This paper considers the dynamic optimization of a particular multistage reactor system whose behavior is nonstatic owing to stochastic changes in its input and output. A variational approach, in which the constraints on the manipulatable variables are included by a parametric representation, leads to a bang-bang, sampled-data, optimal control law. Inclusion of the inequality constraints by a penalty function leads to a set of nonlinear Euler-Lagrange equations specifying the control law.

Fluid flow characteristics of concurrent gas-liquid flow in packed beds, Weekman, Vern W., Jr., and John E. Myers, **A.I.Ch.E. Journal, 10,** No. 6, p. 951 (November, 1964).

Key Words: Heat Transfer-9, Two-Phase-5, 8, Flow-6, 7, Packed Bed-10, 8, Spheres-10, 5, Pulses-7, 9, Pressure Drop-7, Surfactant-4, Foaming-5, 9, Radial-7, Gas Phase-5, Liquid Phase-5, Reactors-10, Velocity-7, Liquid Distribution-7, Wave-7, 9.

Abstract: Pressure drop, liquid distribution, and pulse characteristics were studied for two-phase, concurrent flow of air and water through a 3-in. I.D. vertical column randomly packed with spheres. Three regimes of flow were recognized, and the liquid and gas rates necessary to achieve these regimes are given. In studies of the pulsing flow regime, it was found that the liquid pulses traversing the packed bed did not bridge the entire column diameter but rather had the shape of a wavelike torus. A two-phase, pressure-drop correlation for packed beds is presented in an extension of the Lockhart and Martinelli derivation for two-phase pipe flow.

To detect the dependence of the interdiffusion coefficient on composition, three alternative methods may be used: (1) measurement and evaluation of quasi-stationary concentration profiles within the disk, as discussed by Barrer (*5*) and Jost (*6*); (2) measurements with reservoirs of drastically different volumes; (3) series of measurements over a range of initial compositions such that, in each experiment, the initial concentration *difference* across the disk is small (*7*). Conversely, the results of such experiments cannot be expected to conform to theories assuming a constant interdiffusion coefficient even if these theories are successful for reservoirs of equal volume and the initial condition (*5*).

NOTATION

C_A = concentration of A, given as volume fraction, dimensionless

C_A' = concentration of A in left reservoir, dimensionless

C_A'' = concentration of A in right reservoir, dimensionless

d = thickness of disk, cm.

D_A = diffusion coefficient of A, sq. cm./sec.

D_B = diffusion coefficient of B, sq. cm./sec.

J_A = flux of A, cc. cm.$^{-2}$ sec.$^{-1}$

S = surface area of disk available for diffusion, sq.cm.

u = rate of liquid-phase convection in disk, cm./sec.

V = reservoir volume, cc.

x = space coordinate normal to disk boundaries, cm. (disk extends from $x = 0$ to $x = d$)

LITERATURE CITED

1. Hartley, G. S., and J. Crank, *Trans. Faraday Soc.*, **45**, 801, Sec. 6 and 7 (1949); see also J. Crank, "The Mathematics of Diffusion," pp. 219-221, Clarendon Press, Oxford (1956).
2. Bearman, R. J., *J. Phys. Chem.*, **65**, 1961 (1961); Horrocks, J. K., and E. McLaughlin, *Trans. Faraday Soc.*, **58**, 1357 (1962); see also Prager, S., *J. Chem. Phys.*, **21**, 1344 (1953); Adamson, A. W., *J. Phys. Chem.*, **58**, 514 (1954); Irani, R. R., and A. W. Adamson, *J. Phys. Chem.*, **64**, 199 (1960); Miller, L., and P. C. Carman, *Trans. Faraday Soc.*, **58**, 1529 (1962).
3. Gilliland, E. R., R. F. Baddour, and D. J. Goldstein, *Can. J. Chem. Eng.*, **35**, 10 (1957).
4. Present, R. D., "Kinetic Theory of Gases," McGraw-Hill, New York (1958); McCarthy, K. P., and E. A. Mason, *Phys. Fluids*, **3**, 908 (1960).
5. Barrer, R. M., *Proc. Phys. Soc.*, **58**, 321 (1946).
6. Jost, W., "Diffusion in Solids, Liquids, Gases," p. 14-15, Academic Press, New York (1952).
7. Helfferich, Friedrich, *J. Phys. Chem.*, **67**, 1157 (1963); Bidlack, D. L., and D. K. Anderson, *J. Phys. Chem.*, **68**, 206 (1964).