$\Delta \mathbf{u}$ = velocity of secondary motion
$\Delta u, \Delta v, \Delta w$ = components of $\Delta \mathbf{u}$
x = normalized radial coordinate

Greek Letters

γ = shear rate
δ = gap between cylinders
ϵ = dimensionless wave number
η = viscosity function
η_0 = rheological coefficient, Equation (6)
θ = rheological coefficient, Equation (6)
λ = rheological coefficient, Equation (4)
ν = rheological coefficient, Equation (6)
ρ = density
$\boldsymbol{\tau}, \tau_{ij}$ = extra stress tensor
$\Delta \boldsymbol{\tau}$ = stress from secondary motion
ϕ = transformed linearized velocity, Equation (5)
Φ = transformed linearized velocity, Equation (10)
ψ = transformed linearized velocity, Equation (5)
Ψ = transformed linearized velocity, Equation (10)
ω = rheological coefficient, Equation (4)
Ω = rotational speed

Subscripts

c = critical
0 = undisturbed flow

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Gas Separation Through Expansible Tubing

The basic difficulty in membrane separations has always been their inherent slowness, resulting in high area requirements. Thus fine-bore tubing becomes of considerable interest. Studies showed that some materials will expand appreciably and reversibly and gas flow rates which are multiples of those in the unexpanded condition can be obtained.

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SCOPE

The availability of fine-bore tubing and hollow fibers has resulted in a great deal of research in the use of bundles of these materials for mass transfer operations. The basic difficulty of membrane separation processes has always been their inherent slowness and resulting high area requirements.

With present hollow fiber technology it has become possible to crowd a large diffusion area into a relatively small space. One example of this is the Permasep equipment of the du Pont Company for water purification where as many as 1.7 million hollow fibers can be accommodated in a tube of about 10 cm O.D. and 2.5 m long (Cooke, 1969-70). Also, numerous proposals and prototype models of blood oxygenators and artificial kidney units can be found in the literature (Salyer et al., 1971a, 1971b; Skiens, 1971). Thus, it is to be expected that this type of arrangement will go far to make gaseous diffusion operation competitive with existing separation operations.

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CONCLUSIONS AND SIGNIFICANCE

To investigate the potential usefulness of fiber bundles we constructed a number of diffusion cells and used several varieties of hollow fibers and capillary type tubing. For the sake of simplicity, most trials were made with air and its components. A not unexpected finding was that silicone rubber tubing expanded in the studied pressure range. The expansion effect seemed to be dependent on the physical size of the tubing. For relatively large silicone rubber tubing the change in size with pressure was hardly noticeable, but for one particularly thin tube the change in physical size was remarkable.*

By using the expandability of silicone rubber tubing the diffusion rate of a gas in a given length of tubing is improved in two ways: first, when pressure is applied to the inside of a tube the diameter increases, thus causing the walls to become thinner; and second, when the diameter increases the transfer area becomes larger. For most silicone rubber tubing this increase in permeability is not substantial, but for the special expansion discovered in one particular type this increase gave rise to a multiple of the normal diffusive gas flow.

THEORY

Expansibility

Although the increase in permeability for relatively large silicone rubber tubing is not great compared to the expansion of a very thin wall, it was easily detected by a simple oxygen permeability test on a bundle.

If the tubes would not expand the permeability constant for oxygen K_{O_2} could be calculated by the following equations, (Barrer and Chio, 1965):

$$K_{O_2} = \frac{F \ln\left(\frac{d_o}{d_i}\right)}{2\,\pi\, L\, \Delta P} \tag{1}$$

or

$$F = \frac{2\,\pi\, K_{O_2}\, L\, \Delta P}{\ln\left(\frac{d_o}{d_i}\right)} \tag{2}$$

The deviation from Equation (2) can be predicted by mechanics of deformable bodies. For the expansion of a thick-walled tube, the increase in a radius $u(r)$ is given by (Stippes et al., 1961):

$$u(r) = \frac{1}{E}\,\frac{R_o^2\, R_i^2}{R_o^2 - R_i^2}\left[(1-\nu)\left(\frac{P_i}{R_o^2} - \frac{P_o}{R_i^2}\right) r + (1+\nu)\,\frac{P_i - P_o}{r}\right] \tag{3}$$

where ν is Poisson's ratio for rubbers 0.40-.49 (Nielsen, 1962).

If we consider an expandable ribbon originally dr thick, after expansion it will be $d[r + u(r)]$ thick. The flow rate through this ribbon is given by

$$F = K_p\, 2\,\pi\, L\,[r + u(r)]\,\frac{dp}{d[r + u(r)]}$$

or

$$\frac{1}{r + u(r)}\, d[r + u(r)] = \frac{K_p\, 2\,\pi\, L\, dp}{F}$$

Integrating both sides from R_i to R_o and from the inside pressure P_i to the outside pressure P_o yields

$$F = \frac{K_p\, 2\,\pi\, L\,(P_i - P_o)}{\ln\left(\frac{R_o + u\,(R_o)}{R_i + u\,(R_i)}\right)} \tag{4}$$

Equation (3) holds for thick-walled tubes where the ratio of change in diameter to the diameter is small ($<$ 0.2). Most silicone rubber tubes fall in this region. The elastic modulus must also be linear over the range studied.

Separation Models

Weller and Steiner (1950) treat two types of diffusion in a cell. The Case I model considers a permeation cell in which the gas is completely mixed on both sides of the membrane.

Case I can be calculated by the simultaneous solution of Equations (5) and (6)

$$\frac{y_p}{1 - y_p} = \frac{\alpha^*\;(P_i\, x_o - P_o\, y_p)}{P_i\,(1 - x_o) - P_o\,(1 - y_p)} \tag{5}$$

and

$$y_p\, \theta = x_i - (1 - \theta)\, x_o \tag{6}$$

Case II behavior can be predicted by the Naylor-Backer Equation (Naylor and Backer, 1955), which is actually equivalent to the Weller-Steiner Equation (Hwang, 1969). The Naylor-Backer model assumes plug flow on the high pressure side of the barrier. It also assumes that there exists a constant effective separation factor α at any point along the barrier. The model results in the following equations:

$$(1 - \theta) = \frac{1 - x_i}{1 - x_o}\left[\frac{1 - x_i}{1 - x_o}\cdot\frac{x_o}{x_i}\right]^{\frac{1}{\alpha - 1}} \tag{7}$$

where

$$\alpha = \frac{\alpha^*\,\dfrac{1 - x_i}{1 - y_i}}{\dfrac{1 - x_i}{1 - y_i} + \dfrac{P_o}{P_i}\,(\alpha^* - 1)} \tag{7a}$$

and y_i is given by

$$\frac{y_i}{1 - y_i} = \frac{\alpha^*\;(P_i\, x_i - P_o\, y_i)}{P_i\,(1 - x_i) - P_o\,(1 - y_i)} \tag{7b}$$

APPARATUS

Seven tube types and six cell designs were tested. The design used for most cells is shown in Figure 1. This design was both very easy to construct and to maintain. The header was constructed by molding the tubing with silicone rubber in a small section of Tygon tubing. When dry, the header could be removed and mounted in another section of Tygon which was inserted into a plastic shell of the same inside diameter as the outside diameter of the Tygon (see Fig. 1). This type of fitting was leakproof up to 200 cm Hg. For the special expansible tubes excess volume was allowed on the permeate side for the expansion. This cell was connected to a simple apparatus consisting of a pressure regulator to control pressure in the tubes, a bubble flow meter to measure permeate and

* Product of Medical Engineering Corp., Racine, Wis.

reject flow rates, and an oxygen analyzer to measure compositions of the streams. The permeate pressure P_o was always atmospheric.

EXPERIMENTAL RESULTS

At 25°C the value of K_{O_2} for silicone rubber is $60 \times 10^{-9} \frac{(\text{Std cc})(\text{cm})}{(\text{sec})(\text{sqcm})(\text{cmHg})}$ (Major and Kammermeyer, 1962). This value should remain constant with pressure; however, it does not, since the tubing expands. Figure 2(a, b, c) shows this expansion for three different sizes of silicone rubber tubing (see Table 1). The ordinate is the effective permeability constant K'_{O_2} given by Equation (1) assuming the tubes do not change inside and outside diameters. The solid line represents Equation (1) for the case where the tubes did not change dimensions. The points and the dashed curve signify actual data.

For extruded tubing, the elastic modulus E in the machine direction often differs from that in the transverse direction. The value for E in the transverse direction was calculated from Equations (3) and (4) and the actual data to be 600 to 700 lb./sq.in. (40.82-47.63 atm). The value for the machine direction was measured with dead weight on a section of tubing as 300 lb./sq.in. (20.41 atm). The value for Poisson's ratio ν was assumed to be 0.45 [average of 0.40 and 0.49 (6)] since no literature value could be found. Using 650 lb./sq.in. (44.22 atm) for E and 0.45 for ν, the permeated flow rate can be calculated from Equation (4) for thick-walled silicone rubber tubes within 5% of the experimental values.

For most silicone rubber tubing a maximum of 10 to 20% increase in the permeated flow rate would be obtained from the expansion of the tube in the 0 to 150 cm Hg over pressure range. The one exceptional tube that did not follow this moderate increase in permeation rate has prompted intensified research in expandable tubing. Such a tubing with an O.D. of 0.381 mm and I.D. of 0.254 mm showed an increased permeated flow rate 20 times that predicted by Equations (2) or (4). The reason for this dramatic increase in flow rate is that when pressure is applied to this tubing the diameter is increased 3 to 4 times the original size. These tubes apparently have a critical inside and outside diameter which allows them

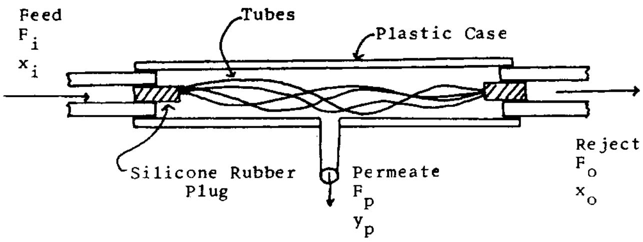

Fig. 1. The design used for most cells.

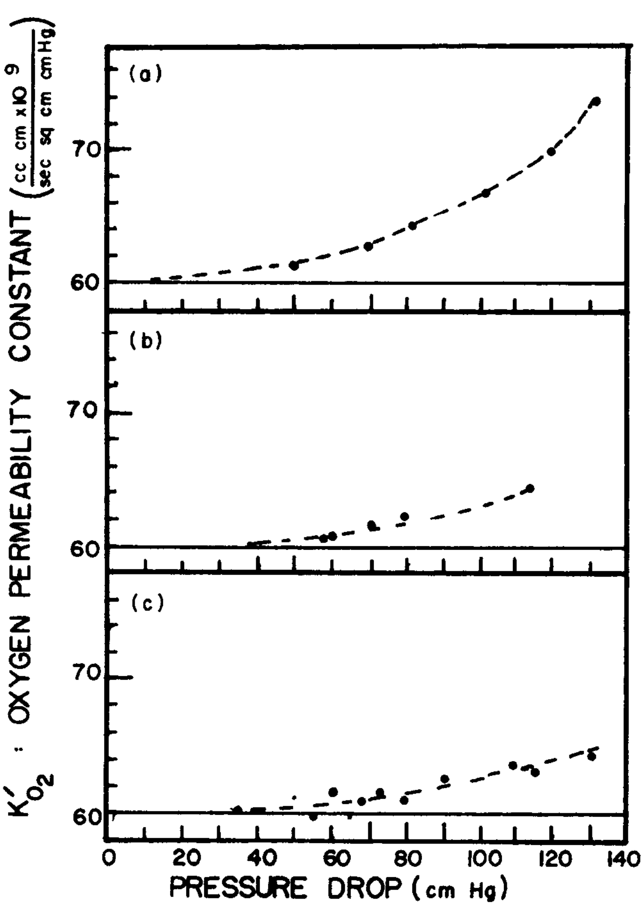

Fig. 2. Permeability vs. pressure for: (a). 77 mil O.D. (1.955 mm), 58 mil I.D. (1.473 mm) silicone rubber tubing; (b). 50 mil O.D. (1.27 mm), 30 mil I.D. (0.762 mm) silicone rubber tubing; and (c). 25 mil O.D. (0.6350 mm), 12 mil I.D. (0.3048 mm) silicone rubber tubing.

TABLE 1. SILICONE RUBBER TUBING TESTED

	Size (mils) O.D.	I.D.	Expansion	Manufacture
(a)*	77	58	slight	Dow Corning Corp.
(b)	50	30	slight	Medical Engineering Corp.
(c)	25	12	slight	Dow Corning Corp.
	15	10.5	large	Medical Engineering Corp.

* As in Figure 1.

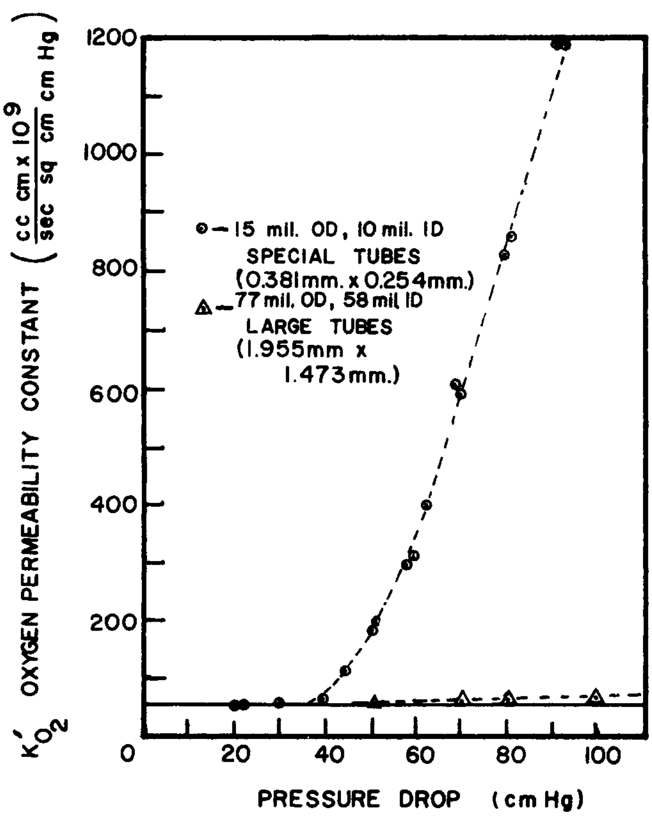

Fig. 3. Permeability vs. pressure for special expansion found in thin wall silicone rubber tubes.

to expand beyond the linear elastic region without ruptures, just like a balloon.

Figure 3 shows this increased flow rate caused by the large change in physical dimension. As before, instead of plotting flow rate, the effective permeability constant for oxygen K'_{O_2} is plotted to show the deviation from the predicted K_{O_2}. The data for 1.956 mm O.D., 1.473 mm I.D. tubes are also included to show how much more the expandable tubes are affected by pressure than a tube with a thicker wall.

As the pressure is slowly increased on the inside of these tubes no noticeable physical change takes place until the pressure reaches a critical value at which the tubes suddenly increase in diameter three- to four-fold. After this initial change in size there is not much visible change in appearance. Figure 3 shows that this critical pressure is approximately at 40 cm Hg. The rise in K'_{O_2} in Figure 3 would be sharper if all of the tubes in the experimental bundle (30 tubes, 25 cm long) expanded at the same time. The tubes are not exactly alike; therefore, they expand at different critical pressures.

It was also noticed that the K'_{O_2} curve changed with the number of times the tubes were stretched. Figure 4 shows the shift in the critical pressure for each expansion until finally there is no noticeable change from expansion to expansion. This change is due to the change in the stress-strain relationship when the tubes are stretched repeatedly.

The reason for this unusual expansion behavior can be found in the stress-strain curve for silicone rubber tubing after a number of expansions (Figure 5). Note that the stress-strain curve diverges upward. This means that the tube is becoming stronger and more rigid as the pressure increases, thus explaining the tube strength in the inflated state.

When some thick-walled tubes were pressure tested to obtain the same large expansion effect as with the exceptional tubes, the tubes ruptured without appreciable expansion. To date these particular tubes with a O.D. of 0.381 mm and I.D. of 0.254 mm are the only tubes found that exhibit this large change in diameter.

To show that the increase in permeability was not due to pinholes, nitrogen gas was also tested in the tubes. The results of this test can be seen in Figure 6. Since the curves for oxygen and nitrogen do not converge and

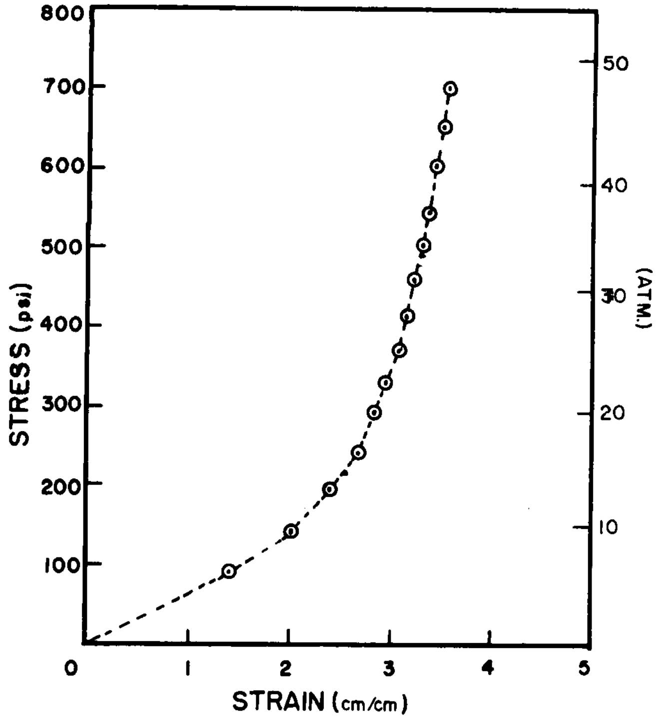

Fig. 5. Stress vs. strain in machine direction for expandable silicone rubber tubes.

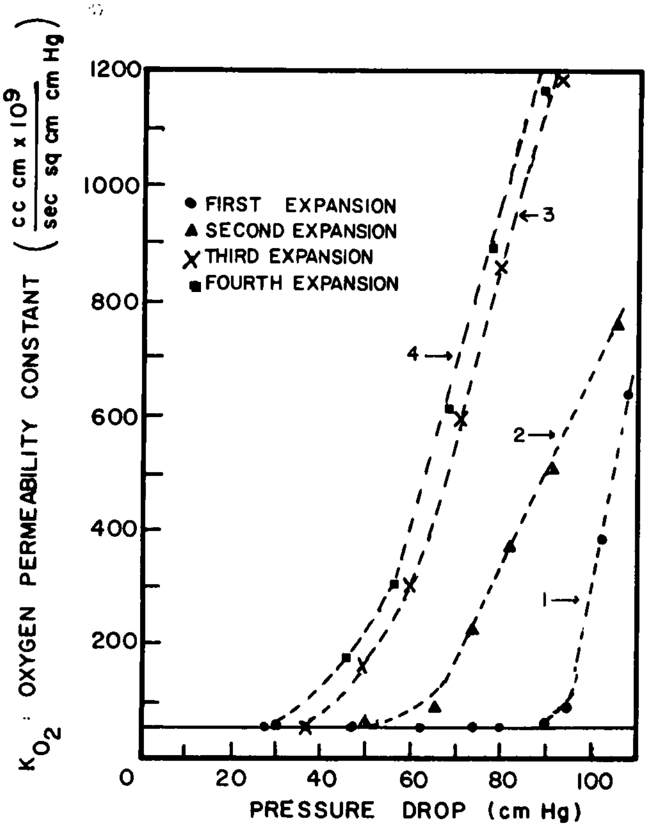

Fig. 4. Permeability vs. pressure for successive expansion of special tubes.

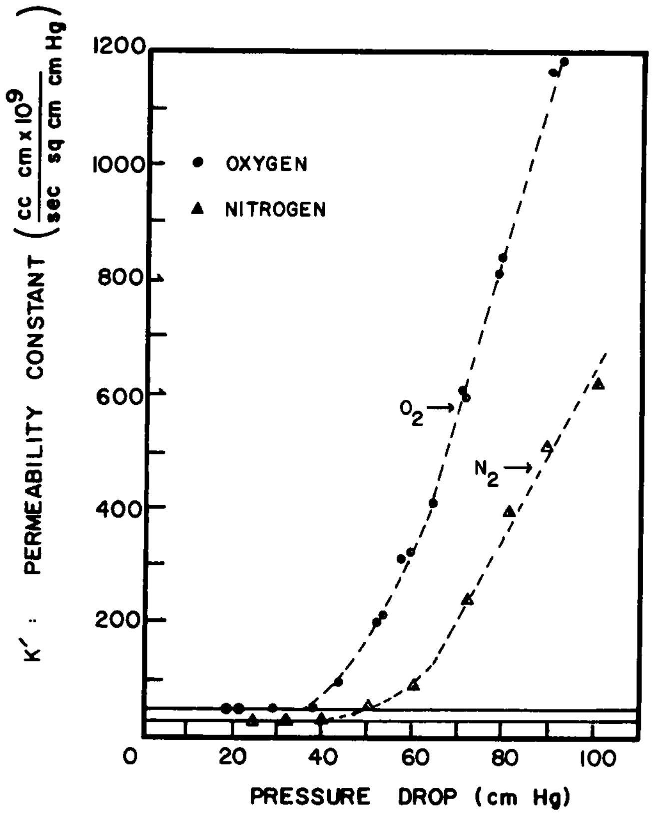

Fig. 6. Permeability vs. pressure for expanded special tubes.

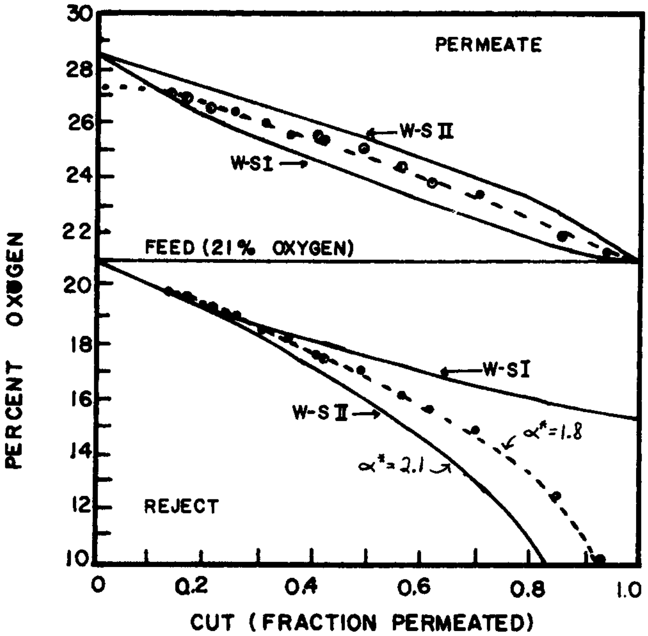

Fig. 7. % oxygen vs. cut for an airfeed to an inflated special silicone rubber tubing bundle W–S I, II → Weller-Steiner Case I, II. ● Data.

the ratio of any two vertical points remains constant at approximately 2.0, it can be assumed that there were no pinholes.

This method of increasing pern ed flow promises to have commercial value; therefore, separation experiments were conducted. Air was used as the feed stock to the permeation cell.

The curves calculated for Case I and Case II are shown in Figure 7 along with the data points taken for air, with the tubes in the expanded state at a pressure drop ΔP of 106 cm Hg. The separation factor α^* for unstretched silicone rubber is 2.1 (ratio of lit. values 60×10^{-9} to 28×10^{-9} (Major and Kammermeyer, 1962)). Note that the Case II curve for $\alpha^* = 2.1$ does not fit the data. If a separation factor of 1.8 is used there is an almost perfect fit to the Case II theory.

Roberts and Kammermeyer (1963) have shown that the permeabilities of gases through silicone rubber are decreased by the strain applied to the membrane. In the expanded state the permeability of oxygen is decreased more than the permeability of nitrogen, thus causing the separation factor to be lower. The Naylor-Backer model should fit the data since the flow inside the tubes was laminar (Reynolds number was less than 300 for a cut of 0.3 in all the cells tested).

CONCLUSION

Although these exceptional tubes have a lower separation factor for the O_2-N_2 system and presumably other gas combinations, they still have a great advantage over other silicone rubber tubes in that their permeated flow is so much higher. Diffusion cells can be made at least 10 times smaller with these expandable tubes than with conventional tubing.

Since these exceptional tubes are a relatively new product and were originally not intended to be used in the expanded state they occasionally fail during operation. These failures usually result where the tube wall is thinner at some spots than the rest of the tube. For sections of tubing where the tube wall is uniform no problems with failures have been encountered to date. Some cells have been cycled as much as 20 times and held up over 6 days of continuous operation without tube failure. If the problem of tube uniformity can be solved, the application of these expandable tubes is only limited by the imagination of the user.

NOTATION

α = effective separation factor
α^* = separation factor; ratio of permeabilities
d_o = outside diameter
d_i = inside diameter
E = elastic modulus
F = flow rate
K = permeability $-\dfrac{(\text{Std cc})(\text{cm})}{(\text{sec})(\text{sqcm})(\text{cm Hg})}$
K' = effective permeability
L = length
ΔP = pressure drop
P_o = absolute outside pressure (atmospheric pressure)
P_i = absolute inside pressure
R_o = outside radius
R_i = inside radius
r = radius
$u(r)$ = change in radius due to pressure
ν = Poisson's ratio
x_i = concentration of faster permeating gas into diffusion cell
x_o = concentration of faster permeating gas rejected from diffusion cell
y_p = concentration of faster permeating gas in permeate
y_i = concentration of faster permeating gas in the first incremental section of tubing
θ = cut or fraction permeated

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