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The Relationship Between One-Dimensional and Two-Dimensional Separation Processes

One-dimensional, time dependent separations are analogous to two-dimensional, steady state separations, and the equations for the former can be transformed to the latter by the transform $t \rightarrow \theta/w$. This analogy is used to develop and provide the solutions for the two-dimensional analogues of several variations of chromatography, parametric pumping, and pressure swing adsorption.

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SCOPE

Many different separation techniques have been developed for the separation of complex mixtures using adsorbents and various chromatographic packings. For preparative separations, a variety of operating techniques including straightforward scale-up of elution development, cyclic operation, and two-dimensional operation (reviewed by Conder, 1973; Wankat, 1974; Sussman, 1976, respectively) have been developed. These methods are all attempts to increase throughput and/or continuously separate multicomponent mixtures. The prototype of the two-dimensional chromatograph is a packed annulus which is rotated past a fixed feed point while solvent or carrier gas is continuously fed to the entire annulus. The schematic of this rotating cylinder system is shown in Figure 1. The solutes move up the annulus in helical flow paths depending upon the rotational velocity, the carrier velocity, and the amount they are adsorbed. Since the steady state separation occurs in the z and θ directions, the process is commonly called a two-dimensional separation. This two-dimensional flow path contrasts with usual chromatographic and adsorption systems, where separation occurs in only the z direction, but is also time dependent.

The purpose of this study was to formalize the relationship between time dependent, one dimensional separation processes such as elution development in chromatography or cyclic operation of adsorption columns and the two-dimensional separation techniques. Then this formalized analogy will be used to compare existing processes, and, finally, the analogy is used in a systematic study to develop new two-dimensional separation techniques. This work thus serves as a bridge to connect three intensively studied separation techniques and helps to explain the somewhat unfamiliar two-dimensional techniques. In addition, a powerful tool for looking for new separation techniques is developed.

The relationship between time dependent, one-dimensional and steady state, two-dimensional processes has been discussed briefly in the literature. Martin (1949) used the analogy between these processes to suggest the first two-dimensional chromatograph. This relationship between the rotating annulus device and usual elution development has been occasionally mentioned in the literature since then. Wankat (1972) extended this analogy to staged systems when he noted the relationship between countercurrent distribution and two-dimensional stage systems. This analogy was further extended to cyclic systems when Wankat et al. (1976) noted the analogy between cycling zone adsorption and continuously regenerated two-dimensional systems.

CONCLUSIONS AND SIGNIFICANCE

Comparison of the material and energy balances, equilibrium relation, and mass transfer expression for the time dependent, one-dimensional and the steady state, two-dimensional separations in the geometry of Figure 1 shows that the equations and appropriate boundary conditions for the one-dimensional system can be transformed into the equations and boundary conditions for the two-dimensional system if the transform $t \rightarrow \theta w$ is made where t is time, θ is the angular coordinate, θw is the angular velocity, and diffusion and dispersion can be neglected. Thus, under condition of negligible diffusion and dispersion, the two techniques are mathematically similar. The separations obtained will thus be similar. The analogy is applied to the limiting periodic state of cyclic operations and the steady state of the two-dimensional apparatus. This analogy thus makes it possible to apply

solutions developed for one process to the other process.

The analogy between the two processes was also employed to develop several new two-dimensional separation techniques. Although mathematically similar, the one- and two-dimensional processes are physically very different and some of the new techniques may be of considerable practical interest. These new processes are the two-dimensional analogues of programmed operations of chromatography, the analogue of the programmed multiple development (PMD) technique of thin layer chromatography (Figure 2), the analogue of multiple bed cross flow chromatography (Figure 3), the analogues of several variations of parametric pumping (Figures 4 and 5), and the analogue of pressure swing (heatless) adsorption (Figure 6).

The significance of this work is threefold. It delineates the relationship between common time dependent separation techniques and less commonly employed steady two-dimensional separation techniques. Second, several new two-dimensional separation techniques are described, some of which may eventually become commercially important. Finally, the use of this analogy allows us to predict the separation achieved from the known results for one-dimensional systems.

Many methods for achieving large scale separation in adsorption, ion exchange, and chromatographic systems have been developed. These include straightforward scale-up of the analytical method of elution development which has been extensively reviewed by Conder (1973), moving-bed systems with either countercurrent flow of solid and fluid or two-dimensional cross flow which are reviewed by Sussman and Rathore (1975) and Sussman (1976), and cyclic methods involving cycling a thermodynamic variable such as temperature or pressure which are reviewed by Wankat (1974). Although the goals of these processes are the same and the mathematical descriptions are similar, the techniques are physically very different and have appealed to different groups. Because of this, few attempts have been made to consolidate the knowledge in these fields.

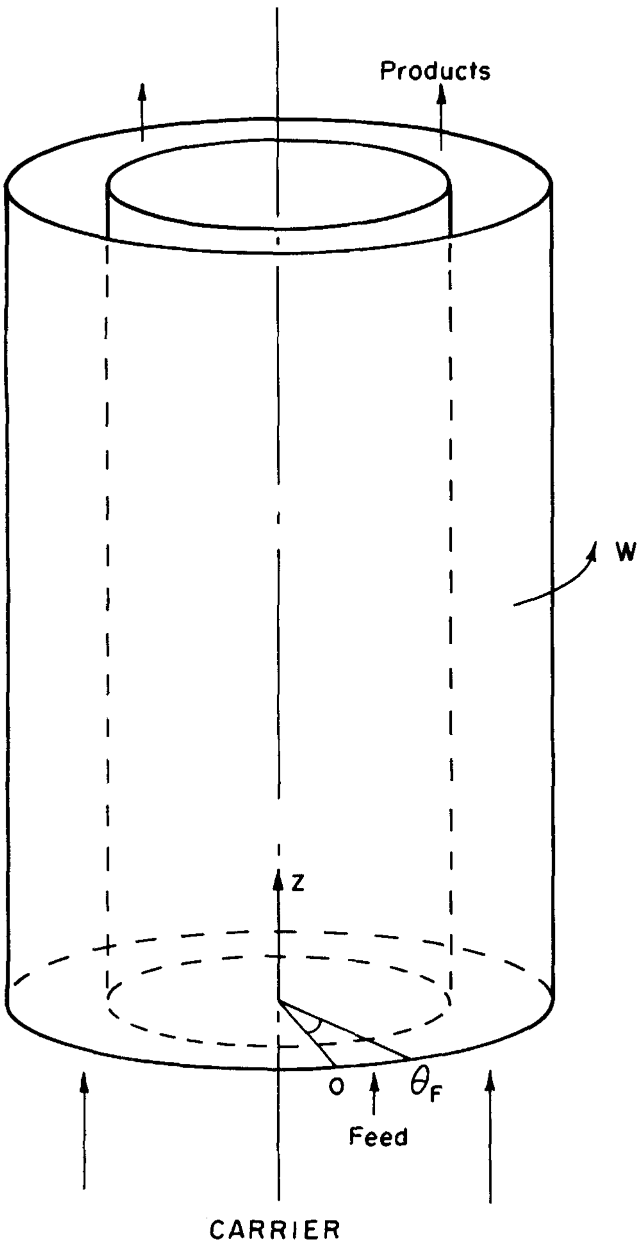

Fig. 1. Rotating annulus apparatus for continuous chromatography.

In this paper, the relationships between these processes will be explored by first considering time dependent chromatographic and cyclic processes and comparing these to steady two-dimensional separations. Then, the analogy developed from these considerations will be used to develop several new two-dimensional processes. The mathematical models for these processes can be obtained by transforming the existing models for the analogous one-dimensional techniques.

Although the analogy between one- and two-dimensional separation process has not been formally studied, it has been used in the development of two-dimensional processes. Thus, Martin (1949) first suggested two-dimensional separation in a rotating device by considering the analogy with elution development in chromatography. The most common form of two-dimensional device dates from this pioneering work and consists of a cylinder which is rotated past a fixed feed point as shown in Figure 1. The cylinder can be a series of columns arranged as in a Gatling gun, a circle of paper for paper chromatography, or a packed annulus. Each individual column or vertical segment receives a pulse of feed when it is rotated past the feed point and then is developed by continuous introduction of carrier fluid. The analogy with a stationary column receiving a pulse of feed is obvious, but the rotating apparatus is continuous and steady state. This analogy has been mentioned many times in the literature and has been used many times to make mechanical separations continuous. Examples are rotating drum filters, moving belt filters, and a rotating carousel device for high gradient magnetic separation.

The analogy was extended to staged systems by Wankat (1972) who developed a continuous two-dimensional staged system based on countercurrent distribution. He noted that the steady state solute mass balances for the two-dimensional system were identical to the countercurrent distribution equations if he related stages in the second spatial dimension to the discrete time variable.

The two processes thus have identical solutions, although one process separates the feed on a time basis while the other is steady state and separates the feed on the basis of spatial direction.

Wankat et al. (1976) used the analogy between one- and two-dimensional systems to develop a continuously regenerated steady state system that could separate multicomponent mixtures. The process was patterned after a multicomponent cycling zone adsorption scheme. The explicit analogy between one-dimensional cycling zone adsorption and the two-dimensional apparatus was recognized for staged systems, but the explicit relation was not recognized for continuous contact systems.

MATHEMATICAL RELATIONSHIP

The usual form of the solute balance for adsorption or chromatography in a packed column assumes plug flow and ignores radial gradients in velocity, concentration, and temperature. This balance for nonreacting systems is

$$\epsilon \frac{\partial c}{\partial t} + \epsilon v \frac{\partial c}{\partial z} + (1-\epsilon)\rho_s \frac{\partial q}{\partial t} - D \frac{\partial^2 c}{\partial z^2} = 0 \quad (1)$$

The energy balance for an adiabatic packed column with negligible heat of adsorption is

$$\rho_f C_f \epsilon \frac{\partial T}{\partial t} + \rho_s C_s (1-\epsilon) \frac{\partial T_s}{\partial t} + \rho_f C_f \epsilon v \frac{\partial T}{\partial z} - D_T \frac{\partial^2 T}{\partial z^2} = 0 \quad (2)$$

The solute balance on the solid phase is

$$\rho_s (1-\epsilon) \frac{\partial q}{\partial t} = k_M a (c - c^*) \quad (3)$$

At equilibrium, the solid and fluid concentrations are related by an equilibrium expression of the general form

$$q = q(T, c^*) \quad (4)$$

These two equations can be compared to the equations for steady state operation in the two-dimensional rotating annulus system shown in Figure 1. Radial gradients are again assumed to be negligible, and the resulting solute balance in cylindrical coordinates is

$$\epsilon w \frac{\partial c}{\partial \theta} + \epsilon v \frac{\partial c}{\partial z} + (1-\epsilon)\rho_s w \frac{\partial q}{\partial \theta} - D \frac{\partial^2 c}{\partial z^2} - D \frac{1}{r^2} \frac{\partial^2 c}{\partial \theta^2} = 0 \quad (5)$$

The rotation of the annulus results in a solid body rotation of both phases. The energy balance for an adiabatic system is

$$\rho_f C_f \epsilon w \frac{\partial T}{\partial \theta} + \rho_s C_s (1-\epsilon) w \frac{\partial T_s}{\partial \theta} + \rho_f C_f \epsilon v \frac{\partial T}{\partial z} - D_T \frac{\partial^2 T}{\partial z^2} - D_T \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} = 0 \quad (6)$$

For isothermal systems or systems using direct external heating, the temperatures will be assumed to be fixed, and the energy balances are not required. The solute balance on the solid phase for the steady state rotating system is

$$(1-\epsilon)\rho_s W \frac{\partial q}{\partial \theta} = k_M a (c - c^*) \quad (7)$$

The equilibrium expression is the same as Equation (4).

Comparison of Equations (1) and (2) to (5) and (6), respectively, shows that there is an extra diffusional term in the latter set of equations. Under conditions where mass or thermal diffusion are important, the one- and two-dimensional systems are not analogous. However, the diffusional terms can commonly be ignored at least for a first approximation. Under the conditions of negligible diffusion and dispersion, there is a term-by-term correspondence between Equations (1) and (5), Equations (2) and (6), and Equations (3) and (7). If the simple transformation

$$t \rightarrow \theta / w \quad (8)$$

is made, then Equations (1), (2), and (3) are transformed into Equations (5), (6), and (7), respectively, for the case with negligible diffusion. As long as q is not a function of t or θ, this transformation is valid regardless of the equilibrium relationship, Equation (4), which is used. Equation (4) is unaffected by the transformation.

Appropriate boundary conditions for isothermal operation of a column when diffusion can be neglected are

$$c = c_f \quad 0 < t \leq t_f, \quad z = 0 \quad (9)$$

and

$$c = 0 \quad t_f < t < t_{\text{cycle}}, \quad z = 0 \quad (10)$$

where the cycle repeats for $t > t_{\text{cycle}}$. For the rotating two-dimensional system, the appropriate boundary conditions are

$$c = c_f \quad 0 \leq \theta \leq \theta_f \quad z = 0 \quad (11)$$

$$c = 0 \quad \theta_f < \theta < \theta_{\text{cycle}} \quad z = 0 \quad (12)$$

where

$$\theta_{\text{cycle}} = 360° / (\text{integer}) \quad (13)$$

The boundary conditions for the column transform into the boundary conditions for the two-dimensional system if the transformation shown in Equation (8) is employed. This relates t_f to θ_f and t_{cycle} to θ_{cycle}

$$t_f = \theta_f / w \quad (14)$$

$$t_{\text{cycle}} = \theta_{\text{cycle}} / w \quad (15)$$

for equivalent boundary conditions. Nonisothermal boundary conditions such as those required for cycling zone adsorption will also transform to the appropriate boundary conditions for the two-dimensional system when diffusion can be neglected.

The analogy relates conditions for limit cycle operation of one-dimensional systems, where each cycle is a repeat of previous cycles to steady state operation of the two-dimensional system. A limit cycle has been reached when

$$c(z, t')|_{\text{cycle } n-1} = c(z, t')|_{\text{cycle } n} = c(z, t')|_{\text{cycle } n+1}$$

Since the partial differential equations and the boundary conditions can be transformed from the time dependent, one-dimensional form to the steady state, two-dimensional form, the systems are analogous, and the solutions obtained for the column system can also be employed for the two-dimensional system. This analogy requires that diffusion be negligible and that w is adjusted in Equation (15) so that Equation (13) is satisfied. The analogy holds strictly for comparison of column operation to the rotating cylinder type of two-dimensional apparatus with axial flow shown in Figure 1. For other two-dimensional geometries (see Sussman and Rathore, 1975; Sussman, 1976), the mathematical equivalence is no longer valid, but a loose analogy between one- and two-dimensional systems can be used as a guide for developing new separation processes.

The application of the solution from a one-dimensional system to a two-dimensional system will be illustrated in the following sections. It should be emphasized that the solution for the two-dimensional system applies only to steady state operation and does not include start-up. Also, application of this relationship between systems does not require any further assumptions, although these assumptions may be required to obtain an analytical solution. If further assumptions are made (for example, external mass transfer is controlling), they must be made for both systems. The analogy holds for nonequilibrium systems as long as the lumped parameter mass transfer expressions [Equations (3) and (7)] are valid expressions for the system being considered.

This analogy between time dependent, one-dimensional systems and steady state, two-dimensional systems can also be extended to staged systems. This was done for isothermal systems by Wankat (1972) and for nonisothermal cyclic systems by Wankat et al. (1976).

APPLICATIONS WITH EXISTING SYSTEMS

Applications of the analogy to existing two-dimensional systems will first be covered. The two-dimensional system analogous to isothermal adsorption or chromatography is the rotating annulus device shown in Figure 1. Solutions to the mass balance equations for a column can be applied to the two-dimensional apparatus if diffusion is neglected. For example, if the assumption of local equilibrium between solid and fluid is made, the mass and energy balance equations for a column are easily solved by the method of characteristics for both linear and nonlinear isotherms (Sherwood et al., 1975). These solutions are easily transformed to the two-dimensional system. The solution for the two-dimensional system shows the same types of concentration and thermal waves as the one-dimensional system, except that the wave velocities are transformed into slopes at which the concentration or thermal wave moves up the annulus. These slopes S are related to the predicted wave velocities u (Sherwood et al., 1975) by the expression

$$S = \frac{u}{w} \tag{16}$$

If favorable nonlinear isotherms are employed in the analysis, shock waves are predicted if a dilute solution is displaced by a more concentrated one (Sherwood et al., 1975). Shock waves are also predicted for the two-dimensional system, and the slope of the shock wave is related to its velocity in the corresponding column system by Equation (16). Thus, there is a one-to-one correspondence between the solutions and the physical phenomena occurring in the column and the two-dimensional systems if diffusion can be ignored.

Nonequilibrium solutions for the mass balance equations (Sherwood et al., 1975; Vermeulen et al., 1973) can also be transformed to the two-dimensional system if diffusion is negligible. Solutions for paper chromatography can also be applied to two-dimensional paper chromatography (Sussman, 1976).

A specific example of this analogy is the relationship between multicomponent cycling zone adsorption (Wankat, 1975) and continuously regenerated two-dimensional adsorption (Wankat et al., 1976). The two-dimensional system with input of hot feed is analogous to the traveling wave mode cycling zone adsorption, and the two-dimensional system with vertical external heaters is analogous to the standing wave mode cycling zone adsorption. To obtain additional zones, several rotating apparatuses would be used in series.

The two-dimensional system with an external heater slanted at an angle is not analogous to the cycling zone systems. Instead, it is analogous to chromatothermography (Zhukhovitskii, 1960), where a heater is moved along the length of the column. The velocity of the heater in the one-dimensional system and the slope of the heater in the two-dimensional system are related by

$$S_{\text{heater}} = u_{\text{heater}}/w \tag{17}$$

Solutions for one of these systems can then be applied to the other system by transforming the variables.

NEW TWO-DIMENSIONAL CHROMATOGRAPHY METHODS

The analogy between one- and two-dimensional separations can be used to generate new two-dimensional chromatographic techniques based on several of the variations used in chromatography. In this section, several possible new techniques will be discussed. The method for developing the analogue to a one-dimensional system is straightforward. A plot of feed condition (that is, concentration, temperature, flow direction) vs. time is made for a complete cycle. If conditions along the length of the column vary, graphs of condition vs. time are made at varying values of z. Each of these graphs is converted to a plot of condition vs. θ/w using the transform $t \rightarrow \theta/w$ and Equation (15) to relate t_{cycle} and θ_{cycle}. These graphs are then used to sketch a rotating annulus device which will generate the desired graphs. With a little practice, the intermediate step of drawing the graphs can be dispensed with. This procedure produces a two-dimensional apparatus where conditions along the z axis are the same as in the one-dimensional apparatus. Transformation of the solutions for models with negligible dispersion is straightforward and will not be covered.

One obvious two-dimensional device would be to form a flexible thin layer chromatography sheet into a cylinder and rotate this cylinder past a fixed feed point. This apparatus is then similar to rotating paper chromatography equipment (Sussman and Rathore, 1975; Sussman, 1976).

A second two-dimensional chromatographic system can be developed by considering temperature programming in gas chromatography. In temperature programming, the entire column is heated while the feed is being separated. The two-dimensional analogue would be to use vertical heaters to heat the rotating annulus at different values of θ. Figure 1 would be modified to include a series of vertical heaters. The segment of the annulus before the feed location would be cooled. This is equivalent to cooling the entire column before injection of the next pulse. t_{cycle} and θ_{cycle} are related by Equation (15). The angular location of a heater at a given temperature is related to the time at which this temperature occurs in the temperature programming by

$$\theta = tw \tag{18}$$

The two-dimensional system would be continuous instead of time dependent.

A two-dimensional system analogous to solvent programming in liquid chromatography can also be developed. For this system, the device shown in Figure 1 would be modified by feeding in solvent of different concentration along the perimeter of the annulus. Solvent to recondition the system would be added before the feed point. The angular location of the solvent of a given concentration

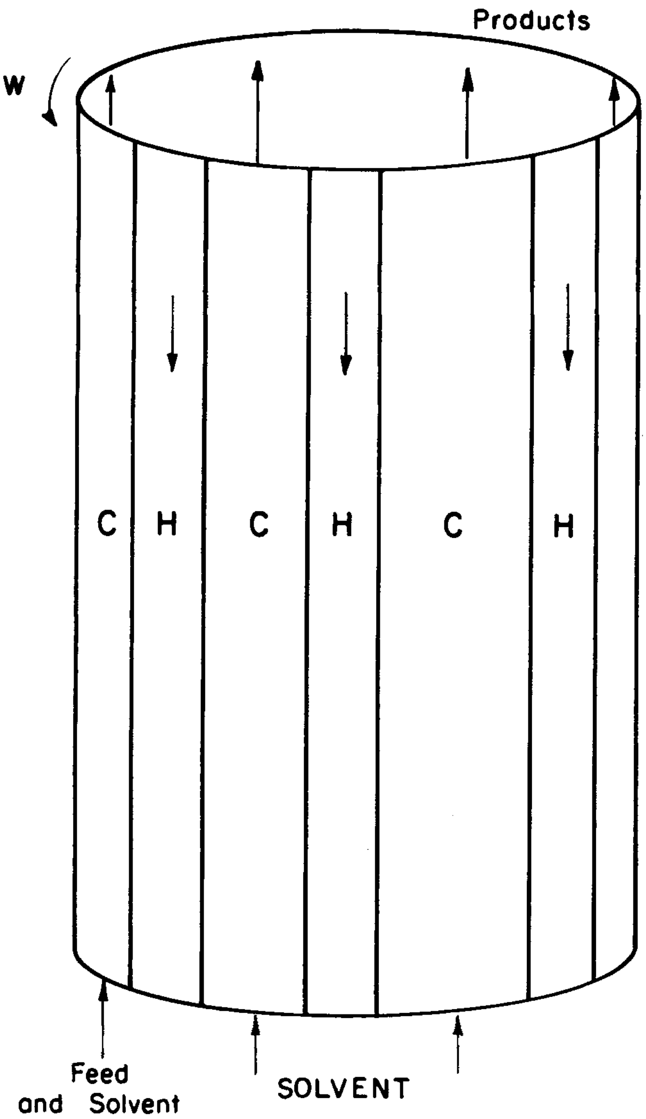

Fig. 2. Two-dimensional analogue of programmed multiple development.

can be compared to the time it would be input in solvent programming by Equation (18) applied to points of equal solvent concentration.

A recent development of considerable interest is Programmed Multiple Development (PMD) for thin layer chromatography (Perry et al., 1975). In this process, development of the feed spot proceeds for a set period of time, and then the solvent is evaporated by heating the chamber. As the solvent evaporates, the solvent front retreats. The retreating solvent front reconcentrates the spot so that resolution is sharper than in usual thin layer chromatography. The operation is repeated several times until the desired separation is obtained. The corresponding two-dimensional apparatus is shown in Figure 2. A thin layer sheet formed into a cylinder is rotated past fixed heaters. Feed is continuously added to one of the cold strips, and products are withdrawn at the top of the device. In the hot strips, the solvent is evaporated. Note that the cold segments increase in size since the solvent front must move further after each evaporation step. Angular locations for heaters can be related to the time a heater is turned on in PMD through Equation (18). Although the conceptual picture of the apparatus is relatively simple, actual construction might be complex.

The two-dimensional analogy can also be applied to the multiple-layer chromatography with cross flow recently developed by Wolf and Vermeulen (1976). In this apparatus, selective packings are layered in a column, and removal of the product is done by a series of cross flows with the axial flow temporarily stopped. The analogous two-dimensional apparatus is shown in Figure 3. It consists of a rotating annulus packed with several layers of selective adsorbents. The annulus rotates past a fixed portion where no axial flow of carrier is input, but instead a cross flow elution is used. This cross flow elution is placed so that all components are separated from each other and each can be eluted as a pure component. The appropriate apparatus dimensions can be obtained by using Equation (18) to relate angular distance θ in the two-dimensional apparatus to time t in the apparatus of Wolf and Vermeulen (1976). If the annulus is divided into segments by vertical dividers, angular dispersion will be prevented, and the two-dimensional and column apparatuses are exactly analogous during axial flow. The cross flow portions will be analogous if the thickness of the annulus is much less than the annulus radius. When these conditions are met, the staged solution developed by Wolf and Vermeulen (1976) can be applied to the rotating annulus system with the appropriate changes in variables.

TWO-DIMENSIONAL PARAMETRIC PUMPING

Parametric pumping has been extensively studied and was recently reviewed by Rice (1976). A two-dimensional apparatus can be used for either batch or continuous operation of many of the variations of parametric pumping. If diffusion and dispersion effects can be neglected, the equations for parametric pumping and the two-dimensional analogue are the same after the variables are transformed using Equation (8). Thus, the two-dimensional apparatus can be used to produce a steady state separation completely analogous to the time dependent parametric pump operating at its limit cycle. This process will be more extensively covered than the chromatographic processes covered earlier.

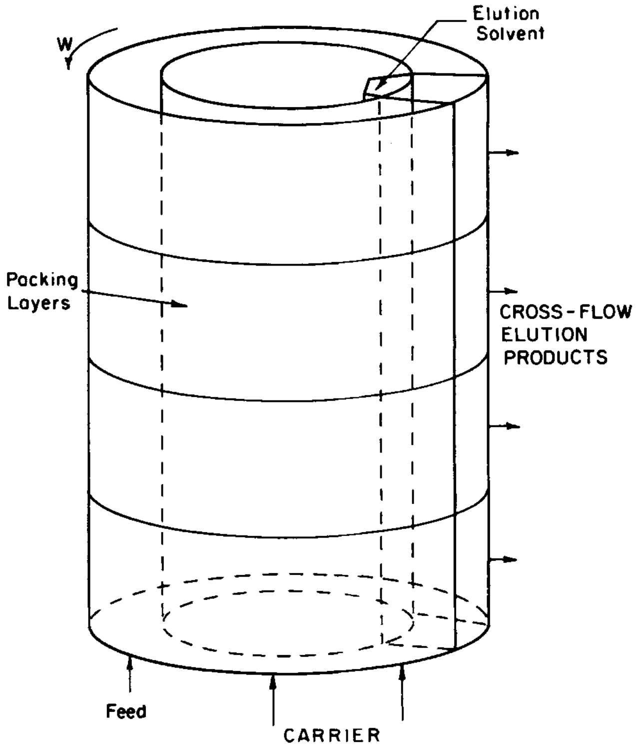

Fig. 3. Two-dimensional layered chromatograph with cross flow.

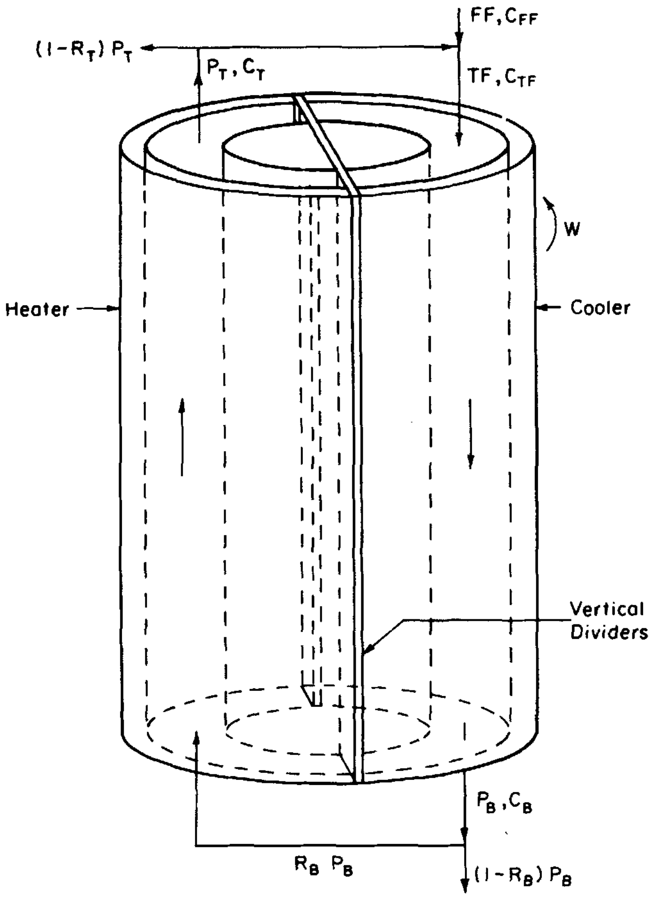

Fig. 4. Two-dimensional direct mode parametric pump. Top feed with completely mixed reservoirs.

The two-dimensional analogue of continuous thermal direct mode parametric pumping with completely mixed reservoirs and feed during the cold portion of the cycle is shown in Figure 4. The feed is input during downflow into the cold adsorbent bed, and regeneration is done during upflow in the hot bed. In Figure 4, the right side of the annulus has downward flow and the left side upward. A series of vertical dividers would allow for flow reversal in the annulus. Some of the dilute product is used as purge to regenerate the bed, and some of the concentrated product is refluxed to increase the concentration of the concentrated products. The equivalent of batch operation is obtained if both products and the feed are stopped and reservoir material is recycled. With usual adsorbent behavior, where solutes are adsorbed less strongly at higher temperatures, this device can produce almost pure solvent in the bottom product and concentrated but not pure top product. With competing solutes or ions, a bottom product which contains only the sorbate which is less strongly sorbed at the cold temperature can be obtained. The top product will be concentrated but not pure. If a pure top product is desired, bottom feed can be used, but then the bottom product will not be pure. To purify multicomponent mixtures, several devices in series can be employed with feed between two of the apparatuses.

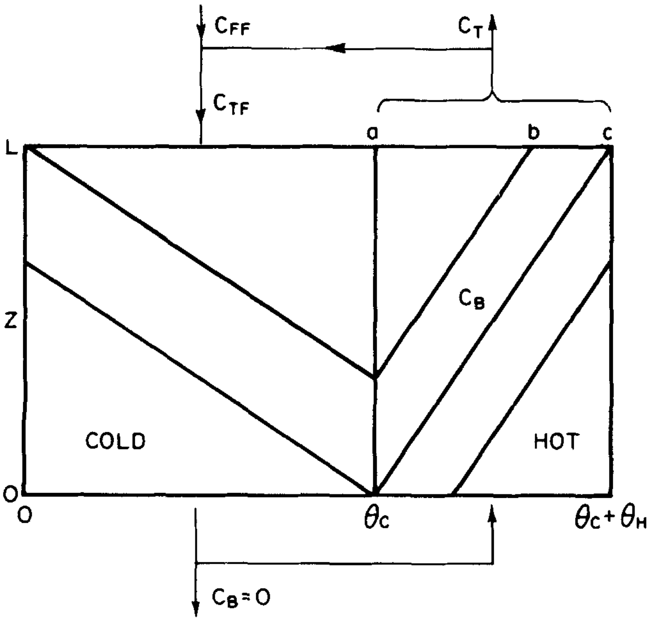

Fig. 5. Characteristics for steady state direct mode parametric pump with mixed reservoirs, top feed. System has linear isotherms and solution is for steady state.

The two-dimensional apparatus will eventually reach a steady state operation. At steady state, the operation of the annulus is equivalent to a parametric pump which has reached a limit cycle where each cycle is a repeat of the previous cycle. Under these conditions, the parametric pump solutions obtained for the conditions of negligible dispersion (Rice, 1976) can be used for the rotating apparatus after the variables are transformed according to Equation (8). This would include the large number of local equilibrium solutions which have been developed (Rice, 1976) or the solutions including a finite mass transfer rate but with negligible dispersion (the stop-go algorithm) (Sweed and Wilhelm, 1969; Sweed and Rigaudeau, 1975).

This procedure for transforming solutions will be illustrated using the local equilibrium model. The local equilibrium solution for the two-dimensional parametric pump can be obtained by simplifying Equations (5) and (6) and solving them using the method of characteristics. Alternatively, the existing solutions for open parametric pumps operating in the limit cycle where each cycle is a repeat of the previous cycle can be used if t is transformed to θ using Equation (18). The local equilibrium solution for the direct mode thermal parametric pump is obtained using the method of characteristics. The characteristics for a parametric pump with linear isotherms are straight lines on a graph of z vs. t and have slopes equal to $u_c(T)$ (Rice, 1976):

$$u_c(T) = \frac{v}{1 + \dfrac{1-\epsilon}{\epsilon}\rho_s A(T)} \tag{19}$$

where $A(T)$ is the constant for linear equilibrium $q = A(T)c$. This characteristic solution for the one-dimensional system is directly applicable to the two-dimensional equipment shown in Figure 4 if Equation (18) is used, and the graph is read as z vs. θ/w. The slopes of the characteristics remain u_c on this plot. However, it will generally be more convenient to plot z vs. θ. This is illustrated in Figure 5 for the system shown in Figure 2 for a single dilute solute with linear isotherms. Since a z vs. θ plot multiplies the abscissa by w and divides the slope by w, the characteristics on Figure 5 have a slope of $u_c/w = S_c$. Thus, from Equation (19), S_c is

$$S_c = \frac{v/w}{1 + \dfrac{1-\epsilon}{\epsilon}\rho_s A(T)} \tag{20}$$

The same equation for S_c and the same solution as shown in Figure 5 are obtained if Equations (5) and (6) are solved directly.

The characteristic solution shown in Figure 5 is for steady state operation. The concentrations are constant along each characteristic until the temperature is changed. Then the solute redistributes between the solid and fluid phases. The new fluid concentration can be determined from a mass balance. For linear isotherms, the change in solute concentration simplifies to

$$\frac{c_{i+1}}{c_i} = \frac{S_{i+1}}{v_{i+1}} \Big/ \frac{S_i}{v_i} \tag{21}$$

The product concentrations can be determined by following characteristics and counting the number of temperature changes they undergo. The product concentration is then the properly weighted average of concentrations existing from that end of the apparatus. For the particular case shown in Figure 5, which is not the only possible case, the bottom product contains no solute (in practice, C_B will be very low but not zero), and the top product consists of a mixture of pure solvent and material which has been concentrated once according to Equation (21). This would correspond to a separation such as toluene, *n*-heptane, and silica gel, where batch separation factors as high as 10^5 have been obtained (Wilhelm et al., 1968). The concentration of the top product and the concentration of material fed to the column will depend upon the fraction of material refluxed and the fraction of top product which has undergone concentration.

For a completely mixed top reservoir, the external mass balances for the system are

$$(1 - R_B)P_B + (1 - R_T)P_T = (FF) \tag{22}$$

and

$$(1 - R_T)c_TP_T + (1 - R_B)c_BP_B = (FF)c_{FF} \tag{23}$$

The terms are defined in Figure 4. For the characteristics shown in Figure 5, the top material exiting from *a* to *b* is concentrated once following Equation (21), and the material from *b* to *c* exits at concentration c_B since it is concentrated once and diluted once. Using the ratios *ab*/*ac* and *bc*/*ac*, and following the characteristics in Figure 5, we can determine the top concentration c_T. The ratios can be determined from the geometry of the characteristics. To determine c_T and c_B for the general case where $c_B > 0$, these equations must be combined with a mass balance around the top reservoir. This is straightforward, but the algebra is messy (Rice, 1976; Wankat, 1978).

For the special case where $c_B = 0$, the value of c_T can be found from the overall mass balances Equations (22) and (23) plus the relationship between P_B, P_T, and FF. For the case where $c_B = 0$

$$c_T = \frac{c_{FF}(FF)}{(1 - R_T)P_T} = \frac{c_{FF}(1 - R_TR_B)}{(1 - R_T)R_B} \tag{24}$$

The bottom product will remain pure as long as

$$|S_c\theta_c| < |S_h\theta_h| \text{ and } |S_c\theta_c| < L \tag{25}$$

$|S\theta|$ is the distance that a characteristic will penetrate into the annulus during a given portion of the cycle.

Several alternatives to the basic parametric pump have been developed and can be extended to two-dimensional operations. Thompson and Bowen (1972) showed that the separation in a batch parametric pump increased much more rapidly if the reservoirs were plug flow without any mixing. This idea was extended to continuous parametric pumping (Wankat, 1978) and is easily extended to a two-dimensional parametric pump. The apparatus shown in Figure 4 would be modified so that products with different values of θ are not mixed. The most concentrated material is withdrawn at the top, and the least concentrated material is removed at the bottom. The other material is selectively refluxed to the appropriate location in the annulus. The solutions obtained by Wankat (1978) can be applied to the rotating annulus by applying Equation (18). The solution of the external mass balances shows that mixed and unmixed reservoir systems give the same results if $c_B = 0$, but if $c_B > 0$ the unmixed reservoir system with selective reflux gives better separation.

The original parametric pumping studies (see Rice, 1976) used the recuperative mode of operation. In this mode, the column is adiabatic and the fluid is either heated or cooled before it enters the column. Thus, temperature waves occur in the column. Sweed and Rigaudeau (1975) used the local equilibrium model and the stop-go model to analyze batch recuperative parametric pumping, and Wankat (1978) studied continuous recuperative mode systems. The two-dimensional analogue to the traveling wave mode of continuous parametric pumping would be similar to Figure 4 except the annulus is adiabatic and heat exchangers are used on the reflux lines. The recuperative mode has the advantage that since external heaters are not required, the equipment would be easier to build and scale-up. In the recuperative mode, the bed in each portion of the apparatus (up or downflow) is no longer isothermal. An energy balance must be used to determine the progression of the thermal wave into the bed and the temperature at each point. The simplified local equilibrium mass and energy balance equations have been solved for the limit cycle of the continuous recuperative mode parametric pump analogous to the two-dimensional parametric pump (Wankat, 1978), and those solutions and the conclusions made there are directly applicable to the two-dimensional apparatus.

The two-dimensional parametric pump operating in the recuperative mode is similar to a conceptual design shown by Gidaspow and Onischak (1973). Those authors were using a separate hot gas for desorption and did not report any theoretical or experimental work. A somewhat different two-dimensional design using a countercurrent radial flow of steam to desorb an activated carbon adsorbent held in a rotating annulus was discussed by Bowen (1971). Bowen discussed results achieved with a commercial apparatus but did not present an analysis. The radial flow rotating annulus system is not directly analogous to the time dependent column systems for which solutions have been obtained.

Up to now, only the removal of solutes has been considered. Camero and Sweed (1976) have shown that a batch parametric pump can separate multicomponent mixtures of ions or of solutes which compete for sorbent sites, and a continuous pump can do a binary separation. A continuous top feed separator similar to that shown in Figure 4 can produce a bottom product which contains only the ion which is least strongly adsorbed at the low temperature. The top product will be concentrated with the other ion. A system with bottom feed can produce a pure top product, while two rotating annuluses with center feed will produce pure top and bottom products. The mathematical analysis for competing sorbates is somewhat more complex than the calculations presented previously. Fortunately, this analysis has already been done by Camero and Sweed (1976) for the parametric pump. Their results for the steady periodic state can be used for

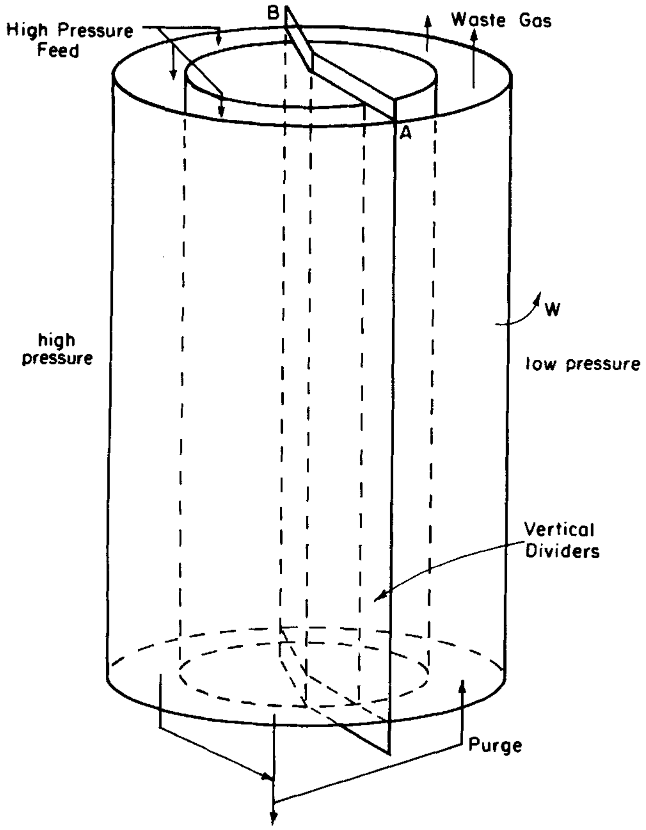

Fig. 6. Two-dimensional analogue of pressure swing adsorption.

steady state operation of the rotating annulus system after the variables are transformed according to Equation (8). This transformation is valid only for converting their periodic steady state results to steady state two-dimensional separations.

TWO-DIMENSIONAL PRESSURE SWING ADSORPTION

Heatless or pressure swing adsorption involves adsorption of a gas at high pressure and desorption at low pressure (Skarstrom, 1972). The steady state two-dimensional analogue of pressure swing adsorption is shown in Figure 6 for the case with completely mixed reservoirs and reflux at the bottom of the column using a low pressure purge. A common modification in pressure swing adsorption is to save some of the blowdown gas for repressurization. The equivalent two-dimensional operation would be to reflux some of the low pressure waste from point A to point B. If the apparatus were designed to depressurize and repressurize portions of the annulus in steps, this reflux could be obtained without additional compression.

Shendalman and Mitchell (1972) used a local equilibrium model with negligible dispersion and linear isotherms to model heatless adsorption. Mitchell and Shendalman (1973) relaxed the assumption of local equilibrium but retained the assumption of negligible dispersion. When the transformation given in Equation (8) is applied, the mass balances and boundary conditions for both of these theories are transformed into the appropriate steady state, two-dimensional equations. This requires that the annulus be constructed with suitable vertical dividers to prevent flow of gas in the θ direction when the pressure is changed and applies only to the limit cycle of pressure swing adsorption. Conditions at any value of (z, θ) in the two-dimensional apparatus can be related to conditions at (z, t) in pressure swing adsorption by relating θ and t through $\theta = tw$. Thus, the solutions obtained by Shendalman and Mitchell (1972) and Mitchell and Shendalman (1973) for the periodic repeating state can be applied to the two-dimensional apparatus if the appropriate changes in variables are made. The start-up solutions are not directly comparable.

DISCUSSION

The analogy between time dependent, one-dimensional and steady state, two-dimensional separations has, like all analogies, limits of applicability. The analogy is only strictly applicable when diffusion and dispersion can be ignored and when the fluid velocity in the flow direction is constant. This latter restriction prevents strict application of the analogy to radial flow two-dimensional systems (Bowen, 1971; Sussman, 1976). Although the analogy cannot be applied in a strict mathematical sense, it can be used outside its limits of applicability to help understand two-dimensional separations and to help design new separators.

There are other situations besides those covered in this paper where this analogy can be helpful. One set of examples involves mechanical separators such as filters or magnetic separators where rotating drums or carousels are routinely used to make a batch process continuous. The analogy can also be applied to relate the unsteady operation of packed-bed thermal regenerators to the steady state operation of thermal recovery heat wheels. In this case, the appropriate equations are analogous if thermal diffusion can be neglected.

One other intriguing application of this analogy is to compare steady state, two-dimensional systems to steady state, one-dimensional countercurrent systems. Steady state countercurrent systems can be mimiced in a fixed-bed system by using the simulated countercurrent technique (Broughton, 1968) of moving all feed and product withdrawal points continuously. The simulated countercurrent system is, from a stationary observer's viewpoint, a time dependent one-dimensional system. If dispersion and diffusion can be neglected, the simulated countercurrent system is analogous to a steady state, two-dimensional apparatus with feed and product withdrawals set at an angle in the z-θ plane. Thus, this two-dimensional system and the countercurrent system must give the same separations. This application will be explored in detail in a later paper.

Although the dispersive forces have been neglected here to show the analogy clearly, in real systems dispersion will reduce the separation which occurs. Thus, all of the calculations with nondispersive models will predict more separation than will actually occur. Nonequilibrium models will be more realistic than the equilibrium models. Any additional mixing caused by channeling, convection cells, or excessive dead volume in the two-dimensional apparatus will greatly reduce the separation achieved.

Finally, a word needs to be said about construction and operation of the two-dimensional apparatus. Bowen (1971) discusses a commercial rotating apparatus, Applegate (1974) discusses commercially available thermal wheels which are similar to these separators, Sussman (1976) discusses the operation of many experimental devices, and Wankat et al. (1976) discusses the operation of the two-dimensional equivalent of cycling zone adsorption. These studies show that considerable care must be taken to avoid channeling or mixing within the annulus. A series of vertical walls which divide the annulus into chambers will help prevent these problems and also allow for different flow directions in different portions of the annulus. These vertical dividers were schematically indicated in Figures 4 and 6. Also, the necessary rotating seals are simpler if low pressure operation is being employed. There are problems in the construction and operation of the rotating equipment, but these problems can be overcome.

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NOTATION

$A(T)$ = linear equilibrium constant $q = A(T)C$, l/g dry solid
a = interfacial area for mass transfer, cm^2
c = solute concentration, g/l
c^* = solute concentration in fluid in equilibrium with solid
C_f = heat capacity of fluid, cal/g°C
C_s = heat capacity of solid, cal/g°C
D = mass molecular diffusivity cm^2/min
D_T = thermal molecular diffusivity, cm^2/min
FF = fresh feed flow to annulus (Figure 4), g/min
k_m = mass transfer coefficient
L = length of column or of annulus, cm
P_B, P_T = total downward and upward flows in annulus (Figure 4), g/min
q = solid phase concentration, g/g dry solid
R_B, R_T = bottom and top internal reflux ratios (Figure 4)
r = radial coordinate, cm
S_c = slope concentration wave moves up two-dimensional annulus, cm/deg
T = temperature, °C
TF = total feed flow to annulus (Figure 4), g/min
t = time, min
t_{cycle} = period of cycle, min
t_f = time period feed is introduced, min
t' = time since beginning of cycle
u_c = concentration wave velocity, cm/min
v = interstitial fluid velocity, cm/min
w = rotational velocity, deg/min
z = axial coordinate, cm

Greek Letters

ϵ = void fraction
θ = angular coordinate, deg
θ_{cycle} = angular distance equivalent to one cycle, Equation (12)
θ_F = angular distance feed is introduced, deg
ρ_s = density of solid, g/l

Subscripts

B = bottom
c = concentration
C = cold
f = fluid
F = feed
FF = fresh feed
H = hot
Heater = slope or velocity of external heater, Equation (17)
i = conditions before a thermal boundary
$i+1$ = conditions after a thermal boundary
S = solid
T = top
TF = total feed

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