

ey 2
cy. 2msg.

University of California

RECEIVED
LAWRENCE
RADIATION LABORATORY

NOV 6 1968

LIBRARY AND
DOCUMENTS SECTION

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

AN EQUILIBRIUM THEORY OF THE PARAMETRIC PUMP

Robert L. Pigford, Burke Baker III,
and Dwain E. Blum

September 1968

Berkeley, California

38

ey. 2
cy. 2msg.

UCRL-18483

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

To be submitted to:
Ind. Eng. Chem.

UCRL-18483
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

AN EQUILIBRIUM THEORY OF THE PARAMETRIC PUMP

Robert L. Pigford, Burke Baker III,
and Dwain E. Blum

September 1968

SHORT SUMMARY

An Equilibrium Theory of the "direct mode" Parametric Pump is presented.

The origin of the separation is discussed in terms of a graphical representation of the system's characteristics.

AN EQUILIBRIUM THEORY OF THE PARAMETRIC PUMP

Robert L. Pigford, Burke Baker III,
and Dwain E. Blum

Department of Chemical Engineering
and Lawrence Radiation Laboratory
University of California
Berkeley, California

SUMMARY

Very large separation factors have been obtained by Wilhelm and his coworkers (1968a, 1968b) using cycling flow of a binary mixture upward and downward through a column containing a fixed bed of solid adsorbent which is alternately heated and cooled. The theory of such separations is developed here on the assumption of local equilibrium between solid and fluid phases. The origin of the separation is the ability of the solid phase to store solute deposited on it by fluid flowing from the bottom of the column and to release this solute later into another fluid stream which flows into the column from a top reservoir containing enriched mixture. The proposed mechanism takes into account the difference in the speeds of propagation of concentration waves through the packing during upward and downward flow.

INTRODUCTION

The "parametric pump" described by Wilhelm, Rice, and Bendelius (1966), by Wilhelm, Rice, Rolke, and Sweed (1968b), by Wilhelm and Sweed (1968a), and by Wilhelm (1966), is a device which uses pulsating fluid motion and pulsating heat input to a tube filled with a fixed bed of solid adsorbent to effect a separation of the components of the fluid. Figure 1 is taken from Wilhelm, Rice, et al. and shows how the separation apparatus is operated in the "direct mode". Heat flows through the walls of the tube containing the fixed bed of solid adsorbent.

particles. When the flow of heat is in phase with the changes in direction of the flow, as in Fig. 2, there develops a net transport of matter along the flow direction which leads eventually, after several cycles, to a steady state difference in the concentrations in reservoirs of fluid at the ends of the column.

Thus, simultaneous forcing of flow and thermal parameters in the partial differential equation of transport produces a "pumping" of components of the fluid which is able to sustain a concentration gradient along the flow coordinate.

Wilhelm, Rice, Rolke, and Sweed demonstrated the main idea experimentally, showing that very large ratios of top and bottom concentrations could be obtained under some conditions. They also showed that numerical solutions of the equations of transport yielded performance curves which agreed at least qualitatively with the observations. The separation factors were predicted to increase gradually with each thermal-flow cycle and to be limited finally only by the mass transfer resistance to diffusion of material between solid and fluid phases.

Despite the success of the computer calculations of separation factors reported by Wilhelm and his coworkers, one wonders what is the origin of the separation. The equations of transport used in the numerical work are so unwieldy that only very qualitative explanations were offered. It was noticeable, however, in the computer results reported by Wilhelm et al. (1968b) that, despite the large differences in composition at the ends of the column of adsorbent, the local differences between fluid composition were always small. Thus, one is led to speculate whether the assumption of perfect local equilibrium between the solid and fluid phases might lead to equations and solutions having simpler behavior. We call the theory of the parametric pump which is based on this assumption the "equilibrium theory". The simplest form of this theory, in which the concentrations on the solid and in the fluid are proportional, is found to yield attractively simple results.

THE EQUATION OF TRANSPORT

If we let x and y represent, respectively, the ratios of moles of solute to mass of solid or moles of fluid, the conservation equation for the fluid and the solid phase is

$$\epsilon \rho_F \frac{\partial y}{\partial t} + \epsilon \rho_F v \frac{\partial y}{\partial z} + (1 - \epsilon) \rho_S \frac{\partial x}{\partial t} = 0 \quad (1)$$

where ϵ is the fractional void space in the packing, ρ_F and ρ_S are fluid and solid densities, and v is the interstitial velocity of the fluid. If the equilibrium relationship is linear,

$$x = M(T)y \quad (2)$$

where M , a function of local temperature, is the equilibrium constant, we can eliminate x , obtaining

$$(1 + m) \frac{\partial y}{\partial t} + v \frac{\partial y}{\partial z} = - \frac{dm}{dT} \cdot \frac{\partial T}{\partial t} \cdot y \quad (3)$$

Parametric pumping action occurs when $m(T) = \rho_S(1 - \epsilon)M(T)/\rho_F\epsilon$ and $v(t)$ are made to vary synchronously, as the following development will show.

Equation 3 is a hyperbolic partial differential equation which can be solved by the method of Lagrange-Charpit, sometimes called the method of characteristics. We form the pair of ordinary differential equations,

$$\frac{dt}{1 + m} = \frac{dz}{v} = \frac{-dy}{\left(\frac{dm}{dT}\right)\left(\frac{\partial T}{\partial t}\right) y} \quad (4,5)$$

The first equality represents characteristic curves in the z - t plane along which solution of the second equality yields values of $y(z,t)$. Thus, values of the fluid concentration are propagated along the characteristic lines from the boundaries, at which concentrations are known.

Consider operation of the apparatus in the "direct mode" described by

Wilhelm, Rice, Rolke, and Sweed (1968b) and in which the fluid velocity is either upward or downward but always at a constant speed, v_0 , represented by the square-wave function,

$$v = v_0 \text{ sq}(\omega t) \quad (6)$$

The synchronous temperature change produces an in-phase, square-wave change in the equilibrium constant, which gives

$$m = m_0 - a \text{ sq}(\omega T) \quad (7)$$

The negative sign before the time-dependent term in this equation is owing to the fact that heating of the bed, which occurs during periods of up-flow, causes a reduction in the ratio of equilibrium solid-to-fluid concentrations. Equations 4 and 5 become

$$\frac{dz}{dt} = \frac{v_0 \text{ sq}(\omega t)}{1 + m_0 - a \text{ sq}(\omega t)} = \frac{u_0 \text{ sq}(\omega t)}{1 - b \text{ sq}(\omega t)} \quad (8)$$

representing the characteristics and

$$\frac{d \ln y}{dt} = - \frac{d \ln(1 - b \text{ sq}(\omega t))}{dt} \quad (8)$$

representing the change in y along the characteristic directions.

At the mean temperature, the velocity of propagation of concentration waves through the packing is $u_0 = v_0 / (1 + m_0)$, which is smaller than the fluid velocity. Obviously, the characteristic curves are straight lines having slopes of $u_0 / (1-b)$ or $u_0 / (1+b)$ in the hot and cold periods, i.e. the up-flow and the down-flow periods, respectively. Equation 8 indicates that along a characteristic path composed of connecting straight line segments, the product $y(z,t)(1-b \text{ sq}(\omega t))$ is constant. Thus, $y(z,t)$ undergoes a change in value proportional to the ratio $(1+b)/(1-b)$ when the characteristic line passes from a cold region into a hot

one, or in the ratio $(1-b)/(1+b)$ when the change is from heating to cooling. Along each of the straight segments of a characteristic line $y(z,t)$ is constant. The problem of constructing a solution is therefore reduced to the geometrical problem of locating the characteristics in the $z-t$ plane and counting the number of changes in slope which each characteristic experiences.

CALCULATION OF ENRICHMENT FOR DIRECT MODE

Fig. 3 shows several characteristic lines crossing the $z-t$ plane for a column which operates in the direct mode. Time periods of heating, each of duration π/ω , alternate with cooling periods. During each such half cycle the characteristics have all the same slopes; these slopes change when the temperatures change.

The average characteristic slope, or, more accurately, the slope at the average temperature depends on the fluid velocity, v , and on the average equilibrium constant. During passage through the column the fluid behind the wave front remains constant in composition unless the temperature changes during the passage. Therefore, if u_0 is great enough it is possible for some of the material to leave one of the end reservoirs and to pass through the column into the other reservoir without enrichment and thereby to decrease the separation effect. To avoid this it is necessary to have $\frac{u_0}{1-b} < \omega Z/\pi$, which is the basis of the construction in Fig. 3. Note that the method of operation described by Wilhelm et al. (1968b) was such that the volume of fluid in each of the end reservoirs was equal to that in the column, corresponding to $v_0(\pi/\omega) = Z$ or to $\pi u_0/Z = 1/(1+m_0) < 1$, as assumed.

The operation begins with the column filled with fluid of concentration y_0 , everywhere at equilibrium with the solid. The initial temperature is high.

In addition, there is fluid of the same initial concentration in a cylinder, at the bottom of the column, of volume equal to the free volume of the column.

The first fluid motion is upward and the column is hot.

We call the mean composition of the fluid leaving the top of the column during the hot period $\langle y_T \rangle_n$; to find this quantity it is necessary to find the source of the characteristic lines which cross the line $z = Z$ during the hot half cycle and for each characteristic to count the number of concentration changes which occur owing to temperature changes inside the packing. During the first half cycle, $0 < \omega t < \pi$, the characteristic lines which cross $z = Z$ all begin along the line $t = 0$, where $y(z, t) = y_0$. This concentration remains constant along each of the characteristic lines crossing the z - t plane diagonally in region A of the figure and leads to the following concentration of the top product during the first hot half-cycle:

$$\langle y_T \rangle_1 = y_0 \quad (9)$$

Note that this is also the concentration of the fluid fed to the top of the column during the cold part of the first cycle.

During this period, $\pi < \omega t < 2\pi$, all the characteristic lines crossing $z = 0$ have originated on $z = 0$ during the just preceding hot half-cycle; there the fluid concentration was $y(0, t) = y_0$ and this concentration has been preserved until the vertical line at $\omega t = \pi$ is reached. There a change in slope occurs and the concentration changes to $y_0(1-b/1+b)$, which continues to the bottom of the column. Therefore,

$$\langle y_B \rangle_1 = y_0 \left(\frac{1-b}{1+b} \right) \quad (10)$$

Note that this will be the concentration of material entering the column during the second hot half-cycle.

During the second cycle two kinds of characteristics cross the upper boundary, $z = Z$. Those in region C have come from the upper reservoir and have the composition $\langle y_T \rangle_1 (1+b/1-b) = y_o (1+b)/(1-b)$. The enrichment comes from the fact that these characteristics cross the vertical line at $\omega t = 2\pi$, where there is a favorable temperature change. Other characteristics in region B originate in the initial contents of the column, however. For these the concentration, y_o , is preserved because there are compensating temperature changes before they leave the top of the column. To find the mean of the two compositions leaving the top, we must determine the fractions ac/ad and cd/ad . From the slopes of the characteristic lines it is easily determined that

$$ac/ad = \frac{1-b}{1+b} \quad (11a)$$

$$cd/ad = \frac{2b}{1+b} \quad (11b)$$

and the weighted average value of the second hot stream is

$$\langle y_T \rangle_2 = y_o \left\{ \left(\frac{1+b}{1-b} \right) \left(\frac{1-b}{1+b} \right) + (1) \left(\frac{2b}{1+b} \right) \right\} = y_o \left(1 + \frac{2b}{1+b} \right) \quad (12)$$

The increasing enrichment is evident. For the second cold stream it follows that

$$\langle y_B \rangle_2 = y_o \left(\frac{1-b}{1+b} \right)^2 \quad (13)$$

After the second full cycle the initial composition of the column no longer affects the solution. Then we can find a general solution for the top and bottom compositions. For the construction shown in the figure

$$\langle y_T \rangle_n = \langle y_T \rangle_{n-1} \left(\frac{1+b}{1-b} \right) \cdot \left(\frac{1-b}{1+b} \right) + \langle y_B \rangle_{n-2} \left(\frac{2b}{1+b} \right) \quad (14)$$

and

$$\langle y_B \rangle_n = \langle y_B \rangle_{n-1} \left(\frac{1-b}{1+b} \right) \quad (15)$$

This pair of difference equations can be solved easily. From Eq. (15)

$$\langle y_B \rangle_n = y_0 \left(\frac{1-b}{1+b} \right)^n \quad (16)$$

and from Eq. (14), using Eq. (12) as an initial condition,

$$\begin{aligned} \langle y_T \rangle_n &= y_0 \left\{ 1 + \frac{2b}{1+b} + \frac{1-b}{1+b} \left[1 - \left(\frac{1-b}{1+b} \right)^{n-2} \right] \right\} \\ &= y_0 \left\{ 2 - \left(\frac{1-b}{1+b} \right)^{n-1} \right\}; \quad n > 0 \end{aligned} \quad (17)$$

Thus the separation factor, $\alpha = \langle y_T \rangle_n / \langle y_B \rangle_n$, is given by

$$\alpha_n = 2 \left(\frac{1+b}{1-b} \right)^n - \left(\frac{1+b}{1-b} \right); \quad n > 0 \quad (18)$$

As the cycling operation continues without limit the separation factor approaches infinity, owing to the first factor. (The separation factor for a real system would be limited only by the resistance to mass transfer between phases.) Fig. 5 is a plot of Eq. (16) and (17) for two values of the parameter b , proportional to the change in the equilibrium constant. The figure shows that, although the top composition continues to increase as the operation proceeds, the rate of increase becomes progressively smaller as the bottom composition falls toward zero. This is of course in agreement with Eq. (14), which indicates that $\langle y_T \rangle_n = \langle y_T \rangle_{n-1}$ in the limit.

THE ORIGIN OF THE SEPARATION

Referring to Fig. 3, note that the pattern of characteristics over one complete cycle has three different regions, one in which the characteristics

originate along the line $z = 0$ (Type 1), one in which they do not enter or leave the column (Type 2), and one in which they cross the line $z = Z$ (Type 3). There is a net upward movement in a characteristic as time goes on, owing to the fact that the increase in the velocity of a concentration wave during the hot half cycle is greater than the subsequent decrease which occurs when the equilibrium constant increases owing to cooling; consequently, a particular characteristic eventually moves into all the regions. Thus the boundaries of each region are not defined by a single, continuous characteristic.

Of primary importance, however, is that over each half cycle, each section of the column is crossed at different times by two of the three types of characteristics. This, coupled with the concentration shifts in the column when the temperature changes, results in a net flow of solute from the bottom reservoir along Type 1 characteristics, then by Type 2 characteristics, and finally into the top reservoir via Type 3 characteristics.

The parametric pumping action of the column arises from concentration changes which the fluid experiences while it is in the column. The fluid which flows into the column from the upper chamber maintains its original concentration until the temperature changes. Then there is a sudden increase in the concentration of this stream just as the flow reverses, made possible by the previous transport upward of adsorbed solute molecules from one packing piece to the next one higher. Likewise, lean fluid from the bottom reservoir experiences no change in composition as it flows upward into the packing, until the temperature changes. The material which flows downward, back into the bottom reservoir, has just experienced a temperature drop while it was in the column. If this fluid had any solute when it went in, some of this solute will have been retained on the solid owing to the temperature drop and will eventually work its way to the top of the column.

Now it is easy to see why, as reported by Wilhelm et al., the temperature and velocity changes must be either in phase or 180° out of phase for the maximum separation to occur.

If they are just 90° out of phase, the characteristics will exactly repeat themselves over each cycle, i.e. there will be no net upward movement as shown in Fig. 4. Furthermore, considering the bottom reservoir, only two situations will occur over one cycle, beginning with a switch to the upflow velocity. Over part of the period characteristics enter the column which ultimately undergo two exactly compensating temperature changes; along them there is no net change in concentration when they leave the column. Over the remainder of the period characteristics enter which undergo no temperature changes; again there is no concentration change when they leave. A similar situation holds for the top reservoir. There may be a small separation during the first cycle because of the initial condition of the column, but there will be no progressive growth of the separation factor.

The case in which the temperature and velocity are 180° out of phase is the reverse of the in-phase case and results in the bottom becoming the rich end and the top, the lean end.

COMPARISON OF EQUILIBRIUM THEORY WITH DATA

Wilhelm et al. (1968b) presented data for the separation of binary liquid mixtures of n-heptane and toluene in a column filled with silica gel particles, using different frequencies and slightly different temperature changes. Values of the equilibrium constant, m_0 , and of its change with temperature, a , were not given so the equilibrium theory cannot be applied directly to forecast the

separation. It is possible, however, to compute values of b from the reported compositions at the bottom of the column at one time during each run and then to use these values to construct curves of the separation factor vs. cycle number for the whole of each run. Fig. 6, which is based on Fig. 4 of the paper of Wilhelm et al., shows the results of such computation and illustrates the approximate agreement between theory and these preliminary data. The shapes of the curves given in Fig. 4 of the paper by Wilhelm et al. (1968b) are nearly the same as those computed. Evidently the separation factors might have gone much higher than the already high values observed during about sixty cycles, the limitations owing to finite mass transfer rates not yet having been felt very strongly.

CONCLUSIONS

The theoretical computations reported here, although based on a very simple set of equations for the transient response of the parametric pump, are capable of giving maximum values of the separations which can be obtained in a system having linear distribution isotherms. The separation factors increase without limit as pumping proceeds, until mass transfer resistance becomes important, as was indicated by Wilhelm and his coworkers (1968b). The origin of the separation effect lies in the ability of the column to store solute temporarily on the solid adsorbent particles, withdrawing it from the lean bottom product and subsequently adding it to the top product as each of these penetrates portions of the column in turn. The vertical transport of solute along the packing is owing to the projection of characteristics into all sections of the column, enabling transport of material into the packing by fluid from below and, subsequently in another part of the cycle, the emission of temporarily stored material into fluid which will emerge eventually from the top of the column. As a result there is a net displacement of adsorbed material from the bottom to the top of the column.

NOMENCLATURE

- a = equilibrium constant change.
- b = $a/(1 + m_0)$, equilibrium constant change parameter.
- M = equilibrium constant (temperature dependent).
- m = equilibrium constant parameter, proportional to M.
- n = number of cycles.
- T = temperature, °C.
- t = time, sec.
- u = velocity of propagation of concentration wave, cm/sec.
- v = interstitial velocity, cm/sec.
- x = solids concentration, moles solute/mass of adsorbent.
- y = fluid concentration, moles solute/mole of fluid.
- y_0 = initial fluid concentration, moles solute/mole of fluid.
- Z = bed length, cm.
- z = axial position in bed.

Greek Letters

- α = separation factor.
- ϵ = void fraction in packing.
- ρ = phase density.
- ω = cycle frequency.

Subscripts

- B = column bottom reservoir.
- F = relating to fluid phase.
- n = cycle number.
- o = at the mean temperature.
- S = relating to solid phase.
- T = column top reservoir.

ACKNOWLEDGEMENTS

These studies were supported by AEC Contract W-7405-eng-48. Additional support through NASA Predoctoral Traineeship NSG(T)-117-2 was provided to one of us. We also thank Mr. T. G. Springer for many valuable discussions.

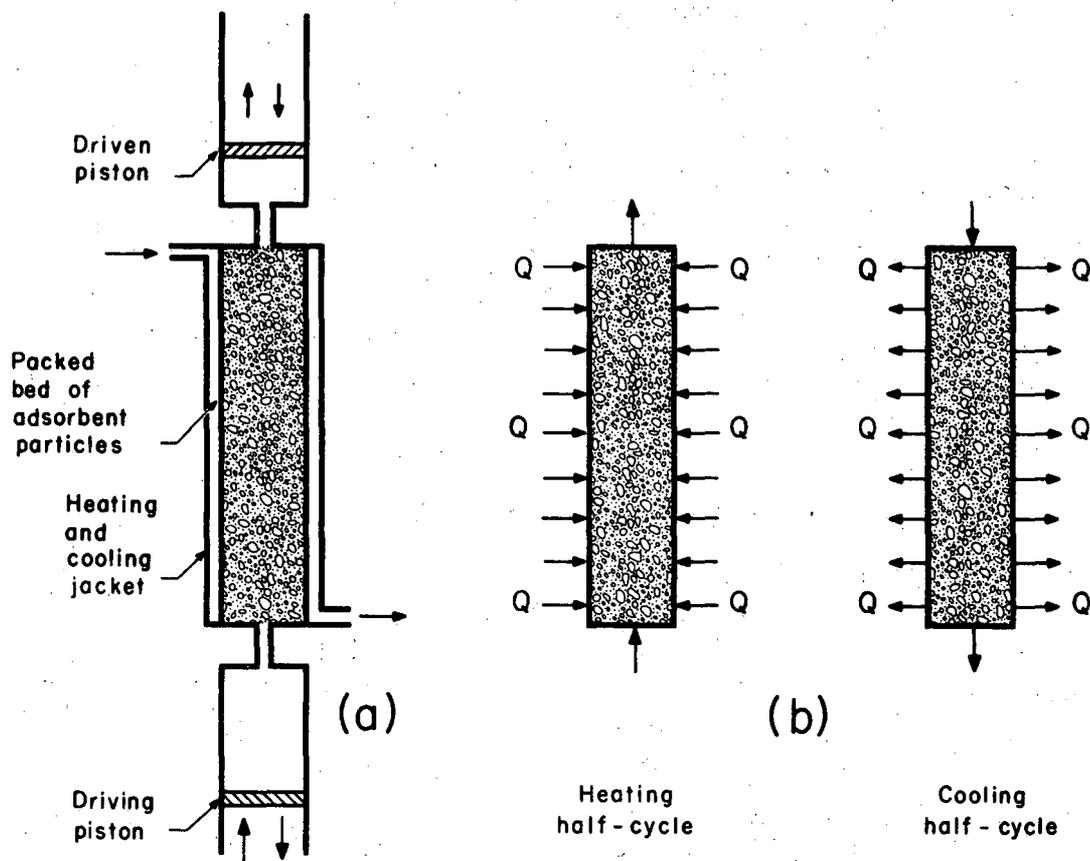
LITERATURE CITED

Wilhelm, R. H., "Parametric Pumping. A Model for Active Transport," in "Intracellular Transport," p. 199., Academic Press, New York, 1966.

Wilhelm, R. H., Rice, A. W., Bendelius, A. R., IND. ENG. CHEM. FUNDAMENTALS QUART., 5, 141 (1966).

Wilhelm, R. H., Sweed, N. H., Science 159, 522 (1968a).

Wilhelm, R. H., Rice, A. W., Rolke, R. W., Sweed, N. H., IND. ENG. CHEM. FUNDAMENTALS QUART., 7, 337 (1968b).



XBL689-6822

Fig. 1. Diagram of column for parametric pumping in direct mode (from Wilhelm, Rice, Rolke, and Sweed (1968b)).

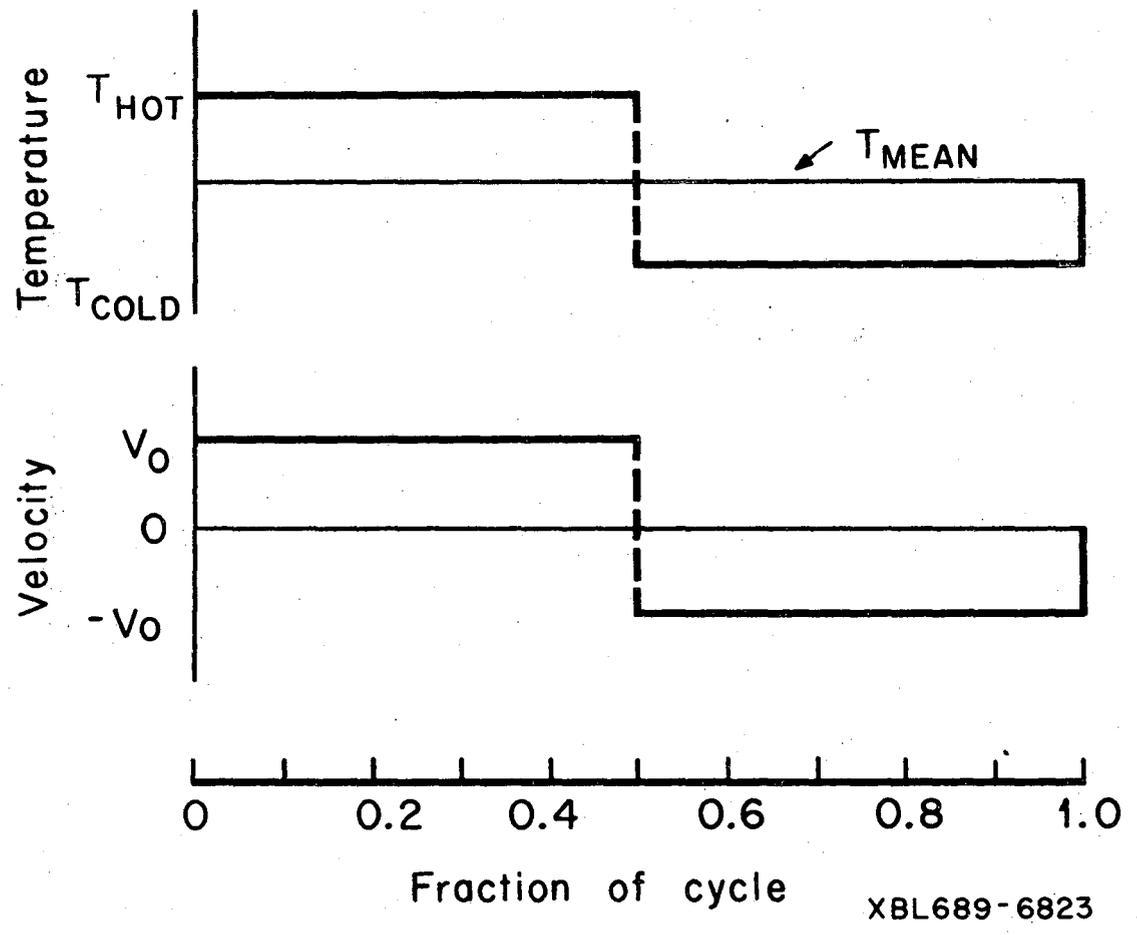
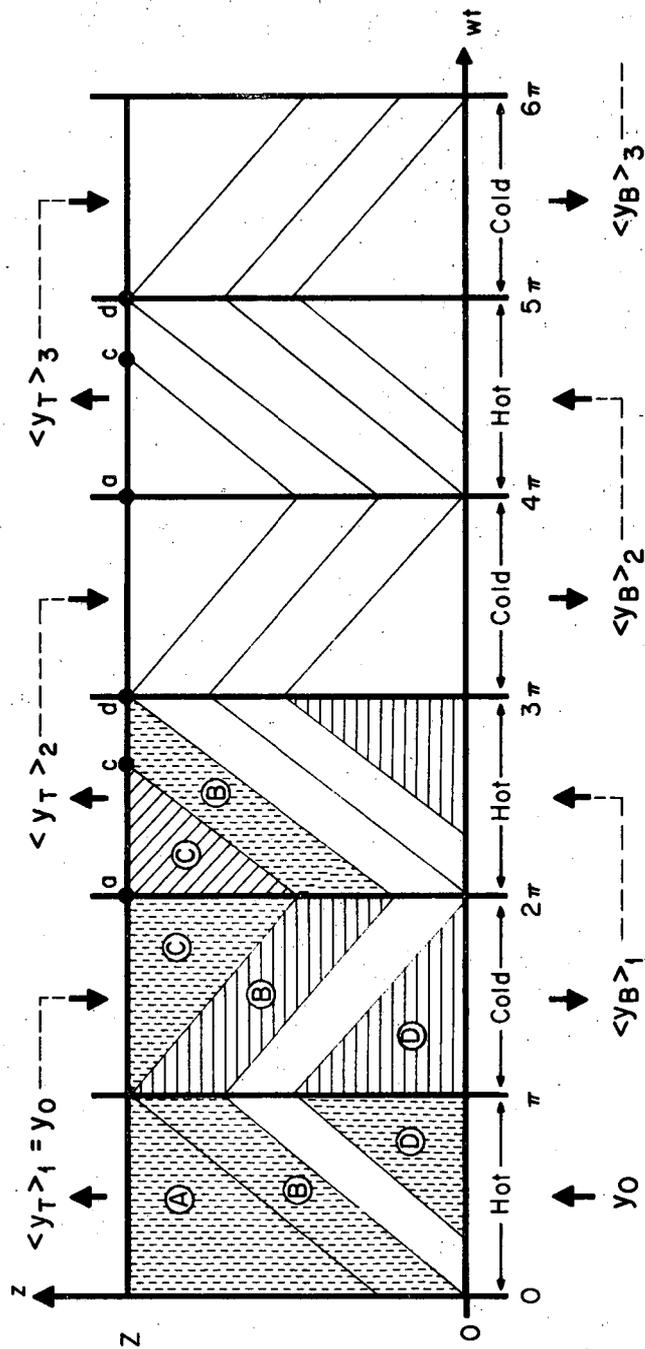


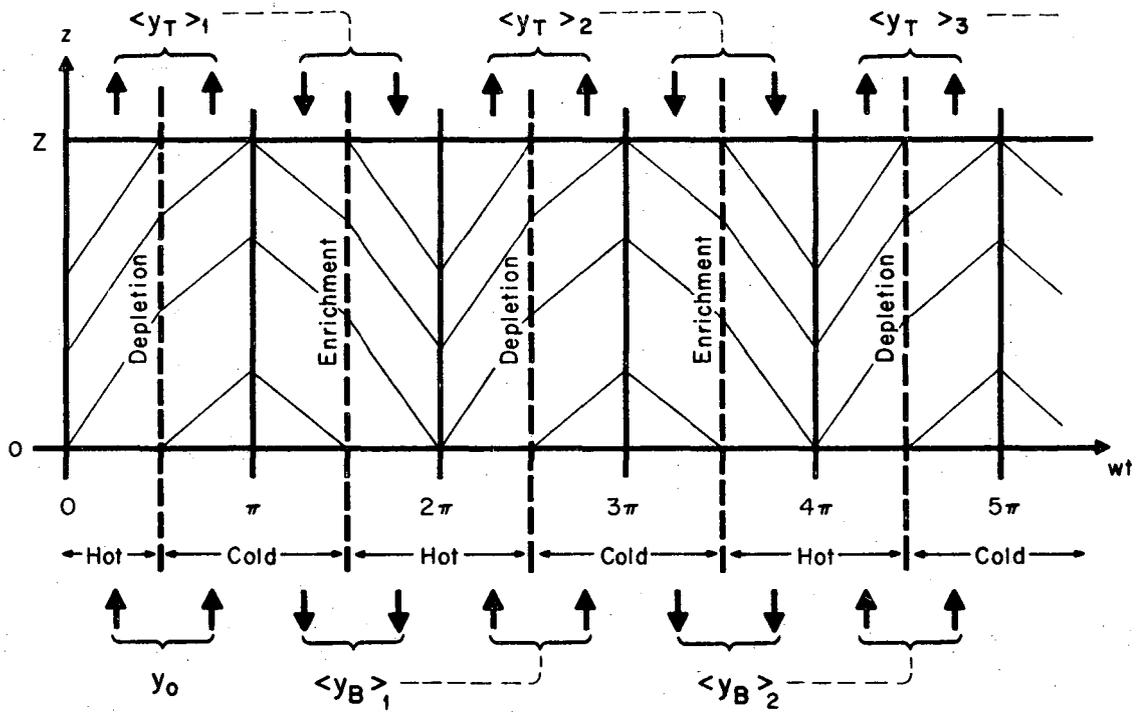
Fig. 2. Velocity and temperature at a point in the bed as a function of time.

XBL689-6823



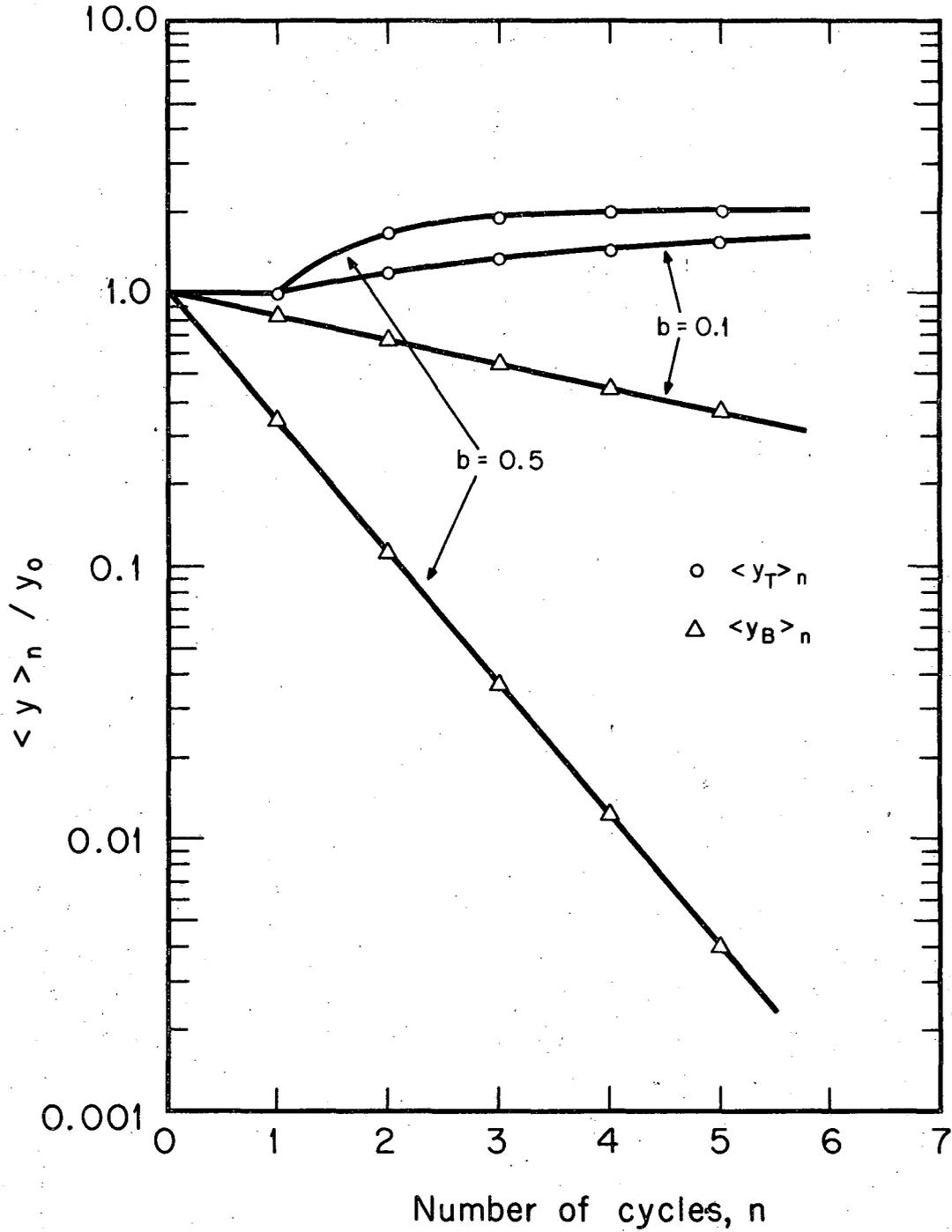
XBL689-6824

Fig. 3. Characteristic lines used for solution by equilibrium theory (up-flow and heating in phase).



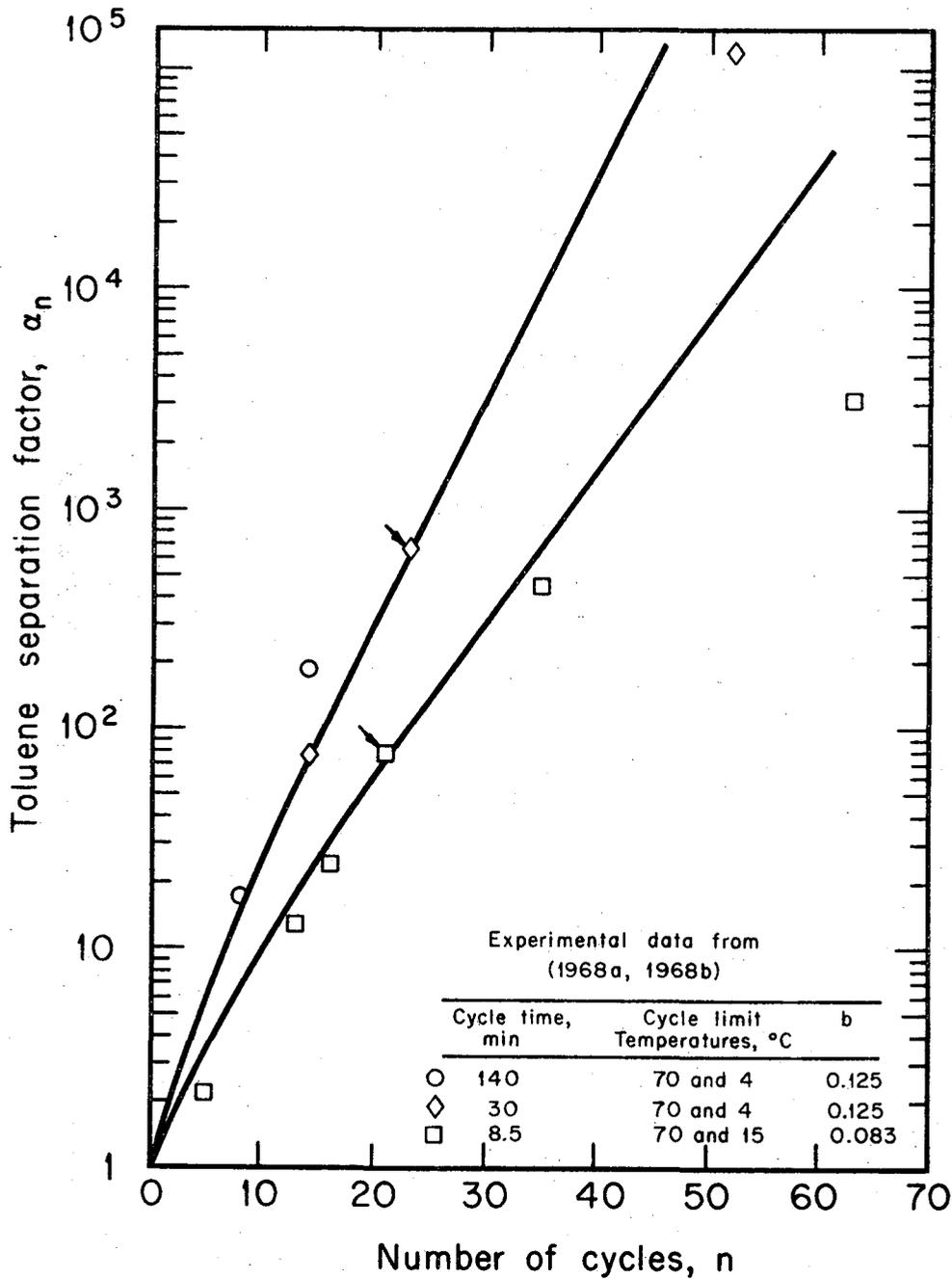
XBL 689-6825

Fig. 4. Characteristic lines used for solution by equilibrium theory (heating leads up-flow by ninety degrees).



XBL689-6826

Fig. 5. Calculated compositions of top and bottom products obtained by parametric pumping.



XBL689-6827

Fig. 6. Comparison of separation factors according to equilibrium theory with observations of Wilhelm et al. (1968b) for the system n-heptane-toluene in silica gel column.

Lines are computed from the equilibrium theory after fitting equation for bottoms composition at a point indicated by arrow. Values of b so chosen are shown on the figure. The theory gives the maximum possible separation; deviations of the data below curves are owing to finite mass transfer resistance between phases.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.