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

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To cite this Article Wankat, Phillip C.(1974) 'Cyclic Separation Processes', Separation Science and Technology, 9: 2, 85 — 116
To link to this Article: DOI: 10.1080/00372367408056067
URL: http://dx.doi.org/10.1080/00372367408056067

SEPARATION SCIENCE, 9(2), pp. 85–116, 1974

REVIEW

Cyclic Separation Processes

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Abstract

This review covers cyclic separation methods used for adsorption, ion exchange, and chromatographic separation processes where the cyclic parameter is a thermodynamic variable which changes the equilibrium distribution coefficients of the solutes. The cyclic methods reviewed include heatless or pressure-swing adsorption, parametric pumping, and cycling zone adsorption. These cyclic techniques have been studied as a possible preparative chromatographic separation method or for continuous production from adsorption or ion exchange columns.

OPERATIONAL METHODS

Before discussing cyclic separation techniques in detail, we will see how they compare with other operational techniques for preparative chromatography, adsorption, and ion exchange. In the simplest operational scheme these are batch processes using a fixed bed. Typically, an adsorption step would be followed by a desorption step and then the process would be repeated. This can be considered a cyclic process, and in some cases there is no clear-cut dividing line between the cyclic processes to be discussed here and usual batch operation. In other cases the technique is clearly a cyclic technique because of the complexity of the cycles. The usual batch processes for adsorption and ion exchange are discussed in a variety of references (*1–3*).

For preparative chromatography the obvious approach is to increase the column diameter and operate in the usual batch mode with pulses of feed followed by solvent or carrier gas. This straightforward scale-up of the usual analytical technique has received considerable attention and is now being used commercially (*4*), but it has been plagued by decreased separation as the column diameter increases and by relatively low throughputs of feed. Aspects of this preparative chromatographic technique are discussed in detail in a recent collection of papers edited by Zlatkis and Pretorius (*5*).

A second approach which has been employed is to move either the solid material or the column in such a way that the fluid flow is either countercurrent or at right angles to the solid movement. The major difficulties with this type of apparatus have been attrition of the solid and mechanical problems with the complicated apparatus. Application of this approach to chromatographic separations has been extensively studied and reviewed by Barker (*5*, *6*). Moving bed systems have been studied and are in commercial use for ion exchange and adsorption and are discussed by Dorfner (*7*) and Dodds et al. (*8*). An alternative that is similar to the moving bed system is to simulate countercurrent flow by changing the feed and product locations. These systems have been studied by Broughton (*9*) and by Barker and Deeble (*10*) and are now in commercial use (*9*, *11*).

The third and newest approach utilizes the cyclic variation of a thermodynamic variable to force the separation. Pressure, concentration, and temperature have all been used as the cyclic variable. All these cyclic separation processes depend on the fact that the distribution coefficient will vary when the cyclic variable changes and the solid can be made to alternately store and lose solute to the fluid. By proper switching of the product stream, a separation can be obtained. In this review we will discuss systems based on cyclic pressure changes, cyclic concentration changes, cyclic temperature changes, and finally related cyclic techniques.

SYSTEMS BASED ON PRESSURE CYCLES

The process called heatless adsorption or pressure swing adsorption was invented by Skarstrom (*12*, *13*). In this technique adsorption of solute from a gas stream is done at a high pressure and desorption is done at low pressures. At high pressures considerably more solute can be adsorbed than at low pressures. The bed can then be purged at low pressures by using a fraction of the high-pressure product stream. In Skarstrom's original device (*12*, *13*), two columns were used. One column would be adsorbing at high pressure with upward flow of the gas while the second column would desorb with downward flow of the gas at low pressure. After several minutes the beds would be interchanged. A product with less than

1 ppm water vapor was obtained with a feed containing 4000 ppm. Operation is not isothermal because the beds become hotter while adsorbing water and cooler while desorbing. Because of the short cycle times and the low heat capacity of the air, most of the heat liberated during adsorption is retained in the column and is available to supply the heat for desorption. No theoretical analysis was presented. Skarstrom (*12*) noted that the process was commercially available.

Despite the fact that it is a commercial success and has been considered a major breakthrough (*14*), no further reference was made to heatless adsorption in the open literature for years. (There are many references in the patent literature which will not be discussed here.) Alexis (*14*) discussed the application of heatless adsorption to purify low-grade hydrogen streams. Alexis showed an improved version of Skarstrom's two-bed system which included a small guard chamber before each adsorber to remove heavy hydrocarbons and had three adsorbers in parallel. The third adsorber is used to depressurize the bed that had just finished adsorbing and thus increase the hydrogen recovery. Cost estimates were given which indicate that heatless adsorption can competitively produce 95–98% hydrogen when compared to palladium diffusion or cyrogenic processes. Neither experimental nor theoretical results were presented.

Katira et al. (*15*) discussed the optimization of an even more complicated pressure swing adsorber for hydrogen purification. This patented system contained four beds in parallel and had two internal recovery steps. The inlet stream containing 98 mole % hydrogen and 2.0 mole % methane was fed to the system at pressures ranging from 150 to 400 psig and produced a 99.999 mole % hydrogen product. This process was thus used to obtain a much purer product than that obtained by Alexis (*14*). Activated carbon was found to be the most economic adsorbent for this separation. The economic optimization performed for this one separation problem showed that the ratio of amount of purge gas to amount of feed gas should be kept as low as possible without decreasing the product purity. Operation should be fast, with a total cycle time of less than 8 min (each column adsorbs for 2 min). Neither experimental results nor calculations of bed concentrations and product concentrations as a function of time were presented. The calculations that were made utilized overall mass balances and equilibrium relationships, and assumed that the columns were isothermal.

Lee and Stahl (*16*) compared a series of patented pressure-swing processes for producing oxygen-rich gas from air. The different processes use different numbers of beds, change the cycles around, and use different adsorbents. The most economic process will depend upon the separation and the objectives of the separation.

Shendalman and Mitchell (*17*, *18*) present detailed theories for the operation of the heatless drier system. The purpose of these papers was to gain insight into the operation of heatless adsorbers by studying the system CO_2–helium–silica gel in a two-bed system similar to Skarstrom's original system (*12*). In the first paper (*17*) a simplified mathematical model was employed which assumed local equilibrium between gas and solid at all times, a linear adsorption isotherm, and negligible axial dispersion. These assumptions greatly simplify the equations and allow for an analytical solution by the method of characteristics. The solution technique is similar to that used by Pigford et al. (*19*) for parametric pumping although the heatless adsorption results are complicated by the repressurization and blowdown portions of the cycle. Since this model was in good agreement with experimental results for parametric pumping (*19*), good agreement would be predicted for heatless adsorption. This was not the case. The experimental results showed a sawtooth pattern of concentration vs time while the theory predicts a step decrease in concentration. The theory predicts a much faster cleanup rate than was experimentally observed. The experimental results did approach the theoretical predictions as the purge-to-feed ratio increased. Both theory and experiment show there is a critical purge-to-feed ratio which must be exceeded to obtain complete cleanup of the high-pressure product, but the critical values obtained were not in agreement. Apparently the simplified local equilibrium theory is inadequate for heatless adsorption because of nonlinear isotherms, dispersion, rate processes, and the complex flow behavior during repressurization and blowdown. The simple theory does point out the importance of the purge-to-feed ratio.

In their second article Mitchell and Shendalman (*18*) developed a nonequilibrium model which also attempted to model the blowdown and repressurization parts of the cycle. The controlling mass transfer step was assumed to be transport in the pores, and a single lumped parameter expression was used to model the mass transfer. Axial dispersion was again assumed to be negligible and the column was assumed to be isothermal. For the blowdown and repressurization steps the authors assumed that either (a) the gas and solid were in equilibrium throughout the pressure changes, or (b) that pressure change was so rapid that gas and solid concentrations were frozen. The first technique predicted more separation than was actually achieved, while the second technique predicted much less separation than was obtained experimentally. The method of characteristics was used to reduce the equations to ordinary differential equations which were then solved by finite difference. The new theory did predict a sawtooth pattern when concentration was plotted vs time, but did not completely predict the effect of the purge-to-feed ratio or of the dynamic capacity. The experiments showed the unexpected result that CO_2 concentration goes through a minimum as the dynamic capacity is increased.

Heatless adsorption is apparently considerably more complicated to model than the other cyclic methods which have been successfully modeled. In addition to the depressurization and repressurization steps which still need to be modeled accurately, nonisothermal effects will need to be included for systems removing large amounts of impurities. Considering that heatless adsorption has been commercially available for over 14 years, very little has been published on this process. It is hoped that other companies will follow the lead of Esso Research and Engineering (*12*, *17*, *18*), Chemical Design (*14*), Union Carbide (*15*), and Grace (*16*) and publish their research on heatless adsorption. Heatless adsorption should be a good research problem for industrial-academic cooperation since some relatively fundamental (from an industrial viewpoint) research is needed for an existing process.

A second periodic adsorption process utilizing pressure changes for separation of gases has been studied by Kadlec and his co-workers (*20*, *21*). In this process a high-pressure gas stream is fed into an adsorber. The feed is then turned off and gas from the column is exhausted at the feed end of the column. Cycling is done extremely rapidly and a second product stream is withdrawn continuously from the other end of the column. The original development of this process was apparently done without knowledge of Skarstrom's process. Turnock and Kadlec (*20*) developed a theory for the process which assumed local equilibrium, Freundlich isotherm, and no axial dispersion. Agreement with experimental results on the removal of methane from nitrogen on molecular sieve was good. The much better agreement between theory and experiment than that obtained for heatless adsorption (*17*, *18*) is probably due to the difference in the processes. Turnock and Kadlec (*20*) included the depressurization and repressurization steps (where flow occurs) in their analysis. The nitrogen concentration in the high-pressure product stream increased as the ratio of the product rate to the feed rate decreased. This agrees with the results obtained for heatless adsorption (*17*, *18*) since the ratio of product-to-feed is essentially 1 − (purge/feed). A very interesting result was obtained by operating at 24, 0, and −77 °C. At −77 °C separation was greatly inhibited and the observed separation was considerably less than the separation predicted by the equilibrium theory. At this temperature, rate processes apparently become important. Turnock and Kadlec (*20*) observed a decrease in flow capacity due to attrition of the molecular sieve. This could be solved by use of hard spheres which were used in subsequent work (*21*).

In the second paper on this process, Kowler and Kadlec (*21*) found that there was an optimum cycle time of approximately 3 sec. This cycle would include a short period with no flow to minimize the exhaust. The optimization was based on maximizing the product composition and minimizing the exhaust rate. The N_2 concentrations in the high-pressure product obtained under the optimum conditions were considerably less than those obtained previously (*20*) at lower product-to-feed ratios. It is unclear whether this difference was caused by a different adsorbent or different operating conditions. The optimum conditions will obviously vary depending upon exactly what is being optimized for. Kowler and Kadlec (*21*) also note that shorter columns would require faster cycling, and then the response of the solenoid valves may become the limiting factor. For the theoretical analysis of the optimum operating sequence, a simplified cell model was used because the more exact equilibrium model (*20*) was too complex to work with. This cell model was a poor predictor of output concentrations, but a good predictor of optimum operating conditions. The experimental results with the new adsorbent were not compared with the theoretical predictions from the equilibrium model (*20*), even though mass transfer resistances may now be important. These results should be useful in the design of heatless adsorbers.

SYSTEMS BASED ON CONCENTRATION CYCLES

Since pressure changes have a large effect on gas systems but only a small effect on liquid systems, other variables must be used for cyclic separation of liquids, and can also be employed for gas separations. Concentration waves have long been used in batch operation as either a regenerant for ion exchange (*1*, *2*), as a displacer in adsorption (*3*, *9*), or to modify distribution coefficients in solvent programming in liquid chromatography (*22*). Despite their common use in batch operations, very little use has been made of concentration changes in cyclic separations.

Thompson (*23*) and Reilley et al. (*24*) both considered alternating pure feed with carrier gas in gas chromatography. Thus the cyclic variable is concentration of the carrier gas. The separation is based on retarding one of the components in the feed more than the other components so that it exits when the carrier gas does. Thompson (*23*) studied the separation of light hydrocarbon mixtures using a sinusoidal variation of gas composition. Fast cycles (periods from 1/2 to 3 sec) were used. Separation factors (defined analogously to relative volatility) between the two components of the feed of up to 4.6 were obtained. This seems suprisingly good for a packed section 8 mm long with a 4-mm i.d. Some of the outlet concentration waves were notably unsymmetric. Thompson (*23*) hypothesized that pressure or flow fluctuations caused this effect. This hypothesis is strengthened by the papers on pressure-induced separations, and suggests that concentration and pressure changes might be superimposed to obtain a stronger separation. It should also be noted that this system can also be considered a cycling zone adsorber (discussed later) with one zone.

Reilly et al. (*24*) studied the response of gas chromatographs to a variety of inputs. They were mainly interested in analytical aspects, but also considered some preparative work. For repetitive input functions they discussed several analytical applications, but did not discuss preparative separations.

Concentration cycles have also been used to separate liquids. Broughton (*9*) gives a sketchy report on a cyclic adsorption column where a liquid feed was alternated with a displacer. Details of the experimental and theoretical work are not given. Small unpacked zones allowed mixing to occur and destroyed the separation. Axial mixing could also have a major detrimental effect. Because of these problems and because of the essentially batch nature of the product streams, the cyclic technique was abandoned in favor of the simulated countercurrent bed. This paper thus serves as a challenge to the development of cyclic separation processes since it reports that an alternate method was found to be more acceptable.

Sabadell and Sweed (*25*) studied the use of pH as the cyclic variable in a parametric pump. This article will be discussed in the section on parametric pumping.

The use of concentration changes to force separation in a cyclic process appears to be an area where future research would be profitable. The challenge is to find a chemical which has a large effect on the distribution coefficients and can be easily recovered from the product streams.

SYSTEMS BASED ON TEMPERATURE CYCLES

The majority of the work on cyclic separation techniques has utilized temperature as the cyclic variable. To some extent this is suprising since in gas systems pressure can be cycled much faster and in liquid systems chemical concentration usually has a much greater effect on the distribution coefficients (*22*). Temperature does have the advantages that it can easily be applied and removed externally, and the product stream is not contaminated.

The current interest in cyclic separation techniques was sparked by the development of "parametric pumping" by Wilhelm and his co-workers and of "cycling zone adsorption" by Pigford and his co-workers. Parametric pumping has been reviewed and discussed in detail by Sweed (*26*, *27*). We will first discuss the large number of papers on parametric pumping and then those on cycling zone adsorption.

Parametric Pumping: Initial Studies

Parametric pumping was first described by Wilhelm et al. (*28*, *29*) in 1966. In this process the fluid to be separated is pumped up through a solid stationary adsorbent into a reservoir and then down through the bed into a second reservoir. The cycle is then repeated. In the original "recuperative" mode of operation (*28*, *29*) the fluid is heated in a heat exchanger before flowing up through the bed and cooled before flowing down through the bed. The adsorbent will hold more solute when the fluid is cool. Thus the solute is held by the adsorbent on the cold half cycle and released to the fluid on the hot half cycle. During the hot half cycle the solute will be carried up to the upper reservoir. Eventually, under ideal conditions, all of the solute will be "pumped" to the upper reservoir and the lower reservoir will contain no solute. In principle, an infinite separation factor (defined as the ratio of concentration of solute in the upper reservoir to concentration of solute in the lower reservoir) can be obtained. The original operation was batch, but later papers have extended the technique to continuous and semicontinuous operation.

Wilhelm et al. (*28*) demonstrated parametric pumping in the recuperative mode of operation by removing NaCl from water on a mixed bed of ion exchange resins. A limiting separation factor of 1.2 between product streams was obtained for a completely open system where fresh feed was introduced each half cycle. The mass and energy balances for parametric pumping were presented, but not solved. Extensions of the principle to adsorbents, chromatographic solids, gas separations, and variation of other thermodynamic variables were discussed. In a second paper Wilhelm (*29*) discussed parametric pumping as a possible model for intracellular active transport. In this article the parametric pumping idea was extended to a variety of oscillating fields such as electrical, magnetic, or chemical potential. Wilhelm (*29*) noted that there would be difficulties in proving or disproving his hypothesis and suggested some experiments. Further papers on this suggestion will be discussed later.

An alternate operating procedure called the "direct mode" was developed independently by Wakao et al. (*30*) and Wilhelm and Sweed (*31*). In the direct mode of operation the stationary bed is heated by external sources (usually a water jacket) before upward flow of the fluid, and the bed is cooled by external sources before downward flow of the fluid. During each half cycle the bed is usually considered to be isothermal. Wakao et al. (*30*) used a cold temperature of 3°C and a hot temperature of 65°C to separate benzene from *n*-hexane on silica gel. Separation factors (defined as the ratio of benzene concentration in the top reservoir to benzene concentration in the bottom reservoir) up to approximately 22 were obtained. The authors used a graphical solution of a staged equilibrium model to calculate separation. The number of stages was estimated as the volume of liquid in the column divided by the reservoir volume. Agreement between theory and experiment was good when the height per stage was large. Although this paper appeared at the same time as the work of Wilhelm and Sweed (*31*), it has had very little impact on subsequent research. This lack of impact was probably caused because Wakao et al. (*30*) published their paper in Japanese and it was relatively inaccessible to most researchers in the United States.

Wilhelm and Sweed (*31*) reported preliminary results on direct mode separations which were reported in more detail by Wilhelm et al. (*32*). Wilhelm and Sweed (*31*) studied the separation of toluene from *n*-heptane using chromatographic grade silica gel as the adsorbent. This article showed a fantastic experimental separation of a 10^5 to 1 concentration ratio for toluene between the top and bottom reservoirs. The separation could have been increased by running for more cycles, increasing the temperature difference, or increasing the cycle time. The differential mass balance and an approximate rate expression were presented. Solutions were presented that were obtained by numerical computer calculations, but the calculation procedure was not presented. The theory was in qualitative agreement with the experimental results. Unfortunately, this theory is too complicated to explain clearly the reasons for the separation.

Wilhelm et al. (*32*) studied both direct and recuperative parametric pumping. For the direct mode the experimental results presented earlier (*31*) are presented in more detail. The theory presented earlier (*31*) is also presented in more detail and theoretical results are presented in more detail. Again the complexity of the equations obscures the reasons for the separation. The recuperative mode results presented greatly amplify the work reported earlier (*28*). More experimental results were presented for NaCl separations in an open system. The theoretical model (*28*) was solved numerically for both open and closed systems using a mixing cell model. With sine changes in velocity there is a region of optimum separation, but this region is not physically accessible for liquids with currently available resins. The authors (*32*) also discuss the principles of parametric pumping and suggest several alternatives such as an open system with reflux, staging in multicolumn arrays, and use of liquid systems. This paper can be considered as the first definitive study of parametric pumping, but naturally many questions were left unanswered.

Parametric Pumping: Recuperative Mode Separation of Liquids

Next two additional studies on the recuperative mode of operation for liquid separations will be discussed before considering the many papers on liquid separations via the direct mode. Rolke and Wilhelm (*33*) did precise modeling of open recuperative parametric pumping without any recycle (*28*, *32*). The model included heat and mass transfer in the column including dispersive effects. Intraparticle mass transfer was modeled by either a lumped parameter model or a distributed parameter model. The latter model was considerably more accurate, but required ten times more computation time. The equations were solved by finite difference computer calculations. The parameters needed for the computer model were obtained experimentally, and the model was checked with chromatographic pulse experiments. The experimental runs were simulated accurately by the distributed parameter model but not by the lumped parameter model. An average separation factor of 1.11 and a maximum separation factor of 1.22 were obtained. Sweed (*27*) reports on the Masters thesis of J. Rigaudeau who found that the temperature wave originating at one end of the column must pass through the entire column to obtain large separations. This was not done by Rolke and Wilhelm (*33*). This paper (*33*) represents the most complete and precise modeling for any of the cyclic separation techniques discussed in this review.

Sabadell and Sweed (*25*) used pH changes to remove K^+ and Na^+ from water. This concentration driven system was mentioned previously. The separation utilized the recuperative mode of operation with the low pH end being closed (except for addition of HCl to keep the pH constant) and the high pH end open (fresh feed and product withdrawal every half cycle). Sweed (*26*) calls this semibatch operation. The cations were concentrated in the acidic reservoir, but there was little separation of the two cations in most runs. The maximum separation factor obtained for total

$K^+ + Na^+$ was 1.84. The energy for the separation comes from the neutralization reaction which occurs in the column. The separation studied by Sabadell and Sweed (*25*) does not appear to use this energy efficiently, but they did not make any attempt to optimize the separation. Sweed (*26*) notes that theoretical calculations for pH parametric pumping will be more difficult than for thermal parametric pumping. This process and parametric pumping in general was also featured in a news article (*34*).

Except for the work of McAndrew (*35*) on gas separations, which will be discussed later, this completes the work on the recuperative mode of operation. The limited success obtained with this technique is somewhat surprising considering the success that has been obtained with the similar "traveling wave" mode of operation for cycling zone adsorbers (*36*). In this reviewer's opinion the recuperative mode should not be abandoned. None of the separations studied have large shifts in distribution coefficient, and the thermal system studied did not have any recycle. The recuperative mode does have the advantage that heat recovery is potentially better (*32*, *33*). A fair test of the recuperative mode of operation would be to optimize the recuperative separation of toluene and *n*-heptane on silica gel and compare the results on the basis of separation per unit of energy consumption with that obtained with the direct mode (*31*, *32*).

Parametric Pumping: Batch Direct Mode Separation of Liquids

Most of the parametric pumping research has concentrated on direct, thermal separation of liquids. We will discuss batch separations and then open separations. For the batch separations the papers will be grouped according to the type of theoretical analysis used.

The theoretical analysis developed by Wilhelm et al. (*32*) was reasonably successful in predicting the separations achieved, but had the disadvantages of being time consuming and so complex that the reasons for separation were obscured. The first advance after this was the "equilibrium" theory developed by Pigford et al. (*19*) and generalized by Aris (*37*). The basic assumption in this theory is that the solid and fluid are locally in equilibrium. This assumption greatly simplifies the equations since rate equations are not needed. In addition, axial dispersion was neglected and the equilibrium relationship was assumed to be linear. With these assumptions the resulting equation is an hyperbolic partial differential equation which can be solved analytically by the method of characteristics. The characteristic lines can be used to show graphically the development of the separation, and to show when separation will not occur. Pigford et al. (*19*) also fit their theory to the data of Wilhelm et al.

(*31*). This was done by fitting one parameter, the equilibrium constant change parameter *b*, to the data. When this is done, the parameter *b* will include other effects such as dispersion and rate limitations which occur in the column and will not agree with the value calculated from equilibrium data. This same technique was used later by other authors. This paper has been very influential because for the first time it clearly explained the reasons for separation, and since then the equilibrium theory has become a very popular analysis method. Because of the many simplifying assumptions, exact agreement with experimental data should not be expected.

Aris (*37*) pointed out that Pigford et al. (*19*) had chosen a special case and he presented the general solution. In a short note, Baker et al. (*38*) concurred with Aris' analysis.

This work has also initiated considerable correspondence. Rhee and Amundson (*39*) suggested that deviations from the theory were due more to the nonlinearity of the isotherms than to mass transfer resistances. In his reply Baker (*40*) agreed that nonlinear isotherms would affect the separation, but noted that the ultimate separation is not necessarily limited by nonlinearities. Harris (*41*) stated that equilibrium stage concepts should be employed, that there is no staging in time, and that the equilibrium model (*19*) is not a valid predictor of separations. Baker (*42*) and Sweed (*43*) answered Harris (*41*) by stating that the equilibrium stage concept is not necessarily *the* fundamental idealization (*43*), that the equilibrium theory is a good predictor of the maximum possible separation (*42*, *43*), and that the batch systems do have staging in time. It appears that successful use of the equilibrium theory for many problems has proved that this theory is a useful idealization.

The original equilibrium theory (*19*, *37*) assumes that there is no dead volume in the reservoirs and that the reservoirs are perfectly mixed. In practice some dead volume is always present. The equilibrium theory was extended to include reservoir dead volume by Gregory and Sweed (*44*) and Chen and Hill (*45*). Both of these papers were concerned mainly with open instead of batch systems and will be discussed in detail later. For the batch system both results (*44*, *45*) agree with Aris (*37*) in the limiting case where the reservoirs have no dead volume. However, their results do not appear to agree with each other so care should be taken in applying these results. Thompson and Bowen (*46*) studied the assumption that the reservoirs are perfectly mixed. They showed theoretically that with no mixing in the reservoir a much greater maximum separation can be achieved. This requires that many separate products be removed from each reservoir. Thompson and Bowen (*46*) also discuss a two-column arrangement where the two columns are operated back-to-back to minimize mixing. In this arrangement the outer ends of the columns can be connected so that the pump operates without reservoirs. This paper presents some interesting ideas which may be difficult to augment experimentally, but should be tried.

The equilibrium theory was used by Butts, Gupta, and Sweed (*47*) to study separations of multicomponent mixtures. The mixtures were assumed to have linear, noncompetitive equilibria. The separation was achieved in a batch parametric pump by using unsymmetric cycles with greater flow to one of the reservoirs. Different solutes will penetrate different distances into the column during each half cycle. The fluid displacements during the hot and cold portions of the cycle can be adjusted so that one solute will migrate upward while the other solutes migrate downward. The authors develop the theory for two processes for separating multicomponent mixtures and discuss how two columns could be used to isolate any desired component. In actual practice a batch process like this would require large reservoir dead volumes to allow sufficient cycles for separation before all of the liquid was pumped to the bottom reservoir. Thus the open systems discussed later are probably better choices for multicomponent systems. Also, the best a single column can do is to separate a binary pair of solutes or make a split within a series of solutes.

Butts, Sweed, and Camero (*48*) utilized a different approach to separate multicomponent mixtures of cations on Dowex 50 × 8 resin. In these experiments binary mixtures of K^+ and H^+ could be adjusted so that K^+ would migrate to the top reservoir and H^+ to the bottom reservoir in normal batch operation. Separation factors in the thousands were obtained in some experiments. This is opposite to the prediction (*18*) of the simple equilibrium theory that all species would move in the same direction to the top reservoir. Butts et al. (*48*) explained their results by noting that electroneutrality must be preserved. Thus when K^+ desorbs, H^+ must adsorb. As a result H^+ must move in an opposite direction than would normally be expected. In addition to this effect a "total separation" effect was observed which was the general movement of both ions to the top reservoir. This was caused by the swelling and shrinking of the resin as the temperature changed. This total separation effect was amplified when the displacement per half cycle was decreased. A modified equilibrium theory was employed to explain this effect. Additional experiments were done with ternary mixtures. By proper adjustment of variables, K^+ could be made to concentrate in the top reservoir, H^+ in the bottom reservoir, and Na^+ in the middle of the column. As outlined by the authors, this method has exciting possibilities for separating multicomponent mixtures of ions. This paper appears to present a new and unexpected use of parametric pumping for complete fractionation of ionic mixtures.

The next calculational procedure appeared shortly after the equilibrium theory (*19*). This is the STOP-GO algorithm developed by Sweed and Wilhelm (*49*). In this technique the partial differential equations are first reduced to ordinary differential equations (ODE) using the method of characteristics, but the solid and fluid are not assumed to be in equilibrium and the equilibrium relationship does not have to be linear. The spatial and time domains are divided into increments and the ODE are then solved numerically by first flowing the fluid without interphase transfer (GO), and then transferring solute between phases without flow (STOP). If each spatial increment were given enough time to come to equilibrium, this algorithm would be identical to countercurrent distribution calculations (*50*). The STOP-GO method was then used to show that separation increased as the mass transfer coefficient increased, as the fluid velocity decreased, as the cycle time increased, and as the reservoir dead volume decreased. The experimental data of Wilhelm and Sweed (*31*) could be fit very closely with this model by adjusting the dead volume parameter. When this is done, the dead volume now includes other effects that were not modeled. The STOP-GO model is more realistic than the equilibrium model, but it requires numerical computer calculations. This more realistic model predicts that separations first increase exponentially and then level off to some limiting value as the number of cycles increases. The experimental data of Wilhelm and Sweed (*31*) were also replotted to show that a given separation was reached in the shortest time when short cycle times are used. This more realistic model still will not predict the separations accurately a priori, but requires adjustment of one parameter (dead volume). The STOP-GO model would be preferred over the equilibrium model for process calculations.

Sweed and Gregory (*51*) used the STOP-GO method to simulate some new data on the separation of NaCl from water using an ion retardation resin. Modest separation factors of approximately 10 were obtained. Unfortunately, this data cannot be compared directly with the recuperative results (*28*, *32*, *33*) because a different resin was used and the direct mode results included reflux. The mass transfer coefficient was determined by simulating experimental breakthrough curves, and three parametric pumping runs were used to calculate the velocity dependance of this coefficient. Once this was done the model was used to simulate successfully two additional parametric pumpings runs where the fluid displacement was varied. This model was then used to predict the expected separation for an open system. This paper showed that batch, direct mode parametric pumping can be accurately modeled if data on pump operation is available to fit the variables. It is unclear whether reservoir void volume was again (*49*) used as an adjustable parameter. A more definitive check of the theory would be to obtain all parameters independently (i.e., in a noncyclic system) and then predict a priori a parametric pumping separation. If this were done, the quantitative fit of the data would probably be poorer.

Equilibrium staged models have also been employed to model parametric pumping (*52*, *53*). Hung and Lee (*52*) used the equilibrium plate theory to model parametric pumping in continuous contact columns. By adjusting the number of theoretical plates the model could simulate experimental data and agreed with other simulations, but this model did not agree with the equilibrium theory (*19*) since infinite separations were not predicted. Wankat (*53*) utilized two equilibrium stage theories to analyze liquid–liquid extraction parametric pumping. The possible application of parametric pumping to systems other than adsorption and ion exchange had been previously mentioned by Wilhelm et al. (*32*) and Sweed and Wilhelm (*49*). Several methods for holding a liquid solvent stationary were presented and experimental separations of acetic acid from water using diethyl ether as the solvent were run for a horizontal helix and a test tube system. Separations were small. The helix was modeled with a continuous flow staged system and the test tube system was modeled with a discrete transfer countercurrent distribution model (*50*) which is similar to the STOP-GO method (*49*). The experimental and theoretical results agreed qualitatively, but quantitative agreement was poor. With the test tube system this was mainly due to evaporative losses since a carefully run experiment would be expected to give excellent agreement with theory (*50*). The qualitative predictions of the staged model agree with the predictions of the STOP-GO model (*49*), although this agreement is not obvious since different variables are held constant in these papers. Application of parametric pumping principles to extraction is not so promising as adsorption or ion exchange applications for two reasons. First, temperature often has little effect on the distribution coefficients, and second, the cyclic system would have to compete with a steady-state countercurrent system.

A mixing cell model was employed by Gupta and Sweed (*54*) to simulate nonequilibrium parametric pumping. In the mixing cell model the number of cells was decreased to a manageable number by lumping part of the dispersion due to finite mass transfer rates into the diffusivity. The equations for the cell model are solved by either matrix exponentiation or by use of Laplace transforms. The authors also present a theory for near equilibrium operation which is similiar to the equilibrium staged models (*52*, *53*). The near equilibrium model requires considerably less computer time than the other techniques, but is not as accurate. The experimental data of Sweed and Gregory (*51*) was fit very well by the cell model when the experimentally determined mass transfer coefficients were used. The number of cells had to be adjusted to give a good fit. The reservoir void volumes used in the calculation are not specified. A two-column arrangement for continuous separation of mixtures containing two solutes is also presented. The authors give computation times for a given separation problem, but do not compare these times with the time required for the STOP-GO method. Although the model was not applied to find the effect of a large number of parameters, one would expect predictions similar to those of other nonequilibrium models (*49*, *51–53*).

Parametric Pumping: Separation of Liquids in Open Systems

Various open parametric pumping systems have been suggested and studied which separate liquids continuously or semicontinuously in the direct thermal mode. The first suggestions for such open systems were contained in some of the original articles by Wilhelm et al. (*28*, *32*). The first detailed presentation with theoretical calculations was presented by Horn and Lin (*55*), and the first experimental data was discussed by Sweed (*26*).

Horn and Lin (*55*) studied a parametric pump arrangement with center feed into a central reservoir and product withdrawal from the two end reservoirs. Flows and temperatures in the two-column sections were in phase with each other. The apparatus was described in general mathematical terms and a geometric interpretation of the separation was presented. The "enrichment problem" where a single solute is to be concentrated was discussed and the steady-state counterpart was shown to be the dual-temperature separation process that has been used for isotope separation (*56*). The "split problem" where two components are to be separated from each other was developed by assuming that the components would be soluble in a suitable carrier liquid. The steady-state counterpart of this process is the two solvent countercurrent extraction. For both problems the parametric pump has the advantage that only one phase is moved, but the disadvantages of heat recovery and control may be more difficult. A possible parametric pumping electrophoresis system was also discussed briefly. This paper is presented in very general terms without any specific examples or experimental data.

Gregory and Sweed (*44*) used the equilibrium theory (*19*) to model two open systems. Both systems are semicontinuous in the sense that feed and products are withdrawn only during a portion of each cycle. One system was nonsymmetric since flow down the column was greater than flow up the column, and the second system was symmetric. For both systems three regions were found for the bottom product concentration; only one region has a limiting product concentration of zero. The constraint [switching point in the nomenclature of Chen and Hill (*45*)] that must be satisfied to obtain a limiting zero concentration is that the bottom reflux ratio (defined as the ratio of amount of bottom product per cycle to bottom reservoir displacement) must be greater than a limiting value dependent upon the equilibrium constants. The top reservoir concentrations for the two systems are different. These two systems were also compared after being optimized for a specific objective. The equilibrium theory is useful since it clearly delineates the conditions under which very large separations can be expected, but as noted in a later paper (*57*), more realistic models are preferred for real systems.

In a paper discussed previously, Sweed and Gregory (*51*) simulated the nonsymmetric parametric pump for the removal of NaCl from water using parameters experimentally determined in batch runs. The STOP-GO model was used. Separation factors of less than 2 were predicted. A calculation using the data presented shows that the simulated operation is not in the region where infinite separation is predicted by the equilibrium theory (*44*).

Chen and Hill (*45*) used the equilibrium theory to study a batch pump and four open systems. The open systems studied were two completely continuous systems with feed at either the top or the bottom of the column and two semicontinuous systems with feed at either the top or bottom of the column. The semicontinuous system with top feed is different from the systems of Gregory and Sweed (*44*) since products are not withdrawn during the same portions of the cycle. The authors introduce the idea of "penetration distance" as the distance a concentration front will move into the column during a half cycle. The switching points for different operating regions are determined in terms of these penetration distances. The batch pump and the open systems with top feed have regions where the limiting bottom product concentration is zero (infinite separation factor), but the open systems with bottom feed cannot produce a zero concentration product. For the systems with top feed the bottom product concentration will jump from zero to some nonzero value when a switching point is passed. The authors show that the semicontinuous pump can produce more zero concentration bottom product per cycle than the continuous pump. However, they do not point out that at equal average bottom product flow rates the internal downflow rate will be less (possibly considerably less) in the continuous pump. Thus the continuous pump is less likely to be flow limited.

Sweed (*26*) discusses separations obtained in an open semibatch system and separations obtained in the symmetric and nonsymmetric open systems discussed previously (*44*). The results for the symmetric and nonsymmetric open systems are very similar to the experiments reported in a later paper by Gregory and Sweed (*57*) and will be discussed when that paper is discussed. In the semibatch apparatus, fresh feed enters the cold reservoir during the cold half cycle while the material leaving the column is removed as product. The hot reservoir end of the column is closed. This operation is similar to the pH experiments (*25*, *26*) except that operation was in the direct instead of the recuperative mode. The work reported was from the B.S. theses of R. J. Goldstein and F. R. Bringhurst at Princeton. The experiments removed urea from water using activated carbon. During an initial transient, urea concentration dropped to a limiting value, and the product concentration remained at this limiting value for several hundred cycles until the column capacity was approached. Then the product concentration slowly increased up to the feed concentration. This technique concentrated the solute considerably, but was inefficient since a large fraction of solute fed left with the dilute product. Comparison with the results of Chen and Hill (*45*) suggests that a more efficient operation might result if a nonsymmetric semibatch operation were utilized with feed at the hot end of the column and product withdrawal from the cold end only. Flow would be greater during the cold half of the cycle. A large, hot reservoir dead volume would allow for longer operating times before breakthrough.

Gregory and Sweed (*57*) compared four open systems and one batch system using the STOP-GO theory. The symmetric and nonsymmetric semicontinuous modes analyzed previously (*44*) were studied experimentally and the experiments were simulated using the STOP-GO theory. The parameters obtained previously in batch separations (*51*) were used in the simulations. As would be expected, the STOP-GO model fit the data very well. The equilibrium theory (*44*) predicted more separation than was obtained experimentally. When the equilibrium theory predicted infinite separation factors, the actually observed separation factor was approximately 2. Sweed (*26*) presents similar experimental results with somewhat different reflux ratios. The five modes of operation were optimized with the specific objective of minimizing bottom product composition with constant feed and bottom product withdrawals. For this objective the nonsymmetric system discussed previously (*44*, *51*) was best when operated at its optimum conditions. The STOP-GO simulation predicts that there is an optimum bottom reflux ratio while the equilibrium theory predicts no effect of reflux ratio. If the objective is changed, the optimum system may change. The systems considered here are different from those of Chen and Hill (*45*) so a direct comparison cannot be made. This paper clearly illustrates that the results predicted by the equilibrium theory must be employed with caution. The STOP-GO algorithm will accurately predict experimental open system separations when the model parameters are determined from batch parametric pumping experiments.

Gupta and Sweed (*54*) discuss a different open system for separation of two components. This system has feed to a reservoir between two columns. The columns are run out of phase with each other so that one is hot while the other is cold and flows are in opposite directions. The mixing cell model (*54*) discussed previously was used to simulate the system and to predict an excellent separation of the two components. This system is different from that of Horn and Lin (*55*) since in that system flows and temperatures on both sides of the feed were in phase. A system similar to this was briefly mentioned by Chen and Hill (*45*).

Chen and his co-workers (*58*–*62*) have studied open systems extensively, both experimentally and theoretically, in addition to the theoretical paper already discussed (*45*). Chen, Rak, Stokes, and Hill (*58*) studied experimentally the continuous parametric pump with top feed. The theoretical solution method for this pump using the equilibrium theory was presented earlier (*45*). In this paper the equations for the concentration transients are presented without derivation [these equations were not given earlier (*45*)]. The continuous pump was used to separate toluene from *n*-heptane on silica gel. In the region where the equilibrium theory predicts infinite separation factors, an experimentally determined separation factor of over 600 was obtained for 14 cycles and larger separations could have been obtained with more cycles. As expected, separation was much less when the pump was operating in the other regions. The equilibrium parameters were estimated by fitting the theory to the data obtained for the parametric pumping run with the largest separation. As mentioned before, this technique will include some of the nonequilibrium effects of the column operation in the values of the equilibrium parameters. The values of the parameters obtained were in reasonable agreement with values obtained by approximating the equilibrium data. However, agreement between theory and experiment would have been worse if an a priori prediction were used. For this system, transfer rates are apparently quite high and the equilibrium theory is a good approximation. The continuous parametric pump can thus be used to obtain very large separations for this easy to separate mixture [separation factors of 10^5 obtained by batch operation (*31*)].

In a second paper Chen, Jaferi, and Stokes (*59*) studied the multicomponent separation of fructose and glucose from water using Fullers earth. Pure component equilibrium isotherms were obtained and fit to the Langmuir equation. There was considerable difference in the isotherms for the two sugars, and their equilibrium change parameters, *b*, differed significantly. Transfer rates were very slow with over 2 hr being required to reach equilibrium. To compensate for this, the continuous parametric pump with top feed (*45*, *58*) was operated with a 6-hr cycle time. The system was run so that the equilibrium theory (*45*, *58*) predicted that glucose should be completely removed from the bottom product stream and fructose only partially. Although only six cycles could be obtained because of the breakdown of the Fullers earth, the data agreed qualitatively with these predictions. The theoretical predictions were not shown, but from the given *b* values the separation can be estimated from the equilibrium theory (*58*) as being considerably greater than was experimentally obtained. The equilibrium theory requires that the two solutes adsorb independently of each other, that the equilibrium relationship is linear, and that local equilibrium be attained. Since all of these assumptions are doubtful, the lack of agreement is not suprising.

The semicontinuous parametric pump with top feed (*45*) was studied experimentally by Chen, Reiss, Stokes, and Hill (*60*). The concentration transients obtained from the equilibrium theory (*45*) are presented since they were not given earlier. The toluene–*n*-heptane–silica gel system was again studied so that the results could be compared with the continuous pump with top feed (*58*). The values of the equilibrium parameters obtained earlier with the continuous pump (*58*) were employed again. Agreement for the bottom product concentrations was not as good as that obtained previously, which is an indication that the equilibrium parameters measured include some column effects. Chen and Hill (*45*) predicted that the semicontinuous pump could be operated at a greater throughput and still have an infinite separation factor. This was again concluded (*60*), but the authors were unable to show this experimentally [note that on Fig. 5 (*60*) the ϕ_B have different meanings for the two pumps] because of experimental limitations. As was pointed out earlier, the semicontinuous pump will have larger internal flow rates at the same bottom product rate.

The article by Chen, Park, and Rak (*61*) is essentially an experimental continuation of the previous articles (*58*, *60*) and the comments made previously are valid. Seven runs are reported, two of which are almost exactly the same as two runs reported previously (*58*, *60*). The other runs show that smaller *b* values caused by a smaller temperature change cause less separation. Cycle time is unimportant as long as it is considerably greater than the time required to reach equilibrium. The last run reported used short cycle times. Equilibrium theory was not valid, and considerably less separation was obtained than in the other runs.

In the last paper on open systems, Chen, Stokes, and Lin (*62*) studied the separation of mixtures of toluene, aniline, and *n*-heptane on silica gel in a continuous parametric pump with top feed. Operation was similar to the separation of fructose–glucose–water discussed previously (*59*). The equilibrium theory can be applied to this separation by treating the multicomponent mixture as a series of pseudo-binary mixtures. The equilibrium change parameters, *b*, found by fitting binary separations, were 0.15 and 0.31 for toluene and aniline, respectively. The continuous pump could then be run so that the bottom product concentration of both aniline and toluene would approach zero or only the aniline concentration would approach zero. The first operation removes all solutes from the heptane. The second gives a bottom product containing toluene and heptane and a top product containing all three components. Some arrangement with several pumps would be required to obtain pure components from a multicomponent system. Agreement between theory and experiment was roughly equivalent to that obtained previously (*58*, *60*, *61*).

The research on separation by open, direct mode, thermal parametric pumping has shown that it is possible to obtain continuous or semicontinuous separations. Large separation factors are obtained when the shift of equilibrium with temperature is large and mass transfer is fast. Under these conditions the equilibrium theory is a good predictor. When mass transfer is slow, less separation is obtained and the equilibrium theory should not be used. A large variety of open systems have been considered and many more variations are possible. Different variations will be useful when the objective of the separation changes. If parametric pumping is to be used for large-scale separations, undoubtedly an open system will be employed.

Parametric Pumping: Separations of Gases

Considerably less work has been done on the parametric pumping separation of gases than for liquids. The first reported work was Mc-

Andrew's (*35*) study of the application of the recuperative mode to the separation of methane from nitrogen on fibrous carbon. Theoretical calculations showed several problems. Under normal conditions the large difference between gas and solid heat capacities makes it difficult to heat the bed using the recuperative mode. This problem can be overcome by operation at conditions where the ratio of the volumetric heat capacities of solid and gas is close to unity. Special equipment arrangements are required for atmospheric operation. The second major problem is inherent in the separation of gases by thermal cycles and will limit separations in the direct mode also. The characteristic *P-V-T* behavior of gases requires that either pressure or volume must increase when the temperature increases. If operation is at constant pressure, the increase in volume causes flow of the gas and mixing which decreases separation. At constant volume the pressure increase causes an increase in adsorption which opposes the decrease in adsorption caused by the temperature increase. McAndrew (*35*) was unable to obtain experimental separations, but he did predict conditions which should allow more separation.

In a short note Jenczewski and Myers (*63*) reported preliminary results on the first direct thermal mode separation of gases. The separation of ethane–propane on activated carbon was studied in a constant volume apparatus. Operation consisted of fast flow periods with longer periods for equilibration after each flow period in a horizontal column. Separation factors of approximately 2.0 were obtained after 60 cycles. The difficulties with thermal parametric pumping were not mentioned, but the use of pressure cycles was suggested.

Jenczewski and Myers (*64*) reported further studies on batch, direct mode separations of gases. Argon–propane and ethane–propane mixtures were successfully separated, while as expected a propane–propylene mixture for which temperature has no effect on the equilibrium isotherms was not separated. Operation was again in a constant volume system with rapid flow of gases followed by long equilibration periods without flow. Because of the very low gas thermal conductivities, the temperature variations inside the bed were considerably less than those imposed on the water jacket around the column. The STOP-GO model (*49*) was modified to include axial mixing of the gases caused by temperature variations in the bed. When the actually measured temperature variations inside the bed were used in the theoretical model, agreement between theory and experiment was good. Unfortunately, this model could not be used a priori without knowledge of the actual temperature variations in the bed.

Patrick et al. (*65*) studied the batch, direct thermal mode separations of air–SO_2 on silica gel. Compared to other studies, very large temperature changes of up to 300°F were used. Flow was again fast, followed by long heating and cooling periods. Operation was at constant pressure which required axial flow to or from one of the reservoirs whenever the temperature was changed. The cycle time ranged from 12 to 28 min and had no effect. This indicates that sufficient time was available to reach equilibrium during heating or cooling. A limiting separation factor of approximately 130 was obtained. The equilibrium theory (*19*) predicted a separation several orders of magnitude greater than was observed. As noted by the authors, the equilibrium theory does not account for the axial flow caused by the pressure changes. A model including this axial flow should have been employed instead.

Thermal parametric pumping does not appear to have great promise for gas separations. The pressure-swing adsorption processes discussed earlier (*12–21*) are more promising.

Parametric Pumping: Miscellaneous Applications

Parametric pumping was proposed by Wilhelm (*29*) as a possible method of active transport in biological cells. This paper explained the basis of recuperative mode parametric pumping, but did not detail a cell model. Booij (*66*) looked at this hypothesis in more detail and concluded that there are major difficulties in scaling the process down to cell dimensions, and that conclusive experimental evidence would be difficult to obtain. Recently, Tverdisl et al. (*67*) reported that parametric ion separation could be the method of active transport.

Apostolopoulos (*68*) presented a perturbation approach to study near-equilibrium parametric pumping and applied this theory to use of the direct, thermal parametric pump as a chemical reactor. The reaction considered was a reversible catalytic reaction which required adsorption before reaction and then desorption. If certain criteria are satisfied, the parametric pump was predicted to increase reaction conversion and concentrate the product. The theoretical results were not checked for agreement with other theories in limiting cases. Four examples were given, but none of these refer to a real system.

Kim (*69*) also considered a theoretical analysis of parametric pumping in a catalytic chemical reactor. Both heterogeneous and homogeneous reactions were studied, and both cases showed that substantial improvement could result with parametric pumping. The author noted that favorable systems could be identified by studying the overshoot in relaxation curves.

Cycling Zone Adsorption

Cycling zone adsorption was first developed by Pigford et al. (*70*). This process is similar to parametric pumping except the fluid to be separated does not flow back and forth through a single bed, but instead flows in a single direction through a series of columns. In the "direct" or "standing wave" mode of operation, the columns are heated or cooled by external sources such as water jackets. The temperatures of the columns are changed cyclically between the cold temperature and the hot temperature. In addition, adjacent columns are out of phase with each other in that when one column is hot the columns adjacent to it are cold. During the first half of each cycle the column sequence is hot, cold, hot, cold, etc., and during the second half of the cycle the column sequence is cold, hot, cold, hot, etc. Pigford et al. (*70*) call each region of constant temperature a "zone." In the "traveling wave" mode of operation the columns are adiabatic and the fluid entering each column is alternately heated or cooled in a heat exchanger. Fluid leaving a zone is sent to a heat exchanger to be heated or cooled before entering the next zone. Adjacent zones should again have their temperatures out of phase. This operational mode is obviously related to the recuperative mode of parametric pumping. After a start-up period, cycling zone adsorption will reach a limiting state where concentrations and temperatures repeat themselves every cycle.

Pigford et al. (*70*) presented the basic operational technique and discussed the operation in detail. Preliminary results from four experiments were presented. These were a standing wave single-zone separation of methane from helium, single and double-zone standing wave separations of acetic acid from water, and a single-zone traveling wave separation of acetic acid from water. As expected, the two-zone system produced a larger separation than a single zone. The experiments also showed that the traveling wave separation was superior to the direct mode separation for a single zone. The reasons for this somewhat unexpected result were explained in a later paper by Baker and Pigford (*36*). Pigford et al. (*70*) used a simplified theory based on the equilibrium theory of parametric pumping (*19*) to explore the direct mode of operation. Considerable theoretical extensions to make the theory quantitative were presented later (*36*). The reason for the separation is clearly the ability of the solid to remove solute from a fluid of low concentration, temporarily store this solute, and then give this solute up on command (the signal being a temperature increase) to a fluid of high concentration. Since the use of several zones allows more opportunities to do this, the separation is enhanced when several zones are used.

Baker and Pigford (*36*) presented both experimental and theoretical aspects of the separation in considerably more detail. It was shown that the direct or standing wave mode could be considered a traveling wave mode with an infinite thermal wave velocity. This relationship allowed the authors to solve for both modes simultaneously. This is certainly efficient, but is somewhat confusing when the paper is first read. The local equilibrium theory (*19*) is used with the assumptions of local equilibrium, no axial dispersion, and no heat of adsorption. With these assumptions the simplified energy balance can easily be solved for given input conditions. The prediction is that a temperature wave will pass through the column at a characteristic thermal wave velocity without changing shape or amplitude. The simplified mass balance can be reduced to two ordinary differential equations by utilizing the method of characteristics. For linear isotherms an analytical solution can be obtained which predicts that the separation factor becomes infinite as the number of zones becomes very large. For standing waves the results are identical to a parametric pump with the number of zones replacing the number of cycles. Nonlinear isotherms prevent the separation from becoming infinite. For the travelling wave case with linear isotherms, an infinite separation factor can be obtained in a single zone if the thermal wave velocity can be adjusted to be equal to or to lie between the velocities of the concentration waves at the hot and cold temperatures. When the thermal wave velocity is adjusted properly, all of the concentration waves are forced to exit during the hot portion of the cycle. This adjustment of the thermal wave velocity was not done experimentally, but the authors (*36*) discussed how it might be done. Experimental separations of acetic acid from water utilizing activated carbon as the adsorbent were reported for one and two zone standing and traveling wave systems. The traveling wave system resulted in somewhat better separations even though the thermal wave velocity was much greater than its optimum value. Agreement between theory and experiment was quite good considering that all required equilibrium parameters were obtained from equilibrium experiments and not from fitting the separation runs. This paper is not the easiest paper to read, but it will well reward the reader who makes the necessary effort.

Gupta and Sweed (*71*) independently developed an equilibrium theory utilizing the method of characteristics for the direct mode of operation. When the different nomenclatures are converted, their result agrees with that of Baker and Pigford (*36*). Gupta and Sweed (*71*) carefully delineate the conditions necessary to get reinforcement from region to region, and they show that the fluid displacement must be correctly chosen to get an increasing separation. This was not done in detail by Baker and Pigford (*36*). The results of a computer model showed that finite mass transfer rates and axial dispersion prevent the formation of an infinite separation. Since this article does not discuss the solution method used, it is helpful to refer to the article by Pigford et al. (*19*) on use of the method of characteristics for parametric pumping.

Cycling zone adsorption was applied to the separation of oxygen and nitrogen from air on molecular sieve adsorbent by Van der Vlist (*72*). This adsorbent preferentially adsorbs nitrogen so that gas leaving a cold zone should be concentrated in oxygen. Upon heating, a greater amount of nitrogen is desorbed so that gas leaving a hot zone should be concentrated in nitrogen. A two zone direct mode system was used. The temperatures of the two zones did not change as square waves, but were closer to sine waves. Product from zone two was concentrated in oxygen when zone one was hot and zone two was cold. Only one experimental run was reported with a maximum oxygen separation factor of 10.6. The experimental results were not compared with any theoretical predictions. The author does note that with high concentrations of solute there will be large flow fluctuations caused by alternate adsorption and desorption. An additional effect not noted by the author is that temperature increases will cause an increase in flow due to gas expansion. Application of theories would be further complicated by the nonlinear isotherms at the high solute concentrations studied. Since cycling zone adsorption is essentially an open system, *P-V-T* effects should not be as detrimental as they are in parametric pumping, but they will decrease the separation obtained.

Ginde and Chu (*73*) studied the removal of NaCl from water using a mixed bed of ion exchange resins in a single zone cycling zone adsorber. The operation is different than the basic process (*36*, *70*) in that product streams are sent to well-mixed hot and cold reservoirs and the material from these reservoirs is recycled. Operation was in a combined direct and traveling wave mode. In the hot portion of the cycle, fluid is fed from the hot reservoir and the column is heated externally. In the cold portion, fluid from the cold reservoir is cooled in a heat exchanger before being fed to the column, but the column was not cooled externally. Two columns were used in parallel so that both hot and cold fluids are cycled continuously. This can then be considered an unsteady state batch cycling zone adsorber with complete recycle. The total amount of liquid in the system, the flow rate, and the cycle time will influence the amount of recycle and thus the separation obtained. The authors found that with complete recycle, separation was increased if two temperature cycles were used instead of one cycle. Use of three cycles caused a decrease in separation.

The authors felt this effect was due to experimental difficulties. Since Gupta and Sweed (*71*) have shown that timing is critical, an alternate explanation is that the device was not properly timed to increase the separation. The effects of several other variables were also studied experimentally. Increasing flow rates gave better separation because the resulting temperature profile in the column was much closer to a square wave. No theoretical analysis was attempted. A theoretical analysis for this system would be difficult because of the interaction of direct heating, traveling waves, recycle, and mixing in the reservoirs.

Rieke (*74*) studied cycling zone adsorbers operating in the standing wave mode with and without partial recycle. For a single zone without recycle, experimental separations of toluene from *n*-heptane on silica gel showed that separation could be optimized by switching temperatures at an optimum frequency, by use of small diameter adsorbent particles, and by use of a temperature response that very closely approximated a square wave. The optimum switching time can be estimated by requiring that the solute undergo only one temperature change while it is in the column. Experiments with partial recycle of product from a single zone showed that recycle can increase separation, but the recycle liquid must be stored for a half cycle before being returned to the column. Longitudinal mixing is the major factor limiting the separation. A theoretical study of cascades with recycle from one zone to another zone showed that large separations could be attained even though the separation in a single zone was modest. This thesis leads toward design of large-scale cycling zone adsorbers for removal of single solutes from a liquid stream.

Wankat (*75*, *76*) studied the extension of cycling zone adsorption to extraction in both the direct (*75*) and the traveling wave (*76*) modes of operation. A countercurrent distribution type system (*50*) with discrete transfer and equilibrium steps was employed to keep one liquid phase stationary. Recursion relations were developed for both the unsteady startup problem and for the limiting repeating cycle. The optimum cycle time (number of transfers per half cycle for countercurrent distribution) was predicted by an argument similar to that used by Rieke (*74*). The theoretical results for the direct mode (*75*) showed an increase in separation from zone to zone if the cycle time was optimized, and a partial cancellation of separation for nonoptimum cycle times. Experimental results for diethylamine–water–toluene obtained in test tube systems agreed qualitatively with theory, but quantitative agreement was only fair. The experiments showed an oscillatory startup behavior that was not predicted by theory.

For the traveling wave mode of operation (*76*), the theory was similar to the direct mode (*75*) theory with the addition of an energy balance. The theoretical calculations showed that the separation could be greatly increased by optimizing the thermal wave velocity, but infinite separation factors were never obtained. The optimum thermal wave velocity lies between the velocities of the concentration waves at the hot and cold temperatures. Experimental results were again obtained in test tube systems for the diethylamine–water–toluene system. Theory and experiment agreed qualitatively but not quantitatively. When the thermal wave velocity was adjusted by using different types of test tubes, separation was enhanced if the thermal wave velocity was close to the concentration wave velocities. The traveling wave separations (*76*) were less than the direct mode results (*75*) because the thermal wave velocity was too low, but the traveling wave separation would be considerably greater if the thermal wave velocity was optimized. For both operational modes the experimental results could be improved if a completely closed system were employed. The countercurrent distribution theory is similar to the STOP-GO model (*49*) and can be considered as a model for continuous operation. This model now includes dispersion effects and predicts finite separations for the traveling wave mode instead of the infinite separations predicted by the local equilibrium theory of Baker and Pigford (*36*). Both models predict large increases in separation when the thermal wave velocity is optimized.

Cycling zone separations appear to have great promise for separation of liquids, but less promise for large separations of gases. Several modifications have been developed which increase the separation obtained in a simple apparatus. Compared to parametric pumping, cycling zone adsorption has the advantages that it is inherently an open system and does not require flow reversal, but it has the disadvantage of one less degree of freedom so that some flexibility may be lost.

GENERAL THEORY OF CYCLIC PROCESSES

Two papers concerned with the general theory of cyclic processes will be discussed. Ritter and Douglas (*77*) considered the general response of nonlinear systems. They showed how perturbation theory can be used to determine regions where nonlinear systems can be linearized for analysis. This theory was then applied to a continuous stirred tank reactor and to a steam heated heat exchanger. Although cyclic separations were not studied, this theory could be applied to cyclic separations. The authors also generalized the definition of parametric pumping so that the processes studied in the paper could be considered as parametric pumping processes.

The second paper by Lavie and Reilly (*78*) is directly concerned with cyclic separation techniques. The cyclic behavior of fixed beds was studied by utilizing the method of characteristics with negligible axial dispersion and by utilizing a mixing cell theory. The authors were mainly interested in what they call a "limit cycle" which is the limiting case where the cycle repeats itself every cycle. The cycles studied consisted of a flow period followed by a transition period during which the flow was stopped and the fluid and solid phases come to equilibrium at the new operating conditions. For cocurrent flow the flow at the end of each transition is in the same direction. In this case the authors were able to prove that limit cycles exist using both theories, and the solution for the method of characteristics was presented. For countercurrent flow the flow reverses direction at each transition. The authors proved that the limit cycle exists for the method of characteristics and presented the solution. For the mixing cell theory numerical solutions always converged to a limit cycle, but a general proof was not obtained. The authors noted that the method of characteristics is very valuable since it gives a physical picture of what is happening. The cocurrent flow case is obviously related to cycling zone adsorption while the countercurrent flow cases are related to parametric pumping and Skarstrom's operation of heatless adsorption (*12*, *13*).

RELATED SEPARATION TECHNIQUES

This completes the review of cyclic separation techniques considered in this article. In order to obtain some perspective, related techniques will be very briefly considered. As was noted in the introduction, cyclic separations can be compared with usual batch operation for adsorption and ion exchange (*1–3*), and the straightforward scale-up of chromatography (*4*, *5*). The dividing line between these techniques and the cyclic separations considered is not sharp. Various moving bed techniques (*6–11*) are an alternative method of obtaining preparative separations. Baker and Pigford (*36*) note that cycling zone adsorption is similar to Zhukhovitskii's (*79*) chromathermography where a heater is rotated around a circular loop of a chromatographic column. Cyclic operation of many separation techniques has been studied where the cyclic variable is the flow rate in the column. This technique has been reviewed by Schrodt (*80*) and some more recent papers are discussed by Dodds et al. (*8*). This technique differs from the techniques discussed here since extensive instead of intensive thermodynamic variables are cycled. The possible cyclic operation of field flow fractionation was mentioned by Giddings (*81*). Paul (*82*) presented a theoretical study of membrane purification of gases in a cyclic operation where the applied pressure was cycled. These papers show that cyclic variation can be used in other ways than those discussed here, and that the results obtained with cyclic operation can also be obtained by utilizing other operational methods.

SUGGESTIONS FOR FUTURE WORK

At the completion of this review I wish to suggest a few areas where in my opinion future research might be particularly profitable. Studies investigating concentration as the cyclic variable or coupling two different thermodynamic variables should be tried. Recuperative parametric pumping separation of liquids should be tried under favorable conditions, and the results should be compared with the direct mode on the basis of separation obtained per unit of energy. More work should be done on separations of multicomponent mixtures. Extension of the cyclic processes to gas–liquid and liquid–liquid chromatography should be studied. A study of gas *absorption* or stripping with pressure and/or temperature cycles would be interesting. Finally, except for heatless adsorption, considerable work on scale-up and process economics is needed. Naturally, other workers will have their own list of priorities. In any case, we can confidently look forward to seeing considerable stimulating new work on cyclic separations.

Acknowledgments

The aid of Professors H. T. Chen, C. Hamrin, H. Lim, N. H. Sweed, and Dr. J. E. Mitchell in preparing this review is gratefully acknowledged. This work was partially supported by NSF Grant No. GK-32681.

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Received by editor October 19, 1973

Note Added in Proof: Since submission of this review the following papers on parametric pumping have appeared:

R. G. Rice, *Ind. Eng. Chem., Fundam.*, *12*, 406 (1973).
R. G. Rice and M. Mackenzie, *Ibid.*, *12*, 486 (1973).
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The following review article on molecular sieves includes several commercial processes utilizing pressure swing adsorption.

G. R. Landolt and G. T. Kerr, *Separ. Purific. Methods*, *2*, 283 (1973).