Reports

Parametric Pumping: Separation of Mixture of Toluene and n-Heptane

Abstract. *Parametric pumping, a dynamic separation technique, comprises alternating axial displacement of a fluid mixture in a column of adsorptive particles upon which a synchronous cycling temperature is imposed. With direct coupling, separations of* $10^5:1$ *between column ends have been obtained, with indications of great potential for further separation. A mathematical model and its solution describe the behavior of the system.*

We demonstrate through experiment and supporting theory the great separative capability of the parametric pumping technique; specifically, 30-ml liquid mixtures of toluene and *n*-heptane have been separated to the extent of a $10^5:1$ concentration ratio of toluene. In principle the technique is applicable to any fluid mixture that adsorbs on a second phase, the extent of separation, however, depending highly on the system and on the details of operation.

Parametric pumping involves a dynamic coupling between periodically reversing displacements between fluid and adsorbent phases, on the one hand, and a cycling of the adsorptive equilibrium, on the other.

In the case of the direct mode of thermal parametric pumping that we illustrate, a periodic cycling of the temperature "parameter" causes a sequence of coupled periodic actions: cycling in the adsorbent-phase equilibrium, alternation in the interphase diffusive driving force, and finally alternation in the interphase diffusive solute flux. A sustained, time-average, axial separation of mixture components develops in both phases as a result of the final coupling of this diffusive interphase flux with the alternating, axial, convective solute flux that stems in turn from the relative fluid-adsorbent position displacements. The amount of separation depends partly on the action of synchronism and the phase angle between the periodic, interphase, diffusive, and axial convective fluxes. Separation takes place at the ultimate expense of thermal energy.

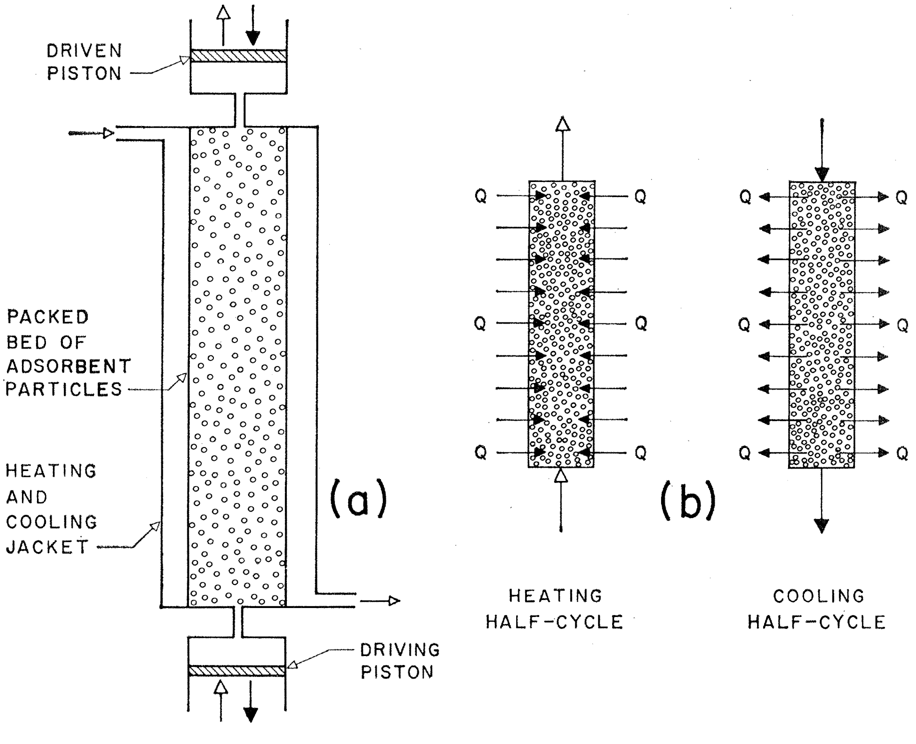


Fig. 1. (a) Experimental arrangement for direct mode of thermal parametric pumping. (b) Relations between flow alternations and periodic heat fluxes Q.

As to experiment, the equipment (Fig. 1) consists of a jacketed glass column (100 by 1 cm in internal diameter) packed with particles (30 to 60 mesh) of chromatographic-grade silica gel (*1*), a constant-rate, positive-displacement, dual-syringe, infusion-withdrawal pump (*2*), sources of hot and cold water for the jacket (not shown), and a programmed-cycle timer. The timer is adjusted to reverse periodically the direction of the fluid stream; also to cycle the jacket temperature by connection to hot or cold sources. Both alternations have the same frequency and are in phase. Adjustments of pump and timer render the alternating velocities always uniform and equalize the displacements in each half-cycle.

For comparison of experiments, each run was started under identical conditions: the interstitial fluid was a mixture of 20 percent by volume of toluene in *n*-heptane and was in equilibrium with the silica gel at ambient temperature. The bottom syringe was filled initially with 30 ml of the same mixture, this volume being approximately equal to the interstitial volume in the column; the top syringe was initially empty. Temperature limits between hot and cold sources are shown in Fig. 2.

At the beginning of a run, the syringe pump is started, and hot water is circulated through the jacket. When 30 ml has been displaced upward, the pump reverses direction, and the jacket is switched to the cold-water source. This process continues until 30 ml is pumped back downward through the column and one cycle is completed. Since no product is removed, we call this method total reflux.

In order to secure for analysis a sample of mixed product in each piston, the final cycle of each run is carried to about 90-percent completion. All products containing more than about 1 percent toluene are analyzed by means of refractive index with a sodium D-line source; those containing less, by ultraviolet absorption (*3*). Separation factor is defined as the ratio of mixed average toluene concentrations by volume in a syringe, top compared to bottom.

Figure 2 shows the results of three experimental separation runs, each performed with a different cycle time; experimental points represent fresh starts from initial conditions to the numbers of cycles noted on the abscissa. The separation factor first increases approximately exponentially with the number of cycles and finally leans toward a limiting separation. The potential for even greater separation by further increase in the number of cycles is evident in each run. The true toluene composition in each piston, from which the separation factor is calculated, is indicated for selected experiments; the larger value is the mixed average concentration of a full 30 ml of solution in the upper syringe at the end of the upstroke; the smaller is the concentration in the lower syringe at the end of the downstroke.

Let us consider now qualitatively the actions involved in separation: As the solution flows upward, the system is heated and the adsorbent transfers toluene to the fluid phase, causing an upward convective flux of toluene. On the reverse, downward stroke, the system is cooled, and toluene is transferred from fluid to adsorbent phase, decreasing thereby the downward convective flux of toluene. A multiple succession of these adsorption-desorption actions tends to cause accumulation of toluene at one end of the column and depletion at the other. A large separation potential exists when the traffic of solute exchange, between adsorbent and solution, is great in the transfer time available in each half-cycle. Thus, for set temperature-cycling limits and adsorbent properties, the separation pump-up rate per cycle is greatest for the longest cycle period (Fig. 1). Separation is retarded ultimately by two counteractions: (i) axial, fluid-phase diffusive losses caused by molecular diffusion and by fluid-mixing processes in the interstices between particles; and (ii) dispersion due to noninstantaneous interphase transfer. The losses that tend to limit separation are fortunately clearly light, so that large separations are permitted to develop (Fig. 2).

To display more fully the mechanisms contributing to a "parapump" separation system, we next present a mathematical model in terms of material balances, rate equations, and equilibria. Material conservation for the *i*th component in the fluid and solid phases contained in a differential, axial section of the column, *dz*, is expressed through this equation:

$$\underset{\text{(a)}}{\alpha f(t)\frac{\partial \phi_{f_i}}{\partial z}} + \underset{\text{(b)}}{\frac{\partial \phi_{f_i}}{\partial t}} + \underset{\text{(c)}}{\kappa \frac{\partial \phi_{s_i}}{\partial t}} - \underset{\text{(d)}}{\eta \frac{\partial^2 \phi_{f_i}}{\partial z^2}} = 0 \qquad (1)$$

Dependent and independent variables are dimensionless, having been normalized through reference to initial fluid concentration, total column length, and frequency of displacement alternation.

An approximate rate equation, convenient in its simplicity for expressing interphase transport and suitable for first-order explorations, is:

$$\underset{\text{(c)}}{(\partial \phi_{s_i}/\partial t)} + \underset{\text{(e)}}{\lambda(\phi^*_{f_i} - \phi_{f_i})} = 0 \qquad (2)$$

Model formulation is completed by expressions for interphase equilibrium as follows:

$$\underset{\text{(f)}}{\phi^*_{f_i}} = \underset{\text{(g)}}{\phi^*_{f_i}[\theta(t),\phi_{s_1},\phi_{s_2},\ldots,\phi_{s_i},\ldots,\phi_{s_{n-1}}]} \qquad (3)$$

There are *n* components taking part in the separation, so that (*n*–1) material-balance equations are required, the final degree of freedom being utilized in the total continuity equation. Furthermore, the constant-density assumption for a liquid assures through the latter equation the independence

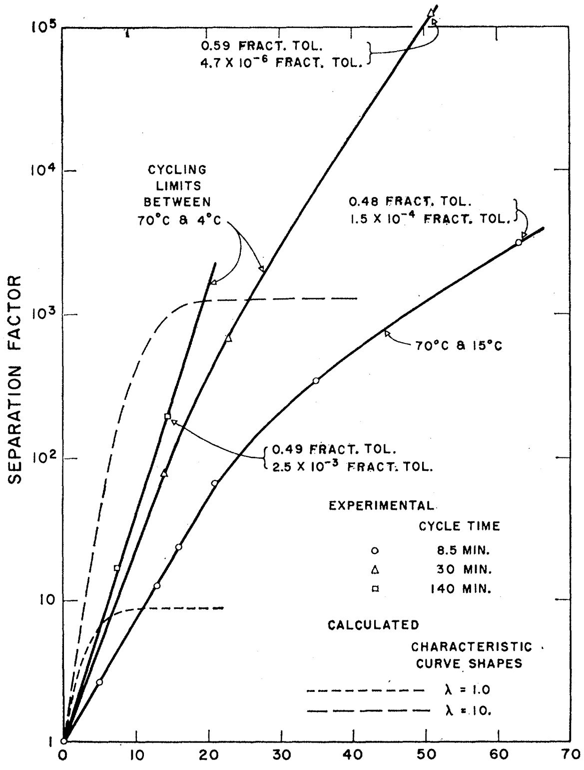
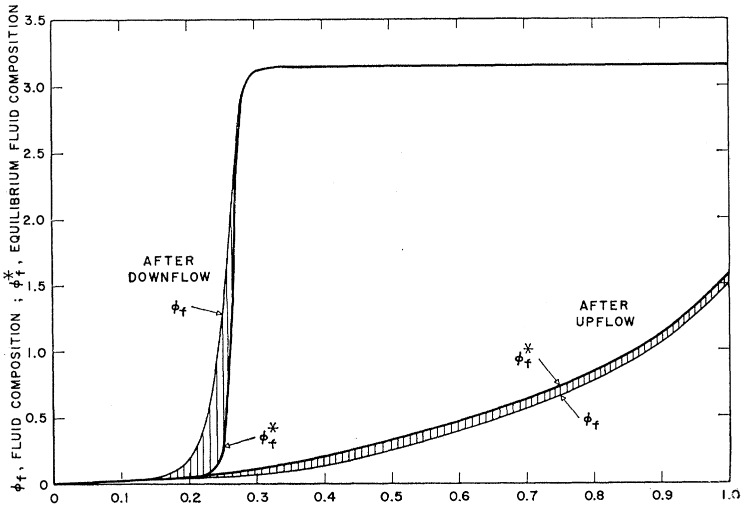


Fig. 2 (left). Experimental separation factor for toluene-*n*-heptane versus number of cycles counted from initial compositional uniformity. Concentrations indicated, for selected experimental points, refer to volume fraction of toluene in mixture in pistons at column ends. Also indicated are theoretical curve shapes computed from the mathematical model. Fig. 3 (below). Computed dimensionless interstitial-fluid composition, ϕ_f, and adsorptive-phase equilibrium composition, ϕ^*_f, versus axial position in the bed at two instants in the cycle, after completion of upflow and downflow.



in position of the fluid velocity, which is the coefficient $\alpha f(t)$ in term (a) (Eq. 1).

For brevity we omit initial and boundary conditions necessary for a complete statement of model. Suffice it to indicate, however, that the degree of separation depends not only on the coupled actions expressed in Eqs. 1–3, but also, in the case of the total reflux operation here described, on the total solute content of the system, such content depending on initial conditions.

Dependent variables in the conservation, rate, and equilibrium equations are identified as ϕ_f, ϕ^*_f, and ϕ_s, being, respectively, the dimensionless fluid composition, fluid composition in equilibrium with the adsorbent phase, and the adsorbent-phase composition. Independent variables are the dimensionless time, t, axial position, z, and system temperature, θ.

The terms in Eqs. 1 and 2 express mass conservation contributions attributable to these mechanisms: (a) axial convection, (b) interstitial, fluid-phase transient, (c) adsorptive-phase transient, (d) axial fluid-phase diffusive loss, (e) lumped-parameter interphase diffusive-transport rate.

Parametric action resides in bringing into synchronism and into suitable phase-angle relation the alternating flow velocity in (a), $\alpha f(t)$, with the periodically cycling temperature θ in (g); the effect of this action penetrates the system of equations successively through the terms (f), (e), and (c).

The magnitude of separation by means of "parapumping" depends on the numerical values of the equation coefficients α, κ, η, λ, the function ϕ^*_f [ ], and the balance among them. These experimental results and others (*4*, *5*) serve to demonstrate that the parametric-pumping principle applied to separation is indeed an operable one, and that the system coefficients are physically attainable in workable combinations. Coefficients are identified thus: α, velocity amplitude; κ, ratio of volume of adsorptive phase to that of the interstitial fluid phase; η, dissipative axial diffusivity of solute;

$$\lambda = (D/R^2)(1/\omega)$$

that is, reciprocal characteristic diffusion time D/R^2 relative to the frequency ω of the axial fluid convective displacements. (Term D is a lumped interphase-diffusion constant, and R is the adsorbent-particle radius.) The properties of the adsorptive equilibrium function ϕ^*_f [ ] complete identification of the essential parameters.

We have found the dimensionless rate constant λ to be particularly important, as shown by the ordering of separation results (Fig. 2) according to experimental frequency. Figure 2 also shows that numerical, computer solutions of the equations predict properly the *qualitative* dependence of separation on λ, the development of limiting separations, and the effect of elapsed time. The equations served a priori to predict that large separations were likely, and thereby provided the incentive for performance of these experiments. *Quantitative* matching of the mathematical model with experiment will involve secondary but important factors such as temperature-dependence of system coefficients, detailed thermal responses within the column, and strategy of computation.

Figure 3 presents composition profiles, computed through Eqs. 1 and 2, based on experimental equilibrium values for the toluene-heptane-silica gel system (*6*). The steep wave front after downflow is that of an adsorption wave, and its shape reflects the effect of the nonlinear, Langmuir-type adsorption isotherm; characteristically of such systems the desorption (upflow) wave is relatively diffuse, as shown. The direction of the interphase-diffusion gradient ($\phi^*_f - \phi_f$) is noted to alternate during each cycle. Parametric action serves to build up, through successive adsorption-desorption steps, a steep solid-fluid adsorption wave that constitutes an effective barrier to the passage of fluid-phase solute through the bottom end of the column. With a 180-deg phase shift between temperature and flow variables, the solute barrier is predicted to appear at the top of the column.

Earlier reports about parametric pumping concern the recuperative mode (*4*), in which heat recovery is an intimate part of the system, and a suggestion (*5*) that parametric-pumping separation may serve as a candidate model for active transport through membranes in biological cells, the intensive thermodynamic variable in this instance being *p*H instead of temperature.

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References and Notes

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6. G. S. Robins performed the equilibrium measurements that were employed in these theoretical calculations.
7. Supported by NSF grant GK-1427X. Computations were by the Princeton University Computer Center, which was aided by NSF grant GP-579. One of us (N.H.S.) holds an NSF graduate fellowship. We thank R. W. Rolke for helpful discussions.

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Kornerupine: Its Crystal Structure

Abstract. *Three-dimensional analysis of the crystal structure of kornerupine reveals the crystallochemical formula* $Mg^{VI}_2Mg^{VI}Al^{VI}_6[Si_2O_7]\ [(Al,Si)_2SiO_{10}]O_4(OH)$*, with four formula units in the structure cell of* a = *16.100 (2) Å*, b = *13.767(2) Å*, c = *6.735(2) Å; space group,* Cmcm. *The unusual crystal structure includes walls of Al-O edge- and corner-sharing octahedra, and chains of alternating Mg-O and Al-O octahedra fused to the walls by further edge-sharing to form dense slabs. These slabs are held together by* $[Si_2O_7]$ *corner-sharing tetrahedral pairs and* $[(Al,Si)_2SiO_{10}]$ *corner-sharing tetrahedral triplets.*

The curious mineral kornerupine was named, and described from its type locality in Fiskenaesset, Greenland, by Lorenzen (*1*) after the Danish geologist A. Kornerup. Many other occurrences have since been recorded. The most detailed account of the crystal chemistry of kornerupine, including references to its paragenesis, is by McKie (*2*).

The chemistry of kornerupine has had a tumultuous history which is not surprising in view of its complex crystal structure. Mineralogy texts usually present its formula as $MgAl_2SiO_6$, but recent detailed work by McKie on material from Mautia Hill, Tanganyika, led him to propose the empirical formula $Na_{0.01}Ti_{0.02}Mg_{3.69}Fe^{3+}{}_{0.37}Al_{6.36}$-$Si_{3.71}B_{0.41}O_{21.75}(OH)_{0.25}$, with four such formulas in the structure cell. Unambiguous interpretation of this formidable composition requires careful analysis of the crystal structure, which was undertaken on an eminently suitable crystal from Mautia Hill (*3*).

The structure cell of kornerupine (Table 1) suggested that the most propitious axis of rotation was *c*[001]. Ten levels of three-dimensional data to $2\theta = 70°$ were collected with a Pailred automatic diffractometer using