



The separation of SO₂ and N₂ by permeation through modified vinylidene fluoride membranes
by Dennis Robert Seibel

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemical Engineering
Montana State University
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Abstract:

Vinylidene fluoride resin plasticized with sulfolane was found to make an effective membrane in the separation of SO₂ and N₂. One and two mil. membranes were made with varying weight percent sulfolane added to the vinylidene fluoride resin, which was then dissolved in dimethylformamide, spread evenly over a glass plate and heated to form the membrane. Tests were run at pressures from 100 psi to 500 psi.

Maximum separation was achieved with about 8% sulfolane in the membrane at 400 psi. Increasing the pressure to 500 psi showed little effect on separation over that obtained at 400 psi. At 20% sulfolane no separation took place.

As the temperature increased, the separation achieved at a given pressure decreased. Results at 14°C were only slightly better than those at room temperature.

Permeation rate increased with increasing pressure. Also, rate generally increased with increasing amount of sulfolane in the membrane.

Membrane thickness had little effect on separation. However, permeation rate decreased with increased thickness.

It was also noted that feed composition had a significant effect upon separation and permeation rate.

Feeds of 2%, 4%, 6%, and 12.5% SO₂ were tested. As the amount of SO₂ increased in the feed, the percent SO₂ in the permeate also increased, as did the rate of permeation. The greatest separation achieved was with a feed of 12.5% SO₂ at 400 psi and 23°C. The permeate at these conditions was 93.5% SO₂. The flux was 1.86 ft³(STP)/ft²/day.

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by

DENNIS ROBERT SEIBEL

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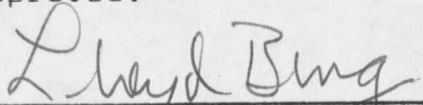
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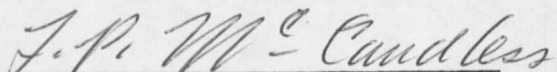
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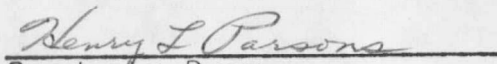
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ABSTRACT

Vinylidene fluoride resin plasticized with sulfolane was found to make an effective membrane in the separation of SO_2 and N_2 . One and two mil. membranes were made with varying weight percent sulfolane added to the vinylidene fluoride resin, which was then dissolved in dimethylformamide, spread evenly over a glass plate and heated to form the membrane. Tests were run at pressures from 100 psi to 500 psi.

Maximum separation was achieved with about 8% sulfolane in the membrane at 400 psi. Increasing the pressure to 500 psi showed little effect on separation over that obtained at 400 psi. At 20% sulfolane no separation took place.

As the temperature increased, the separation achieved at a given pressure decreased. Results at 14°C were only slightly better than those at room temperature.

Permeation rate increased with increasing pressure. Also, rate generally increased with increasing amount of sulfolane in the membrane.

Membrane thickness had little effect on separation. However, permeation rate decreased with increased thickness.

It was also noted that feed composition had a significant effect upon separation and permeation rate. Feeds of 2%, 4%, 6%, and 12.5% SO_2 were tested. As the amount of SO_2 increased in the feed, the percent SO_2 in the permeate also increased, as did the rate of permeation.

The greatest separation achieved was with a feed of 12.5% SO_2 at 400 psi and 23°C . The permeate at these conditions was 93.5% SO_2 . The flux was $1.86 \text{ ft}^3(\text{STP})/\text{ft}^2/\text{day}$.

INTRODUCTION AND BACKGROUND

Separation of gas mixtures by membrane processes is rapidly becoming a popular area of research. As man finds it necessary to control his natural environment with regard to pollution, and to control artificial finite environments as those found in space craft and submarines, the separation of gases becomes absolutely necessary. Conventional separation techniques such as scrubbing, adsorption, and cryogenic methods are expensive and often not highly efficient. Membrane separation, on the other hand, has the potential of improving on the short comings of these conventional methods.

To be more specific and accurate, 'selective permeation' would better describe the membrane process of separation. What is sought is the transport across the membrane thickness of specific gas molecules at a much greater rate than other gas molecules in the mixture. Thus, the relative solubility of the components in the membrane film will influence its selectivity.

Previous Work

A U.S. patent was issued in the preparation of liquid films of cellulose impregnated with a polyethylene glycol for the extraction of SO_2 from gas streams. A porous

membrane of a cellulose derivation is prepared, hydrolyzed to cellulose, and the resulting film is impregnated with the polyethylene glycol. This film is reported to be about 3000 times more selective for SO_2 than O_2 or N_2 (7).

Facilitated permeation through polymer membranes with CO_2/O_2 and CO_2/N_2 systems were studied by Tajar and Miller (5). The separation of CO and H_2 by polymeric films was studied by McCandless (2). McCandless also did work in the separation of aromatics and naphthenes using a membrane of vinylidene fluoride plasticized with a sulfone (3), as was used in this study.

In this work, sulfolane was added to the membrane. Sulfolane has received wide interest as a solvent for the removal of acid gases, such as H_2S , CO_2 , COS , and mercaptans, from sour gas streams. Sulfolane has also been used in the recovery of sulfur dioxide from dilute streams through absorption in sulfolane at atmospheric or higher pressures (6). Advantages over water absorption are the recovery of anhydrous sulfur dioxide, the non-corrosive system, and the greater absorptive capacity of sulfolane. These advantages hold true in the membrane separation process, as well. Because of the high solubility of SO_2 in sulfolane, it seemed appropriate to investigate the

separation of SO_2 from a gas mixture by permeation using a membrane made by including sulfolane as a plasticizing agent in a relatively impermeable polymer. (See the Appendix for the properties of sulfolane.)

Sulfur Oxides

Sulfur Oxides are very common air pollutants, resulting from smelting and refining processes. In Montana alone, over 800 tons of sulfur in the form of SO_2 is emitted daily from plants in East Helena and Anaconda. The East Helena plant emits a typical stack gas of 5% to 6% SO_2 ; the Anaconda stack gas is about 6% SO_2 . The Environmental Protection Agency is of course requiring both plants to reduce their emissions by almost 90% in the next four years. Conventional separation techniques will require huge sums of money to be spent in order to meet government specifications. In the past, membrane processes have not been economically feasible because the low permeation rates would require massive areas of membrane.

However, recent development of the modular membrane unit makes possible a tremendous membrane surface area in a small volume of space. This may bring membrane processes into favorable light for commercial applications.

OBJECTIVES OF THIS RESEARCH

Objectives were to determine if a membrane selective for SO_2 could be made by including sulfolane in a vinylidene fluoride film and if so, to determine the effects of membrane composition, temperature, pressure, and gas composition on the separation of SO_2 from dilute gas streams.

EXPERIMENTAL

The permeability cell is diagramed in Figure 1. The cell was fabricated from two stainless steel flanges, $5/8$ inches thick and $4\frac{1}{2}$ inches in diameter. Two circular cavities two inches in diameter were machined in the center of the flanges. One cavity was for the gas inlet, and the other to enable membrane support by a porous stainless steel disc, about the size of a silver dollar. The disc was placed in the cavity and a piece of filter paper was placed over it to pad the surface of the disc. A teflon gasket with a two-inch center hole was then laid on the flange and several pieces of filter paper cut to fit the gasket center hole were put in place to insure a flat secure surface for the membrane, which was then laid across the gasket and filter paper. A second teflon gasket was then placed over the membrane and finally the other flange was placed over the gasket. The two flanges were clamped together by means of eight equally spaced bolts. The membrane surface exposed to the test gas was two inches in diameter.

Initially, the cell was operated at room temperature (23°C) while membranes of varying compositions were tested to determine the composition that brought about maximum

separation.

Then this composition was tested at other temperatures. For this, the permeability cell was mounted in a constant temperature enclosure and connected to the rest of the apparatus as shown in Figure 2. The enclosure was made from a piece of 18-inch diameter by 12-inch high asbestos pipe, sealed at the bottom, and with an insulated asbestos board lid. The wall and bottom were also insulated with fiber glass. Two 500 watt heaters were placed in the bottom of the enclosure and covered with a piece of asbestos board to shield the test cell from direct exposure to the heaters. The heaters were controlled by means of variable transformers. In addition, one transformer was connected with a Thermistemp temperature controller. The thermistor probe, along with a thermocouple, were mounted at the gas inlet to the cell. A glass tube thermometer was also inserted in the enclosure during operation as a temperature check. When testing below room temperature, ice in containers was placed in the enclosure. A small fan provided air circulation in the constant temperature enclosure.

The binary mixture of N_2 and SO_2 was made in one cylinder. This feed gas was brought from the cylinder

through a needle-metering valve, into the enclosure, and then through 30 feet of 1/8 inch stainless steel tubing to bring the gas to the same temperature as the test cell. The pressure in the cell was controlled by a Grove "Mighty Mite" back pressure regulator.

The permeate gas rate was measured by timing the movement of oil through 1/8 inch nylon tubing on the outlet stream. A Swagelock tee containing a silicone rubber septum was connected to the outlet just outside the cell. This allowed sampling of the permeate by inserting a .5 cc syringe into the septum and drawing the sample. The other end of the nylon tubing was immersed in oil. The gas in the tubing could then be drawn out through the septum and oil would then be forced by atmospheric pressure into the tube. This insured that, once the oil was pushed out of the tube by permeate gas, only that gas would be analyzed and not air or permeate of a previous run. The volume of the tube per length was calculated by measuring the volume of water contained in a known length of tube.

When testing a membrane the assembled cell was placed in the enclosure and allowed to reach the desired temperature. The high pressure side of the cell was purged with

the gas to be tested, oil was drawn into the low pressure nylon tube to as close as possible to the cell, then the cell was pressurized. A gas rate of about one liter per hour (STP) was maintained through the high pressure side of the cell, which, as near as possible, assured that a constant volume of gas flowed past the membrane per unit time. The permeating gas was allowed to force the oil completely out of the tube, and for an additional 30 minutes the permeate was allowed to vent through the oil seal to ensure equilibrium had been reached. When three or more samples at each temperature and pressure showed the same composition on the gas chromatograph, equilibrium was assumed.

Stern and his colleagues using similar apparatus reported the accuracy of permeation measurements to be on the order of $\pm 5\%$ (4).

Membranes

Membranes were made by dissolving vinylidene fluoride (Kynar, Grade 301, Penwalt Corp.) in dimethylformamide. Gentle heat was applied until the vinylidene fluoride was completely dissolved in the solvent.

Because SO_2 is soluble in sulfolane (tetrahydrothiophene 1,1-dioxide, Phillips Petroleum Co.), it was

thought that the membrane would be more selective for SO_2 if sulfolane was added to the membrane (See the Appendix for solubility data). Thus, membranes were made with varying weight percents of sulfolane added to the vinylidene fluoride before it was dissolved in the dimethylformamide.

Depending on thickness of membrane desired, three or six thicknesses of paper tape were laid along the long edges of a glass plate measuring $9\frac{1}{2} \times 5 \times \frac{3}{16}$ inches. After heating, the syrup-like solution was then poured onto the glass plate, and a glass rod resting on the tape was used to spread the mixture evenly over the glass. Membrane thickness was about one mil for three thicknesses of tape, and about two mils for six thicknesses of tape. The glass plate was then placed in an electrically heated oven at about 105°C . for approximately twenty minutes to remove the solvent. The resulting membrane was cooled and easily removed from the plate for mounting in the test cell.

Gas Analysis

Both the feed gas and permeate gas mixtures of N_2 and SO_2 were analyzed by a thermal conductivity gas chromatograph operating at the following conditions:

Column: 6 feet x 1/8 inch stainless steel
tubing packed with Porapac Q (Waters
Associates, Inc.)

Column Temperature: 120°C

Detector Temperature: 30°C

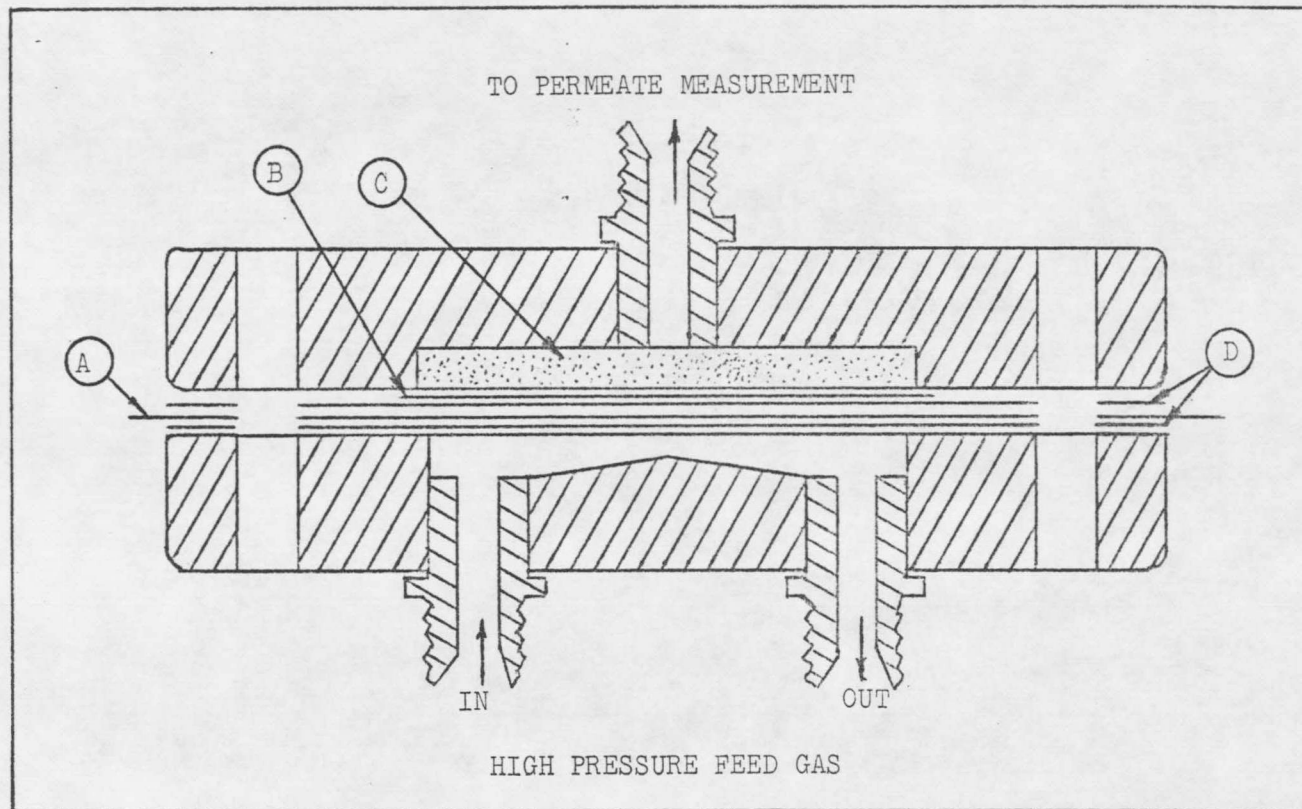
Carrier Flow: 25 cc/min

Detector Current: 215 ma

Attenuation: 64

Carrier Gas: Hydrogen for all samples

A calibration curve for determining the amount of SO₂ in samples was made by injecting known gas mixtures of N₂ and SO₂ into the chromatograph, calculating the areas of the SO₂ curves that resulted on the recorder, and plotting that versus the known percent of SO₂ in the sample. The curve is shown in Figure 1 of the Appendix.



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Figure 1. Diagram of Permeation Cell.
 (A) Membrane, (B) Filter paper, (C) Porous stainless steel plate,
 (D) Teflon gaskets.

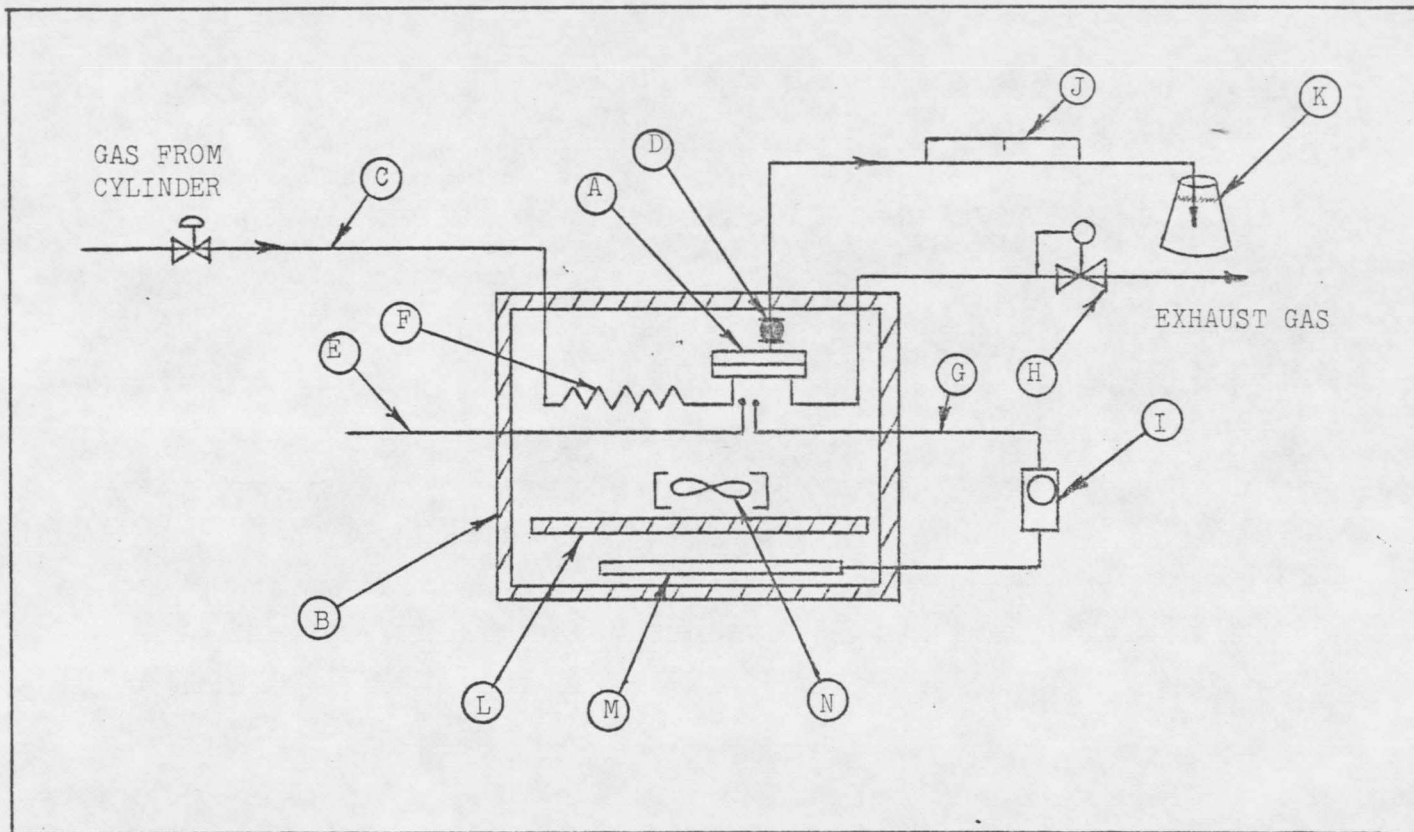


Figure 2. Apparatus for Permeability Measurement.
 (A) Permeation cell, (B) Constant temperature enclosure, (C) Gas inlet,
 (D) Rubber septum, (E) Thermocouple probe, (F) Heat exchanger,
 (G) Thermistor probe, (H) Back pressure regulator, (I) Thermistemp
 temperature controller, (J) Rate measurement, (K) Oil seal,
 (L) Asbestos baffle, (M) Two 500 watt heaters, (N) High speed fan.

RESULTS AND DISCUSSION

The first variable investigated was the effect of the composition of the membrane. As stated earlier, sulfolane was added to the vinylidene fluoride resin which constituted the base of the membrane. Initially, various compositions were tested at room temperature and five pressures, using a feed gas of 6.0% SO₂ and 94.0% N₂. The results of the separation process at various pressures and compositions are listed in Table 1. Five of these compositions are plotted in Figure 3. As can be noted, the maximum percentage of SO₂ in the permeate was 82.5%, obtained when 8.2% (weight) sulfolane was added to the vinylidene fluoride resin. Also, separation varied little with an increase of pressure from 400 psi to 500 psi. As a matter of fact, a majority of compositions showed better separation at 400 psi. Figure 4 shows what effect the percent sulfolane in the membrane had on separation at 400 psi, which is considered an optimum pressure for maximum separation. With 20% sulfolane in the membrane, no separation occurred.

The flux of permeate through the membranes was measured at all membrane compositions (except 20% sulfolane) and are listed in Table 2. The same five compositions as

plotted in Figure 3 are plotted in Figure 5. Flux increased with increasing amount of sulfolane in the membrane. The highest flux obtained with any separation was $1.01 \text{ ft}^3(\text{STP})/\text{ft}^2\text{day}$ when 15.2% sulfolane was in the membrane. With 20% sulfolane, the membrane apparently leaked.

Effect of Temperature

Once the optimum composition had been determined for maximum separation, tests were run at various temperatures using that optimum of about 8% sulfolane in the membrane. Table 3 shows the data obtained at seven temperatures, and these results are plotted in Figure 6. As can be noted, an increase in temperature lowered the percent of SO_2 in the permeate at a given pressure. A minimum of 52.5% SO_2 was obtained at 75°C and 500 psi. However, at 14°C , an increase in separation compared with room temperature was noted at 300 and 400 psi, with a slight decrease noted at 500 psi.

These results can be explained by the fact that SO_2 is more soluble in sulfolane at lower temperatures. (See Table 1 of the Appendix.) Thus as the temperature rises, the acceptance of SO_2 into the membrane becomes more difficult. Hence the separational power of the mem-

brane decreases. On the other hand, at lower temperatures, SO_2 is accepted and transported across the membrane much more freely, with the result of a higher concentration of SO_2 in the permeate. The membranes were not tested below 14°C .

Permeation rates generally increased with increased temperatures. Table 4 lists the data obtained at seven temperatures with an 8% sulfolane membrane. Figure 7 shows how flux increased with increasing temperature. The maximum permeation rate was $.708 \text{ ft}^3(\text{STP})/\text{ft}^2\text{day}$ at 74°C and 500 psi. However, it will be remembered that separation was the poorest at these conditions.

Effect of Membrane Thickness

Theoretically membrane thickness should have no effect on separation, but the flux should decrease with increasing thickness. Doubling the membrane thickness to 2 mils and testing at 14°C and 23°C at 300, 400, 500 psi showed little effect on separation. The changes noted were within the limits of error of the separate measurements. Flux decreased with the 2 mil membranes to about 70% of the rates of the 1 mil membrane.

The 2 mil membranes were more optically uniform and strength was greatly improved over the 1 mil membrane.

Also, it was thought results could be more easily reproducible with 2 mil membranes. Hence, 2 mil membranes were used for the remainder of the research. Table 5 shows a comparison of the SO_2 in the permeate and the flux of both thickness membranes.

Effect of Feed Composition

The percent SO_2 in the feed had an effect both on the separation obtained and the flux through the membrane. The results of four feed compositions are shown in Table 6.. As the percent SO_2 in the feed increased, so did the separation possible at a given pressure. The rate of permeation also increased. These results were expected since there are more SO_2 molecules available to be absorbed and transported across the membrane.

Table 1. Percent of SO₂ in permeate, using vinylidene fluoride membranes with weight percent sulfolane added as shown. The feed was 6% SO₂, 94% N₂; membrane thickness, 1 mil ; temperature for all runs, 23°C.

<u>MEMBRANE</u> % Sulfolane	PERCENT SO ₂ IN PERMEATE AT PSIG*				
	100	200	300	400	500
0.0	20.5	32.0	40.5	57.5	54.5
4.1	28.0	47.5	57.5	59.0	55.0
7.5	25.5	51.5	64.5	79.0	78.5
8.2	12.5	62.0	69.0	80.5	82.5
10.8	23.0	58.0	65.5	71.0	70.5
12.8	22.5	47.0	62.0	66.0	56.0
15.2	13.0	23.5	44.5	46.5	39.5
20.0	No Separation				

*Values taken to the nearest half percent.
PSIG is the difference between inlet and exhaust pressures.

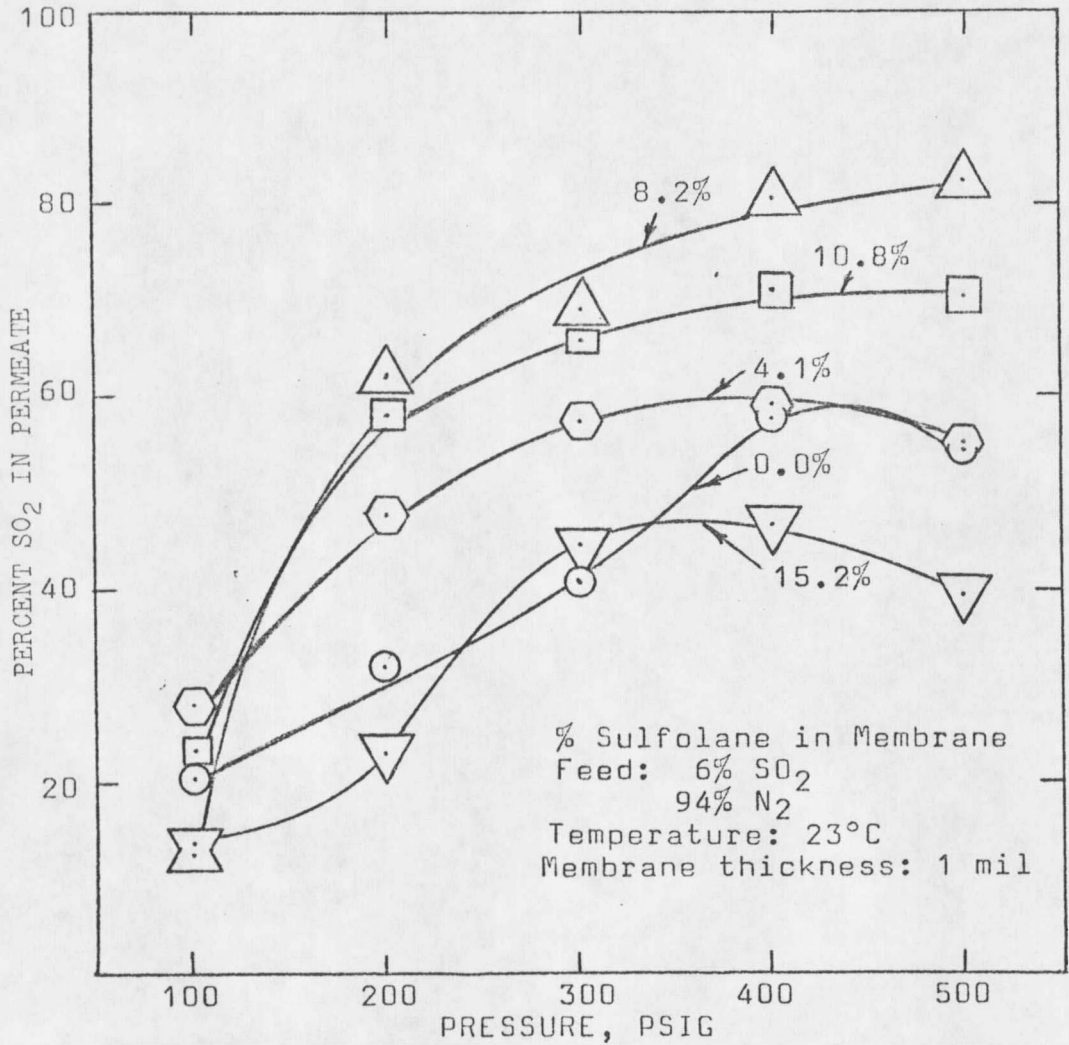


Figure 3. The effects of the amount of sulfolane in vinylidene fluoride membranes on the percent SO₂ in the permeate.

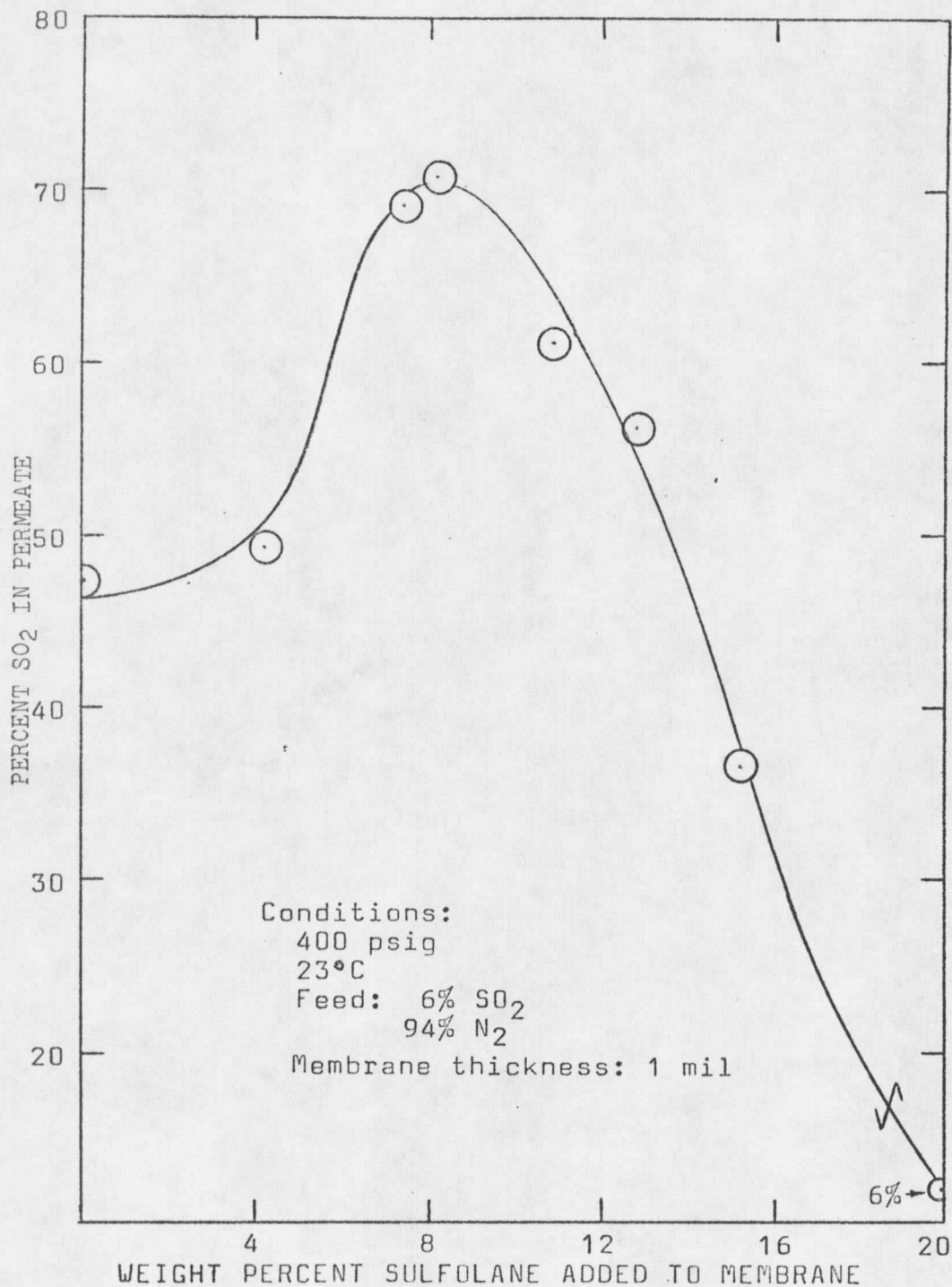


Figure 4. The effects of amount of sulfolane in the membrane at constant pressure and temperature.

Table 2. Permeate flux at 23°C of membranes with weight percent sulfolane added as shown. Feed gas is 6% SO₂. Membrane thickness is 1 mil.

<u>MEMBRANE</u> % Sulfolane	FLUX AT PSIG (ft ³ (STP)/ft ² day)				
	100	200	300	400	500
0.0	.005	.007	.015	.041	.169
4.1	.004	.018	.037	.165	.218
7.5	.009	.043	.083	.154	.267
8.2	.010	.042	.150	.295	.520
10.8	.039	.065	.166	.303	.535
12.8	.028	.048	.159	.282	.494
15.2	.040	.071	.262	.800	1.01

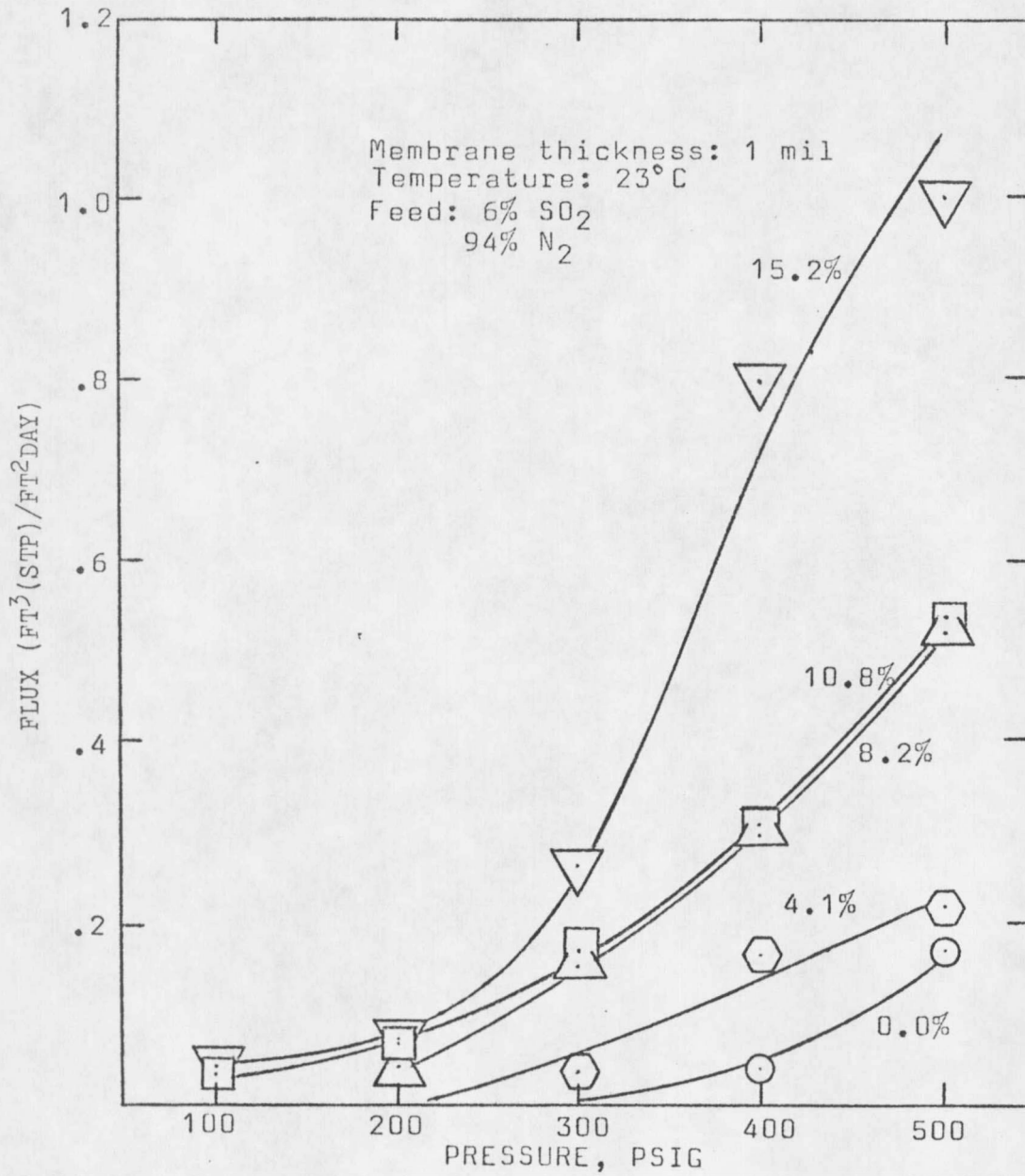


Figure 5. The effects of amount of sulfolane in the membranes on flux.

Table 3. The effects of temperature upon permeate using a 1 mil membrane of 8% sulfolane. The feed gas was 6% SO₂. Values for SO₂ are to the nearest half percent.

TEMPERATURE °C	PRESSURE, PSIG		
	300	400	500
	<u>% SO₂ in Permeate</u>		
14	79.5	82.0	77.5
23	69.0	80.5	82.5
32	66.0	74.0	73.5
42	63.5	70.5	74.2
48	63.0	65.5	68.0
64	57.5	59.0	58.5
74	57.0	58.0	52.5

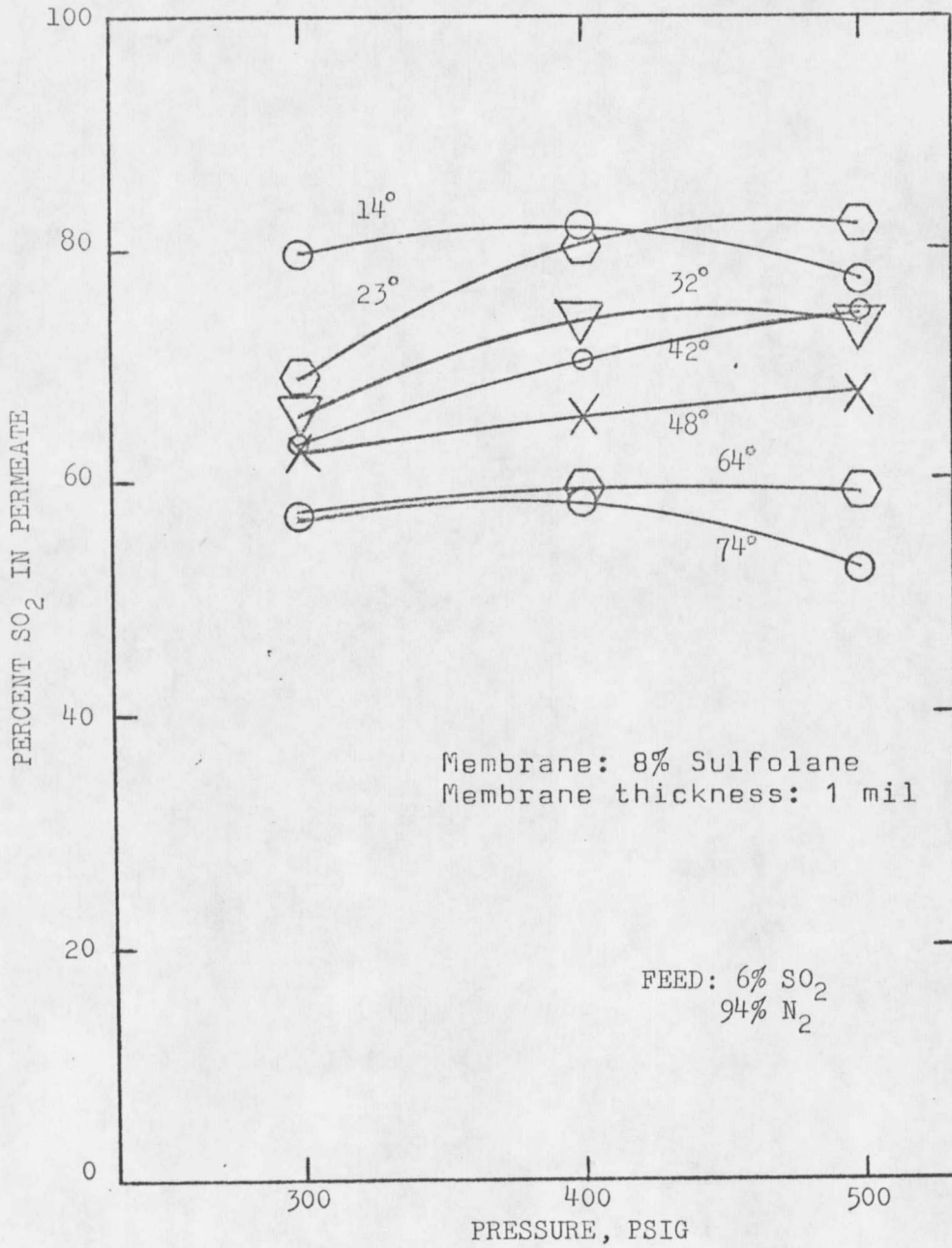


Figure 6. The effects of temperature on permeate using optimum membrane.

Table 4. The effects of temperature upon flux using a 1 mil membrane of 8% sulfolane. The feed gas was 6% SO₂.

TEMPERATURE °C	PRESSURE, PSIG		
	300	400	500
	Flux (ft ³ (STP)/ft ² day)		
14	.097	.239	.365
23	.150	.295	.520
32	.184	.387	.609
42	.191	.355	.555
48	.187	.396	.559
64	.321	.433	.697
74	.356	.570	.699

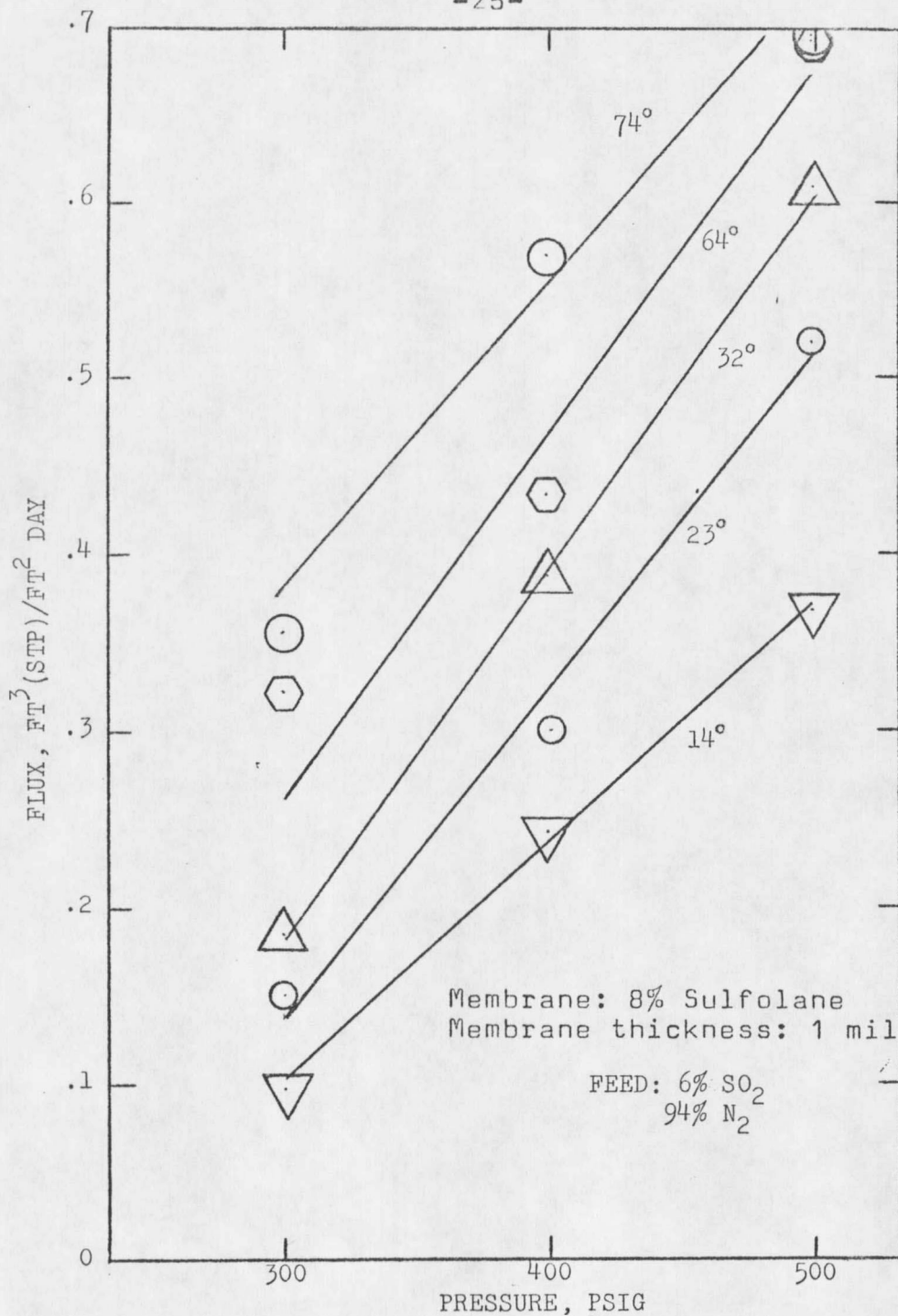


Figure 7. The effects of temperature on flux using optimum membrane.

Table 5. Comparison of values of 1 and 2 mil optimum membranes. Values for SO₂ are to the nearest half per cent. Flux values given as ft³(STP)/ft²day.

<u>1 MIL MEMBRANE</u>			<u>2 MIL MEMBRANE</u>		
psi			psi		
<u>300</u>	<u>400</u>	<u>500</u>	<u>300</u>	<u>400</u>	<u>500</u>
<u>% SO₂ in Permeate @ 14° C</u>			<u>% SO₂ in Permeate @ 14° C</u>		
79.5	82.0	77.5	83.5	84.0	83.0
<u>@ 23° C</u>			<u>@ 23° C</u>		
69.0	80.5	82.5	64.2	78.0	76.5
<u>Flux @ 14° C</u>			<u>Flux @ 14° C</u>		
.097	.239	.365	.062	.157	.213
<u>Flux @ 23° C</u>			<u>Flux @ 23° C</u>		
.150	.295	.520	.077	.181	.264

Table 6. Effect of feed composition upon permeate and flux. Data taken at 23°C with 2 mil membrane with 8% sulfolane.

<u>% SO₂ in feed</u>	<u>% SO₂ in permeate</u>	<u>FLUX (ft³(STP)/ft²day)</u>
	@ 300 psi	
2.	39.5	.012
4.	54.5	.052
6.	58.0	.067
12.5	92.0	.903
	@ 400 psi	
2.	46.5	.025
4.	72.5	.094
6.	78.0	.157
12.5	93.5	1.86
	@ 500 psi	
2.	38.0	.025
4.	78.0	.121
6.	83.5	.264
12.5	Partial pressure exceeds vapor pressure	

CONCLUSIONS

The results of this study have shown that SO_2 can be separated from N_2 using modified vinylidene fluoride membranes at reasonable temperatures and pressures. These results look promising especially in the light of going from 6% to over 80% SO_2 , or from 12.5% to over 90% SO_2 with one pass through the membrane. The disadvantage of such a process is the relatively slow permeation rate. A very large surface area would be necessary to process the SO_2 gas stream from most commercial refining and smelting operations. The modular membrane unit may be the answer to getting a tremendous surface area in a small volume of space. In any case, membrane separation is clearly an important possibility in the separation of SO_2 and N_2 .

The important conclusions of this research are listed below.

1. Vinylidene fluoride membranes impregnated with about 8% by weight sulfolane showed the highest separation obtained at 23°C and 6% SO_2 in the feed gas.

2. As the temperature increased, the separation decreased at a given pressure. No significant gain in separation occurred at 14°C over that at 23°C.

3. Membrane thickness had little effect upon separation, but thicker membranes did slow permeation rate.

4. As the percent SO_2 in the feed increased, so did the separation achieved and the permeation rate.

5. Permeation rates varied greatly, depending primarily on pressure and amount of sulfolane in the film. With good separation (above 75% SO_2 in the permeate), $.3 - .5 \text{ ft}^3(\text{STP})/\text{ft}^2\text{day}$ is a typical rate.

6. The preparation of the membrane is felt to be critical to results obtained. Thus, a minute more or less in the oven may affect how well the membrane performs. Other important factors include the temperature of the oven, the amount of solvent used, and how well the sulfolane was dispersed in the solution. Also, the age of the membrane may affect results.

RECOMMENDATIONS FOR FURTHER WORK

This research was conducted using relatively mild conditions of temperature and pressure. Further study is suggested using higher pressures and perhaps lower temperatures. However, care must be taken not to exceed the low vapor pressure of SO_2 in the gas mixtures. It is felt that permeation rate would increase markedly, hopefully with as good (perhaps better) separation.

Of critical importance and which deserve more study are the factors affecting the membrane itself. The age of a membrane may be important. With constant use, will the membrane act differently when it is six months old than it does when it is one day old? Is there an age when a membrane can no longer be expected to perform?

The same questions apply to membranes in storage. Do they deteriorate, and if so, how fast and how much?

Another factor that should be studied is the affect of the rate of feed gas past the membrane on separation. In this study 1 liter/hour was the feed gas rate. An increase in rate may increase separation. Is there an optimum value for feed rate?

Sulfolane should be studied in other polymeric mate-

rials with the possibility of incorporating a higher percent into the membrane and therefore with the chance of increasing separation and permeation rate.

Other sulfones should be studied for their possible selectivity for SO_2 . 3-Methylsulfolene may prove worthy in the separation of SO_2 from gas streams. Too, thiophene and its derivatives should be included in further study as plasticizing agents in the membrane.

APPENDIX

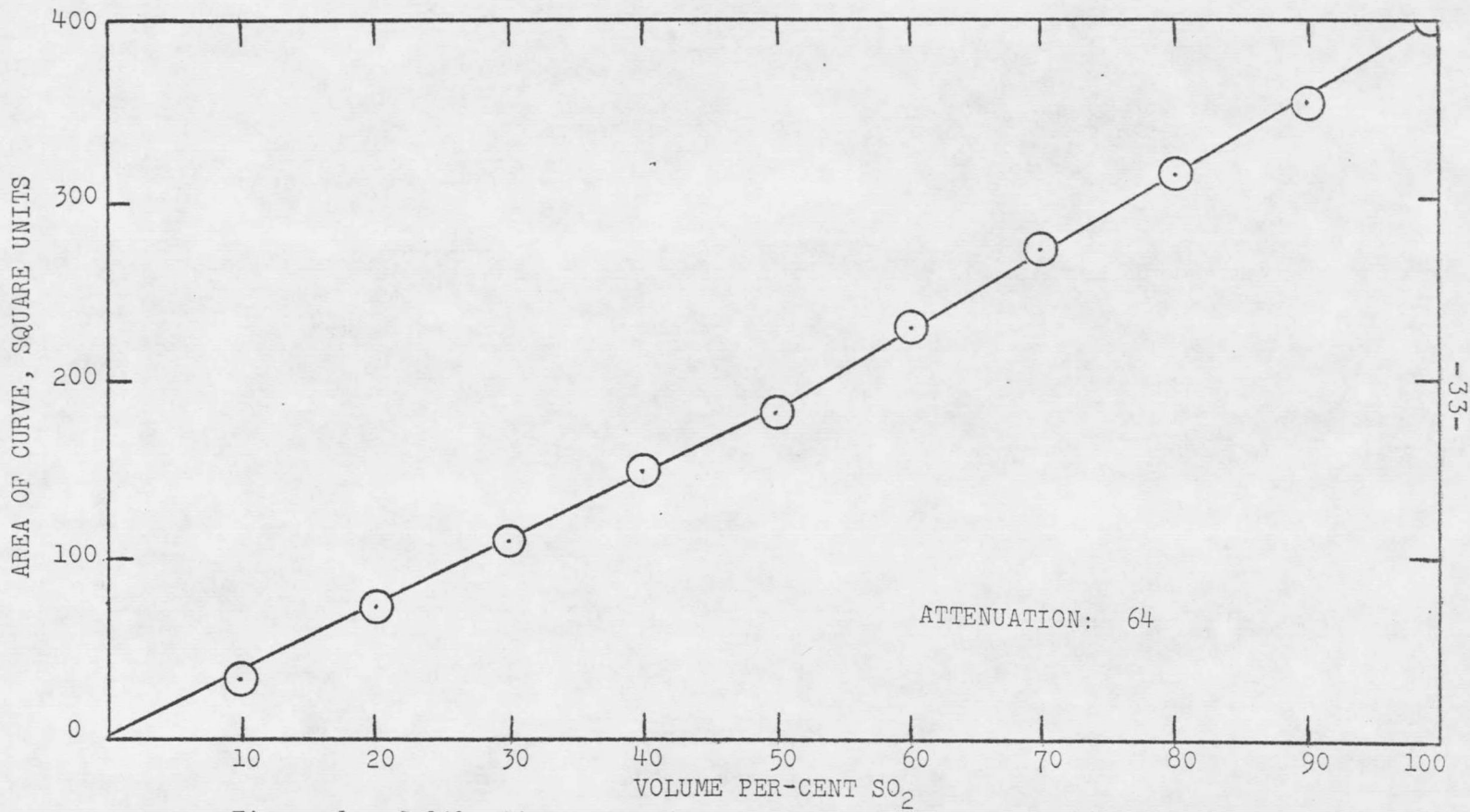


Figure 1. Calibration curve for the gas chromatograph showing area of SO₂ curve versus volume percent SO₂.

INFORMATION ON SULFOLANE (1)

Sulfolane (tetrahydrothiophene 1,1-dioxide), $C_4H_8O_2$, is colorless, highly polar, water-soluble, and is noted for its solvent properties and exceptional chemical and thermal stability.

Table 1. The Physical Properties of Sulfolane.

<u>Property</u>	<u>Value</u>
Specific gravity @ 30°C	1.266
Boiling point, °C	285
Freezing Point, °C	27.4-27.8
Flash Point, open cup, °F	350

The solubility of SO_2 in sulfolane is .65 lb per lb sulfolane at 20°C and 1 atm, and .115 lb per lb sulfolane at 75°C and 1 atm.

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