q = rate of energy transfer to propellant surface, cal./sec. sq. cm.
R = gas constant, cal./g. mole °K.
r = linear burning rate, cm./sec.; r_0 = burning rate at zero gas velocity
T^* = temperature of primary reaction (propellant surface temperature during burning, °K.)
T_i = initial temperature of propellant, °K.
T_g = temperature of core gas during burning, °K.
y_A = mole fraction A in gas phase
ϵ = pressure coefficient in empirical burning rate, Equation (2)
γ = frequency factor in Arrhenius' representation of chemical rate equation
ρ = density of solid propellant, g./cc.

Subscripts

A, B, D = components in the primary surface reaction
g = core gas
i = gas-solid interface

LITERATURE CITED

1. Adams, G. K., and L. A. Wiseman, "The Combustion of Double-Base Propellants," p. 275, Butterworth's Scientific Publications, London, England (1954).
2. Crawford, B. L., C. Huggett, F. Daniels, and R. E. Wilfong, *Anal. Chem.*, 19, 630 (1947).
3. Corner, J., *Trans. Faraday Society*, 43, 635 (1947).
4. Crawford, B. L., C. Huggett, and J. J. McBrady, *J. Phys. Chem.*, 54, 854 (1950).
5. Friedman, N., R. G. Nugent, K. E. Pimbel, and A. C. Scurlock, "Deflagration of Ammonium Perchlorate,"
   p. 612, Reinhold, New York (1956).
6. Geckler, R. E., "The Mechanism of Combustion of Solid Propellants," p. 289, Butterworth Scientific Publications, London, England (1954).
7. Parr, R. G., and B. L. Crawford, *J. Phys. Chem.*, 54, 929 (1950).
8. Rice, O. K., and R. Ginell, *ibid.*, 54, 885 (1950).
9. Schultz, R., L. Green, and S. S. Penner, "Combustion Reviews (AGARD)," Butterworth Scientific Publications, London, England (1958).
10. Summerfield, M., G. S. Sutherland, M. J. Webb, H. J. Taback, and K. P. Hall, paper presented at 13th Annual Meeting American Rocket Society, New York (November, 1958).
11. Wilfong, R. E., S. S. Penner, and F. Daniels, *J. Phys. Chem.*, 54, 863 (1950).

Continuous-Throughput Rectification of Organic Liquid Mixtures with Thermal-Diffusion Columns

DAVID R. LONGMIRE

University of Wisconsin, Madison, Wisconsin

Experiments were carried out with cylindrical thermal-diffusion columns in which the separation chambers were sufficiently narrow so that curvature effects might be ignored. For both open and closed operation, results were obtained for the two binary systems benzene-carbon tetrachloride and n-heptane–benzene as well as the ternary mixture n-heptane–methylcyclohexane-toluene. For the binary systems, correlations are given in terms of dimensionless combinations which arise when the equations of conservation are placed in dimensionless form. The thermal-diffusion coefficients used in the correlations are literature values determined in steady-state–cell (no convection) measurements.

The historical background of thermal diffusion has been covered by Powers and Wilke (1). Except for the many steady-state–cell experiments (no convection), studies with liquids generally have been confined to the vertical or inclined countercurrent thermal-diffusion column conceived by Clusius

David R. Longmire is with Texas Butadiene and Chemical Corporation, Channelview, Texas.

and Dickel (2). Although for continuous throughput the product positions on a Clusius-Dickel column are usually at the extremities, with the feed position at an intermediate point, recent arrangements by A. L. Jones and his associates (3 to 12) include concurrent flat-plate columns operated vertically or horizontally with or without membranes as well as apparatus

with porous walls. Studies have been reported recently on the Clusius-Dickel column operated with packing as well as centrifugal force (13, 14).

In addition to the work of Powers and Wilke (1), the principal quantitative investigations covering thermal-diffusion columns operated with a continuous throughput have been those of Heines, Larson, and Martin (15) and

Thomas and Watkins (16, 17). The former have contributed a large number of data for the system n-heptane–benzene, and their results have been expressed in terms of a dimensionless group $FL/4K_c$, which appears in the earlier theoretical developments of Furry, Jones, and Onsager (18). The thesis by Heines (19) was the first experimental study on continuous-throughput operation for liquids presented as a dimensionless-group correlation. The study of Powers and Wilke (1) was carried out with the system ethanol-water as well as n-heptane–benzene. Variables examined were feed rate, length of column, wall spacing, temperature difference between walls, and the angle of inclination of the apparatus, which was of the flat-plate type. By extrapolation to zero throughput of curves describing the difference of top and bottom product concentrations vs. throughput constants H and K_c for the Furry, Jones, and Onsager (18) equations were determined. Curves then calculated from the equations were generally in good agreement with experimental results. The failure of the equations at high throughputs led Powers and Wilke (1) to a novel theory modification which assumes a linear variation of vertical concentration gradient with the horizontal cartesian coordinate. Thomas and Watkins (17) have presented the first experimental results for continuous-throughput operation of thermal-diffusion columns with concentrated mixtures of ternary gaseous mixtures.

For binary systems this study differs from previous ones in several respects, essentially, in the thermal-diffusion coefficients utilized in the correlations, in the method of developing the correlations, and in the correlations themselves. In view of the disagreement between thermal-diffusion coefficients determined from column experiments (20 to 23) and those arising from steady state thermal-diffusion–cell experiments without convection (24, 25, 26), coefficients which have resulted from steady-state–cell measurement, a more fundamental type of determination, have been used in the correlations. The binary systems benzene–carbon tetrachloride and n-heptane–benzene were selected because of the availability of data on ordinary diffusion (27, 28) and thermal-diffusion coefficients (24, 26). On account of the many assumptions in the classical derivation of Furry, Jones, and Onsager (18); Waldmann (29); and de Groot (30) and in the more recent modification of Powers and Wilke (1), quantitative expressions more general in application were sought. The unintegrated dimensionless equation of mass con-

servation revealed the dimensionless groups and combinations thereof for treatment of operating data.

The study of ternary systems was intended for observation of continuous throughput operation with concentrated solutions for which a composition analysis for each component could be made. Previous investigations for concentrated three-component liquid mixtures are the closed-column experiments of Jones and Milberger (31) as well as of Begeman and Cramer (32).

THEORETICAL CONSIDERATIONS

Fundamental Theoretical Expressions

The theoretical relations are founded on the partial-differential equations of fluid mechanics which describe the
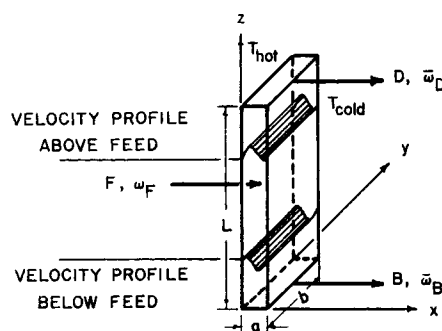

Fig. 1. Vertical flat plate, open thermal-diffusion column.

laws of conservation of mass, momentum, and energy. The nomenclature for the equations, fluxes, and transport coefficients is not given here, but it is identical to that in the review article by Bird (33). The coordinate arrangement is the three-dimensional, orthogonal system of Figure 1.

Application to the Vertical, Countercurrent Thermal Diffusion Column

Physical problem. The column consists of two flat plates, one at a high temperature and one at a low temperature, as described by Figure 1. Both plates of vertical length L and horizontal length b are spaced parallel to each other with a horizontal separation a. The quantity ω is the mass fraction of that component in a binary mixture which migrates toward the hot wall and the top of the column. The definition of $\bar{\omega}$ is

$$\bar{\omega} = \frac{1}{ab} \int_0^b \left[\int_0^a \omega dx \right] dy \quad (1)$$

Before beginning the dimensional analysis of the equations of change, the author omits some of the terms according to the following physical assumptions:

1. Steady state, realized experimentally
2. No chemical reaction, realized experimentally
3. Laminar flow, realized experimentally
4. Pressure and external force diffusion absent, realized experimentally
5. No viscous heat effects, negligible effects at low velocities
6. Insignificance of Dufour effects, radiation heat flux, and flux due to intrinsic energy carried by diffusing species
7. $p = p(z)$
8. $T = T(x)$
9. No variations in the y direction

The Dufour effect is neglected for lack of a descriptive expression as well as the probability that it is small (33). The equation for radiation heat flux is valid only if the flux is in equilibrium with the matter, a prerequisite which usually does not exist (33). This energy flux has been ignored in the past and is not accounted for here. Intrinsic energy carried by diffusing species is discussed in the application of the equation of energy balance in the analysis of the final correlations. The significance of its effect is not known (34).

Dimensionless relations. When analytical solutions of the partial differential equations of fluid mechanics are not easily found, the equations and their boundary conditions can serve as a guide to physical behavior. In the examination of the conservation equations Schlichting's (35) procedure for handling problems in fluid mechanics has been applied. The equations of change and their boundary conditions are placed in dimensionless form, and the resulting dimensionless groups of physical quantities are noted. The groups are the coefficients of the dimensionless derivatives and of other variable terms in the equations of change and their boundary conditions. These dimensionless groups of physical quantities are parameters of any analytical solution to the dimensionless equations of change, no matter how difficult that solution might be.

Above the feed point dimensionless variables are defined as follows:

$$x^* = x/a \quad \omega^* = \frac{\omega - \omega_F}{(\omega_D - \omega_F)_{cc}}$$

$$z^* = z/L$$

$$T^* = \frac{T - T_{cold}}{T_{hot} - T_{cold}} \quad v_z^* = v_z/(v_{av})_D$$

$$(2)$$

Although such a procedure is not entirely sound, for simplicity μ, $\mathcal{D}_{12}$ $\mathcal{D}_i^T$, ρ, and β are assumed constant. In

open-column operation above the feed point

$$(v_{av})_D = \frac{1}{a} \int_0^a (v_z)_D \, dx \qquad (3)$$

A similar relation would define $(v_{av})_B$ below the feed point. For closed-column cases above the feed point

$$\lim_{D \to 0} (v_{av})_D$$
$$= \lim_{D \to 0} \frac{1}{a} \int_0^a (v_z)_D \, dx \qquad (4)$$

with $(v_{av})_B$ being defined by a like relation below the feed point. Dimensionless numbers are formulated as follows:

$$(N_{Re})_D = \frac{a(v_{av})_D}{\mu} \rho \quad \text{Reynolds number}$$

$$N_{Gr} = \frac{a^3 \rho^2 \beta g \, \Delta T}{\mu^2} \quad \text{Grashof number}$$

$$N_{Sc} = \frac{\mu}{\rho \, \mathcal{D}_{12}} \quad \text{Schmidt number}$$

$$N_a = \frac{T_{av} \mathcal{D}_1^T}{\mathcal{D}_{12}} \quad \text{Thermal-diffusion}$$
$$\text{factor}$$

$$N_{\Delta T} = \frac{\Delta T}{T_{av}}$$
$$N_{a/L} = a/L \qquad (5)$$

The quantity T_{av} denotes the arithmetic mean temperature of the hot and cold walls, and ΔT is $T_{hot} - T_{cold}$.

For the given assumptions the equations of change and their boundary conditions have been set down by others (1, 18, 20, 30) and are repeated here in dimensionless form. The equation of energy conservation is

$$\frac{d^2 T^*}{dx^{*2}} = 0 \qquad (6)$$

with boundary conditions

$$T^* = 1 \quad \text{at } x^* = 0$$
$$T^* = 0 \quad \text{at } x^* = 1 \qquad (7)$$

The equation of momentum conservation can be simplified to

$$\frac{d^3 (v^*_z)_D}{dx^{*3}} = -\frac{N_{Gr}}{(N_{Re})_D} \qquad (8)$$

for which the boundary conditions are

$$(v_z^*)_D = 0 \quad \text{at} \quad x^* = 0, 1$$
$$\int_0^1 (v_z^*)_D \, dx^* = 0 \quad \int_0^1 (v_z^*)_D \, dx^* = 1$$
$$\quad \text{closed} \qquad \qquad \text{open}$$
$$\quad \text{column} \qquad \qquad \text{column}$$

The equation of mass conservation becomes

$$[v^*_z(x^*)]_D \frac{\partial \omega^*}{\partial z^*}$$

1 LEVEL INDICATOR
2 FEED FLOWRATOR
3 FLOW CONTROL VALVE
4 PRODUCT FLOWRATOR
5 SHUTOFF VALVES
6 COLD WALL THERMO-
   COUPLES
7 HOT WALL THERMO-
   COUPLE
8 SEPARATION CHAMBER
9 SAMPLE TAP
10 VARIABLE REACTANCE
11 WATER VALVE
12 WATER ORIFICE
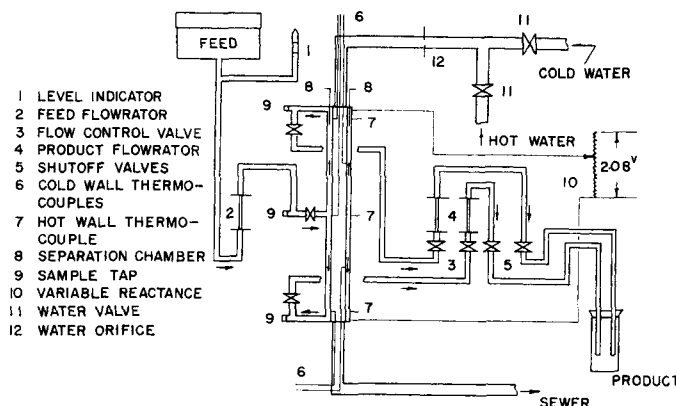
Fig. 2. Process flow scheme.

$$= \frac{1}{(N_{Re})_D N_{Sc} N_{a/L}} \frac{\partial^2 \omega^*}{\partial x^{*2}}$$
$$+ \frac{N_{a/L}}{(N_{Re})_D N_{Sc}} \frac{\partial^2 \omega^*}{\partial z^{*2}}$$
$$+ \frac{N_a N_{\Delta T}}{(N_{Re})_D N_{Sc} N_{a/L}}$$
$$\{1 - 2[(\overline{\omega}_D - \omega_F)_{cc} \omega^* + \omega_F]\} \frac{\partial \omega^*}{\partial x^*}$$

(10)

and has the boundary conditions

$$\frac{\partial \omega^*}{\partial x^*} + \left[\omega^* + \frac{\omega_F}{(\overline{\omega}_D - \omega_F)_{cc}} \right]$$
$$\{1 - [\omega^*(\overline{\omega}_D - \omega_F)_{cc} + \omega_F]\}$$
$$N_a N_{\Delta T} = 0 \quad \text{at} \quad x^* = 0, 1 \quad (11)$$

$$\frac{\overline{\omega}_D - \omega_F}{(\overline{\omega}_D - \omega_F)_{cc}} = \frac{\omega_F}{(\overline{\omega}_D - \omega_F)_{cc}}$$
$$\left(-1 + \int_0^1 v^*_z \, dx^* \right) + \int_0^1 \omega^* v^*_z \, dx^*$$
$$- \frac{N_{a/L}}{(N_{Re})_D N_{Sc}} \int_0^1 \frac{\partial \omega^*}{\partial z^*} \, dx^*$$
$$\text{at} \quad z^* = 1$$
$$\omega^* = 0 \quad \text{at} \quad z^* = z^*_F$$

above the feed point.

Solutions to the equations of energy and momentum conservation, Equations (6) and (8), have been established by previous investigators (1, 18, 20, 30), although not explicitly in this nomenclature. The integration of Equation (6) gives a linear variation of T with x. Above the feed point the solution for Equation (8) and its boundary conditions (9) becomes

$$[v^*_z(x^*)]_D = \frac{N_{Gr}}{(N_{Re})_D} f_1^*(x^*)$$
$$+ f_2^*(x^*) \qquad (12)$$

Although Equation (8) can easily be integrated, the general expression, Equation (12), suffices for this illustration. Substitution of Equation (12) for $[v_z^*(x^*)]_D$ in Equation (10) gives

$$\left[f_1^*(x^*) + \frac{(N_{Re})_D}{N_{Gr}} f_2^*(x^*) \right] \frac{\partial \omega^*}{\partial z^*}$$
$$= \frac{1}{N_{Gr} N_{Sc} N_{a/L}} \frac{\partial^2 \omega^*}{\partial x^{*2}}$$
$$+ \frac{N_{a/L}}{N_{Gr} N_{Sc}} \frac{\partial^2 \omega^*}{\partial z^{*2}} + \frac{N_a N_{\Delta T}}{N_{Gr} N_{Sc} N_{a/L}}$$
$$\{1 - 2[(\overline{\omega}_D - \omega_F)_{cc} \omega^* + \omega_F]\} \frac{\partial \omega^*}{\partial x^*}$$

(13)

For Equation (13) and its boundary conditions (11) an analytical solution of the form $\omega^* = \omega^*(x^*, z^*)$ is difficult because of the nonlinearity of both the partial differential equation and its boundary conditions. Although they have been carried through with ingenuity (1, 18, 29, 30), existing solutions are approximate and of the form $\omega^* = \omega^*(z^*)$.

With $N_{a/L}$ being of the order 10^{-3}, terms with coefficients of $(N_{a/L})/(N_{Gr} N_{Sc})$ were neglected in accordance with Schlichting's procedure for comparing dimensionless terms (35). Then any solution to Equation (13) and its boundary conditions must be a relation of the following type:

$$\omega^* = \omega^* \left[x^*, z^*, \frac{\overline{\omega}_D - \omega_F}{(\overline{\omega}_D - \omega_F)_{cc}}, \right.$$
$$(\overline{\omega}_D - \omega_F)_{cc}, \omega_F, \frac{(N_{Re})_D}{N_{Gr}},$$
$$\left. N_a N_{\Delta T}, \frac{N_a N_{\Delta T}}{N_{Gr} N_{Sc} N_{a/L}} \right]$$

(14)

Actually when physical properties of liquids in the column vary to some extent as they did here, particularly on the z axis, these properties might be described as dimensionless variables with boundary conditions corresponding to ρ_D, ρ_F, $(\mathcal{D}_{12})_D$, etc. Then dimensionless ratios such as ρ_D/ρ_F, etc., would become parameters of a solution to the dimensionless equations of

TABLE 1. BINARY SYSTEMS—OPERATING DATA FOR CLOSED COLUMN RUNS

System	Run	T_{av}, °C.	ΔT, °C.	L, cm.	a, cm.	$\overline{\omega}_D$	$\overline{\omega}_B$	ω_F
C_6H_6-CCl_4	I-C-2	39.8	33.5	183	0.043	0.968	0.004	0.337
	I-C-7	40.1	34.6	183	0.079	0.523	0.175	0.337
	I-C-9	40.2	34.3	36.6	0.079	0.930	0.899	0.903
nC_7-C_6H_6	II-C-1	33.5	36.0	183	0.043	0.965	0.004	0.577
	II-C-2	38.9	37.8	36.6	0.079	0.609	0.540	0.549

change. The experimental data have been examined only with the aid of the groups incorporated in Equation (14). The group $N_a N_{\Delta T}/(N_{Gr}N_{Sc}N_{a/L})$ multiplied by $9!/6!$ is identical with the quantity HL/K_c, which results from an integration of the Furry, Jones, and Onsager (18) transport equation for the vertical closed column in the steady state with longitudinal diffusion neglected.

EXPERIMENTAL WORK

Experimental Apparatus

Thermal-diffusion column. The column consisted of two concentric tubes. Except for physical dimensions, it was similar to the multiple port device described by Jones and Milberger (31), the annulus between the two tubes serving as the separation chamber. The tubes were of 304 stainless steel and formed a separation chamber 183 cm. in length. Annulus width, varied by use of alternate inside tubes, was either 0.043 or 0.079 cm. The outside tube was equipped with iron-constantan thermocouples, one at the center and one near each extremity of the tube. A nichrome heating element was wrapped on the outside tube, the inside wall of which served as the hot wall of the annulus. Each of the two tubes which could be used as the inside tube was equipped with five copper-constantan thermocouples installed at equal intervals in the tube wall as shown in Figure 2.

Cooling. The inside wall of the annular space was maintained at lower temperatures than the hot wall by cold water

passing in turbulent flow through one of the two center tubes available for this purpose. The temperature of the cold water could be varied by mixing it with hot water.

Feed and product lines. From the feed reservoir copper tubing led through a rotameter and stainless steel needle valve into one of the column ports. The two ports at the extremities of the column served as product ports to which copper tubing lines were connected. The product lines each led through stainless steel needle valves to upper and lower product-line rotameters and finally to a product reservoir. Construction materials exposed to the chemical systems studied were copper, brass, stainless steel, glass, and Teflon.

Instruments. A precision potentiometer indicated thermocouple potentials. For closed-column runs a six-point recording potentiometer was used during periods of absence by the operator. Although steady state throughput was indicated by rotameters, actual flow rates were measured by allowing liquid product to pass into small sealed bottles placed at the ends of the product lines, which otherwise emptied into a large collection bottle used for replenishing the feed reservoir. The small bottles were weighed on an analytical balance, collection time having been measured with a stop clock.

Power devices. A variable reactance controlled voltage across the column heating element. A household type of electric fan placed about 6 ft. from the center of the column and turning at a low speed helped to equalize the temperatures along the hot wall. At larger values of ΔT layers of Fiberglas insulation added near the

column extremities reduced the heat leak and temperature gradient between the midpoint and ends of the column.

Analytical equipment. The two binary systems were analyzed with a refractometer at 25°C. The first six runs with the ternary system were analyzed with a double-beam infrared recording spectrophotometer. The remaining ternary-system runs were analyzed with a vapor fractometer.

Equipment Operation

Continuous throughput runs. The increase in temperature of the cooling water was about 1.5°C. or less. The cold-wall temperature fluctuation was not greater than ± 0.1°C. Lengthwise the hot-wall variation in temperature was about 2°C. or less with fluctuations of about ± 0.2°C. at any one of the three thermocouple positions. The rotameter floats were held to a fluctuation of 2 to 4% of the indicated float level. A run was considered complete when liquid compositions at the ends of the product lines were the same as, or within 1% of, those at the sample taps on the upper and lower ends of the column.

Closed-column runs. Before such experiments were begun, the top and bottom product lines leading from the column were disconnected and the port caps designed for those ports were put in place, the connection between the center feed port and feed reservoir being maintained. After the annulus had been filled with liquid, the valve at the feed port was closed and operation commenced.

When the operator was absent, the average hot-wall temperature might fluctuate as much as 2°C. for ΔT values of about 35°C. For lower ΔT values the fluctuation in average hot-wall temperature was proportionally lower. Usually at the end of 48 hr. any change in $\overline{\omega}_D$—$\overline{\omega}_B$, the composition difference between the top and bottom of the column, would be less than 0.5% over a period of 12 hr.

DISCUSSION OF EXPERIMENTAL RESULTS

Binary Systems

Separation curves. Conditions which were varied were feed rate, temperature difference, wall spacing, column length, and feed concentration. For continuous throughput runs the quantity F was varied, with all other conditions remaining constant when each of the quantities ΔT, a, L, or F was studied. Curves describing $\overline{\omega}_D - \overline{\omega}_B$ vs. F appear elsewhere (36) and are similar in form to those reported by other investigators (1, 15). Samples of the closed column and continuous throughput operating results are given by Tables 1 and 2, in which ω refers to benzene in the system benzene–carbon tetrachloride and to n-heptane for the combination n-heptane–benzene.

Construction of correlations. The results for the two-component systems

TABLE 2. BINARY SYSTEMS—OPERATING DATA FOR CONTINUOUS THROUGHPUT RUNS

System	Run	D, g./sec.	B, g./sec.	L, cm.	a, cm.
C_6H_6-CCl_4	I-5	0.00210	0.00162	183	0.043
	I-12	0.00188	0.00197	183	0.043
	I-17	0.00383	0.00375	183	0.043
	I-51	0.00544	0.00528	183	0.079
	I-55	0.0109	0.0108	183	0.079
nC_7-C_6H_6	II-18	0.00456	0.00406	183	0.043
	II-24	0.00656	0.00658	183	0.079

System	Run	T_{av}, °C.	ΔT, °C.	$\overline{\omega}_D$	$\overline{\omega}_B$	ω_F
C_6H_6-CCl_4	I-5	39.8	33.6	0.560	0.157	0.328
	I-12	40.2	22.0	0.458	0.186	0.331
	I-17	39.7	9.4	0.350	0.310	0.331
	I-51	40.2	34.5	0.464	0.207	0.337
	I-55	40.2	34.5	0.443	0.234	0.337
nC_7-C_6H_6	II-18	35.5	35.0	0.597	0.520	0.562
	II-24	38.9	37.2	0.629	0.532	0.577
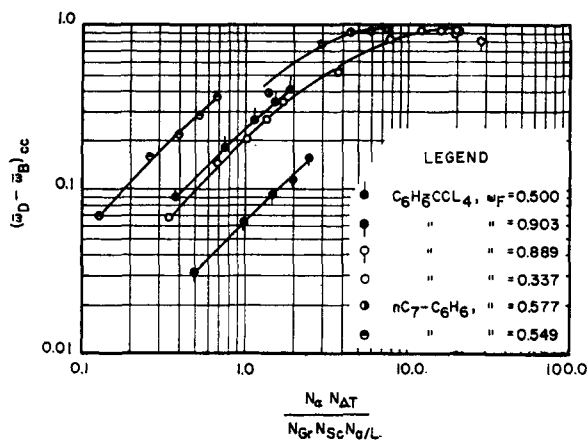
Fig. 3. Binary-system correlation of closed-column separations with parameter of feed composition.

ALL BINARY SYSTEM CLOSED COLUMN RUNS

$$10^3 \cdot \left[\, \omega_F(1-\omega_F)\right]^{1.3} \frac{N_a^{0.37} N_{\Delta T}}{N_{Gr} N_{Sc} N_{a/L}}$$

Fig. 5. Final closed-column correlation for two binary systems.

have been expressed in the form of correlations constructed from the dimensionless quantities included within Equation (14). Literature sources were utilized for the transport coefficients and density data which made the correlations possible. For the system benzene–carbon tetrachloride the thermal-diffusion coefficients had been determined in cells by Tichacek, Kmak, and Drickamer (26), the ordinary diffusion coefficients by Caldwell and Babb (27), the coefficients of shear viscosity by Thorpe and Rodger (37), and the density by Hubbard (38). For the system n-heptane–benzene the thermal-diffusion coefficients had been measured in cells by Huse, Trevoy, and Drickamer (24), the ordinary diffusion coefficients by Trevoy and Drickamer (28), and both viscosity and density by Heines (19). In the correlations absolute values of thermal-diffusion coefficients are used.

The closed-column correlation is discussed initially. In the experiments the composition measurements correspond to $\bar\omega_D$, $\bar\omega_B$, and ω_F. Therefore for

closed-column operation and for Equation (14)

$$\int_0^1 \omega^* \, dx^* = 1 \quad \text{at} \quad z^* = 1$$

and $(\bar\omega_D - \omega_F)_{cc}$ becomes a function of

$$\omega_F, \; N_a N_{\Delta T}, \; \frac{N_a N_{\Delta T}}{N_{Gr} N_{Sc} N_{a/L}} \quad (15)$$

a similar statement being possible for $(\omega_F - \bar\omega_B)_{cc}$ below the feed. In the dimensionless numbers average fluid properties have been taken at the

TABLE 3. BINARY SYSTEMS—THERMAL DIFFUSION FACTORS N_a USED IN CORRELATIONS

System	ω	T_{av}, °C.	N_a	Ref.
C_6H_6-CCl_4	0.113	40.0	1.37	26
	0.336	40.0	1.43	26
	0.670	40.0	1.48	26
nC_7-C_6H_6	0.561	38.7	0.342 to 0.371	24

arithmetic mean temperature and arithmetic mean composition for that portion of the column above or below the feed point. After a combination of dimensionless numbers had been computed for both top and bottom portions of the column, the arithmetic average of the two computations was used in the correlations. The group N_{Re}/N_{Gr} has not been considered, since the average value of N_{Re} is zero at any position z for the closed column operating in the steady state. The closed-column separation, $(\bar\omega_D - \bar\omega_B)_{cc}$, has been plotted vs. $N_a N_{\Delta T}/(N_{Gr} N_{Sc} N_{a/L})$ in Figure 3. The sets of points appear to be stratified according to the feed concentration ω_F. The quantity $\omega_F(1 - \omega_F)$ has been used to form the group $[\omega_F(1 - \omega_F)]^{1.3} N_a N_{\Delta T}/(N_{Gr} N_{Sc} N_{a/L})$ which has been plotted against $(\bar\omega_D - \bar\omega_B)_{cc}$ in Figure 4. Included is a closed-column separation reported by Trevoy and Drickamer (22) with a column 4 in. in height. The upper line corresponds to n-heptane–benzene and the lower to benzene–carbon tetrachloride.

$$10^3 \left[\, \omega_F(1-\omega_F)\right]^{1.3} \cdot \frac{N_a N_{\Delta T}}{N_{Gr} N_{Sc} N_{a/L}}$$

Fig. 4. Binary-system closed-column correlation with feed composition incorporated.

$$\frac{N_{Re}}{N_{Gr} N_a N_{\Delta T}}$$

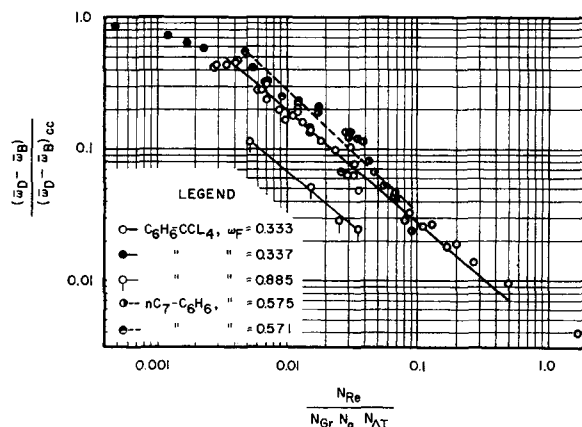Fig. 6. Correlation of continuous throughput separations with parameter of feed composition.
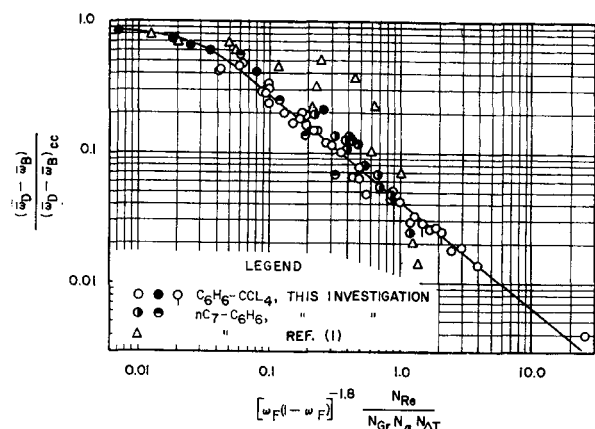
Fig. 7. Final binary-system continuous-throughput correlation with feed composition incorporated.

Fig. 9. Closed-column separation for ternary mixture; $a = 0.079$ cm.

The dimensional analysis of the equations of change gives N_a in either of the two groups $N_a N_{\Delta T}$ or $N_a N_{\Delta T}/(N_{Gr} N_{Sc} N_{a/L})$. If the terms of the equation of energy conservation containing partial molal enthalpy are omitted in the solution of the equations of change, N_a never occurs alone and cannot be obtained by intermultiplication of the groups which remain. It is possible to merge the two sets of points of Figure 4 by multiplying the abscissas of the points by a factor of $N_a^{-0.63}$ to give the result in Figure 5, which is presented with the reservation that N_a and $N_{\Delta T}$ occur only as $N_a N_{\Delta T}$ unless the terms containing partial molal enthalpy are accounted for.

The continuous throughput results have been related to the closed-column separations. In the theoretical discussion concentration was defined

$$\omega^* = \frac{\omega - \omega_F}{(\omega_D - \omega_F)_{cc}}$$

One reason is that in a series of runs for which the only factor varied is the feed rate, the closed column, steady state concentration difference between the top and feed point $(\omega_D - \omega_F)_{cc}$ is greater than that for any run with a throughput. Furthermore, Heines (15) has had success with a correlation by beginning at this point. He has introduced the following expression which is conveniently in terms of the product compositions of the experimental runs:

$$\frac{\overline{\omega}_D - \overline{\omega}_B}{(\overline{\omega}_D - \overline{\omega}_B)_{cc}} \quad (16)$$
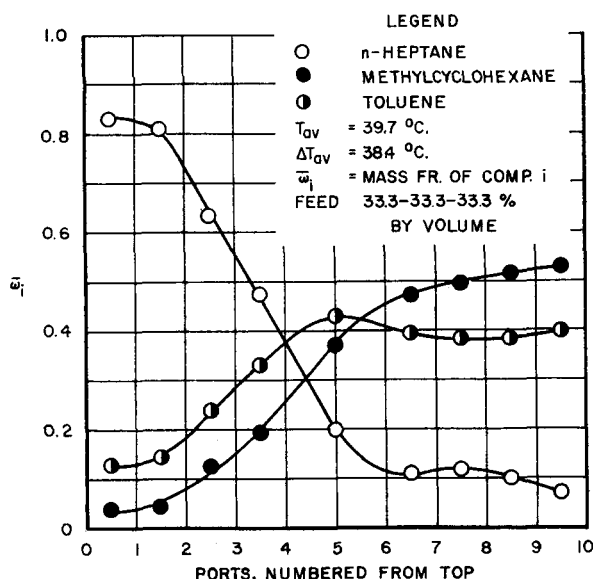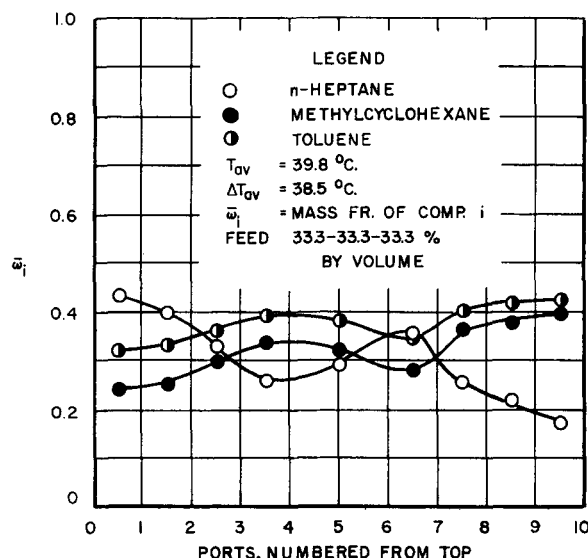
Except for four runs for which no values of $(\overline{\omega}_D - \overline{\omega}_B)_{cc}$ were determined, the concentration data for all the continuous-throughput, two-component runs have been placed in the form of the ratio (16).

Since feed rate was varied in all of the sets of continuous-throughput runs, the dimensionless group into which the feed rate could be incorporated, N_{Re}/N_{Gr}, was investigated initially. The ratio has been averaged in the following manner:

$$\frac{N_{Re}}{N_{Gr}} = \frac{1}{2}\left[\left(\frac{N_{Re}}{N_{Gr}}\right)_D + \left(\frac{N_{Re}}{N_{Gr}}\right)_B\right] \quad (17)$$

In a series of runs in which the ratio of product rates, B/D or D/B, in the two sections of the column was varied with F being approximately constant, the Powers (20) data for ratios in the range 1 to 1 through 1.5 to 1 show a variation in rectification between top and bottom fractions of perhaps several per cent of total rectification. In this investigation similar behavior was noted, and an attempt was made to keep the ratios of product rates as close to unity as possible.

As N_{Re}/N_{Gr} was increased, the ratio $(\overline{\omega}_D - \overline{\omega}_B)/(\overline{\omega}_D - \overline{\omega}_B)_{cc}$ decreased for both binary systems with considerable scattering of points for benzene–carbon tetrachloride. The plots are given elsewhere (36). Although the points for one system appeared to be displaced from those of the other by a factor almost equal to N_a, the ratio $(\overline{\omega}_D - \overline{\omega}_B)/(\overline{\omega}_D - \overline{\omega}_B)_{cc}$ has been plotted vs. $N_{Re}/(N_{Gr} N_a N_{\Delta T})$ for both binary systems in Figure 6, since N_a occurs as $N_a N_{\Delta T}$ in the dimensionless groups. In Figure 6 between the

Fig. 8. Closed-column separation for ternary mixture; $a = 0.043$ cm.

abscissa values of 0.0025 and 1, the straight lines are least-squares representations of the data. The four points toward the lower left-hand region of Figure 6 correspond to runs for a dilute solution of carbon tetrachloride in benzene. The forms D/H and B/H which occur in the Furry, Jones, and Onsager developments (18) include a constant 6!. Except for this constant, the combination $N_{Re}/(N_{Gr} N_a N_{\Delta T})$ is similar to D/H and B/H.

The quantity $\omega_F (1 - \omega_F)$ has been used together with Figure 6 to form the combination $[\omega_F(1 - \omega_F)]^{-1.8} N_{Re}/N_{Gr} N_a N_{\Delta T})$ which is the abscissa of Figure 7. The n-heptane–

LEGEND

O   n-HEPTANE
●   METHYLCYCLOHEXANE
◑   TOLUENE
T_{av} = 39.3 °C.
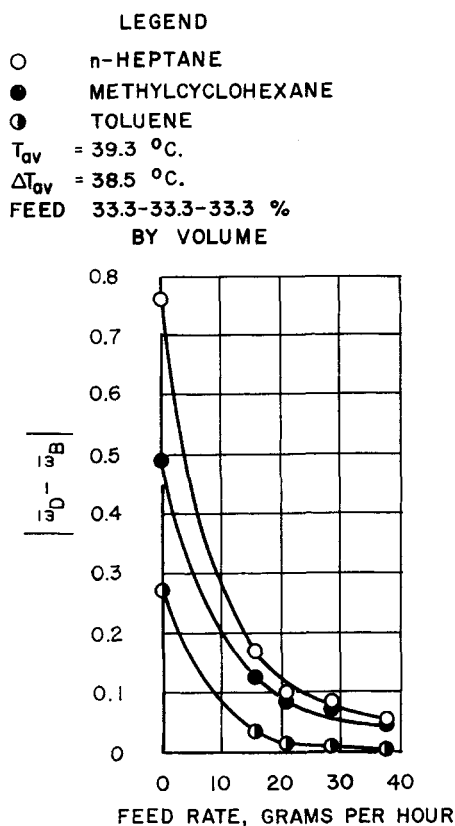ΔT_{av} = 38.5 °C.
FEED   33.3-33.3-33.3 %
BY VOLUME

Fig. 10. Continuous-throughput separations for ternary mixture; $a = 0.043$ cm.

benzene points of Powers and Wilke (1), also shown on Figure 7, were not included in the least-squares computation for the straight portion of the line. The values of $(\omega_D - \omega_B)_{cc}$ for the Powers and Wilke points were estimated from the closed-column correlation of Figure 4.

Analysis of correlations. In Figures 4 and 5 the variation in N_{Gr} was about twenty-five-fold, N_{Sc} 1.7 fold, N_a fourfold, $N_{a/L}$ ninefold, and ω_F from 0.34 to 0.90 fold. For the straight portion of the curve in Figure 5

$$N_a = 1.2 \times 10^{-9} \left(\frac{N_{Gr} N_{Sc} N_{a/L}}{N_{\Delta T}} \right)^{2.7}$$

$$\frac{(\omega_D - \omega_B)^{2.8}_{cc}}{[\omega_F(1 - \omega_F)]^{3.5}} \quad (18)$$

The possible error in N_a if determined from closed-column experiments as conducted in this investigation can be as high as 30%; the most probable error is about 16%. For definitions of these errors see reference 39.

One shortcoming of the continuous-throughput correlation is that the exponent −1.8 on $\omega_F(1 - \omega_F)$ is heavily influenced by the points corresponding to runs conducted with dilute solutions. Also in the experiments no assurance was made that the feed was equally distributed about the circumference of the annulus. Although the arithmetic mean circumference b does not enter into the group $N_{Re}/(N_{Gr}N_a N_{\Delta T})$, it is necessary to use b to compute N_{Re} from the top and bottom product rates. Short-circuiting would cause the effective b to be smaller than its true value if any tendency exists for the solution concentration to vary circumferentially. This problem has been studied by Jones (40), but nothing quantitative appears to have been established.

For the convection effect due to the x direction concentration gradient it is possible to define a Grashof group different from that given by Boelter (41). It is

$$N^\omega_{Gr} = \frac{a^3 \rho^2 \beta_\omega g (\Delta\omega)_{\text{constant } z}}{\mu^2} \quad (19)$$

In neither the continuous throughput nor the closed-column correlations does the group N^ω_{Gr} appear. An accurate measurement of the derivative $\partial\omega^*/\partial x^*$ would be essential for calculating N^ω_{Gr}. By the use of theoretical relations of de Groot (30) for the system benzene–carbon tetrachloride the ratio N^ω_{Gr}/N_{Gr} was estimated to be about 0.10. Since the effect of N^ω_{Gr} must be greater for benzene–carbon tetrachloride than for n-heptane–benzene, the curves of Figure 4 probably should be closer together, which would modify the exponent on N_a for Figure 5. Dimensionless terms such as $\dfrac{N_{Pr}}{N_{Sc}N_{\Delta T}}$

$$\left[\frac{1}{M_1 C_p T_{av}} \frac{\partial H_1}{\partial x^*} \right] \text{ and } M_1/M_2 \text{ arise}$$

(36) when partial molal enthalpy is treated in the dimensionless equation of energy conservation, partial molal enthalpies being a function of temperature, pressure, and composition (42). How these groups would affect the correlations is not known. As has been pointed out, variations in physical properties such as μ, $\mathcal{D}_{12}$, etc., introduce additional parameters which have not been included in the dimension-

less-group treatment. In the correlations the absolute value of N_a is used. In the strict meaning N_a would have a negative value when that component which migrates toward the hot wall is considered.

Ternary System

Separation curves. For the ternary combination n-heptane–methylcyclohexane–toluene the factors studied were F and a. The closed-column runs are reported in Figures 8 and 9. When placed in the thermal-diffusion column under closed-column conditions 50 mole % methylcyclohexane–toluene mixtures had little tendency to separate, a result observed by others (31, 32). Figures 8 and 9 show an improvement in the rectification of methylcyclohexane and toluene by the addition of the third component n-heptane.

For the continuous-throughput runs an attempt was made to maintain the product rates as nearly alike as possi-

LEGEND

O   n-HEPTANE
●   METHYLCYCLOHEXANE
◑   TOLUENE
T_{av} = 39.2 °C.
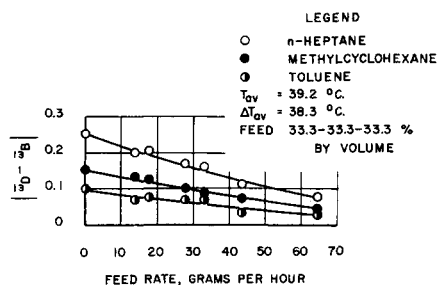ΔT_{av} = 38.3 °C.
FEED   33.3-33.3-33.3 %
BY VOLUME

Fig. 11. Continuous-throughput separations for ternary mixture; $a = 0.079$ cm.

ble for each run. The absolute value of the difference in mass fraction between the top and bottom ports for each component in the mixture has been plotted vs. feed rate in Figures 10 and 11. At high feed rates the separations tended to be smaller. The separations for larger annulus width were greater than those for smaller annulus width at the higher throughputs. This behavior for annulus width and throughput is similar to that observed with binary systems.

CONCLUSIONS

For the binary solutions benzene–carbon tetrachloride and n-heptane–benzene and for the conditions under which they were studied in this investigation it is possible to correlate thermal-diffusion–column operating variables on the basis of thermal-diffusion coefficients determined in cell experiments. The correlating combinations of dimensionless groups can be obtained from the equations of conservation and their boundary conditions in dimensionless form. With the

ternary system n-heptane–methylcyclohexane–toluene, variations in feed rate and wall spacing gave results similar to those observed in binary systems.

NOTATION

a = distance between hot and cold walls

B = bottom product rate, mass per unit time

b = arithmetic mean circumference of hot and cold walls forming an annulus in a cylindrical thermal-diffusion column or horizontal width of heat transfer plates for a flat column

C_p = heat capacity per unit mass at constant pressure

D = top product rate, mass per unit time

$\mathcal{D}_{12}$ = concentration diffusion mass transport coefficient in a binary mixture of components 1 and 2

$\mathcal{D}_1{}^T$ = thermal diffusion mass transport coefficient for component 1 in a binary mixture

F = feed rate, mass per unit time

f^* = arbitrary function, dimensionless

g = acceleration of gravity

H = thermal-diffusion–column parameter from physics literature

H_1 = partial molal enthalpy of component 1 in a binary mixture

K_c = thermal-diffusion–column parameter from physics literature

L = vertical length of column

M = molecular weight

T = absolute temperature

T_{av} = arithmetic mean temperature of hot and cold walls

v = mass average velocity

x = Cartesian coordinate perpendicular to heat transfer surfaces

y = horizontal cartesian coordinate parallel to the heat transfer surface

z = Cartesian coordinate parallel to the heat transfer surface and perpendicular to the x, y plane

Greek Letters

β = volumetric coefficient of thermal expansion

β_ω = volumetric coefficient of expansion from concentration variation

μ = coefficient of shear viscosity

ρ = mass density

ω = mass fraction of that component in a binary mixture which migrates toward the warm wall and is enriched toward the top of the column

Dimensionless Variables

$T^* = (T - T_{cold})/(T_{hot} - T_{cold})$

$v^*{}_z = v_z/v_{av}$

$x^* = x/a$

$z^* = z/L$

$\omega^* = (\omega - \omega_F)/(\omega_D - \omega_F)_{cc}$

Dimensionless Numbers

N_{Gr} = Grashof number for heat transfer

$N^\omega{}_{Gr}$ = Grashof number for mass transfer

N_{Re} = Reynolds number

N_{Sc} = Schmidt number

N_{Pr} = Prandtl number

N_a = thermal-diffusion factor (called α in physics literature)

$N_{a/L}$ = a/L, geometric factor

Subscripts

B = quantity pertaining to the bottom product

D = quantity pertaining to the top product

F = quantity pertaining to the feed

1 = component in a binary mixture which migrates toward hot wall

2 = component in a binary mixture which migrates toward cold wall

cc = closed column

LITERATURE CITED

1. Powers, J. E., and C. R. Wilke, *A.I.Ch.E. Journal*, **3**, 213 (1957).
2. Clusius, Karl, and G. Dickel, *Naturwissenschaften*, **26**, 546 (1938).
3. Jones, A. L., U. S. Patent 2,720,976 (1955).
4. ———, U.S. Patent 2,720,979 (1955).
5. ———, U. S. Patent 2,723,034 (1955).
6. ———, and P. S. Fay, U. S. Patent 2,723,033 (1955).
7. Jones, A. L., R. A. Gardner, and C. W. Seelbach, U. S. Patent 2,720,978 (1955).
8. Jones, A. L., and E. C. Hughes, U. S. Patent 2,734,633 (1956).
9. Jones, A. L., and E. C. Milberger, U. S. Patent 2,712,386 (1955).
10. Jones, A. L., C. W. Seelbach, and David Frazier, U. S. Patent 2,720,975 (1955).
11. Gary, J. H., U. S. Patent 2,751,082 (1953).
12. Thomas, J. W., U. S. Patent 2,720,980 (1955).
13. Sullivan, L. J., T. C. Ruppel, and C. B. Willingham, *Ind. Eng. Chem.*, **47**, 208 (1955).
14. *Ibid.*, **49**, 110 (1957).
15. Heines, T. S., Jr., O. A. Larson, and J. J. Martin, *ibid.*, p. 1911.
16. Thomas, W. J., and S. B. Watkins, *Chem. Eng. Sci.*, **5**, 34 (1956).
17. *Ibid.*, **6**, 26 (1956).
18. Furry, W. H., R. C. Jones, and L. Onsager, *Phys. Rev.*, **55**, 1083 (1939).
19. Heines, T. S., Jr., Ph. D. thesis, Univ. Mich., Ann Arbor (1954).
20. Powers, J. E., UCRL 2618, U. S. Atomic Energy Comm., Washington, D. C. (1954).
21. Prigogine, I., L. de Brouckere, and R. Amand, *Physica*, **16**, 577 (1950).
22. Trevoy, D. J., and H. G. Drickamer, *J. Chem. Phys.*, **17**, 1120 (1949).
23. Velden, P. F., van, H. G. P. van der Voort, and C. J. Gorter, *Physica*, **12**, 151 (1946).
24. Huse, E. S., D. J. Trevoy, and H. G. Drickamer, *Rev. Sci. Instr.*, **21**, 60 (1950).
25. Thomaes, G., *Physica*, **17**, 885 (1951).
26. Tichacek, L. J., W. S. Kmak, and H. G. Drickamer, *J. Phys. Chem.*, **60**, 660 (1956).
27. Caldwell, C. S., and A. L. Babb, *ibid.*, 51 (1956).
28. Trevoy, D. J., and H. G. Drickamer, *J. Chem. Phys.*, **17**, 1117 (1949).
29. Waldmann, Ludwig, *Z. Physik*, **114**, 53 (1939).
30. Groot, S. R. de, *Physica*, **9**, 801 (1942).
31. Jones, A. L., and E. C. Milberger, *Ind. Eng. Chem.*, **45**, 2689 (1953).
32. Begeman, C. R., and P. L. Cramer, *ibid.*, **47**, 202 (1955).
33. Bird, R. B., in "Advances in Chemical Engineering," Vol. 1, Academic Press, New York (1956).
34. ———,private communication (1956).
35. Schlichting, Hermann, "Boundary Layer Theory," pp. 248-253, Pergamon Press, New York (1955).
36. Longmire, D. R., Ph. D. thesis, Univ. Wis., Madison (1957).
37. Thorpe, T. E., and J. W. Rodger, *J. Chem. Soc. (London)*, **71**, 360 (1897).
38. Hubbard, J. C., *Z. Phys. Chem.*, **74**, 207 (1910).
39. Sherwood, T. K., and C. E. Reed, "Applied Mathematics in Chemical Engineering," 1 ed., pp. 368-378, McGraw-Hill, New York (1939).
40. Jones, A. L., U. S. Patent 2,720,977 (1955).
41. Boelter, L. M. K., *Trans. Am. Inst. Chem. Engrs.*, **39**, 557 (1943).
42. Hougen, O. A., K. M. Watson, and R. A. Ragatz, "Chemical Process Principles," Part 1, 2 ed., Wiley, New York (1954).