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Differential Permeation of Hydrogen Sulfide through a Microporous Vycor-Type Glass Membrane in the Separation System of Hydrogen and Hydrogen Sulfide

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NOTE

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Abstract

The differential permeation of hydrogen sulfide through a microporous Vycor-type glass membrane was found in the hydrogen and hydrogen sulfide separation system. Separation factors of less than 1.0 were obtained at 10°C under higher pressures of a feed gas mixture having a low hydrogen concentration.

INTRODUCTION

The separation process through a microporous Vycor glass membrane is based on Graham's law and Knudsen flow, while the strong effect of surface flow upon the separation behavior has been recognized (*1–3*). Since the surface flow is caused by adsorbed molecules, it seems to occur most markedly at low temperatures and high pressures. Under these conditions the magnitude of surface flow may exceed that of gas flow, which results in the preferential permeation of heavier gas molecules. Preferential permeation has been observed at lower temperatures in the following systems: C_6H_{12}–CH_3OH (*4*), C_6H_{12}–C_2H_5OH (*4*), O_2–CO_2 (*5*), and CH_4–C_3H_8 (*6*).

This report shows that the preferential permeation of hydrogen sulfide through microporous Vycor-type glass membrane occurred under higher pressures of a feed gas mixture containing a low hydrogen concentration in the H_2–H_2S separation system. The H_2–H_2S separation system will become of great importance for the recovery of hydrogen from hydrogen sulfide (*7–9*).

EXPERIMENTAL SECTION

A schematic diagram of the apparatus used is given in Fig. 1. The feed gas mixture (A) of hydrogen and hydrogen sulfide is introduced into the high-pressure section and permeates through porous membrane (E) into the atmospheric pressure section. The unpermeated stream is taken off from the high-pressure section. The pressure of the feed gas mixture is controlled by a pressure regulator (B). The diffusion cell (C) is made of stainless steel. Recrystallized nonporous alumina tubing (H) is set close to the inner surface of the cell wall to prevent the sulfurization of the diffusion cell by hydrogen sulfide at high temperatures. Before a feed gas mixture is introduced into the diffusion cell, both sections are filled with

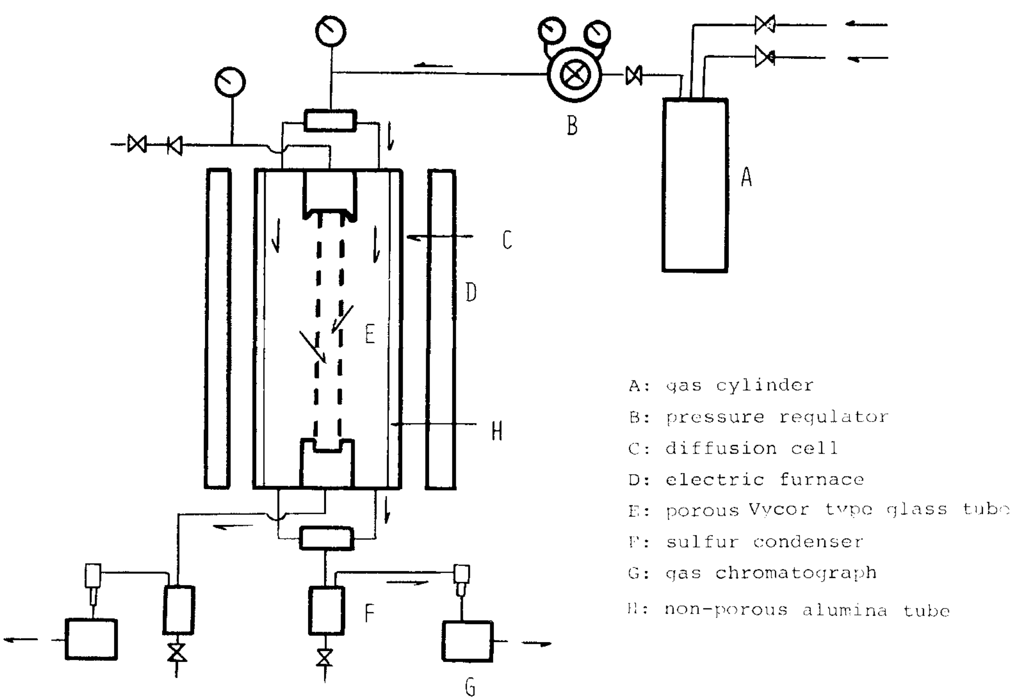

FIG. 1. Schematic diagram of the apparatus used for the separation of an H_2–H_2S gas mixture.

nitrogen gas at 1.0 atm. The flow rate is measured by means of a soap bubble meter. Gases flowing through the porous glass membrane are allowed to vent to the atmosphere. The mole fractions of feed, permeated, and unpermeated gases are analyzed by the same gas chromatograph (G) as Fukuda used (*8*).

Microporous Vycor-type glass tubing used as the membrane was supplied by Toshiba Kasei Co. (Japan) and its specifications were 600 mm in length, 15 mm in outer diameter, and 3.0 mm in thickness. Its chemical composition was 96.60 SiO_2, 2.91 B_2O_3, 0.42 Al_2O_3, and 0.07 Na_2O in weight-%. The maximum distribution of the pore diameter was measured to be 45 Å, and almost 86% of the total pore volume fell within ±10 Å. The porosity and the specific surface area of the porous glass were 0.79 and 191 m^2/g, respectively. These specifications are similar to the so-called porous Vycor glass. The mean free path of hydrogen molecules is known to be 1230 Å, while that of hydrogen sulfide molecules was calculated to be 430 Å under 1 atm at 25°C.

Separation measurements were made at 10°C over a wide range of a feed gas pressure ($P = 3.39 - 17.71$ atm) and mole fraction of hydrogen ($X = 0.040 - 0.778$) in a feed gas mixture. Gas permeability (Q) through the porous glass was measured for hydrogen, hydrogen sulfide, and nitrogen gases.

RESULTS AND DISCUSSION

The permeabilty of hydrogen sulfide is much larger than that of nitrogen gas (Table 1) in spite of the fact that the molecular weight of hydrogen sulfide is greater than that of nitrogen. It also increases remarkably with higher mean pressures (P'). If their Q values can be extrapolated to zero pressure, the permeability of hydrogen sulfide should be larger than that of nitrogen and also close to the curve reported by Hwang (*10*).

Typical differential permeation phenomena for hydrogen sulfide are shown in Table 2. Eighty-five percent of all runs agreed within ±2% of the material balance. The cut was 0.32 ± 0.04 in all runs. Preferential permeation of hydrogen sulfide, which means that the measured separation factor (α_m) is smaller than 1.0, is clearly observed under higher pressures of a feed gas mixture with a low hydrogen concentration. For example, α_m is 0.37 at $P = 17.71$ in the case of $X = 0.04$.

The amounts of adsorption of hydrogen sulfide and hydrogen gases on the porous glass at 10°C under 0.70 atm were measured to be 6.01 and 0.037 cc/g, respectively. Moreover, the critical temperatures of hydrogen

TABLE 1

Gas Permeability Data for Porous Glass at 10 °C[a]

Hydrogen		Nitrogen		Hydrogen sulfide	
P'	$Q \times 10^5$	P'	$Q \times 10^5$	P'	$Q \times 10^5$
2.18	3.99			2.18	1.53
3.15	4.16	3.15	1.31	3.15	1.94
4.11	4.32	4.36	1.40	4.11	2.02
7.02	4.49	6.78	1.56	7.02	2.35
8.71	4.83	8.71	1.61	9.20	2.80

[a] P' in atmosphere. Q in std-cc/sec-cm^2-cmHg.

TABLE 2

Effects of Pressure and Mole Fraction of a Feed Gas Mixture on the Separation Factor of the H_2–H_2S Separation System at 10 °C[a]

Feed gas pressure, P	Permeated gases, N	Permeated H_2, Y	Separation factors, α_m
$X = 0.040$			
3.39	16.40	0.048	1.21
7.26	57.98	0.046	1.16
12.78	90.68	0.037	0.92
17.71	144.71	0.015	0.37
$X = 0.288$			
3.39	23.15	0.319	1.16
7.26	70.42	0.315	1.14
13.07	131.20	0.303	1.07
16.45	192.94	0.282	0.97
$X = 0.460$			
3.39	28.94	0.518	1.26
7.26	72.35	0.508	1.21
13.07	131.20	0.490	1.13
16.45	192.94	0.470	1.04

[a] P in atmospheres. N in std-cc/min, $\alpha_m = Y(1 - X)/X(1 - Y)$.

sulfide and hydrogen gases are known to be 100.4 and −239.9°C, respectively. Both a large amount of adsorption and the high critical temperature of hydrogen sulfide gas may result in the differential permeation of hydrogen sulfide through the surface flow (*11*). The inversion of α_m between

P values of 7.26 and 12.78 at $X = 0.04$ (Table 2), therefore, is a perfectly normal phenomenon. Mathematical analysis of the differential permeation of hydrogen sulfide through a porous membrane is now under investigation.

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