Hollow Fiber Gas Membranes

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Gas membranes can be used to rapidly remove volatile solutes like hydrogen sulfide and sulfur dioxide from dilute aqueous solutions. The gas membranes are supported by microporous hydrophobic hollow fibers. The aqueous feed containing the volatile component flows down the fiber lumen, and an aqueous stripping solution bathes the outside fiber surface. Thus the membrane consists of gas trapped in the hydrophobic pores. The fluxes across these membranes, which can be much faster than those across polymer films, are consistent with a nonlinear mechanism which includes solute ionization.

SCOPE

Membrane separations can be conveniently considered as two groups, solid membranes and liquid membranes (Lonsdale, 1982; Matson et al., 1983). Solid membranes often contain small pores and act as filters. When a solution is forced through this type of membrane, small solutes pass easily through the pores but large solutes are retained. Thus the selectivity of the membrane is frequently controlled by the solute size, and the analysis of membrane performance is often made by analogy with filtration.

In contrast, liquid membranes are essentially pore-free. Instead of passing through pores, the solutes dissolve in the membrane and diffuse to the other side. Very soluble, mobile solutes pass easily through these membranes, but insoluble, immobile solutes are retained. Thus the selectivity of these membranes is controlled by solubility, and the analysis of the membranes depends on parallels not with filtration, but with liquid-liquid extraction (Cussler, 1984).

In this paper, we explore gas membranes, a third group useful for membrane separations. These membranes consist of a gas layer separating two aqueous solutions (Watanabe and Miyauchi, 1976; Imai et al., 1982; Zhang and Cussler, 1985). The gas layer is stabilized within the pores of a hydrophobic microporous filter in the same way that liquid membranes are most commonly immobilized. Solutes which are volatile can pass across these membranes, but nonvolatile solutes like electrolytes are completely retained. Moreover, such gas membranes are stable for at least months, even when they are separating solutions whose acid concentration differs by ten or more pH units.

In this paper, we identify the range of systems which can be separated with these gas membranes. We measure their speed and their selectivity, and compare these with other membrane processes. Finally, we determine the detailed mechanism by which these membranes function.

CONCLUSIONS AND SIGNIFICANCE

We have measured the flux of nine volatile solutes dissolved in water and transported across gas membranes. The flux can be faster than that observed across polymer membranes or carrier-facilitated liquid membranes. This high flux occurs when the solute is volatile and when it is relatively insoluble in water. Interestingly, the requirement of high volatility seems less restrictive than that of low solubility. Within these restrictions, membrane selectivity is higher than in many polymer membranes, but lower than that observed for carrier-assisted diffusion.

We have studied in detail the gas membrane separation of hydrogen sulfide, sulfur dioxide, and ammonia. We chose these three solutes because their removal can be a problem in industries such as paper, textiles, and tanning. We have developed a mechanism explaining the operation of these membranes, and have verified this mechanism experimentally. Not surprisingly, the mechanism involves three resistances: mass transfer out of the feed solution, diffusion across the membrane, and mass transfer into the product solution. The first two resistances are more important than the third. However, the overall resistance will not be a simple sum of these resistances when mass transfer in the feed solution is altered by ionization.

Our experiments using hollow fiber gas membranes involve membrane areas/volume of about 1,000 m^2/m^3, which are larger than those commonly found in packed towers (Treybal, 1980). Moreover, gas membranes can carry out gas stripping and gas absorption in the same apparatus. It will be interesting to see whether these membranes can in the future compete with packed towers.

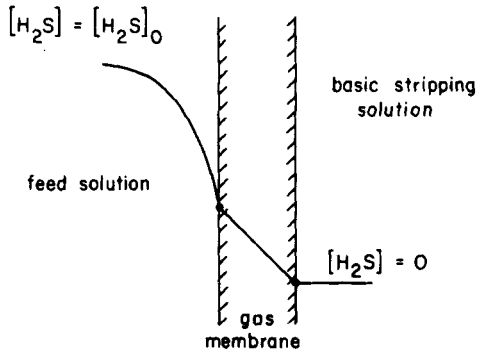

Figure 1. Hydrogen sulfide diffusion across a gas membrane.

H_2S concentration drops from bulk value in aqueous feed (left) to almost zero in stripping solution (right); the drop occurs largely in the feed and across the membrane. The concentrations shown in the membrane actually represent the aqueous concentrations which would be in equilibrium with the local partial pressure.

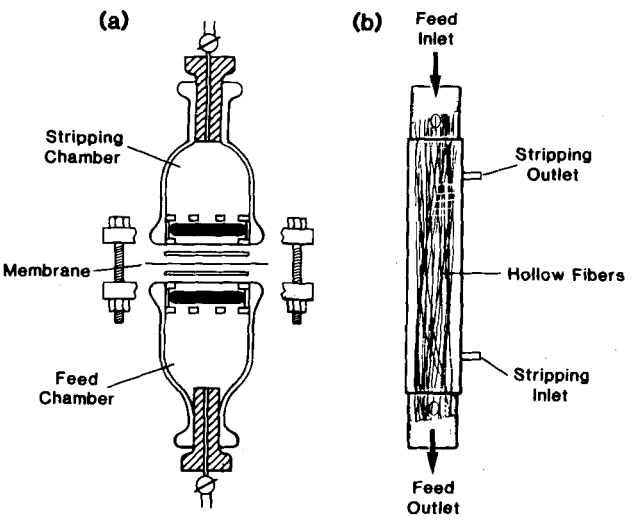

Figure 2. Diffusion apparatus.

(a) Flat membranes installed in the diaphragm cells were used in preliminary studies and in some investigations of the transport mechanism.

(b) Hollow fiber membranes used in the remaining experiments are a geometry of practical potential.

INTRODUCTION

The gas membranes described in this paper are essentially a gas layer, about 30×10^{-6} m thick, separating two aqueous solutions. In many cases, one of the solutions is strongly acidic and the other is strongly basic. The gas membrane separating these solutions is contained within the pores of a microporous, hydrophobic polymer film. As a result, the acid and base cannot mix.

The operation of this type of membrane for the case of hydrogen sulfide is shown schematically in Figure 1. The membrane is represented by the shaded region between the two vertical lines. A feed solution containing H_2S flows on the left of this membrane, and a stripping solution containing NaOH flows on the right. As a result, H_2S diffuses from left to right, where it reacts to form the nonvolatile sulfide.

The overall rate of H_2S transport depends on three resistances in series. First, the H_2S is transferred from the bulk of the feed to the membrane's lefthand interface. Second, it evaporates, diffuses across the gas membrane, and dissolves in the stripping solution on the right side. Third, it diffuses and reacts in this basic stripping solution. This sequence is familiar in many engineering courses on heat or mass transfer; the only unusual aspect is that the membrane is a gas.

In this paper, we report experiments with this type of gas membrane. We show that membrane transport can be faster than that across most liquid or polymer membranes. We show that these membranes can function both in diaphragm cells used for fundamental research, and as hollow fibers having commercial potential. Finally, we show that the three step mechanism qualitatively sketched in Figure 1 can be quantitatively complicated.

EXPERIMENTAL

All chemicals were reagent grade and were used as received. Hydrogen sulfide was made by adding 1 M phosphoric acid to sodium sulfide, warming to release the gas, and capturing the gas in distilled water. Sulfur dioxide was made analogously, but with sodium sulfite replacing sodium sulfide. Hydrogen sulfide and sulfur dioxide concentrations were measured by adding known amounts of iodine and than titrating the remaining iodine with sodium thiosulfate, using starch as an indicator. Ammonia concentrations were found by titration with hydrogen chloride, using methyl orange as an indicator (Snell and Hitton, 1966).

Two different types of membrane experiments were made in this work. Experiments of the first type used flat membranes to test the feasibility of separations of a variety of solutes. Experiments of the second type utilized hollow fibers to determine details of the membrane's mechanism and to explore the practical possibilities of this type of separation. Every experiment of each type was made in triplicate.

Experiments with flat membranes used modified diaphragm cells like those shown in Figure 2a. These cells, which are similar to those used for liquid membrane experiments (Duffey et al., 1978; Zhang and Cussler, 1985), consist of two compartments, each of about 0.02 dm^3 and each stirred magnetically at 240 rpm. The flat membrane which separates the two compartments was microporous polypropylene (Celgard 2500, Celanese, Charlotte, NC), with an area of 3.1×10^{-4} m^2, an average pore diameter of 3×10^{-8} m, a void fraction of about 0.45, and a thickness of 25×10^{-6} m. These membranes were used as received, so that their pores initially contained only air. Experiments with H_2S are typical: The cell was assembled, the lower compartment was filled with a known solution of H_2S and any other desired solutes, and the upper compartment was filled with a basic stripping solution. The cell was then immersed in a constant temperature bath for the desired time, and the solutions in both compartments were sampled for analysis. These solution concentrations were analyzed by the equation (Cussler, 1984)

$$k = \frac{V_d}{2At} \ln\left[\frac{\Delta c(t=0)}{\Delta c(t)}\right] \tag{1}$$

where the various symbols are defined in the notation section at the end of the paper. This equation is basic to the analysis of the flat membrane experiments described below.

Experiments with hollow fiber membranes used modules like those shown schematically in Figure 2b. These modules, originally made for use in an Amicon model CH2 ultrafiltration apparatus, were attached with our own connections to feed and stripping reservoirs via two Manostat Varistaltic pumps. Two modules were used. One contained 300 fibers, $381 \cdot 10^{-6}$ m I.D., $29 \cdot 10^{-6}$ m thick, 40% voids, and 0.20 m long, giving an area per volume of 550 m^2/m^3. The second contained 400 fibers, $397 \cdot 10^{-6}$ m I.D., $24 \cdot 10^{-6}$ m thick, 20% voids, and 0.20 m long, giving 820 m^2/m^3. Both modules used fibers of microporous polypropylene (Celgard X10, Celanese, Charlotte, NC) having an average pore size of $3 \cdot 10^{-8}$ m. Like the flat membranes, the hollow fibers were used as received. The feed solutions containing the volatile solutes such as H_2S were pumped down the center of the fibers, and the stripping solution was circulated more slowly outside the fibers. The solute concentration in the feed reservoir was measured as a function of time and was used to calculate the mass transfer coefficient k across the fibers' walls:

$$k = \frac{vd}{4L} \ln\left\{1 - \frac{4V}{\pi d^2 vNt} \ln\left[\frac{c(t=0)}{c(t)}\right]\right\} \tag{2}$$

The derivation of this equation is given in the Appendix.

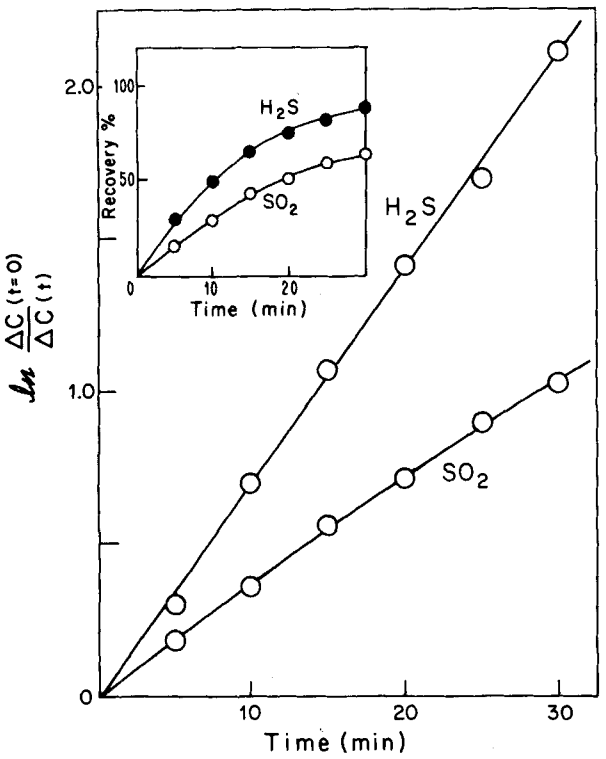

Figure 3. Gas fluxes across flat membranes.

In both sets of experiments, the feed solution contained 10^{-2}M of the volatile species, the stripping solution contained 0.1 M NOH.

Inset: Transport was rapid. For H_2S, the logarithm of concentration varies linearly with time, consistent with Eq. 1 Slight curvature for SO_2 is explained in text discussion.

RESULTS

In this paper, we want to investigate the speed and selectivity of gas membranes. We want to establish a criterion by which we can predict when these membranes will be effective. We want to determine the detailed mechanism by which these membranes function.

Before we can realize these goals, we must first show that these membranes can be described with the equations given above. In particular, for the flat membranes, Eq. 1 predicts that the logarithm of the measured concentration difference in the diaphragm cell should vary linearly with time. This prediction is tested by the data

TABLE 1. GAS MEMBRANE FLUXES FOR VARIOUS SOLUTES

Solute*	Stripping Solution	$\ln \frac{\Delta c(t=0)}{\Delta c}$	k 10^{-6} m/s
Br_2**	0.5 N NaOH	0.77	4.1
H_2S	0.5 N NaOH	0.70	3.7
I_2**	0.5 N NaOH	0.39	2.1
SO_2	0.5 N NaOH	0.35	1.9
NH_3	0.5 N H_2SO_4	0.32	1.7
$(NH_4)_2S$	0.1 N $AgNO_3$ +0.1 N HNO_3	0.18	1.0
CH_3COOH	0.5 N NaOH	0.02	0.1
HCl	0.5 N NaOH	0	~0
Lactic acid	0.5 N NaOH	0	~0

* In each case, initial feed concentration was 10^{-2}M and experiment duration was 10 min.

** Feed was acidified to pH 3.5 using HCl.

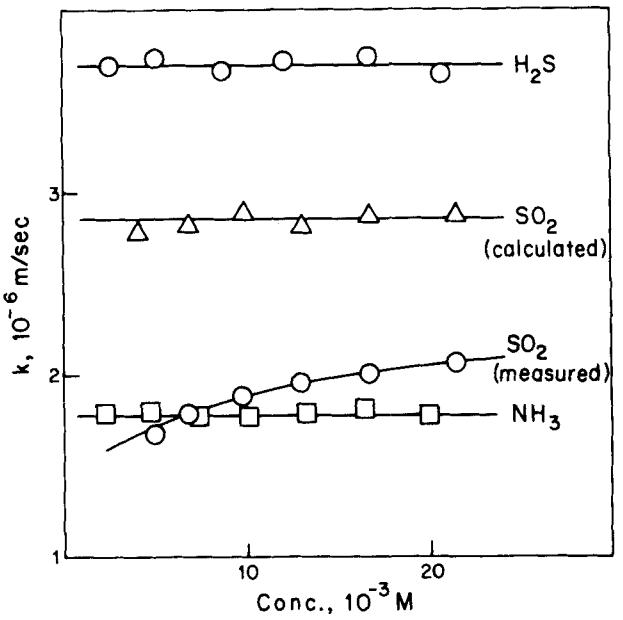

Figure 4. Mass transfer coefficients vs. solute concentration.

If the mechanism shown in Fig. 2 is correct, the data should fall on horizontal lines, as they do for H_2S and NH_3. They do not for SO_2 because of formation of HSO_3^-. When this formation is included, the calculated values of k are also constant.

in Figure 3. For H_2S the variation is linear, but for SO_2 it shows slight negative curvature. We will base our discussion on the initial slopes of these curves, and will explain the curvature for SO_2 later. In passing, note that the half-life for separating these solutes implied by the inset in Figure 3 is about 10 min, more than 50 times faster than is typical of liquid diffusion in similar diaphragm cells.

The mass transfer coefficients across flat gas membranes are shown for a variety of solutes in Table 1. The first column in the table gives the solute, the second describes the stripping solution, and the third reports the concentration after 10 min. The last column gives the overall mass transfer coefficient across the membrane.

The results show that volatile solutes like H_2S often give large mass transfer coefficients, diffusing rapidly through the membrane. However, a high vapor pressure is not enough: the vapor pressure of HCl is high, but its flux is low. As we will show below, a high flux requires not so much a large vapor pressure as a low solubility in the feed.

We have studied the transport of H_2S, SO_2, and NH_3 in more detail. The variation of the mass transfer coefficient with solute concentration in the feed stream is illustrated for flat membranes by the results in Figure 4. For H_2S, the mass transfer coefficient is constant, and for NH_3 it is nearly so. However, for SO_2 the coefficient is constant at high solute concentration but drops at low concentration, suggesting that its mass transfer is not a linear process.

We made a variety of experiments designed to elucidate the detailed mass transfer mechanisms across these membranes. First, we found in scattered experiments that the mass transfer is independent of concentration and flow in the stripping solution. Thus we conclude that the resistance to mass transfer in the stripping step is negligible. Second, we found that the mass transfer coefficient in the flat membranes varies inversely with the membrane thickness, as shown by the results in Figure 5. Third, we discovered that the mass transfer coefficient varies with the flow in the hollow fiber membranes, as shown by the results in Figure 6. It also can vary with added acid, as shown by the results in Figure 7. The implications of these apparently disparate results are resolved in the discussion that follows.

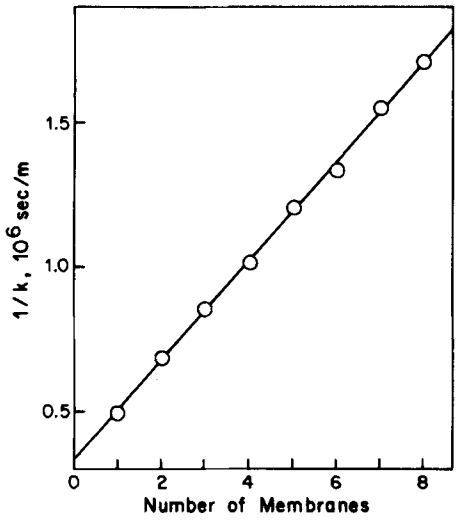

Figure 5. Ammonia mass transfer vs. flat membrane thickness.

Mass transfer coefficient for NH_3 is inversely proportional to membrane thickness, varied by clamping several membranes together. The intercept on this plot is the resistance of the feed solution; the slope is related to membrane resistance per membrane thickness.

DISCUSSION

The results above show that gas membranes can be a rapid, selective separation process for volatile solutes. For example, the initial flux of H_2S inferred from the flat membrane results given in Figure 3 or Table 1 is about $3 \cdot 10^{-8}$ mol/cm^2·s. This is one to three orders of magnitude faster than the fluxes reported for carrier-assisted diffusion in liquid membranes. However, the concentration difference in the gas membranes is about 10 times less than that characteristic of the liquid membranes (Lonsdale, 1982). Under the same concentration difference, the gas membranes would be faster still.

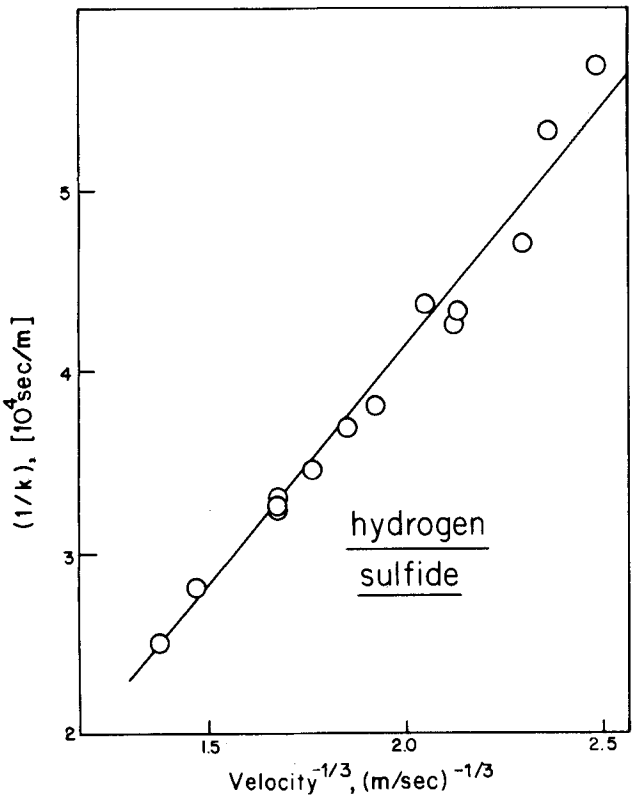

Figure 6. Hydrogen sulfide flux vs. hollow fiber flow.

Mass transfer coefficient varies with cube root of the flow through hollow fibers. This result, consistent with existing correlations for mass transfer, shows that resistance to mass transfer in the feed solution is significant.

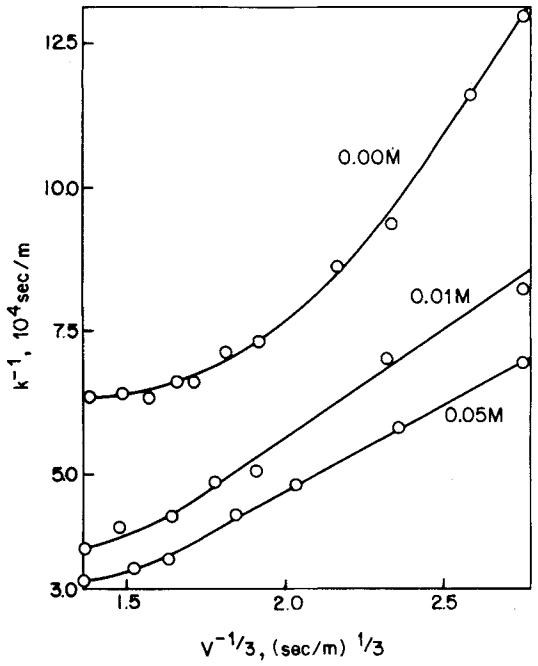

Figure 7. Mass transfer of sulfur dioxide vs. acid concentration in the feed.

Mass transfer coefficient of SO_2 across the hollow fibers varies with flow and with H_2SO_4 concentration in the feed solution. This variation approaches the simple limit of Fig. 6 only at high H_2SO_4 concentration. As explained in text, this more complicated behavior occurs because of the formation of HSO_3^-.

The selectivity in the gas membranes is a function both of the solute's volatility and of the nature of the stripping solution. Again, using H_2S as an example, we can obviously separate H_2S from sodium sulfide, sodium chloride, or any other salt. Less obviously, we can separate H_2S from NH_3 selectively if we use a basic stripping solution. This is because the H_2S reacts with the base but the NH_3 does not.

The selectivity of the gas membranes between two acidic solutes like H_2S and SO_2 is smaller but still interesting. This selectivity depends on the resistances to mass transfer both in the feed and across the membrane. In many practical cases, the feed will be aqueous, so the physical properties in the feed (like the diffusion coefficient) will be nearly equal for both solutes. As a result, the resistances in the feed stream will be nearly the same. If these feed resistances are rate-controlling, then there will be little selectivity between H_2S and SO_2.

On the other hand, when the membrane resistances are rate-controlling, the selectivity of the gas membranes can be greater. These membrane resistances ($1/k_M$) are given by (Cussler, 1984):

$$\frac{1}{k_M} = \frac{\ell}{DH} \tag{3}$$

The membrane thickness ℓ is the same for both solutes, and the diffusion coefficients D fall within a factor of two for most solute pairs (Hirshfelder et al., 1954). Thus when the membrane resistance controls, any selectivity is dominated by differences in the distri-

bution coefficient H. For sparingly soluble solutes, this coefficient is proportional to the vapor pressure divided by the solubility in the feed, i.e., to the Henry's law constant.

Thus the data show that gas membranes offer fast separations selective between solutes with different distribution coefficients. We now turn to the detailed mechanism by which these membranes function.

We expect that the flux across gas membranes is determined by the three resistances implied by Figure 1. These three are the resistance in the stripping solution, the resistance of the membrane itself, and the resistance in the feed solution. As mentioned above, we find that the resistance in the stripping solution is small, for changes in the stripping solution's flow and concentration do not affect the flux across the membrane. As a result, we believe that the mass transfer coefficient in the stripping solution is so accelerated by chemical reaction that it is much greater than the corresponding mass transfer coefficients in the feed and across the membrane (Astarita et al., 1983).

We originally expected that the flux across gas membranes would be given by the usual equation

$$n = k(c - c^*) \tag{4}$$

where k is the overall mass transfer coefficient across the membrane, and c^* is the feed concentration in equilibrium with the stripping solution. Since the stripping solution is present in excess, c^* is zero. Moreover, we expected that

$$\frac{1}{k} = \frac{1}{k_F} + \frac{1}{k_M} \tag{5}$$

where k_F and k_M are the mass transfer coefficients in the feed and across the membrane, respectively. From Eq. 3, we see that $(1/k_M)$ should vary with the total membrane thickness ℓ. Thus for flat membranes, a plot of $(1/k)$ vs. ℓ should be a straight line. The intercept of this line corresponds to $(1/k_F)$, and the slope is closely related to DH. In a similar way, for the laminar flow in hollow fibers, we expect that (Sieder and Tate, 1936)

$$\frac{k_F d}{D} = 1.86\left(\frac{d^2 v}{LD}\right)^{1/3} \tag{6}$$

Thus a plot of the reciprocal of k vs. the reciprocal of the cube root of velocity should be a straight line. The intercept of this line would correspond to the membrane resistance; increases of $(1/k)$ above this intercept represent the flow-dependent resistance in the feed solution.

Some of our results support our original expectation. In particular, for ammonia transport across flat membranes, $(1/k)$ is proportional to the membrane thickness ℓ, as shown in Figure 5. For H_2S transport across hollow fiber membranes, $(1/k)$ varies linearly with $(1/v^{1/3})$, as shown in Figure 6. So far, everything looks benign, consistent with Eqs. 4 and 5.

However, when we look more critically at these data, our simple explanation crumbles. For example, the intercept in Figure 6 is negative, implying that the resistance of the membrane to H_2S is also negative. This does not make physical sense. Moreover, the results for SO_2 are completely inconsistent with this simple picture. The logarithm of SO_2 concentration does not vary linearly with time, as shown in Figure 3; k varies with SO_2 concentration, as shown in Figure 4; and $(1/k)$ is not linear with $(v^{-1/3})$, as shown in Figure 7. Thus the simple picture summarized by Eqs. 4–6 is limited.

We want to develop a more detailed mechanism describing the flux across gas membranes. In particular, we want to show why the conventional picture given above sometimes works, as it does for NH_3 in Figure 5, and why it sometimes fails, as it does for SO_2 in Figures 4 and 7. This mechanism should be capable of explaining all of the results obtained above.

To develop this mechanism, we first not that a chief difference between the three solutes studied in detail is that SO_2 reacts more completely with water. In particular, the pK_a of SO_2 is 1.90, while the pK_a of H_2S is 6.88 and the pK_b of NH_3 is 4.76. This means that for a 10^{-2} M aqueous solution, which is typical of our experiments, SO_2 is 66% ionized, H_2S is 0.4% ionized, and NH_3 is 4% ionized. As a result, the diffusion of sulfur dioxide in the feed includes parallel transport of molecular SO_2, of HSO_3^-, and of H^+. In contrast, the other two solutes diffuse largely as H_2S and NH_3, with only minor amounts of HS^- and NH_4^+.

This ionization can dramatically change the interaction of the mass transfer coefficients k_F and k_M. To see how this occurs, imagine the reaction:

$$\text{species 1} + H_2O \rightleftarrows \text{species 2} + \text{species 3} \tag{7}$$

For example, for sulfur dioxide, species 1 would be SO_2, species 2 would be HSO_3^-, and species 3 would be H^+. We expect that this reaction is so fast that it is essentially in equilibrium, and that water is always present in excess. Thus

$$c_2 c_3 = c_2^2 = K c_1 \tag{8}$$

where K is the equilibrium ionization constant of the reaction in Eq. 7.

As a result, the diffusion of these solutes in the feed is given by

$$\begin{aligned} n &= k_F[(c_1 + c_2) - (c_{1i} + c_{2i})] \\ &= k_F[c - (c_{1i} + \sqrt{K c_{1i}})] \end{aligned} \tag{9}$$

in which the mass transfer coefficient in the feed k_F is taken as equal for all species. The assumption of a single value for the mass transfer coefficient, which implies that all solutes have equal diffusion coefficients, is an approximation made to emphasize the effects of ionization. Removing this assumption is tedious but straightforward numerically; however, our present data give no strong reason to do so.

While the flux in the aqueous feed includes both nonionized and ionized forms, the flux across the membrane is only of the nonionized form

$$n = k_M c_{1i} \tag{10}$$

When we combine Eqs. 9 and 10 to eliminate the unknown interfacial concentration, we obtain Eq. 4, but with k given not by Eq. 5 but by

$$\frac{1}{k} = \left(\frac{1}{k_F} + \frac{1}{k_M}\right)\left[\frac{qi}{(\sqrt{1+qi}-1)^2}\right] \tag{11}$$

where qi is a dimensionless group given by

$$qi = \frac{4c(k_F + k_M)}{k_F K} \tag{12}$$

Equations 11 and 12 are the desired result, capable of explaining all of the data presented above.

The significance of these results is best seen by considering three limiting cases. First, when qi is large, Eq. 11 reduces to Eq. 5. Thus Eq. 11 can predict all the successes of Eq. 5, including the constant mass transfer coefficients in Figure 4, the variation of membrane thickness in Figure 5, and the variation with flow in Figure 6. Note that qi is large under a variety of circumstances: a high solute concentration c, a small mass transfer coefficient in the feed k_F, or a small ionization constant K. Adding excess acid to SO_2 solutions essentially decreases K, increases qi, and forces the SO_2 results closer to this limit, consistent with Figure 7.

The second important limiting case occurs when qi is small, so that Eq. 11 reduces to

$$k = \frac{k_M c}{K} \tag{13}$$

The group qi will be small when (c/K) is small, i.e., when the solute

is very dilute or ionization is extensive. Under these circumstances, we expect k to vary with c, as it does for SO_2 in Figure 4. Moreover, Eqs. 11 and 13 show why the plot of $(1/k)$ vs. $(1/v^{1/3})$ can become nonlinear at small $(1/k)$, as shown in Figure 7. This nonlinearity also explains the apparent negative intercept for the H_2S data in Figure 6: this intercept is false, for data at higher flows (which are experimentally inaccessible to us) would curve to reach a positive intercept.

We can put these ideas on a more quantitative basis by considering a third limit of Eq. 11, which occurs when k_F becomes large. This limit exists, for example, when the flow through the hollow fiber membranes is rapid, as it is in Figure 4. In this case, Eq. 11 becomes

$$k = k_M \frac{\left(\sqrt{1+\frac{4c}{K}}-1\right)^2}{4c/K} \tag{14}$$

The squared quantity in parentheses has the physical significance of (c_1/c), i.e., it is the fraction of the solute which is ionized. Thus, if we divide the experimentally measured values of k by the ratio (c_1/c) calculated from the literature value of K, we should find k_M. That k_M is in fact a constant is shown by the "calculated" values for SO_2 given in Figure 5. These values are a quantitatively successful test of the ionization mechanism developed above.

We have shown that gas membranes can yield rapid fluxes, especially in hollow fibers. For H_2S and NH_3, these fluxes are influenced by the sum of the resistances in the feed and across the membrane. For SO_2, the flux is governed by a nonlinear combination of these resistances. All these fluxes can be explained by a mechanism which includes solution ionization. In more general terms, these gas membranes are alternative to more conventional methods of gas stripping.

Acknowledgment

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NOTATION

A	= membrane area, Eq. 1
c	= total solute concentration
c_1,c_2,c_3	= actual solute concentrations in bulk solution, Eq. 8
c_{1i},c_{2i}	= interfacial solute concentrations, Eq. 9
d	= hollow fiber diameter
D	= diffusion coefficient
H	= distribution coefficient; the dimensionless equilibrium ratio of gas concentration to liquid concentration, Eq. 3
k	= overall mass transfer coefficient
k_F	= feed mass transfer coefficient
k_M	= membrane mass transfer coefficient
K	= equilibrium constant
ℓ	= membrane thickness
L	= hollow fiber length
n	= solute flux
N	= number of hollow fibers
qi	= dimensionless group, Eq. 12
t	= time
v	= velocity inside the hollow fibers
V	= reservoir volume for fiber module
V_d	= diaphragm cell compartment volume, Eq. 1

APPENDIX: THE MASS TRANSFER COEFFICIENT IN THE HOLLOW FIBER MODULE

In our experiments, feed solution is pumped from a reservoir through the hollow fiber module and back into the reservoir. Solute concentration in the reservoir, measured as a function of time, forms the basis for calculating the mass transfer coefficient across the walls of the hollow fibers.

To see how this calculation proceeds, we first make a solute balance on a single fiber:

$$0 = -v\frac{dc}{dz} - \frac{4kc}{d} \tag{A1}$$

subject to the condition of the fiber's mouth

$$z = 0 \quad c = c_0 \tag{A2}$$

Thus

$$\frac{c}{c_0} = e^{-4kL/vd} \tag{A3}$$

where L is the fiber's total length. However, we are using a bundle of N fibers to process a reservoir volume V of solution. A solute balance on this reservoir gives

$$V\frac{dc_0}{dt} = \left(\frac{\pi}{4}d^2v\right)N(c - c_0) \tag{A4}$$

subject to the initial condition

$$t = 0 \quad c_0 = c_0(t = 0) \tag{A5}$$

We combine Eqs. A3 and A4 to eliminate c, integrate, and use Eq. A5 to obtain (dropping the subscript o):

$$\ln\left[\frac{c(t=0)}{c(t)}\right] = \left(\frac{\pi}{4}\frac{d^2vNt}{V}\right)(1 - e^{-4kL/vd}) \tag{A6}$$

This relation, is rearranged as Eq. 2, is used to calculate the mass transfer coefficient k in the hollow fibers.

LITERATURE CITED

G. Astarita, D. W. Savage, and A. Bisio, *Gas Treating with Chemical Solvents*, Wiley, New York (1983).

E. L. Cussler, *Diffusion*, Cambridge, London, 26 (1984).

M. E. Duffey, D. F. Evans, and E. L. Cussler, "Simultaneous Diffusion of Ions and Ion Pairs Across Liquid Membranes," *J. Membrane Sci.*, 3, 1 (1978).

J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1954).

M. Imai, S. Furusaki, and T. Miyauchi, "Separation of Volatile Materials by Gas Membranes," *Ind. Eng. Chem. Proc. Des. Dev.*, 21, 421 (1982).

H. K. Matson, J. Lopez, and J. A. Quinn, "Separation of Gases with Synthetic Membranes," *Chem. Eng. Sci.*, 38, 503 (1983).

E. N. Sieder, and G. E. Tate, "Heat Transfer and Pressure Drop of Liquids in Tubes," *Ind. Eng. Chem.* 28, 1,429 (1936).

F. D. Snell, and C. L. Hitton, Eds., *Encyclopedia Indust. Chem. Anal.*, Wiley-Interscience, New York (1966).

R. E. Treybal, *Mass Transfer Operations*, 3rd ed., McGraw-Hill, New York (1980).

H. Watanabe, and T. Miyauchi, "Permeation of Iodine through a Diaphragm Type Liquid Membrane," *Kagaku Kogaku Ronbunshu*, 3, 262 (1976).

Qi Zhang, and E. L. Cussler, "Bromine Recovery with Hollow Fiber Gas Membranes," *J. Membrane Science*, (in press, 1985).

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