Thermal Separation Column with Vertical Barriers. II. Performance of a Thermal Separation Column with Vertical Barriers

Kazuo Sasaki, Norio Miura, and Tsutomu Yoshitomi
Department of Applied Chemistry, Hiroshima University, Hiroshima 730

(Received January 30, 1975)

The performance of a newly designed thermal separation column has been examined. The apparatus was constructed along the line of mathematical analysis developed in the preceding paper. The column was basically composed of two coaxial cylinders inside of which two additional cylinders of fine stainless steel screen were installed to control the gas flows in the column. An equimolar mixture of argon and nitrogen was used as the test gas. A definite improvement in the magnitude of equilibrium separation was demonstrated in accordance with the theory. In addition, the rate of attainment of steady state was found not so much different from that with open column when temperature exceeded 140 °C or more.

As has been described in the preceding paper,[1] mathematical analysis predicted that the additional installation of a couple of wire gauzes or something like that, which effectively control the relative magnitude of convectional and horizontal flow of gas, will increase the performance of thermal separation markedly. Treacy and Rich[5] studied the effect of several sorts of flow barriers in a Clusius column and reported that the simultaneous use of horizontal and vertical barriers resulted in a remarkable increase in the separation. Their data seems to indicate that the single use of vertical barriers is not so much effective.

The design of column used by them, however, seems not suitable to test our theory and the data presented were so restricted. We thus attempted to construct a column which closely satisfies the assumptions made in the mathematical analysis.

The following is the first full report on the performance of thermal separation column having several types of barriers.

Experimental

Description of the Column. An outline of the column used are shown in Fig. 1. The inner tube (1) of the column was made of iron pipe of 21.7 mm o.d., and 970 mm in its effective length. On the outer surface of this tube, eight long iron bars (2) having square form cross section (2 mm in width, 4 mm in height) were welded parallelly along the direction of the length. Thus the horizontal cross section of the inner tube assembly has a form of a gear. Around this cylinder (30 mmϕ) a 100 mesh stainless steel screen (3) was tightly wound with thin wire.

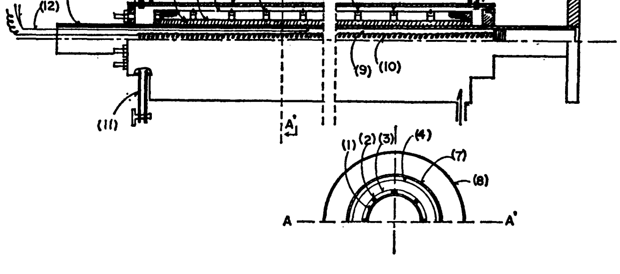

Fig. 1. Apparatus.
1: Inner tube, 2: square bar of iron, 3: inner screen, 4: outer screen, 5: aluminium O-ring, 6: binding wire, 7: outer tube, 8: water jacket, 9: heat mediator, 10: nichrome heater, 11: gas inlet, 12: thermocouple, and 13(13′): sampling port.

Outside the inner tube assembly, another cylindrical stainless steel screen was coaxially suspended (4). In order to keep the shape of cylinder, twenty aluminium O-rings of 38 mm i.d. and 44.8 mm o.d. (5) were placed with a regular distance (4 cm) and the screen was tightly bound onto the aluminium O-rings with steel wire. Each edge of the binding wire (6) was made to contact with the inner surface of the cold wall (52.7 mmϕ) (7) in order to keep, as far as possible, the temperature of the outer screen same as that of the cold wall. This benefited also to hold the suspended outer screen at a proper position. The size of the column and dimensions of each part were determined by purely technical reason except that the value of design parameter a was adjusted to be 1/2. The central hollow cylinder (9) of the inner tube was filled with a mineral oil as the heat mediator in which a 300 W nichrome wire (10) was immersed. The outer cylinder was surrounded by a water jacket (8) of vinyl chloride pipe through which tap water was flown.

The test gas inlet (11) was placed just below the top of the column. No particular gas reservoir was attached.

Operation of the Column. In an actual operation, the whole assembly was evacuated through the inlet tube (11) and the temperature difference was applied. After setting up the steady temperature difference, the test gas, 50% Ar-50% N_2, was introduced until a desired pressure was attained. The temperature of the hot wall was measured at the backside of it by means of a copper-constantan thermocouple (12), while that of cold plate was measured by a thermometer at exit of cooling water. The temperature variation along the direction of column was unable to detect by this method. Since oil was used as the heat mediator the highest temperature available was limited at 200 °C or so. Sample gas was withdrawn by a hypodermic syringe from two sampling ports (13) which were consisted of small silicone rubber stoppers. The progress of the thermal separation was monitored by periodical sampling and analysis with an ordinary gas chromatograph in which a 1 m column of molecular sieve 5 A was installed. By the aid of digital integrater maximum deviation of the readings was able to control within 0.1%.

As the control experiments, several series of data were collected with an open column which was an exact duplicate of the column described above except that no barrier was equipped.

Results

Equilibrium Separation and the Temperature Effect. In Fig. 2, are shown the results of two representative runnings observed with novel and ordinary columns under the same operational condition. In this figure, the scale of the ordinate is expressed by the ratio of direct reading of the gas-chromatographic peak areas of argon and nitrogen. A couple of curves drawn with solid line stand for the measurement with the novel column while another couple with dotted line for the ordinary column. Ascending curves stand for the measurement at the top of the column and descending curves at bottom. The couple of solid curves (novel column) in ascending and descending directions are not exactly symmetrical. The volume of free space at the column top was made slightly bigger than that of the bottom. Accordingly, if this structural assymmetry of the column was the cause, the depression of the curve would be more pronounced in the ascending curves. Local assymmetry of barrier location may be accounted for. On the other hand, the couple of curves observed with the ordinary column (dotted line) are exactly symmetrical. In any case, since the equilibrium was found to attain within five minutes in both columns, q_e data presented in the following were those observed after 20 minutes operation.

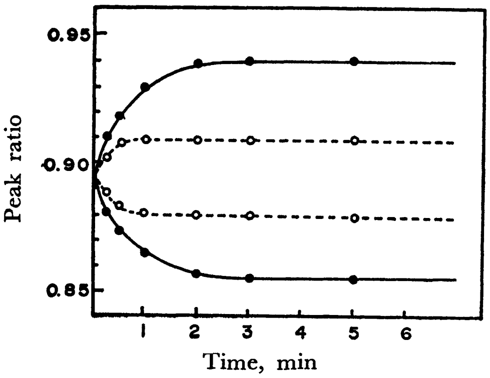

Fig. 2. Progress of separation with time.
Solid line: Column with barriers. Dotted line: Open coulmn. ΔT: 78 °C, pressure: 790 mmHg.

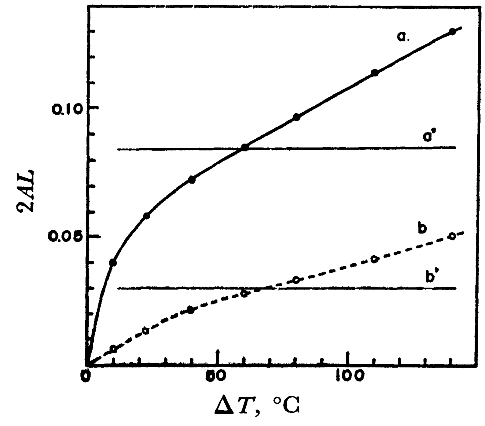

Fig. 3. Logarithm of equilibrium separation against temperature difference. Pressure: 790 mmHg.
Solid line: novel column. Dotted line: open column.

Results of a series of runnings in which the working pressure was kept constant and the temperature difference applied was varied are summarized in Fig. 3. The scale of the ordinate is logarithm of the equilibrium separation factor, ln q_e ($=2AL$).

The curves clearly indicate that, as the theoretical analysis predicted, the magnitude of the equilibrium separation is always greater with novel column (solid line) than with the ordinary one (dotted line). In this figure, the two horizontal lines indicates the theoretical values of the logarithmic equilibrium separation for the novel column (curve a') and ordinary column (b').[6] One thing to be stressed with this figure is not the dissimilarity[7] between the experimental and theoretical curve forms but is that the experimental separations are greater than the theoretical values when the temperature difference exceeds 70 °C or so regardless of the column type. As far as the authors are aware, it is usual that the experimental separation, particularly with hot-wire column, doesn't exceed theoretical value. The present result might be correlated with the shape and sizes of column used.

Pressure Effect. Similarly, the effect of pressure was studied under the condition of constant temperature difference. The results obtained are shown in Fig. 4 in which theoretical curves (a' and b') are drawn using the following relationship.

$$2AL = \frac{1.231\times 24\times \eta DL\alpha}{\rho g w^4 P^2} \tag{1}$$

The numerical factor 1.231 is the correction factor for the cylindricity of the column used (see Eqs. (100) through (111) in Ref. 2). In accordance with the theory (curves a' and b'), the separation factor observed appears to decline with increasing pressure (curves a and b). Curve a, which stands for the observation with the novel column, appears to lie down at the lower pressure region. As has been frequently shown,[2,3] the separation factor makes a maximum at a low pressure. This effect is not seen in curve b which stands for the measurements with ordinary column. In any case, it is apparent that the performance of the novel

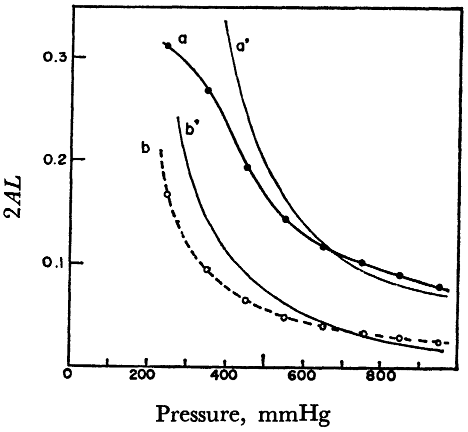

Fig. 4. Pressure effect on the logarithmic equilibrium separation.
a: observed with novel column, b: with ordinary column a' and b' are calculated on the base of Eq. (1). Temperature difference: 78 °C.

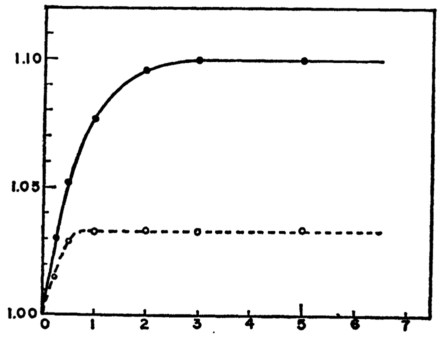

Fig. 5. Progress of thermal separation with time. Temperature difference: 78 °C, Pressure: 790 mmHg. Solid line: novel column, Dotted line: ordinary column.

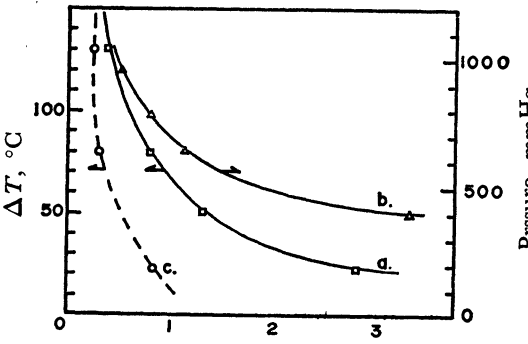

Fig. 6. Change in relaxation time, t_r, against ΔT (curve a) and pressure (curve b). Curve c represents the effect of ΔT observed with open column.

column is always better than that of the ordinary one.

Rate of Attainmnet of Equilibrium Separation. Although it is now undoubted that the magnitude of equilibrium separation is definitely improved, there is another important factor in the practice, *i.e.*, the rate of attainment of the equilibrium separation. This point is answered graphically in Fig. 5, where the scale of the ordinate is expressed by the separation factor q (not to be confused with q_e). It is clearly seen that the separation progresses with higher rate in the novel column than in the ordinary one. Although only two representative curves are shown in this figure, the situation was the same through all measurements in the present study.

The characteristics of the relaxation time was fully studied with the novel column. The effect of temperature difference was studied under a constant pressure of 790 mmHg, while the pressure effect was studied by keeping temperature difference 78 °C. These are shown in Fig. 6 with curves a and b respectively. The behavior of the curves are quite ordinary and the relaxation time decreases with the increase of both temperature difference and pressure.

Discussion

According to the original theory of Jones and Furry, the equilibrium separation does depend neither mean

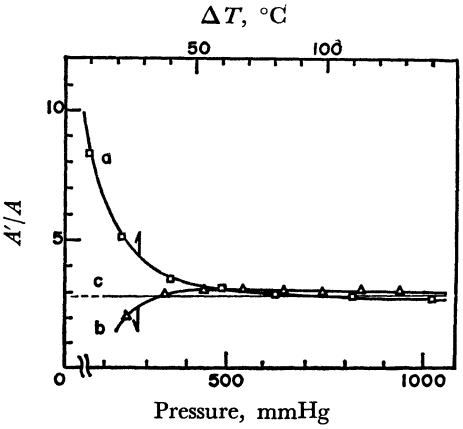

Fig. 7. Quality factor, A'/A, against ΔT (curve a) and pressure (curve b). Curve c represents theoretical value.

temperature nor the temperature difference, if the coefficient K_d is sufficiently less than K_c (see Eqs. (3), (4) and (23) in the foregoing paper). This was the case for the apparatus presently used (calculated K_c is 3×10^3 times greater than K_d). Accordingly, the experimental variation of the equilibrium separation with the change in applied temperature difference, as is exemplified by Fig. 3, is beyond the theory at present.

On the other hand, results shown in Fig. 4 indicate, regardless of the type of column, that the agreement between theory and experiment is quite good when the pressure effect is concerned.

The equilibrium separation factor is correlated with the theoretical transport coefficients by the equation

$$q_e = \exp(2AL), \text{ where } 2AL = HL/(K_c+K_d).$$

Accordingly, in order to see the relative performance of the two types of column, it will be worth to define the "quality factor" f as follows

$$f = \ln q_e'/\ln q_e = A'/A \tag{2}$$

in which primed symbols stand for the novel column. On the base of experimental results shown in Figs. 3 and 4 the quality factor was calculated as a function of both the temperature difference and pressure respectively. This is shown in Fig. 7. It is interesting to see that the quality factor at a difference of 10 °C of temperature is 8.3 and reduces rapidly first and gradually later with increasing temperature difference. At the maximum temperature difference applied (140 °C), the quality factor takes a value of 2.6. This indicates that the performance of the novel column is equivalent to that of an ordinary column having 2.6 times longer length. A graphical estimation indicated that the quality factor will be still more than 2.3 at the temperature difference of 500 °C, which is thought as a practical condition in the gas phase operation.

Curve b in Fig. 7 is drawn for a series of experiments show in Fig. 4. In this case also, the quality factor becomes almost constant at higher pressure region but reduces strongly at lower pressure. The straight line c is the theoretical value[8] which is an only function of the design parameter a. It is obvious that at pressure more than 400 mmHg and the temperature difference exceeding 60 °C, the agreement between theory and experiment is excellent.

According to Jones and Furry,[2] in cases where the equilibrium separation is sufficiently small so that $c(1-c)$ does not change appreciably along the column, the progress of the thermal separation is characterized by

$$\Delta = \Delta_e(1-e^{-t/t_r}) \tag{3}$$

where Δ is the concentration difference at top and bottom of column and suffix e means the value at equilibrium. The relaxation time, tr, is[9]

$$tr = 2mAL/H = mL/(K_c+K_d).$$

In the latter equation, m represents mass of gas in the positive reservoir. Since K_c is sufficiently greater than K_d the ratio of the relaxation times for the two types of column having the same dimension should be the ratio of K_c's.

$$t_r'/t_r = K_c/K_c'$$

According to this equation, the relaxation time of the novel column should be much longer than the ordinary column of the same dimension. Numerical evaluation indicated that the ratio of relaxation time becomes to 11.4 at maximum corresponding to $a=5/8$.

If this prediction was acceptable the benefit of using screens would be worthless because of a long time consumption. This was not the case, however. That the initial rise of curves in Fig. 5 is undoubtedly steeper in the novel column is an indisputable proof. Furthermore, as is seen in curve a in Fig. 6, the relaxation time of the novel column is certainly greater at smaller temperature difference but becomes almost indistinguishable at higher temperature difference. A similar behavior of t_r' is seen in curve b which represents the dependence on pressure. It is readily seen that the temperature difference was even smaller (ΔT was 78 °C in the measurement of curve b), the increase in pressure decreases the relaxation time. Treacy and Rich[5] also stated that the installation of barriers resulted in the increased rate of separation.

The authors are indeed grateful to Professors T. Chiba and M. Ohmori of Mechanical Engineering Department for their collaboration in constructing the separation columns. The authors are also indebted to Dr. Yoshimura of Chemical Engineering Department for his courtesy in giving every facility throughout this work.

Table of Notation

$A = H/2(K_c+K_d)$, [cm^{-1}].
D = self-diffusion coefficient, [cm^2/s].
H = transport coefficient, [g/s].
L = length of column, [cm].
K_c and K_d = transport coefficient, [g·cm/s].
P = dimensionless relative pressure.
g = acceleration of gravity, [cm/s^2].
m = mass of gas in positive reservoir, [g].
q = separation factor at transient state.
q_e = separation factor at steady state.
t_r = relaxation time, [s].
w = half-width of the annular space, [cm].
α = thermal diffusion constant.
ρ = density, [g/cm^3].
η = viscosity, [P].

References

1) K. Sasaki, T. Yoshitomi, and N. Miura, This Bulletin, **49**, 363 (1976).

2) R. C. Jones and W. H. Furry, *Rev. Mod. Phys.*, **18**, 151 (1946).

3) J. W. Corbett and W. W. Watson, *Phys. Rev.*, **101**, 519 (1956).

4) K. Hirota, "Molecular Structure and Related Problems", Monog. Ser. Res. Inst. Appl. Electricity, Hokkaido Univ., No. 4 (1954).

5) J. C. Treacy and R. E. Rich, *Ind. Eng. Chem.*, **47**, 1544 (1955).

6) Theoretical values were calculated by means of the following relationships

$$A = \frac{H}{2(K_c+K_d)} \fallingdotseq \frac{12\alpha\,\eta D}{\rho g w^4}$$

and

$$A' = \frac{H'}{2(K_c'+K_d')} \fallingdotseq 2.82\,\mathrm{A}$$

for the ordinary and novel columns, respectively. In the evaluation of these equations, we adapted 0.102[4] as the α value which seems largest among we found.

7) When K_d is extremely less than K_c, theoretical value of equilibrium separation becomes independent of temperature difference as far as temperature dependence of characteristic constants, η, D, and ρ, are ignored. (see Eqs. (3), (4) and (23) in the preceeding paper).

8) See Eq. (24) in the foregoing paper.

9) This expression is applicable when the column has finite size of reservoirs at both ends (see Eq. (194) in Ref. 2) and thus inappropriate for the present case. It seems, however, the tentative use of this equation dosen't result in a serious error. For instance, if Eq. (163) in Ref. 2 was used in place of this equation, the result was unchanged.