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R. R. Patrick[a]; J. T. Schrodt[a]; R. I. Kermode[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF KENTUCKY LEXINGTON, KENTUCKY

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Thermal Parametric Pumping of Air—SO_2

R. R. PATRICK, J. T. SCHRODT, and R. I. KERMODE

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF KENTUCKY
LEXINGTON, KENTUCKY 40506

Abstract

The separation of air–SO_2 mixtures in a specially prepared silica gel column has been accomplished using a direct mode thermal parapump. The effect of the number of cycles, pumping cycle time, and operating temperature range and level on the extent of separation has been studied over a wide range of operating conditions. The separation factors obtained were several orders of magnitude greater than those typically reported in the literature for gas–solid systems, and compare favorably with those obtained in liquid–solid systems.

INTRODUCTION

The idea of a parametric separation was first suggested by Wilhelm (*1*). He proposed that the intercellular transport of ions in living cells was a parametric separation process, and that the principle was quite general and could be applied to the separation of chemical mixtures on an industrial scale.

The first experimental data (*2*) were for the separation of toluene–*n*-heptane mixtures using silica gel. Separation factors of approximately 100 for 20 cycles or more were reported. A later article (*3*) analyzed the same system using a theoretical approach, and computer generated curves of separation factor versus the number of cycles were given. General material balance and equilibrium relationships had been previously formulated (*2*) and numerical results calculated for the

$NaCl$–H_2O system. These results were then compared with experimental results for the same system. The maximum experimental separation factor obtained was about 1.2.

The complexity of these first models required excessive computer time and made generalization difficult. This difficulty was overcome (*4*) by assuming plug flow, instantaneous gas–solid equilibrium, and a linear equilibrium relationship. The resulting differential equation was soluble by the method of characteristics. Analytical expressions for the top and bottom compositions as a function of the number of cycles and system parameters were presented in the paper. This procedure was later generalized (*5*) somewhat to eliminate the requirement that characteristic solutions eminating from the origin exit from the bed after exactly a time of $3\pi/\omega$. The effect of a nonlinear equilibrium relationship on the separation factor was subsequently analyzed theoretically (*6*). The authors were unable to derive analytical expressions for the separation factor, but they were able to put bounds on the separations obtained for large values of n. The mathematical analysis of parametric pumping was extended (*7*) by considering in detail the effect of product withdrawal and feed addition.

Two other experimental studies are worth noting. The first (*8*) because it used pH as the driving force to separate Na^+ and K^+ in an ion-exchange column. The maximum enrichment obtained was 20 to 30% after 200 to 300 cycles. The second study (*9, 10*) was the separation of the gas mixtures argon–propane and ethane–propane. The largest separation factors reported were less than 100 for 100 cycles.

EQUILIBRIUM MODEL OF PARAMETRIC PUMPING: A QUALITATIVE UNDERSTANDING

Parametric pumping is best understood by a specific example of a packed column filled with adsorbent particles and a two-component fluid phase. Two full cycles of heating and cooling will be examined for the direct mode of operation. The initial state of the system is shown in Fig. 1a with equal volumes of fluid in the column and the bottom storage chamber. The fluid is in equilibrium with the adsorbent at the hot temperature. Initial compositions of the fluid and solid are given by Point 1 of Fig. 2. At the start of the first cycle the fluid in the bottom is pumped upward, displacing the fluid already in the column into the top reservoir, Fig. 1b; compositions are still given by Point 1. The column is

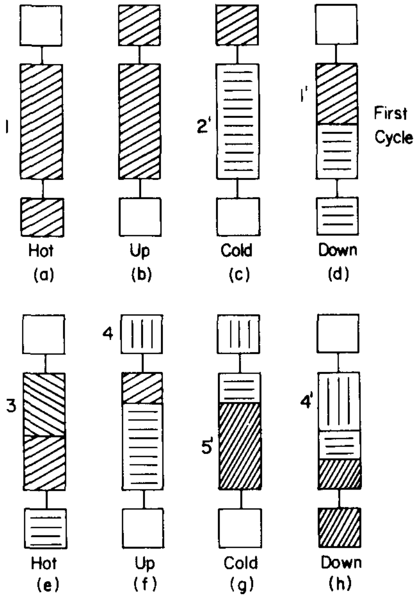

FIG. 1. Schematic of direct mode thermal parapumping system.

now cooled and as the adsorbent cools it removes solute from the fluid. When the cooling is completed, the fluid and solid compositions are y_2' and x_2'. The straight line between 1 and 2′ in Fig. 2 is not meant to describe the actual path but only the direction. The top chamber is sealed off during the cooling and no concentration change occurs there. Finally the fluid in the top chamber is pumped downward, displacing fluid in the column into the bottom chamber. As the fluid from the top chamber moves downward, it comes in contact with the adsorbent which is in equilibrium with a fluid of lower concentration. If perfect local fluid–solid equilibrium and plug flow are assumed, the downward traveling fluid will lose its solute to the adsorbent instantaneously on contact and change to composition y_2'. Thus a concentration wave front is formed which travels in the direction of fluid displacement. This wave front movement may be clarified by considering the following analogy. Picture a caravan of dump trucks loaded with dirt, backing toward the edge of a cliff at some arbitrary speed. The trucks empty their load at the instant they reach the edge, fall over the cliff to a pleateau below, and miraculously continue moving on this plateau at the same speed

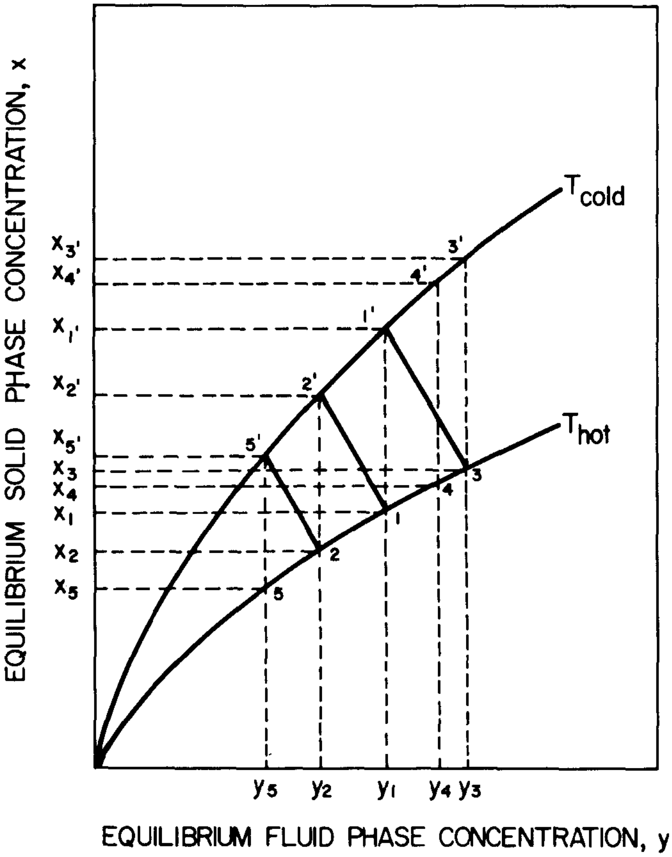

FIG. 2. Equilibrium diagram for a hypothetical parapumping system.

and in the same direction. The dirt dumped by each truck is unloaded at the immediate edge of the cliff and fills in a small length of the lower plateau up to the higher plateau level. Each truck will therefore have to travel a greater distance before emptying its load than the previous truck. As time progresses, the cliff edge moves slowly in the direction the trucks are traveling. The movement of the concentration wave front is analogous to that of the cliff edge.

Because the wave front travels at a slower pace than the fluid, none of the mixture of composition y_1' will reach the bottom of the column. Since the bottom chamber composition y_2' is less than y_1', the first cycle of operation has lowered the solute concentration.

The second cycle begins by heating the column to the hot temperature. After the heating, Fig. 1e, compositions in the two regions are given by 1 and 3 of Fig. 2 for the bottom and top, respectively. The composition in the bottom region merely changes back to the original fluid composition. Since solute is gained by the fluid during the heating, y_3 is greater than y_1 for the upper region. Next the fluid is displaced upward. All of fluid in Region 3 and part from Region 1 go into the top chamber giving a fluid composition of y_4 which is between y_1 and y_3. When the fluid from the bottom chamber contacts the adsorbent which is in equilibrium with a fluid of concentration y_1, solute is desorbed, and a new wave front is formed. At the end of pumping, two concentration regions exist in the column as shown in Fig. 1g.

EQUILIBRIUM MODEL: A QUANTITATIVE APPROACH

Pigford et al. (*4*) present the most easily interpreted mathematical model of the direct mode thermal parapump. In it they assume perfect local temperature and composition equilibrium at all times as well as a linear equilibrium relationship for the adsorbent. The resulting material balance was solved by the method of characteristics to give a closed form solution for the compositions in the top and bottom chambers as a function of the number of cycles and several system parameters. These expressions for the top and bottom composition are:

$$(y_t)_n = y_0\left[2 + \frac{2b}{1+b} - \frac{(1-b)^{n-2}}{(1+b)}\right]; \qquad n > 2 \tag{1}$$

$$(y_t)_n = y_0\frac{(1-b)^n}{(1+b)} \tag{2}$$

If we define a separation factor $\alpha = (y_t)n/(y_t)n$ then

$$\alpha_n = \left(2 + \frac{2b}{1+b}\right)\left(\frac{1+b}{1-b}\right)^n - \left(\frac{1+b}{1-b}\right)^2; \qquad n > 2 \tag{3}$$

In this investigation Eqs. (1), (2), and (3) were compared with the experimental results for the SO$_2$–air system.

APPARATUS

A schematic diagram of the direct mode thermal parapump apparatus is shown in Fig. 3. The adsorption column is made of stainless steel,

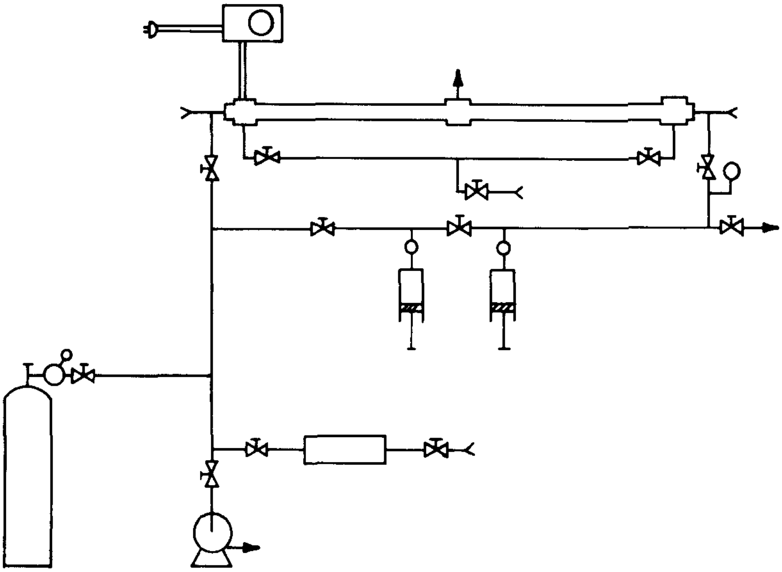

FIG. 3. Schematic diagram of apparatus.

0.625-in. i.d. × 53.0-in. long, packed to a porosity of $\epsilon = 0.40$ with 192.0 g of Davidson Grade 03 silica gel and mounted horizontally to minimize axial mixing of the gases caused by thermal convective forces. Around the column a 2-in. carbon steel pipe forms an annulus through which air may be pumped to remove the heat supplied by the Nichrome wire heating element that coils around the column. Stainless steel shielded copper–Constantan thermocouples extending 1 ft into each end of the column sense the periodically altered hot T_H and cold T_C temperatures of the packing. Two 500-ml gas tight syringes connected to the ends of the column and to one another by three pieces of tubing, each containing a needle valve, are used both as the end collection reservoirs and the fluid displacement pumps. This arrangement permits the gas mixture in the column to be drawn into one reservoir while a mixture in the other is being pumped into the resulting column void, or by adjusting the proper valves the column can be by-passed in the procedure. Rubber septums adjacent to the reservoirs permit gas samples to be withdrawn with small gas tight syringes after every few cycles of pumping. These are needed for composition analyses and determination of the separation. The system's pressure is indicated on a Bourdon vacuum-pressure gauge.

EXPERIMENTAL PROCEDURE

The gas mixtures for the twelve experiments reported on were prepared directly in the evacuated system using anhydrous SO$_2$ and laboratory dried and de-oiled air. These were brought to equilibrium with the adsorbent at either $T_H = 400°\text{F}$ or $T_H = 300°\text{F}$ by pumping them back and forth through the bed until no further composition change was detected by chromatographic analysis. The resulting gas phase compositions were $y_0 = 0.211 \pm 0.02$ at $T_H = 400$ and $y_0 = 0.091 \pm 0.009$ at $T_H = 300°\text{F}$. According to the equilibrium data presented in Fig. 4, these y_0's have the same values of $x_0 = 7.5 \times 10^{-5}$.

Separation of the SO$_2$ and air was started by first pumping the mixture from the left reservoir into the column at T_H, forcing the interstial gas into the right reservoir. With one half of the first cycle completed, the column was cooled to T_C at atmospheric pressure. The latter resulted in gas being drawn into the column from the right reservoir. The volume of gas in this syringe was further reduced to 120 ml, approximately the void volume of the column, by expelling gas out the vent. The cycle was

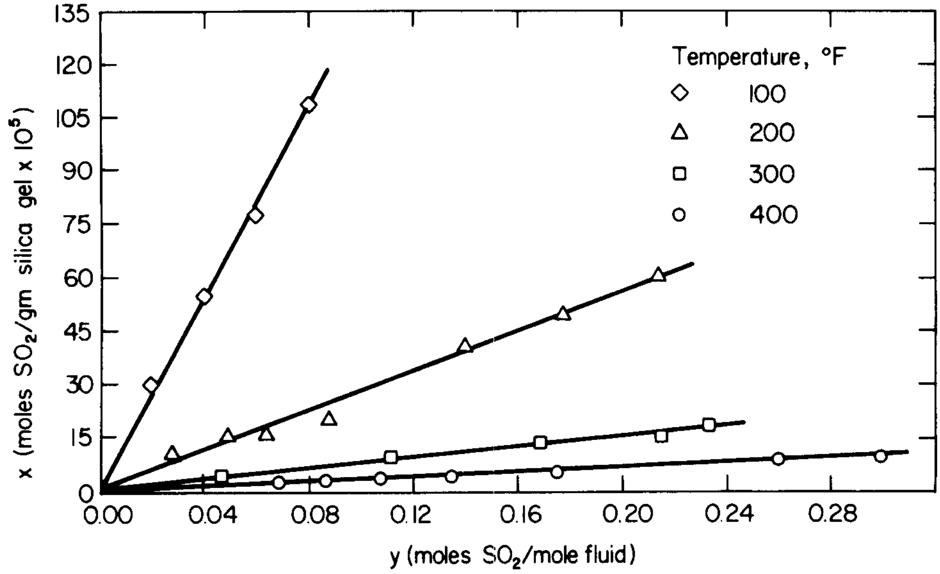

FIG. 4. Adsorption isotherms for SO$_2$–air–silica gel system.

completed by pumping the remaining gas back into the column. Subsequent cycles consisted of heating the column, pumping from left to right, cooling the column, and pumping from right to left. The system was always kept at atmospheric pressure by keeping the valve connecting the column and the right reservoir open. During the heating, gas would be withdrawn from it. Velocity and temperature alternations had about the same frequency (distorted square waves) and were in phase in each run.

One-milliliter gas samples were periodically withdrawn from the septum ports, sealed, and then analyzed by a chromatographic technique discussed elsewhere (*13*).

RESULTS AND DISCUSSION

Results from the experimental studies show that the direct mode of parapumping produced significant separations of the air–SO_2 mixtures in the silica gel adsorption column. In Fig. 5 the separation factors α are

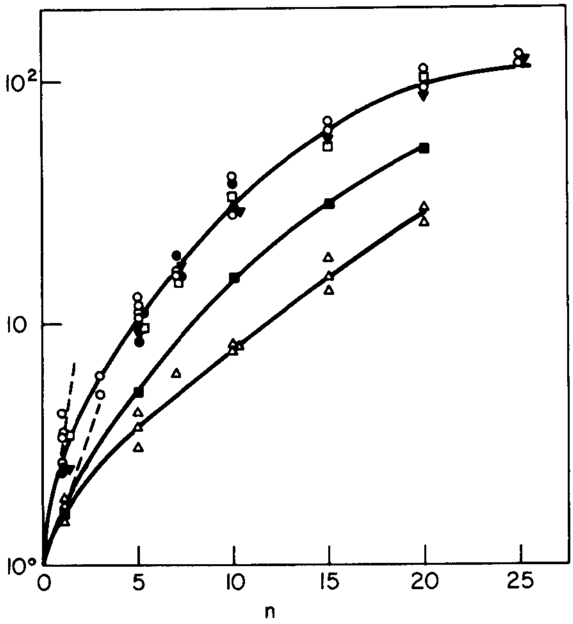

Fig. 5. Separation factors for air–SO_2 mixtures.

TABLE 1

Operating Conditions

Symbol	y_0	$T_H - T_C$ (°F)	τ (min)
○	0.213 ± 0.020	400 – 200	28
●	0.208 ± 0.009	400 – 200	20
▼	0.208	400 – 200	12
□	0.218	400 – 100	20
△	0.091 ± 0.009	300 – 200	12
■	0.205	400 – 300	12

plotted as a function of cycle number n. The initial SO_2 concentrations, temperature oscillations $(T_H - T_C)$, and cycle periods τ corresponding to the α's are presented in Table 1. Dimensionless reservoir concentration of SO_2, defined as y/y_0, are presented in Fig. 6 as a function of n. The equilibrium adsorption isotherms for the system SO_2–air–silica gel at 100, 200, 300, and 400°F are shown in Fig. 4. The 100°F data are those of Miller (*12*), the others were obtained by Patrick (*11*).

Different cycle times of 12, 20, and 28 min had no detectable effect on the separation. This is shown by the data along the top curve of Fig. 5. This implies that the rate of interphase mass transfer was sufficiently great for equilibrium to be reached in less than 12 min. Since Miller (*12*) suggests that the time required for SO_2 and air to reach equilibrium with silica gel is of the order of 15 min, our lowest cycle time of 12 min is reasonable.

The effect of temperature oscillation, $T_H - T_C$, is shown in both Figs. 5 and 6. The separation factors for the experiments at $T_H - T_C =$ 200 and 300°F are clearly double those at $T_H - T_C = 100$°F. This effect is independent of any initial or other operating conditions. It would seem that the data for $T_H - T_C = 300$°F should show a better separation than was detected; however, as indicated by the equilibrium adsorption isotherms in Fig. 4 the amount of SO_2 desorbed in going from 300 to 400°F is considerably less than the adsorbate given up in going from either 200 to 400 or 100 to 400°F. Also, the greatest degree of axial dispersion would be expected for the largest temperature oscillation and this would result in a decrease in the separation.

Axial mixing results from expansion and contraction of the mixture, from adsorption and desorption of the solute, and pulsation of the mix-

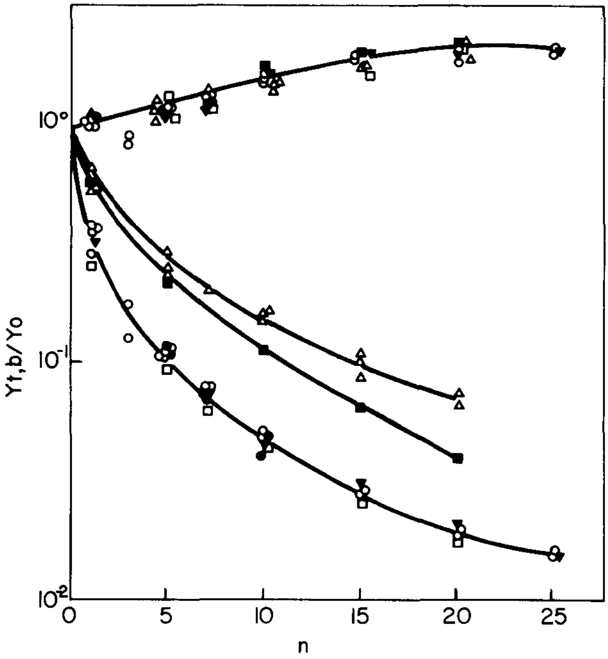

FIG. 6. Dimensionless concentrations of SO_2 in the end reservoirs.

ture. These effects are not nearly as severe in the case of liquid mixtures as in gases. During the heating period the desorbed SO_2 and expanding mixture were allowed to enter the diluting reservoir until the system pressure equalized at $P_T = 1.0$ atm. Upon cooling the mixture contracted and some of the diluting reservoir's mixture was drawn into the column. This tended to destroy the interphase concentration gradients and the periodicity of the axial solute flux. In effect the over-all separation capacity of the system was reduced. It has been suggested (*3*) that small rates of interphase mass transfer are equivalent to axial dispersion effects and both lower the separation in practice (*10*) and in theory (*3, 4*).

The separation was affected by the starting composition of the mixture. Two initial compositions were used in the parapump $y_0 = 0.211 \pm 0.02$ and $y_0 = 0.091 \pm 0.009$. It was found that the smaller starting composition resulted in lower degrees of separation, e.g., $\alpha = 30$ vs. $\alpha = 100$ at $n = 20$. The effect was more severe on the diluting than the concentrating composition. This result agrees with the experimental findings Jenczewski and Myers (*9*), who found that the separation decreased as the mole fraction of propane, the more readily adsorbed component in their propane–ethane–silica gel system, was decreased in the starting mixture. Wilhelm et al. (*2*) also mentioned that the magnitude of separation depends not only on the phase shift of the coupled action but also on the total solute content of the system. The effect of phase angle between the alternating velocity of pumping and the temperature oscillation was not explored in these studies.

Based upon the results it was concluded that the sulfur dioxide–air–silica gel system possesses two characteristics that make its mathematical modeling suitable for the equilibrium theory, viz., linear isotherms and rapid interphase mass transfer. Using the actual physical parameters of the system, given in Table 2, values of m_0 and a in Pigford's model were calculated. The α's predicted from these using Eq. (3) were very close to the experimental α's for the first few cycles as shown in Fig. 5, but were several orders of magnitude greater than those obtained experimentally at $n > 3$. This discrepancy is attributed to the failure of the model to account for the axial dispersion. As suggested by Sweed and Wilhelm (*3*), the latter effect produces an upper limit to the separation and in the case of the present system this appears to be $\alpha \simeq 130$. In the absence of dispersive effects, which are minimal in liquid systems, parametric pumping would seem to increase separation without limit if the isotherms are linear and mass transfer is rapid.

CONCLUSIONS

Significant separations of SO_2 and air were obtained by the direct mode of parapumping in a silica gel adsorption column at fairly high

TABLE 2[a]

Values to Determine m_0 and a

T (°F)	$M(T)(10^3)$	$\rho_F(10^5)$	$m(T)$
100	13.62	3.921	629.3
200	2.736	3.326	148.3
300	0.783	2.888	48.90
400	0.350	2.552	24.73

[a] $\rho_s = (\rho_s)_{\text{bulk}}/(1 - \epsilon) = 1.202$ g dry gel/cc gel.

temperature oscillation levels. The separation increased exponentially for $n < 3$, but approached an upper limit of $\alpha \simeq 130$. This limit of separation appears to be caused by axial despersive effects. The separation was not effected by increasing τ from 12 to 28 min, but did increase with the level of temperature oscillation; this was tempered somewhat by greater axial dispersion at the higher temperatures.

SYMBOLS

a	equilibrium constant change
b	$a/(1 + m_0)$ parameter in Eqs. (1), (2), and (3)
m	equilibrium constant
m_0	mean equilibrium constant
n	number of cycles
T	temperature
x	equilibrium solid phase composition
y	equilibrium fluid phase composition
y_0	initial equilibrium fluid phase composition

Subscripts

b	refers to bottom chamber
C	refers to cooling half of cycle
t	refers to top chamber
H	heating half of cycle
1, 2	numerical subscript refers to a particular fluid composition after a certain number of cycles

Greek Letters

α	separation factor
ϵ	porosity
τ	cycle period
ω	angular frequency

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REFERENCES

1. R. H. Wilhelm, "Parametric Pumping: A Model for Active Transport," in *Intracellula Transport*, Academic, 1966, pp. 199–220.
2. R. H. Wilhelm, A. W. Rice, R. W. Rolke, and N. H. Sweed, "Parametric Pumping. A Dynamic Principle for Separating Fluid Mixtures," *Ind. Eng. Chem., Fundam.*, *7*(3), 337–349 (1968).
3. N. H. Sweed and R. H. Wilhelm, "Parametric Pumping Separations via Direct Thermal Mode," *Ind. Eng. Chem., Fundam.*, *8*(2), 221–231 (1969).
4. R. C. Pigford, B. Baker, and D. E. Blum, "An Equilibrium Theory of the Parametric Pump," *Ind. Eng. Chem., Fundam.*, *8*(1), 144–199 (1969).
5. R. Aris, "Equilibrium Theory of the Parametric Pump," *Ind. Eng. Chem., Fundam.*, *8*(3), 603–604 (1969).
6. H. Ree and N. R. Amundson, "An Equilibrium Theory of the Parametric Pump," *Ind. Eng. Chem., Fundam.*, *9*(2), 303–304 (1970).
7. N. H. Sweed and R. A. Gregory, "Parametric Pumping: Modeling Direct Thermal Separations of Sodium Chloride–Water in Open and Closed Systems," *Amer. Inst. Chem. Eng. J.*, *17*(1), 171–176 (1971).
8. J. E. Sabadell and N. H. Sweed, "Parametric Pumping with pH," *Separ. Sci.*, *5*(3), 171–181 (1970).
9. T. J. Jenczewski and A. L. Myers, "Separation of Gas Mixtures by Pulsed Adsorption," *Ind. Eng. Chem., Fundam.*, *9*(2), 216–221 (1970).
10. T. J. Jenczewski and A. L. Myers, "Parametric Pumping Separates Gas Phase Mixtures," *Amer. Inst. Chem. Eng. J.*, *14*(3), 509 (1968).
11. R. R. Patrick, "The Separation of Sulfur Dioxide–Air Mixtures by Direct Thermal Mode Parametric Pumping," M.S. Thesis, University of Kentucky, 1971.
12. E. B. Miller, "Adsorption by Silica Gel, Theory and Applications," *Colloid Chem.*, *3*, 119–134 (1931).
13. R. Patrick, T. Schrodt, and R. Kermode, "The Determination of SO_2 and Air by Gas Chromatography," *J. Chromatogr.*, *9*(6), 381–382 (1971).

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