Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

On a Transient Effect in Thermal Diffusion

Gerald T. Fisher[a]; John W. Prados[a]; Echol M. Reed[ab]
[a] The University of Tennessee, Knoxville, Tennessee [b] Echol M. Reed is with California Research Corporation, San Francisco, California

To cite this Article Fisher, Gerald T. , Prados, John W. and Reed, Echol M.(1966) 'On a Transient Effect in Thermal Diffusion', Separation Science and Technology, 1: 6, 701 — 708
To link to this Article: DOI: 10.1080/01496396608049475
URL: http://dx.doi.org/10.1080/01496396608049475

SEPARATION SCIENCE, 1(6), 701–708 (1966)

On a Transient Effect in Thermal Diffusion

GERALD T. FISHER,* JOHN W. PRADOS,
and ECHOL M. REED†
THE UNIVERSITY OF TENNESSEE, KNOXVILLE, TENNESSEE

Summary

An effect was observed in thermal diffusion of the $CuSO_4$-$CoSO_4$-H_2O system. During the transient start-up of a Von Halle-Jury horizontal column, which utilizes diffusion through a membrane, the salts diffused in a direction opposite to that predicted by Soret measurements. This is not the "forgotten" effect observed in the Clusius-Dickel column.

Two continuous horizontal thermal-diffusion columns, first used by Von Halle (*1*) and Jury, were operated with the system $CuSO_4$-$CoSO_4$-H_2O. The device is designed to separate the components of a liquid mixture by thermal diffusion and was designed to overcome several shortcomings of the conventional Clusius-Dickel column. A transient effect occurred in the operation of one of them that is interesting and is previously unreported.

The schematic of the equipment is shown in Fig. 1. A solution is forced by external pumps through the space between a solid wall and a porous membrane. A thermal gradient is imposed on the solution perpendicular to the flow direction, and the material diffuses through the membrane under the influence of this gradient.

* Gerald T. Fisher is with Vanderbilt University, Nashville, Tennessee.

† Echol M. Reed is with California Research Corporation, San Franciso, California.

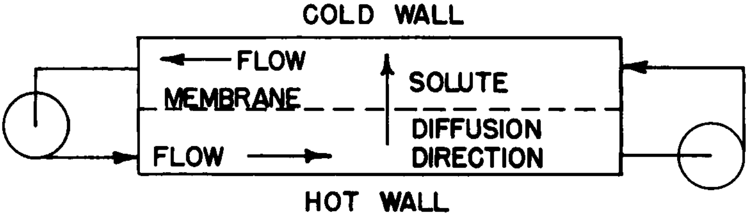

FIG. 1. Schematic representation of a Von Halle-Jury thermal-diffusion column.

Thus the solution, in passing through the flow channel, is enriched (or depleted in the other channel) by action of the diffusion, which is in one direction across the entire length of the membrane.

EXPERIMENTAL

In the first column built, two silicon bronze (95% Cu, 4% Si, 1% Mn) plates 17 × 17 × ½ in. were separated by two layers of 17 × 17 × ⅛ in. cork. Twenty slots ½-in. wide × 14⅝-in. long were cut in the cork and alternate ends connected to form one continuous channel. A layer of du Pont PT-600 (PD-600) cellophane which had been presoaked in distilled water for days was placed between the layers of cork. A layer of ½-mil Teflon was placed on either side of the membrane over the first slot on each end of the plate to prevent thermal embrittlement of the cellophane at low temperatures, leaving 18 slots and their end connections for diffusion, or a total of 0.915 ft^2 of diffusion area. The cellophane, together with each plate, bounded a channel through which a solution could be pumped; diffusion between the two streams could take place through the cellophane membrane. External pumps provided the flow. The top plate was cooled by a Freon 12 refrigeration system, and the bottom plate was heated by electric heaters. The top plate was electrically grounded, but the bottom plate was completely isolated from any ground by an isolation transformer between the heaters and the power source. This electric isolation was necessary to prevent electric currents which were induced by the emf generated by the difference in temperature and compositions of the salt solution in the regions of the plates.

The second column was built in an attempt to explain the behavior of the first. It was similar in construction, but with the following differences. The plates were 16 × 14 × ⅝ in. copper;

a layer of 5-mil Teflon sheet was glued on one 16 × 14 in. surface of each plate with Eastman 910 Adhesive. A ⅛-in.-thick Neoprene sheet was glued on the Teflon with 910 Adhesive, and 18 flow channels, each 11¾ by ½ in. wide, were cut in the Neoprene with alternate ends connected to form a continuous channel. No channels were blocked from diffusion, and this geometry provided an area of 0.702 ft^2 for diffusion.

A feed solution for the first column initially 0.445 *M* in $CuSO_4$ and 0.410 *M* in $CoSO_4$ in H_2O was used to fill the column, and a reservoir of this solution was used to feed the hot-side channel. A solution of 0.483 *M* $CuSO_4$ and 0.481 *M* $CoSO_4$ was used for the second column. Part of the effluent from the hot side was returned to the cold side as reflux, and the balance was returned to the reservoir. The effluent from the cold side was returned to the reservoir, so that the operation was as a closed system. The reservoir composition changed slightly during operation.

The first column was operated with a hot-side temperature of 122°F and a difference in wall temperatures of 70°F. The Teflon wall column operated with a hot side and a difference of 122 and 58°F, respectively.

Except for differences described, the construction and operation of the two columns were identical. A complete description of the equipment is presented by Fisher (*2*), Fisher et al. (*3*), and Reed (*4*).

THE EFFECT

The columns were operated in such a manner that the ratio of x_L, the composition of the effluent from the cold side, to x_D, the composition of the effluent from the hot side, was expected from Soret experiments always to be greater than 1. However, the transient data as shown in Fig. 2 were observed for the first column, and the data of Fig. 3 were observed for the second column. The second column was operated for the first eight days of its operation at flow rates too high to observe any separation; during the eighth day, the flow rates were decreased, and the eighth day is reported as time zero in Fig. 3, which shows the transient behavior during its further operation. From Figs. 2 and 3, it may be observed that the columns start with a uniform solution and then create a concentration change in the direction opposite to that predicted by Soret data and to that in the columns at steady state.

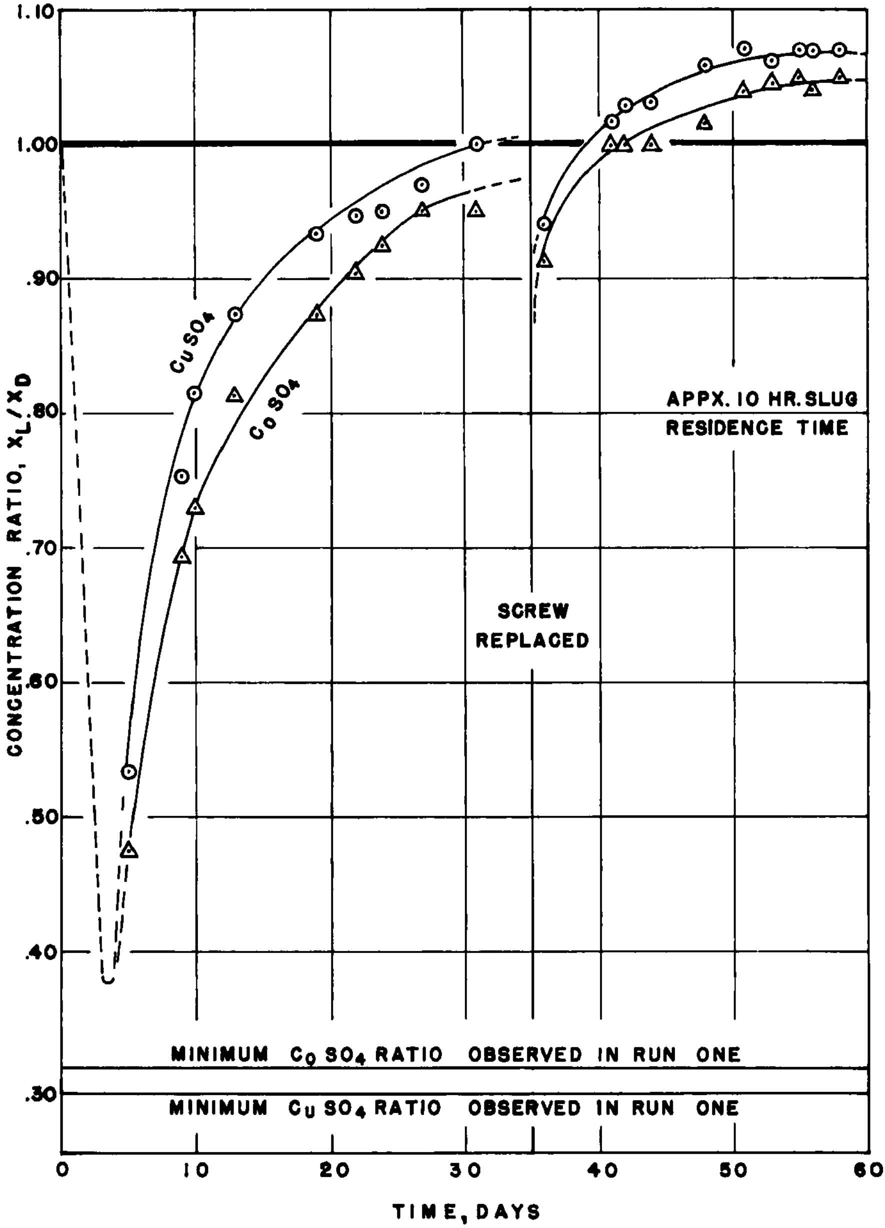

FIG. 2. Transient concentration ratios for silicon bronze column.

During the early stages of these transients (first 15 days), a large amount of water was transported through the membranes. For instance, in the first column the hot-side feed was 33.5 ml/hr and the exit 23.7 ml/hr; the cold-side feed was 14.8 ml/hr and the exit 24.6 ml/hr, or a cross flow of 9.8 ml/hr. This flow of water is from the hot side to the cold side, which is the usual direction for thermal osmosis observed by others (5–7). Operation of the column with no temperature gradient indicated that no flow occurred because of pressure differences across the cellophane membrane. Total reflux operation of the first column was not attempted during start-up; it was simpler to operate the column with set feed rates to each side such that the column was not at total reflux. The effluents from the channels changed as the thermal osmosis transport changed; hence one input flow would have to be continually changed to maintain total reflux. The effluent of the hot channel that was not pumped back into the cold channel automatically overflowed into the system reservoir.

The reversed direction of separation of the second column was caused by the cross flow of water through the membrane;

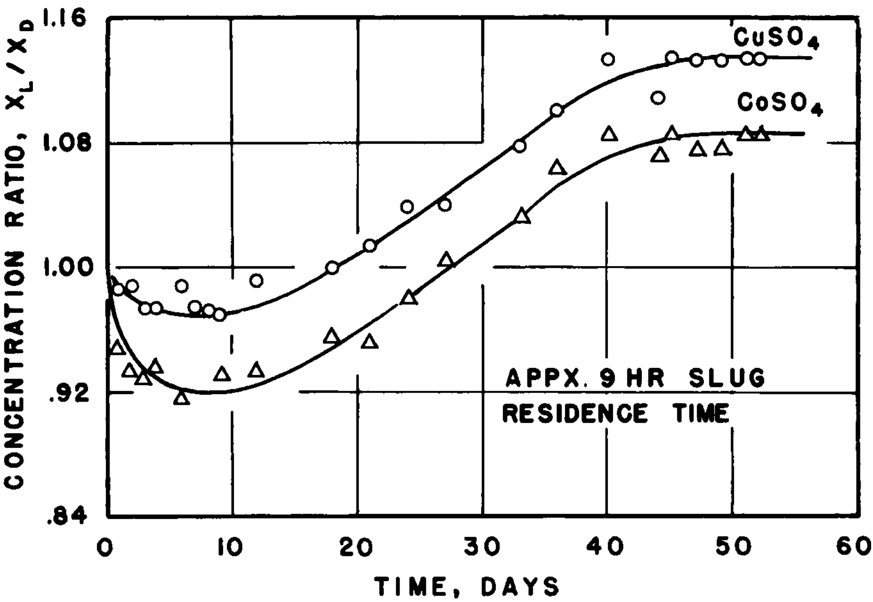

FIG. 3. Transient concentration ratios for the Teflon-wall column.

the large water flow simply diluted the cold stream and concentrated the hot stream. Material balances on the column indicated that the salt was diffusing from the hot side to the cold side as predicted by Soret data. The feed rate of this second column was 24 ml/hr and at total reflux.

The data of the first column, however, cannot be so readily explained. Although the water diffusion created a major part of this large reverse separation, material balances on the column, which checked within the accuracy of the experimental measurements, indicated that each salt was being transported from the cold to the hot side at rates of 2.8 mg-moles/hr for $CuSO_4$ and 3.7 mg-moles/hr for $CoSO_4$, accurate within 10%. The set of compositions and flow rates observed (which indicate this transport) are given in Table 1; these data were for the eighth day of operation of the first of the three runs in which the effect was observed. This transport direction is contrary to steady-state results and to predictions from Soret data. The transport of water through the membrane gradually decreased, until it was not significant at the end of the 58-day transient period. After the thirty-first day, the screw fitting in the entrance port of the hot-side feed corroded out and had to be replaced; the heat and refrigerant were shut off and the screw replaced with one made of Lucite; no difficulty was experienced with the Lucite fitting. At the end of 40 days, the transport was occurring in the opposite and usual direction. This particular type of transient behavior was observed in three runs; the first run resulted in solutions so concentrated that they crystallized and plugged the cold-side entrance port. These measured concentration ratios are given at the bottom of Fig. 2. After

TABLE 1

Compositions and Flow Rates

	Flow rates ml/hr	Concentration, M		Time
		$CuSO_4$	$CoSO_4$	
Hot inlet	33.5	0.493	0.488	8th day
Hot outlet	23.7	0.816	0.851	1st run
Cold inlet	14.8	0.816	0.851	
Cold outlet	24.6	0.381	0.364	

the first run, the column was taken apart and the membrane replaced with new presoaked cellophane. The column was started a second time, and after visually observing a concentrated salt solution leaving the hot-side exit, the column was shut down after 1 day's operation because of pump difficulties. No spectrophotometric measurements were made for this 1-day operation. The column was opened, and the wall of the hot channel was scraped of a green deposit. The same membrane was replaced in the column for the third run. No treatment was given the cold wall. The data obtained after this treatment are reported in Fig. 2. No satisfactory explanation of this behavior has yet been proposed. It should be noted that changes of column flow rates did not cause this anomalous behavior; the behavior resulted only after shutdowns involving taking the column apart. Also, the Teflon-wall column did not exhibit the reverse salt diffusion effect, although it did show the thermal osmosis effect.

The explanation of the reverse diffusion effect is not clear. It could have been caused by a membrane effect; however, the effect was not observed in (a) the Teflon-wall column, (b) in another smaller column made of copper which is described elsewhere (*3*), or (c) in a copper equilibrium cell of the same arrangement used by Bosanquet (*8*). An effort was made to remove all sizing and perhaps age the cellophane by extended soaking and washing in distilled water. Bosanquet (*8*) experienced some other difficulties in Soret measurements which he attributed to surface effects of the hot side and prevented by coating the hot surface with a resin. As a green deposit was observed on the hot surface of the silicon bronze column in this work, a similar surface effect could be hypothesized as causing the effect. The effect was not attributed to electrolytic corrosion and transport, however, as sufficient material was not found deposited on the hot surface to account for the large quantity of salt that was transported.

Acknowledgment

All work described herein was carried out under a research contract with the Chemical Technology Division of the Oak Ridge National Laboratory (operated by Union Carbide Nuclear

Company). The authors wish to express their gratitude for this support and for permission to publish results of the study.

REFERENCES

1. E. Von Halle, Ph.D. Thesis, University of Tennessee, 1959.
2. G. T. Fisher, Ph.D. Thesis, University of Tennessee, 1960.
3. G. T. Fisher, J. W. Prados, and L. P. Bosanquet, *AIChEJ*, **9**, 786 (1963).
4. E. M. Reed, MS Thesis, University of Tennessee, 1962.
5. K. F. Alexander, *Z. Physik. Chem.* (*Leipzig*), **203**, 181 (1954).
6. W. D. Jones, BS Thesis, University of Tennessee, 1958.
7. E. Von Halle, Ph.D. Thesis, University of Tennessee, 1959.
8. L. P. Bosanquet, MS Thesis, University of Tennessee, 1960.

Received by editor August 1, 1966
Submitted for publication August 25, 1966