boundary at a finite distance from the sphere surface has been developed.

ACKNOWLEDGMENT

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The Forgotten Effect in Thermal Diffusion

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The basic equations that describe the thermal diffusion column, including the forgotten effect, were solved numerically. When the density of the liquid in the column varies with concentration, the effect is important in transient batch operation of columns, increasingly so as the wall spacing decreases, but it has no influence at the steady state. Experimental work corroborated the theoretical results.

According to the theory, the instances of concentration reversal reported in the literature cannot be the result of the forgotten effect; the fluids involved could not have had the necessary properties. Attempted duplications of these instances in careful experiments yielded normal behavior. However, theoretical and experimental work on a column with a deliberately nonconstant wall spacing indicated that concentration reversals could occur in the complete absence of any forgotten effect contribution.

The basic theory of the thermal diffusion column, first presented in 1939 (*3, 5*), led to operating equations for the column that have been moderately successful in predicting the effects of the variables on the separations obtained in binary systems of liquids or gases, in both batch and continuous operation. One of the many simplifying assumptions made in these original derivations was that the density of the fluid used in the flow equation is a function of temperature only and not of concentration. In 1943, De Groot et al. (*4*) included the effect of concentration on density in an approximate way. Interest in the effect of concentration was really fired, however, when Prigogine et al. (*14*) in 1950 published a bizarre set of curves of concentration vs. time from batch operation of a column in which the difference in concentration between top and bottom started in one direction, slowed, and then went in the opposite direction, giving separations opposite from the original direction! This behavior, which we call *concentration reversal*, was attributed by them to the influence of concentration on density. Prigogine's article in French was accompanied by an abstract in English, in which *l'effèt oublié*, the term used by both De Groot and Prigogine for the hitherto *neglected* effect of concentration, was translated as the forgotten effect. Jones and Milberger (*8*) used this name in their 1953 article and the amusing appellation has stuck.

Since Prigogine's article, Jones and Milberger (*8*) and John and Bent (*7*) have observed concentration reversal (not to be confused with the forgotten effect), and these

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and many review articles on thermal diffusion have accepted Prigogine's qualitative argument that the forgotten effect is the cause. De Groot et al. (*4*), von Halle (*16*), Baldeschwieler (*1*), and Horne and Bearman (*6*) have incorporated the forgotten effect into the operating equations in an approximate way, but to date there has been no rigorous derivation and nothing that could touch the case of concentration reversal.

The objectives of our work were: to perform numerical solutions of the basic differential equations with the forgotten effect included, to conduct experiments on various columns to check the predictions of the numerical solutions, and to explain the concentration reversals reported in the literature by theoretical and experimental means. We succeeded in the first two and for the third have evidence that tends to refute the customary explanation.

QUALITATIVE DESCRIPTION OF THE FORGOTTEN EFFECT

Between the parallel plates or annular tubes of a thermal diffusion column, the horizontal heat flux sets up a density gradient. The fluid flows by natural convection up the hot wall and down the cold; if viscosity is assumed constant, the velocity profile is the shape of the zero-time curve in Figure 1. At the same time, thermal diffusion proceeds in the horizontal direction, with component *A* diffusing to the hot wall, as shown in Figure 2, *first phase.* *A* is carried to the top of the column and a vertical concentration gradient develops.

If *A* has a smaller density than *B*, the horizontal concentration gradient increases the density gradient (a positive forgotten effect) and the convection velocities become

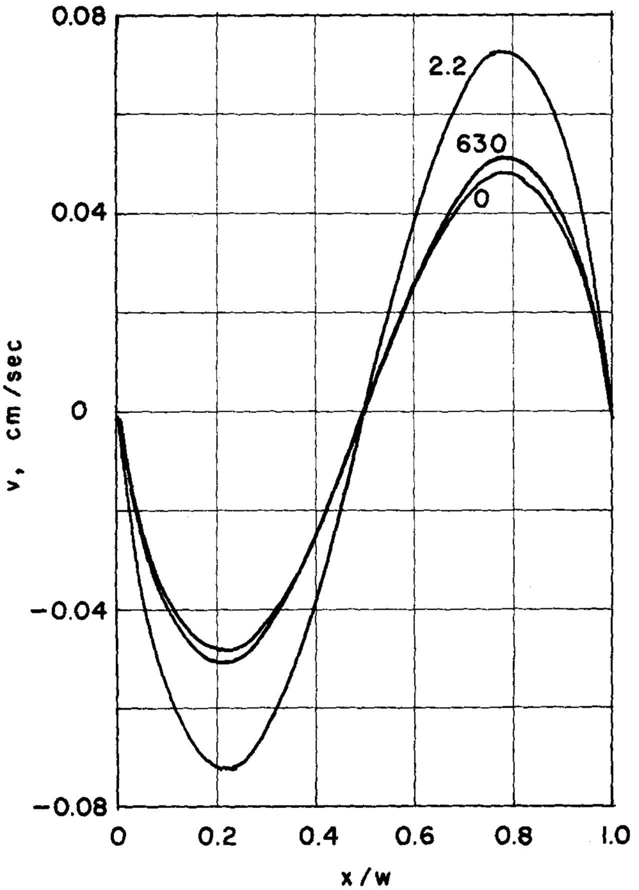
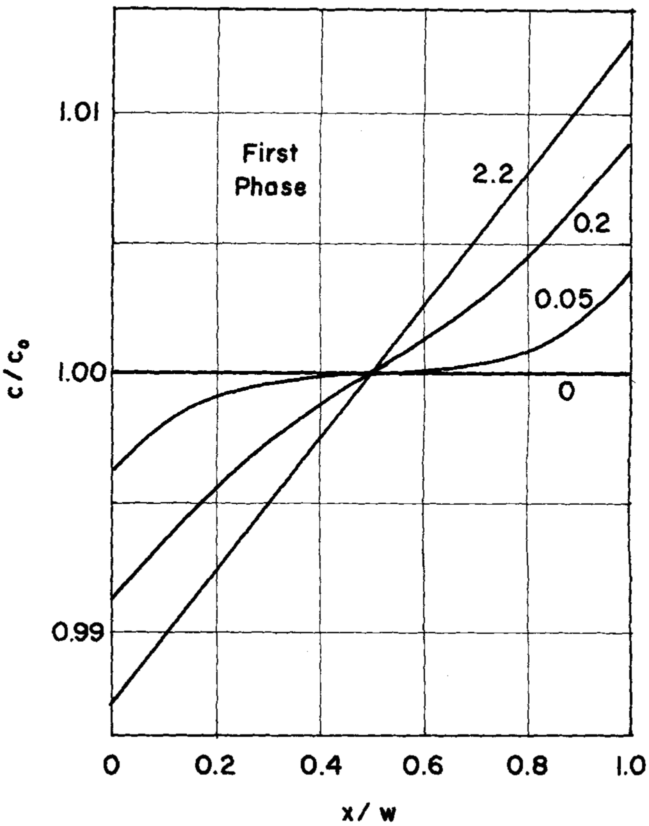


Fig. 1. Variation of convection velocity *v* with horizontal position *x* half way up the column, for a positive forgotten effect ($\gamma = +0.5$). Numbers by the curves are elapsed time in minutes.



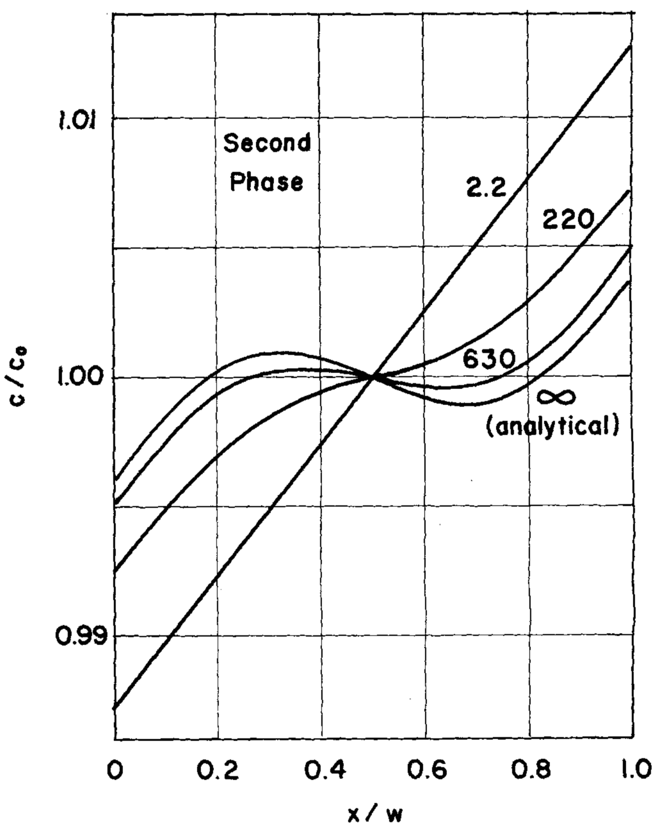


Fig. 2. Variation of concentration *c* with *x* for the same case as in Figure 1. Numbers by the curves are elapsed time in minutes.

greater than without the effect. This can be seen in the 2-min. curve of Figure 1. From the ordinary theory (*11*), one would expect that this increased convection velocity would increase the rate of approach to steady state and decrease the steady state separation. (We find that the first happens and the second does not, as explained below.)

If A has a larger density than B, the horizontal concentration gradient decreases the density gradient (a negative forgotten effect), and the convection velocities become less. One would expect this to lengthen the approach to steady state (which it does) and to increase the steady state separation (which it does not). Furthermore, if the effect is large enough, it is conceivable that the convection currents might eventually reverse themselves and yield flow down the hot wall and up the cold. This is Prigogine's widely circulated explanation of concentration reversal (theoretically possible, but unobservable practically, as noted below).

In this paper we present our theoretical work and the conclusions that can be drawn from it, the experimental corroboration of the theory, and then take up the concentration reversals reported in the literature.

THEORETICAL WORK

The Numerical Solution of the Basic Equations

The basic differential equation for the natural convection flow pattern is

$$\mu \frac{\partial^3 v}{\partial x^3} = g \frac{\partial \rho}{\partial x} \tag{1}$$

Density is a function of both temperature and concentration, so that

$$\frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial T} \frac{dT}{dx} + \frac{\partial \rho}{\partial c} \frac{\partial c}{\partial x} \tag{2}$$

The second term in Equation (2) is the effect ordinarily forgotten, but included here.

In writing equations for mass flux, certain terms ordinarily left out must be included, because we want to simulate concentration reversal, which occurs early in the transient period. During this period, the horizontal concentration profile changes drastically and is not the same at various heights at any one time. Without the forgotten effect, this is of no consequence, but with the forgotten effect, it means that vertical velocity changes with height, and thus horizontal velocity is not zero, as ordinarily assumed. These deliberations yield the basic differential equation

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) - \frac{\alpha \, \Delta T \, D}{w \overline{T}} \frac{\partial c(1-c)}{\partial x} - v \frac{\partial c}{\partial y} - u \frac{\partial c}{\partial x} \tag{3}$$

which is to be solved numerically along with Equation (1).

TABLE 1. PARAMETERS CHARACTERIZING THE THEORETICAL CURVES

Curve shown in Figure	Wall spacing w, in.	Column height L, ft.	$HL/2K$	K, (g.) (cm.)/sec.	γ, relative forgotten effect
1, 2	0.018	1.64	0.731	0.0068	+0.50
3	0.018	1.64	0.731	0.0068	+0.50, 0, −0.50
4	0.040	5.08	0.231	0.412	+0.84
5	0.040	5.08	0.254	1.648	−1.30
7	0.018	5.08	4.23	0.0070	+0.77

We employed the usual scheme in solving these equations without the forgotten effect, namely, using Equation (3) for a solution of c as a function of x only, assuming that the functions of y are given and constant, and writing the so-called transport equation for transport of A in the vertical direction. Using the average concentration $\bar{c}$ at any height, we define the transport τ as

$$\tau = B\rho \int_0^w v\,\bar{c}\,dx - BD\rho \int_0^w \frac{\partial \bar{c}}{\partial y}\,dx \tag{4}$$

and a mass balance on a differential element of height gives

$$\frac{\partial \tau}{\partial y} + B\rho w \frac{\partial \bar{c}}{\partial t} = 0 \tag{5}$$

The boundary conditions for these equations are: c and $\bar{c}$ are uniform at the start, a velocity profile is instantaneously established, horizontal mass flux is zero at the walls all the time. For the column without reservoirs, τ is zero at top and bottom; for the column with reservoirs, τ is related to the change of c in the reservoirs with time.

With the proper mesh sizes and time increments, stable numerical solutions were obtained. The programs were checked by insertion of zero forgotten effect, and the results agreed well with the standard analytical solutions for columns with or without reservoirs.

The theoretical curves that follow can be characterized by three parameters, $HL/2K$ and K, which are both familiar from the standard treatment, and a new parameter γ, which gives the relative importance of the forgotten effect with respect to the effect of temperature on density for maximum horizontal c gradient (whether or not the forgotten effect actually assumes this importance depends on the column dimensions, as noted below). The definitions of these parameters are

$$H = \frac{g\,\alpha\,\rho\,\beta\,w^3\,B\,(\Delta T)^2}{6!\,\mu\,\overline{T}} \tag{6}$$

$$K = \frac{g^2\,\rho\,\beta^2\,w^7\,B\,(\Delta T)^2}{9!\,D\mu^2} + D\rho w B \tag{7}$$

$$\gamma = -\frac{\alpha\,c(1-c)}{\beta\,\overline{T}} \frac{\partial \rho}{\partial c} \tag{8}$$

A positive value of γ means a positive forgotten effect contribution, in which the effect of concentration augments the effect of temperature on density. Values of these parameters, along with some others of interest, are shown in Table 1 for each of the theoretical cases presented. Fluid properties used were usually those of cyclohexane-carbon tetrachloride, except for γ, which was sometimes changed from its proper value for this system to give cases of theoretical interest.

Development of Concentration Profiles During the Transient Period

To understand the influence of the forgotten effect, one must distinguish between two phases in the transient operation of the batch column. For a column with small wall spacing, the horizontal concentration profiles develop very rapidly over essentially the entire height of the column in the manner indicated in Figure 2, *first phase*. This first phase development is the same regardless of the sign of the forgotten effect, since it is entirely due to horizontal diffusion processes, having taken place in a time too short to be affected by the vertical convection. As the vertical concentration gradient develops, fluid is carried by convection up the hot wall into an area richer in A, while at the cold wall fluid is carried into an area less rich in A.

This causes the horizontal concentration profile to be depressed on the hot side and elevated on the cold, following the development shown in Figure 2, *second phase,* and to arrive ultimately at the doubly curved, steady state profile.

The qualitative nature of the curves in the second phase of Figure 2 is the same for positive, zero, or negative γ (providing that γ is not negative enough to cause reversal), but the times at which the curves occur vary with γ. For instance, the curve for $\gamma = 0.5$ and $t = 220$ min., shown in Figure 2, is the same as the curve for $\gamma = 0$ and $t = 340$ min., and the same as the curve for $\gamma = -0.5$ and $t = 630$ min. Furthermore, as time approaches infinity, curves for any γ (barring cases of reversal) approach the limit shown in Figure 2, which was calculated from the analytical solution for $\gamma = 0$ (*11*). The curves at the ends of the column have this same shape for most of the transient period. In other words, the forgotten effect influences the transient behavior but has negligible influence on the horizontal gradient at steady state.

However, in a column with a large wall spacing, say 0.07 in., processes in the vertical direction are very rapid with respect to the horizontal, the vertical profile develops rapidly over the entire column, and the horizontal profiles evolve directly from the flat start into the doubly curved, steady state profile without ever approaching the linear limit shown in Figure 2. The forgotten effect has almost no influence in this case.

Influence of the Forgotten Effect on the Transient Separation Curves

Transient curves for a small wall spacing are shown in Figure 3 for cases which do not lead to concentration reversal. As the horizontal concentration profile develops, it influences the velocity profile more and more, reaching its maximum influence when the concentration profile most closely approaches the linear limit of Figure 2. As the vertical concentration profile begins to develop throughout the column, the horizontal concentration profile begins to drop toward its steady state limit; when that limit is reached, the forgotten effect has no perceptible influence. The initial and final velocity profiles are almost identical and the theoretical concentration curves for the three forgotten effect cases shown in Figure 3 converge at long times. The reason for this is that the concentration profile at steady state is doubly curved, which greatly reduces the concentration gradient as compared to earlier times

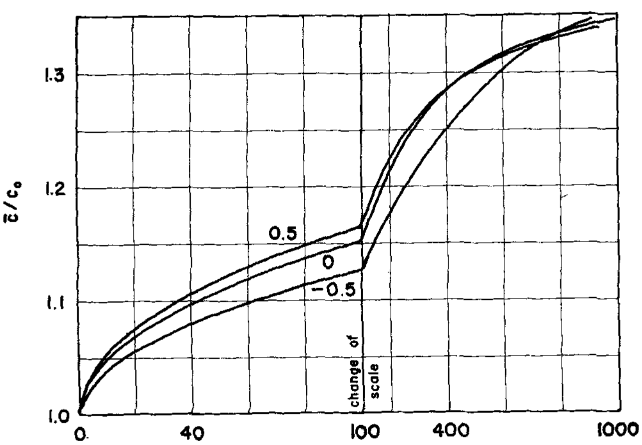


Fig. 3. Influence of the forgotten effect on the transient behavior of the concentration at the top for a small wall spacing. Numbers by the curves are values of γ. The curve for $\gamma = +0.5$ is the same case as in Figures 1 and 2 and the other cases differ only in the value of γ.

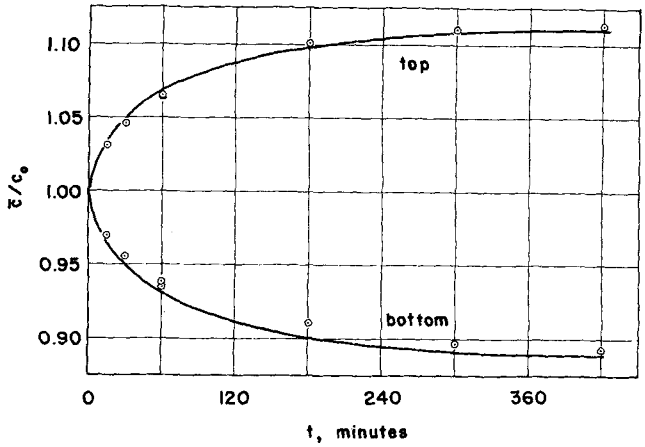


Fig. 4. Transient separation data, cyclohexane-carbon tetrachloride. The curves are the theoretical predictions for $\alpha = 1.82$.

and thus diminishes the importance of the forgotten effect. This means that calculations concerned only with the steady state separation in a batch column can be performed by using the classical equations in the literature without any regard for the forgotten effect!

With a very large spacing, vertical processes are so rapid that the horizontal profiles tend to progress directly from the initial flat state to the steady state form, neither of which has an effect on the velocity profiles, and the forgotten effect has almost no influence on either the transient or steady state separation.

These results apply to liquids in columns with or without reservoirs, down to a wall spacing of 0.010 in.

EXPERIMENTAL VERIFICATION

To check the computer solution against experiment, the system cyclohexane-carbon tetrachloride (which has a large positive forgotten effect) was run in a column 5 ft. high with a 0.04-in. wall spacing (*9*). This size column allows precise data to be obtained easily during the transient period and at the steady state. Data were obtained for three conditions: 50 wt. % cyclohexane, ΔT of 10°C.; 50% cyclohexane, ΔT of 19°C.; and 20% cyclohexane, ΔT of 10°C. The data for the first condition are shown in Figure 4; the demonstration is not significantly different for the other conditions. Agreement with the theoretical curve is good.

For the computer solution, properties of this system listed in the literature were used (some are shown in Table 1), except that α was treated as an arbitrary parameter to obtain a good fit with the data. The values of α obtained were 1.82 at 50%, independent of ΔT, and 1.74 at 20%. These values are within 5% of those calculated from the column data of Horne and Bearman (*6*) for this system (by our theory, not theirs) and within 5% of the value obtained by Korsching (*10*) from a thermal diffusion cell.

CONCENTRATION REVERSAL

According to the theory, if concentration reversal is to be caused by the forgotten effect, γ must be sufficiently negative and the wall spacing must be in a suitable range. At the beginning of the process, the velocity profile is normal, shown by the zero-time curve in Figure 5. As the horizontal concentration profile begins to develop, A is carried up the hot wall and begins to accumulate at the top. Before the horizontal profile reaches the linear limit, the forgotten effect is sufficient to exceed the normal temperature effect and the convection flow reverses. The

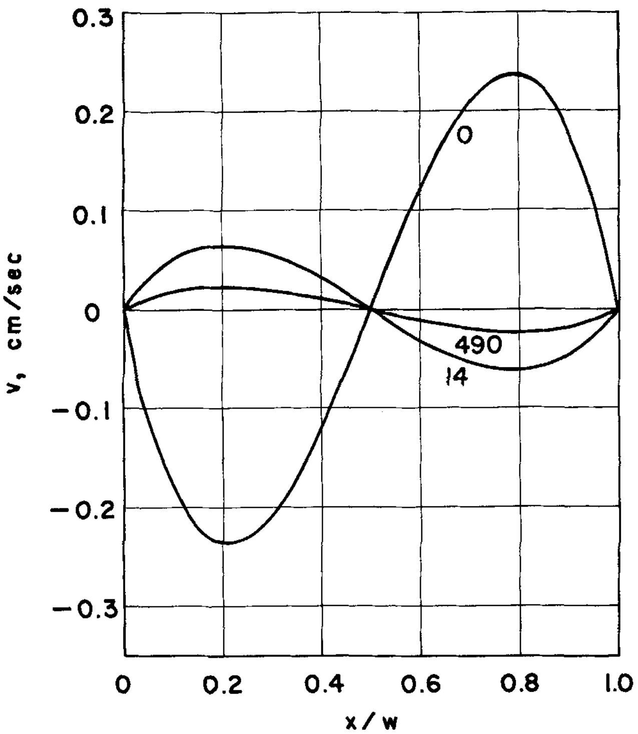


Fig. 5. Variation of v with x for a case in which concentration reversal occurs. Numbers by the curves are elapsed time in minutes.

horizontal concentration profile continues to develop to the linear limit and the velocity profile reaches a maximum in the negative direction at about 14 min., as shown in Figure 5. *A* is now carried down the hot wall and begins to accumulate at the bottom. The reverse vertical profile that now develops has the same effect on concentration as in the normal case, and the horizontal concentration profile is depressed on the hot side and elevated on the cold side, which tends to reduce the influence of the forgotten effect and slows down the convective flow. However, there is no indication in this case that the velocity will ever return to its initial state. As far out in time as we ran the calculations, it appeared that the velocity simply approached zero asymptotically, the vertical transport rate became very small, and the vertical concentration gradients became very large.

This description from the theory is good for small wall spacing, say 0.020 in. or less, with or without reservoirs, which includes all cases of concentration reversal in the literature. With this wall spacing and reasonable values of system properties, reversal would never take more than a few minutes and would create a miniscule concentration rise before reversal, which would certainly be missed in an experiment. The reason is that the cause of reversal is the build-up of a horizontal concentration gradient by horizontal diffusion before the vertical mass transport has much effect. From ordinary diffusion theory, the relaxation time for this build-up will be on the order of $w^2/4D$, which gives a value of 0.3 min. at a wall spacing of 0.01 in., 1 min. at 0.02 in.

We are not presenting one of these theoretical curves here, because the initial concentration blip is too small to be seen and it looks like any other separation curve. Also, in the theoretical calculation we were forced to use a fictitious value of α, because we could find no real systems with a value large enough to cause reversal! It seems that the few systems in which the more dense component is known to diffuse to the hot wall have too small a variation of density with concentration to give a large enough value of γ.

In an effort to duplicate the reversal of Jones and Milberger (*8*), we built a concentric tube column similar to theirs, with a wall spacing of 0.010 in. and a height of 5 ft., and ran their system in it, 50 vol. % toluene-cyclohexane. We were careful to make it as uniform and exact as possible and so checked the wall spacing over the length and heated the column with hot water instead of the electric heat they used. The results are shown in Figure 6, along with theirs. In their work toluene began to concentrate at the top of the column, then reversed itself and eventually became more concentrated at the bottom. This behavior could be explained by the forgotten effect, except that the time involved is far too great, 80 instead of 1 min. In our work toluene went to the top and stayed there, giving no indication whatever of impending concentration reversal.

In an effort to duplicate the concentration reversal of Prigogine et al. (*14*), we built a short column with reservoirs much like theirs, 4 in. tall and with a wall spacing of 0.007 in. The column was made of concentric tubes instead of their parallel plates to avoid possible spacing imperfections and was heated with hot water instead of their bar heaters to avoid irregularities in heat flux and secondary currents. We ran two of their systems, 1,1,2,2-tetrachloroethane–1,1,2,2-tetrabromoethane and bromobenzene-carbon tetrachloride; neither showed reversal. In their case, the tetrachloroethane concentrated at the bottom at the start, then changed direction and concentrated at the top. This would be reasonable behavior for reversal caused by the forgotten effect if the tetrabromoethane diffused to the hot wall. However, cell measurements by Saxton et al. (*15*) and by Childress (*2*) indicate directly that tetrachloroethane diffuses to the hot wall, which makes the forgotten effect positive. Furthermore, their time of reversal of over 2 hr. is much too long to be explained by the forgotten effect; it should have occurred in less than 1 min. In our case the tetrachloroethane went right to the top and stayed there, as would be expected from previous experimental work and theoretical considerations.

These results are in line with the results of Korsching (*11*), who constructed a parallel-plate column with reservoirs similar to that of Prigogine et al. (*14*) (except that the wall spacing was 0.016 in.). He studied these systems as well as bromobenzene-carbon tetrachloroethane and observed, as we did, that in the first system toluene concentrated at the top and in the second system tetrachloroethane concentrated at the top and that there was no concentration reversal. Furthermore, by microscopic observation of graphite flakes, he observed the convection currents directly and noted that in both systems the convection current was upward at the hot wall and downward at the cold at all times.

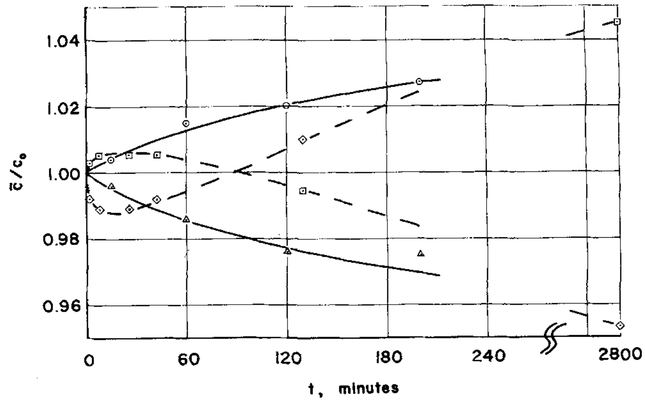


Fig. 6. Experimental transient data, toluene-cyclohexane. For the Jones and Milberger data, □ top and ◇ bottom; for our data, ○ top and △ bottom.

Table 2. Literature Concentration Reversals

System	Wall spacing, in.	Time to reversal, hr.	α required	D required, sq. cm./sec.
Toluene-cyclohexane	0.0115	1.5	>12	$\sim 10^{-7}$
Tetrachloroethane-tetrabromoethane	0.006	2	>2	$< 10^{-8}$
Bromobenzene-carbon tetrachloride	0.006	2 to 3	>23	$\sim 10^{-8}$

Another approach to the problem is to calculate approximate values of α and D for the three literature cases above by using the criteria that γ must be greater than unity and that D must be on the order of $w^2/4t$, where t is their reversal time. The results are shown in Table 2. Five of the six values are beyond the realm of possibility; values of α rarely exceed 3 and D cannot be smaller than 10^{-6}. It is true that the classical thermal diffusion theory without the forgotten effect does not always precisely fit the facts. However, the kinetic constants that one obtains from experiment are rarely more than a factor of two or three different from the theoretical predictions and not the factor of ten or more different shown in Table 2.

In review, the predictions of the theory that concentration reversal should occur in less than 1 min. (or, alternatively, that kinetic constants calculated from literature reversals are unlikely) and the concentration reversal would be too small to see, and the facts that experiments failed to duplicate literature cases and one system involved in a literature case exhibits a *positive* forgotten effect, all suggest that the reversals in the literature were not caused by the forgotten effect.

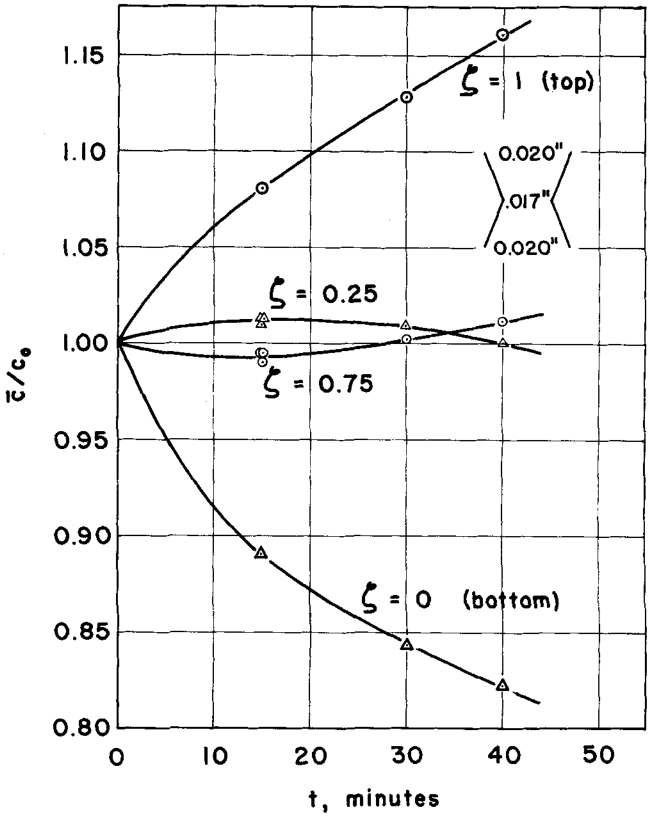


Fig. 8. Experimental concentration reversal in the hour-glass column caused by the deliberately nonconstant wall spacing shown in the sketch; cyclohexane-carbon tetrachloride.

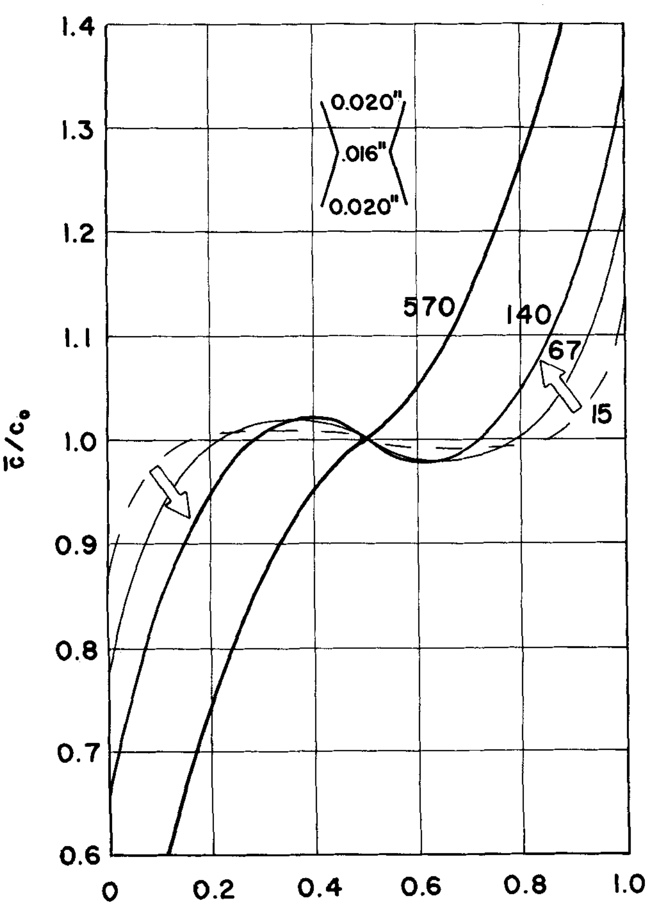


Fig. 7. Theoretical development of vertical concentration profiles for the nonconstant wall spacing shown in the sketch. Numbers by the curves are elapsed time in minutes. Concentration reversal occurs over most of the column (but not at the extreme top or bottom).

EXPERIMENTAL IMPERFECTIONS

In this section we demonstrate that very small irregularities in wall spacing can create concentration reversal and present qualitative arguments to the effect that other irregularities could do the same. We do not claim to explain the literature cases but we do show that these irregularities lead to concentration reversals with time scales similar to those in the literature.

Wall Spacing

Minor variations in wall spacing along the length of a column can cause unusual fluctuations in transient vertical concentration profiles because of the profound variation of mass flux with wall spacing. It is even possible to have a configuration which leads to concentration reversal over much of the column, regardless of the influence of the forgotten effect, as we demonstrated theoretically and experimentally with the cyclohexane-carbon tetrachloride system, which has a *positive* forgotten effect.

For the theoretical calculation, we chose the hour-glass column without reservoirs sketched in Figure 7, 5 ft. long, 0.020-in. wall spacing at the ends, and tapered linearly to 0.016 at the middle. Vertical flux of A increases as wall spacing increases. At the center flux is small and near the top of the column flux is large. Thus the region in between becomes depleted in A, whereas in normal operation it should remain unchanged until it becomes enriched. This can be seen in the developing vertical profiles in Figure

7. After 430 min., the concentration curve crosses the initial concentration only once, so that one can observe concentration reversal over most of the column (though not at the extreme ends). At a distance of 20% from either end, the reversal is complete in about 70 min., which is the order of magnitude of time involved in the cases of reversal in the literature.

For the experimental demonstration, we constructed a similarly tapered column, shown in Figure 8. It showed the same behavior as the computer solution, concentration reversal at intermediate points in the column and no reversal at the ends. Furthermore, reversal occurred at a long time characteristic of vertical processes, since it is vertical flux rather than horizontal diffusion that causes this phenomenon.

In a similar fashion, in columns with reservoirs unusual wall spacings may cause reversal of the concentrations in the column and not in the reservoirs.

Other Imperfections

Anything that causes varying mass flux from one height to another in a column without reservoirs can create reversal, just as imperfect wall spacing does. For example, temperature difference between the walls might vary with height, which is likely in columns heated electrically. If the coils were more closely wound on the ends than in the middle, one would get the same sort of results as with our hour-glass column. Powers (*13*), reporting results from a column manufactured by the Fink Co., says: "Temperature measurements indicated that heat from the spirally-wound nichrome element was not distributed evenly along the outer tube and therefore the columns were stripped bare and rewrapped . . . ." Furthermore, Powers' vertical concentration profiles show irregularities even after the improvement, which probably indicates poor wall spacing, a hazard which is very hard to avoid in such narrow columns.

Sample taps might create zones of reduced temperature. The mass flux into and out of this zone would be normal but the flux in the zone would be reduced, causing an abnormal increase in concentration at the bottom of the zone and decrease at the top and showing reversal if it were the top of the zone that were sampled. Another possibility is the presence of trace impurities in a system, especially if material were continually removed for analysis from the ends of the column during a run.

Columns with reservoirs might produce the appearance of reversal if the reservoirs are imperfectly flushed between runs; some data show no approach to the maximum initial concentration, only a steady movement from that to the reversed condition.

CONCLUSIONS

1. When density of the liquid in the column varies with concentration, the forgotten effect is important in transient batch operation of columns, increasingly so as the wall spacing decreases, but it has no influence at the steady state.

2. Values obtained for α for cyclohexane-carbon tetrachloride, a system with a large positive forgotten effect, agree well with those obtained from the column data of Horne and Bearman and the cell data of Korsching.

3. With regard to concentration reversal:

(a) The theory indicates that reversal caused by the forgotten effect would occur in about 1 min. and would be very small in magnitude, whereas cases reported in the literature occur in over 1 hr. Furthermore, those few systems in which the more dense component is known to diffuse to the hot wall have too small a variation of density with concentration to cause reversal.

(b) Using carefully constructed and operated columns, we were unable to obtain concentration reversal under conditions similar to those in which it has been reported in the literature.

(c) We demonstrated theoretically and experimentally that minor irregularities in wall spacing can create concentration reversal, regardless of the sign of the forgotten effect.

(d) These facts suggest that instances of concentration reversal reported in the literature are not caused by the forgotten effect.

NOTATION

A = component that diffuses to the hot wall
B = component that diffuses to the cold wall
B = third dimension of the column
c = concentration, mass or mole fraction
$\bar{c}$ = concentration averaged over x
c_0 = initial concentration
D = diffusion coefficient
g = acceleration of gravity
H = constant as defined by Equation (6)
K = constant as defined by Equation (7)
L = column height
t = time
T = absolute temperature
$\bar{T}$ = absolute temperature, averaged over x
u = horizontal velocity
v = vertical velocity
w = wall spacing
x = horizontal distance
y = vertical distance

Greek Letters

α = thermal diffusion constant
β = $-\partial\rho/\partial T$
γ = relative forgotten effect as defined by Equation (8)
ζ = y/L
μ = viscosity
ρ = density
τ = vertical mass flux

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