

RECEIVED

JAN 12 1998

OSTI

Direct Methane Conversion to Methanol


Final Report
April 13, 1995 - September 30, 1996

By:
Richard D. Noble
John L. Falconer

Work Performed Under Contract No.: DE-FG21-90MC27115

For
U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
Morgantown Site
P.O. Box 880
Morgantown, West Virginia 26507-0880

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

By 
University of Colorado at Boulder
206 Armory
Campus Box 19
Boulder, Colorado 80309-0019

MASTER

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

DIRECT METHANE CONVERSION TO METHANOL

PROJECT STATUS REPORT -- FINAL

(01/01/95 -- 03/31/96)

PROJECT DESCRIPTION

We proposed to demonstrate the effectiveness of a catalytic membrane reactor (a ceramic membrane combined with a catalyst) to selectively produce methanol by partial oxidation of methane. Methanol is used as a chemical feed stock, gasoline additive, and turbine fuel. Methane partial oxidation using a catalytic membrane reactor has been determined as one of the promising approaches for methanol synthesis from methane. Methanol synthesis and separation in one step would also make methane more valuable for producing chemicals and fuels.

Another valuable fuel product is H_2 . Its separation from other gasification products would make it very valuable as a chemical feedstock and clean fuel for fuel cells. Gasification of coal or other organic fuels as a source of H_2 produces compounds (CO , CO_2 , and H_2O) that require high temperature (1000-1500°F) and high pressure (600-1000 psia) separations. A zeolite membrane layer on a mechanically stable ceramic or stainless steel support would have ideal applications for this type of separation.

PROJECT SUMMARY

A high pressure, high temperature apparatus was constructed to perform the methane and methanol reaction/separation experiments. Many membranes were tested but none of them could selectively remove methanol at the pressure and temperature necessary for methanol formation. As an alternative approach, a cooling tube was inserted inside the

membrane reactor to create a low temperature zone that rapidly quenched the product stream. This system has proven effective for increasing methanol selectivity during methane oxidation. In order to separate CH_3OH from the condensed product mixture, a liquid phase separation system was built and pervaporation experiments are currently being conducted. One of these organic mixture experiments is the separation of acetone and water.

For the H_2 separation phase of the research, we successfully fabricated a silicalite-alumina composite membrane with a γ -alumina layer (5 nm pore diameter) as the substrate. Single gas permeances of H_2 , Ar, $n\text{-C}_4\text{H}_{10}$, and SF_6 were measured and mixtures of $\text{H}_2/i\text{-C}_4\text{H}_{10}$ and H_2/SF_6 were separated to characterize the silicalite membrane. The silicalite membrane demonstrated behavior that was dramatically different from an alumina membrane without the silicalite layer. Permeances for the alumina membrane decreased with increasing temperature, and separation selectivities were lower than values expected for Knudsen diffusion. The silicalite membrane showed activated permeance behavior. The ratio of single gas permeances was as high as 136 for H_2 to SF_6 and 1100 for H_2 to $i\text{-C}_4\text{H}_{10}$ at 298 K. Separation selectivities at elevated temperatures were significantly above Knudsen diffusion selectivity for the silicalite membrane and were larger than ratios of pure gas permeances at the same temperature. Single gas permeation experiments were performed on CH_4 , CO_2 , N_2 , and H_2 using a silicalite-1 membrane with an ideal N_2/SF_6 selectivity of 234. Additionally, this membrane was used for gas separation experiments involving the binary mixture of H_2 and CO_2 .

The separations of interest (CO_2/H_2 , CO/H_2 , $\text{H}_2\text{O}/\text{H}_2$, etc.) will require zeolite membranes with even smaller pore sizes. Efforts were made to produce other zeolite

membranes on alumina or stainless steel supports that have the potential for better H₂ selectivity. Attempts to synthesize zeolite NaA membranes have not resulted in membranes with promising gas separation capabilities. Zeolite ZSM-5 membranes have been prepared with ideal N₂/SF₆ selectivities of 50. These membranes have pore sizes identical to that of silicalite-1 but also have the potential for ion exchange processes that can reduce the effective pore size. In addition, the technique of chemical vapor deposition has been used successfully to improve the gas separation performance of silicalite-1 membranes.

PROGRESS

Acetone Separation

Acetone/water mixtures were separated at ambient temperature using the pervaporation apparatus (Figure 1). This process involves the selective mass transfer of a compound through a membrane layer that is placed between a liquid and a vapor phase. The transfer occurs from the liquid to the vapor side, and the vapor is maintained at low partial pressure either by continuous pumping (vacuum pervaporation) or a sweep gas. In this case, vacuum pervaporation was used to selectively separate acetone from water through a silicalite-1 membrane (stainless steel support). This action occurs because silicalite possesses a high preference for the adsorption of organic molecules smaller than its limiting pore size of 0.6 nm.

A stable separation factor of approximately 11 had been previously obtained for methanol/water mixtures over a wide range of methanol concentrations. Relatively high fluxes and much higher separation factors were seen using the acetone/water mixture.

Figure 2 shows the effect of acetone concentration on the total flux and the selectivity of acetone over water. The highest separation factor was 250 at a low acetone concentration of 0.8 wt% with a total flux of 0.24 kg/(m²h). Conversely, the highest flux of 0.78 kg/(m²h) was obtained at the highest acetone concentration of 43 wt%. Increasing acetone concentration caused a large increase in acetone flux and a smaller decrease in water flux (Figure 3). High concentrations of acetone can be obtained from low feed concentrations by the pervaporation method. Figure 4 is a comparison between the single-stage separation product of pervaporation and the vapor composition from the vapor-liquid equilibrium at 1 atm. The high separations that can be obtained from low feed concentrations can easily be seen by a comparison of separation factors obtained by distillation and by pervaporation (Figure 5). The distillation factors were calculated from vapor-liquid equilibrium data for acetone/water solutions.

Molecular Sieve Membrane Preparation

Two important types of zeolites that have the potential to preferentially separate H₂ from other molecules are ZSM-5 and zeolite A. ZSM-5 zeolites have the same crystallographic structure but vary in their silicon to aluminum ratios. The Si/Al ratio can vary between 15 and infinity (silicalite-1) and imparts some difference in behavior to the different zeolites. All ZSM-5 zeolites have pore channels of two different sizes, 0.54 x 0.56 nm and 0.51 x 0.55 nm. Zeolite A is a strongly hydrophilic zeolite that has a narrowly distributed pore size. The most common of these, zeolite NaA, has a pore diameter of approximately 0.4 nm. This pore diameter is smaller than many hydrocarbons, and makes zeolite A promising for H₂/hydrocarbon separations and gas drying.

ZSM-5 membranes were attempted via an in-situ synthesis on both γ -alumina and stainless steel supports with gels consisting of Si/Al ratios of 60 and 80. Gels with the latter Si/Al ratio proved to be too caustic and SEM analysis showed that the γ -alumina layer on the support was destroyed. Membranes made from the other gels were synthesized on alumina supports and stainless steel supports with a silicalite-1 intermediate. Single gas permeation experiments were performed on these membranes. Results for some of these membranes are as follows:

Membrane M7 - alumina support

Gas	Permeance $10^{-8} \text{ mol}/(\text{m}^2 \text{ s Pa})$	Selectivities
N ₂	142	N ₂ /SF ₆ = 25
SF ₆	5.67	H ₂ /iBut = 170
H ₂	170	nBut/iBut = 7
i-Butane	0.947	
n-Butane	6.59	

Membrane M8 - alumina support

Gas	Permeance $10^{-8} \text{ mol}/(\text{m}^2 \text{ s Pa})$	Selectivities
N ₂	30.4	N ₂ /SF ₆ = 18
SF ₆	1.7	H ₂ /iBut = 53
H ₂	35.4	nBut/iBut = 3
i-Butane	0.67	
n-Butane	2.02	

Membrane M9 - stainless steel with silicalite-1 intermediate

Gas	Silicalite Membrane Only		ZSM-5 With Silicalite Layer	
	Permeance $10^{-8} \text{ mol}/\text{m}^2 \text{ s Pa})$	Selectivity	Permeance $10^{-8} \text{ mol}/\text{m}^2 \text{ s Pa})$	Selectivity
N ₂	38.6	44	35.4	50
SF ₆	0.87		0.72	

Membrane M10 - stainless steel with silicalite-1 intermediate

Gas	Silicalite Membrane Only		ZSM-5 With Silicalite Layer	
	Permeance 10^{-8} mol/m ² s Pa)	Selectivity	Permeance 10^{-8} mol/m ² s Pa)	Selectivity
N ₂	70.8	41	53.1	50
SF ₆	1.73		1.47	

Similar preparation techniques were used to create zeolite NaA gels and their subsequent membranes. Zeolite NaA crystallizes within a narrow composition range, without the organic templates that were successfully applied to the ZSM-5 and silicalite-1 syntheses. The membranes were attempted on γ -supports which showed very little evidence of crystal growth. X-ray diffraction analysis confirmed that the crystals were in fact zeolite NaA, but a continuous layer did not form. SEM experiments also showed that the support was partially damaged by the caustic nature of the zeolite NaA gel.

Numerous attempts were made to synthesize a continuous layer of zeolite NaA on an α -alumina support using the same basic in situ technique that works well for silicalite. All of these syntheses were performed without the use of a structure directing organic template, as in ZSM-5 and silicalite preparation. Because of this fact, high calcination temperatures were not needed. Two different synthesis gels were used for a hydrothermal preparation. The first used standard zeolite NaA molar reactant ratios of 2:1:2:120 for SiO₂:Al₂O₃:Na₂O:H₂O respectively. An autoclave was used with synthesis times from 3.5 to 6 hours and a temperature of 373 K. The second primary gel had vastly different reactant ratios of 5:1:50:1000. Preparation using this gel required milder conditions (333 K) and longer synthesis times (24 hours). Slight variations were made in these reactant ratios and synthesis conditions, but the resulting membranes all possessed N₂/SF₆ ratios of 1.3-1.6.

Two other techniques were combined with these preparations, but they had similar results. First, an preliminary NaA layer was attempted at atmospheric pressure to replicate the "seeding" that is often used for NaA synthesis. This technique produced the most crystals on the support surface but did not affect the N_2/SF_6 ratios on the subsequent membranes. Second, a silicalite membrane (N_2/SF_6 selectivity = 32) was prepared on an α -alumina support to provide an intermediate layer for NaA membrane production. The addition of the caustic NaA gel destroyed the silicalite layer and reduced the selectivity back to a Knudsen type value.

Promising results have been obtained in the area of ZSM-5 synthesis. Again, the synthesis technique was similar to that of silicalite membranes with different conditions and gel compositions. Zeolite ZSM-5 membrane preparation was carried out at 448 K for 24 hours using a gel with a composition of 1 TPAOH: 6 TEOS: 583 H₂O: 4 NaOH: 0.04 Al. A membrane synthesized in this manner was found to have an ideal N_2/SF_6 selectivity of 52 and an H_2/SF_6 selectivity of 163. The aluminum content of this membrane makes ion exchange possible, which in turn can decrease the effective pore size and improve gas separation performance.

The technique of chemical vapor deposition (CVD) has been favorably used to improve existing silicalite membranes. This process may be used to improve the performance of ZSM-5 and NaA membranes as well. In CVD silicon methoxide is deposited in the surface layer. Silicalite-1 membranes with N_2/SF_6 ideal selectivities of approximately 150 have been improved substantially with this modification. The N_2/SF_6 ratio changed to 560 and the ideal H_2/SF_6 selectivity became 2400. It is not known at present whether the process decreases the effective pore size or closes up the

intercrystalline "cracks" in the membrane layer. More characterization of this technique needs to be performed.

X-ray diffraction analysis was performed on crystals grown under reaction conditions similar to the zeolite A membranes. These results indicate that the actual crystal growth is zeolite X, another zeolite with high aluminum content but much larger pores (0.7-0.8 nm). Zeolite X has the ability to preferentially adsorb CO₂, so these membranes may be valuable for H₂/CO₂ separation, especially after they are treated via chemical vapor deposition.

Single Gas Permeation Experiments

Single gas permeation experiments for N₂, CO₂, and CH₄ were carried out through a silicalite-1 membrane at 1.3 bar from 300 to 600 K. The membrane was mounted in a brass module with three ports: feed inlet, feed outlet, and permeate outlet. Silicone o-rings were used to seal the feed inlet and outlet ports, and pipe threads with Teflon tape were used to seal the permeate outlet. Permeate and feed fluxes were measured at each temperature setting using bubble flow meters. The readings were taken at intervals of 15 minutes until consecutive measurements were within 2% precision, indicating steady state. A thermocouple attached to steel tubing that flowed into the bubble meters was used to confirm that the gases were at room temperature.

Figure 6 shows a plot of single gas permeances versus temperature. The permeance values for each component go through a minimum (400 K for CH₄ and CO₂, 350 K for N₂). Experiments performed on a different silicalite membrane also showed the same sort of minima, although the values were shifted approximately 50 degrees higher. Activation energies (E_a) for permeation were calculated for each gas from the portions of

the plots where the permeances increased with temperature. These values and some ideal selectivities can be found below:

Gas	Kinetic Diameter (A)	Ea (KJ/mol)
N ₂	3.64	10.6
CO ₂	3.3	8.5
CH ₄	3.8	9.7

Ideal Selectivity

Gases	@ 300 K	@ 500 K	@ 600 K
CH ₄ /N ₂	1.8	1.2	1.1
CH ₄ /CO ₂	1.4	1.6	1.6

Single gas permeation experiments for H₂, N₂, CO₂, and CH₄ were carried out through a very high quality (N₂/SF₆ = 234) silicalite-1 membrane at 1.3 bar from 300 to 600 K. Figure 7 shows a plot of single gas permeances versus temperature. The results are similar to previous experiments using a silicalite-1 with a lower ideal selectivity (N₂/SF₆ = 80). The permeance values for components other than H₂ again go through a minimum (375 K for CH₄ and CO₂, 350 K for N₂) in the temperature range studied. The values for H₂ appear to level off at room temperature but do not go through an apparent minimum in the experimental temperature range. Activation energies (Ea) for permeation were calculated for each gas from the portions of the plots where the permeances increased with temperature. These values and some ideal selectivities can be found below:

Gas	Kinetic Diameter (A)	Ea (KJ/mol)
H ₂	2.89	3.5
N ₂	3.64	5.1
CO ₂	3.3	4.5
CH ₄	3.8	4.1

Ideal Selectivity

Gases	@ 300 K	@ 500 K	@ 600 K
H ₂ /N ₂	2.7	3.3	3.1
H ₂ /CO ₂	2.4	3.7	3.6
H ₂ /CH ₄	1.7	2.4	2.3

Single gas permeation experiments were also performed on H₂, CH₄, CO₂, and CH₄ at temperatures that were below ambient. The experimental setup was very similar to the one described above. The membrane module was suspended in a bath of dry ice and allowed to equilibrate at 253 K. The ideal selectivities at this temperature were the following: H₂/N₂ = 1.9, H₂/CO₂ = 2.1, and H₂/CH₄ = 1.4. Permeance values of all components increased at the decreased temperature, continuing the trend exhibited by previous experiments.

H₂/CO₂ Binary Gas Experiments

Binary experiments on silicalite-1 were carried out from 300 to 585 K using a gas feed mixture of 55.7% H₂ and 44.3% CO₂ on a molar basis. The experimental setup was identical to that for the single gas experiments with the exception of gas composition

determinations. The retentate and permeate compositions were directly sampled using a gas chromatograph (HP Series III 3396). The feed gas pressure was 25.7 psia for all temperatures and the total differential pressure across the membrane was maintained at 0.9 psi. Permeate gas flows were below 20% of the total to minimize any gradients in driving force along the membrane.

Figure 8 shows a plot of the total gas permeance versus temperature. The total permeance undergoes the same sort of minimum at approximately 400 K that had previously been observed for CO₂ single gas permeation through a silicalite membrane. The total permeance ranges from this minimum of about 2.2×10^{-6} to about 3.4×10^{-6} mol/(m²*sec*Pa). The gas permeances were calculated both using a log mean pressure gradient and the normal pressure gradient across the membrane. Individual gas permeances using the normal gradient are shown in Figure 9 and those calculated with a log mean are found in Figure 10. The primary difference in the two results is the more pronounced minimum that occurs for CO₂ permeances in the log mean calculations.

The binary results do not differ dramatically from the ideal, single gas results for the same membrane (Figure 7). The actual selectivities are graphed as a function of temperature in Figure 11. The values range from 1.7 to 3.5 (for the calculations with a regular driving force) and 1.1 to 2.1 (for the log mean driving force). The ideal selectivities that are shown above are slightly higher than these values. Both the ideal and actual selectivities appear to increase in the higher temperature range.

High Temperature H₂/CO₂ Binary Gas Experiments

Previous experiments were carried out from 300 to 585 K using a gas feed mixture of 55.7% H₂ and 44.3% CO₂ on a molar basis. Data was obtained for the same mixture

over a temperature range of 590 to 700 K for the same membrane. Figure 12 shows a plot of the total gas permeance versus temperature. The total permeance undergoes the same sort of minimum at approximately 400 K that had previously been observed for CO₂ single gas permeation through a silicalite membrane. The total permeance ranges from this minimum of about 2.2×10^{-6} to about 4.3×10^{-6} mol/(m²*sec*Pa), which occurs at 632 K. The higher temperature data indicate that a plateau occurs after this point, and that the total permeance does not increase. Figure 13 shows the change of the permeance of each component (H₂ and CO₂) with temperature. The initial data (for temperatures up to 585 K) indicated that better H₂/CO₂ selectivity could be obtained at higher temperatures. However, the H₂ gas permeance reaches a maximum at 660 K and the CO₂ gas permeance does not change significantly with temperature. The net result is that the highest H₂ selectivity of 3.6 is obtained at 660 K. The H₂ selectivity is simply the ratio of the H₂ permeance to the CO₂ permeance and is shown as a function of temperature in Figure 14.

NaX Membrane Preparation and TIPB Treatment

Zeolite NaX membranes (where Na is the cation in the zeolite X matrix) have been prepared with N₂/SF₆ ideal selectivities of 1.9, which is less than the value for Knudsen diffusion (2.28). However, SF₆ is too small to be a good indicator of the quality of a zeolite X membrane. However, ideal H₂/CO₂ selectivities of 3.6 to 3.8 for these same membranes were obtained, which are higher than the value of 2.4 which was obtained for the best silicalite membrane (N₂/SF₆ = 234). Because of this behavior, a representative zeolite X membrane was used for a binary H₂/CO₂ experiment. In addition, treatment with triisopropylbenzene improved the ideal H₂/CO₂ selectivity of a zeolite X membrane (96ZX05) from 3.8 to a value of 5.7 (see Table 1).

A variety of zeolite membranes were treated with 1,3,5 - triisopropylbenzene (Aldrich, 97%) by soaking in the liquid, followed by heating at high temperature. The theory behind this process is that the triisopropylbenzene is too large (diameter > 0.8 nm) to infiltrate the zeolite pores, but is small enough to permeate into the mesopores, or membrane defects. The dense membrane layer could then be improved by forming carbon deposits in the mesopores during heating. The soaking and heating conditions varied a little for each membrane. All membranes were pre-treated by calcination at 480 °C for 8 hours. The experimental conditions were as follows:

1. Membrane = 96Z512, a ZSM-5 membrane on α -alumina; soaked for 24 hours, heated at 0.01 °C/sec to 480 °C, temperature held for 8 hours, then cooled at 0.05 °C/sec.
2. Membrane = Sil #13, a silicalite on γ -alumina; soaked for 25 hours, heated at 0.017 °C/sec to 480 °C, temperature held for 2 hours, then cooled at 0.017 °C/sec.
3. Membrane = 96ZX05, a NaX membrane on α -alumina; soaked for 25 hours, heated at 0.017 °C/sec to 480 °C, temperature held for 2 hours, then cooled at 0.017 °C/sec.
4. Membrane = 96Z512 (second treatment), a ZSM-5 membrane on α -alumina; soaked for 24 hours, heated at 0.017 °C/sec to 500 °C with a slow N₂ purge, temperature held for 2 hours, then cooled at 0.017 °C/sec
5. Membrane = 96ZX05 (second treatment), a NaX membrane on α -alumina; soaked for 24 hours, heated at 0.017 °C/sec to 500 °C with a slow N₂ purge, temperature held for 2 hours, then cooled at 0.017 °C/sec.

6. Membrane = 96SI26, a silicalite on stainless steel; soaked for 24 hours, heated at 0.017 °C/sec to 500 °C with a slow N₂ purge, temperature held for 30 hours, then cooled at 0.017 °C/sec
7. Membrane = 95SI32, a silicalite on α-alumina; soaked for 24 hours, heated at 0.017 °C/sec to 500 °C with a slow N₂ purge, temperature held for 30 hours, then cooled at 0.017 °C/sec

The membranes were immersed in a glass vial full of triisopropylbenzene during the soaking phase, and the heating occurred with the membranes open to the atmosphere. A nitrogen gas purge was used during the heating stage for a few of the experiments indicated above. There was never any significant change in membrane weight after the treatment with triisopropylbenzene. The gas permeation results were erratic and can be found in the table below:

Table 1

Membrane	Condition	H ₂ Perm.	N ₂ Perm.	CO ₂ Perm.	SF ₆ Perm.	N ₂ /SF ₆ Ideal
96Z512	before TIPB	32	9.40	8.4	0.21	44
	after 1 layer		7.1		0.22	32
	after 2 layers		9.0		1.2	7.6
Sil #13	before TIPB		6.8		0.071	96
	after 1 layer		3.9		0.49	8
96ZX05	before TIPB		0.95		0.49	1.9
	after 1 layer	12	3.2	2.1	1.7	2.3
	after 2 layers	18	4.6	3.7	2.2	2.1
96SI26	before TIPB		1.6		0.36	4.4
	after 1 layer		0.84		0.3	2.8
95SI32	before TIPB		0.0056		0.000086	66
	after 1 layer		0.015		0.014	1.1

* note - Permeance units are mol/(m²*sec*Pa) * 10⁻⁷

H₂/CO₂ Binary Gas Experiments on NaX Membrane

Experiments were carried out from 300 to 540 K using a gas feed mixture of 55.3% H₂ and 44.7% CO₂ on a molar basis. The experimental setup was identical to that for the silicalite-1 binary gas experiments discussed previously. Figure 15 shows the total gas permeance through the zeolite X membrane. The permeance steadily decreases with temperature, which is indicative of Knudsen type diffusion and is not promising for potential gas separations at the high temperatures of interest. The component gas permeances can be found as a function of temperature in Figure 16. Both H₂ and CO₂ gas permeances decrease with temperature, with H₂ decreasing the most in magnitude, although it appears to reach a plateau at 500 K. The H₂ selectivity (Figure 17) stays fairly constant between 4 and 4.5. These results are not promising for high temperature H₂/CO₂ separation, although the possibility exists that the adsorption characteristics will permit improved separation at higher feed pressures.

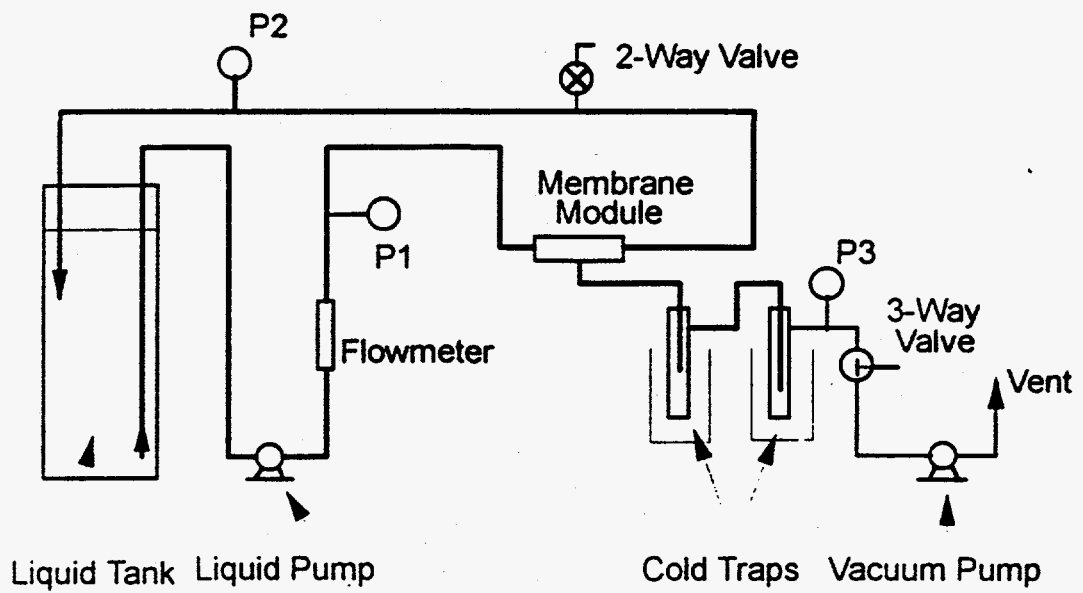


Figure 1: Pervaporation System

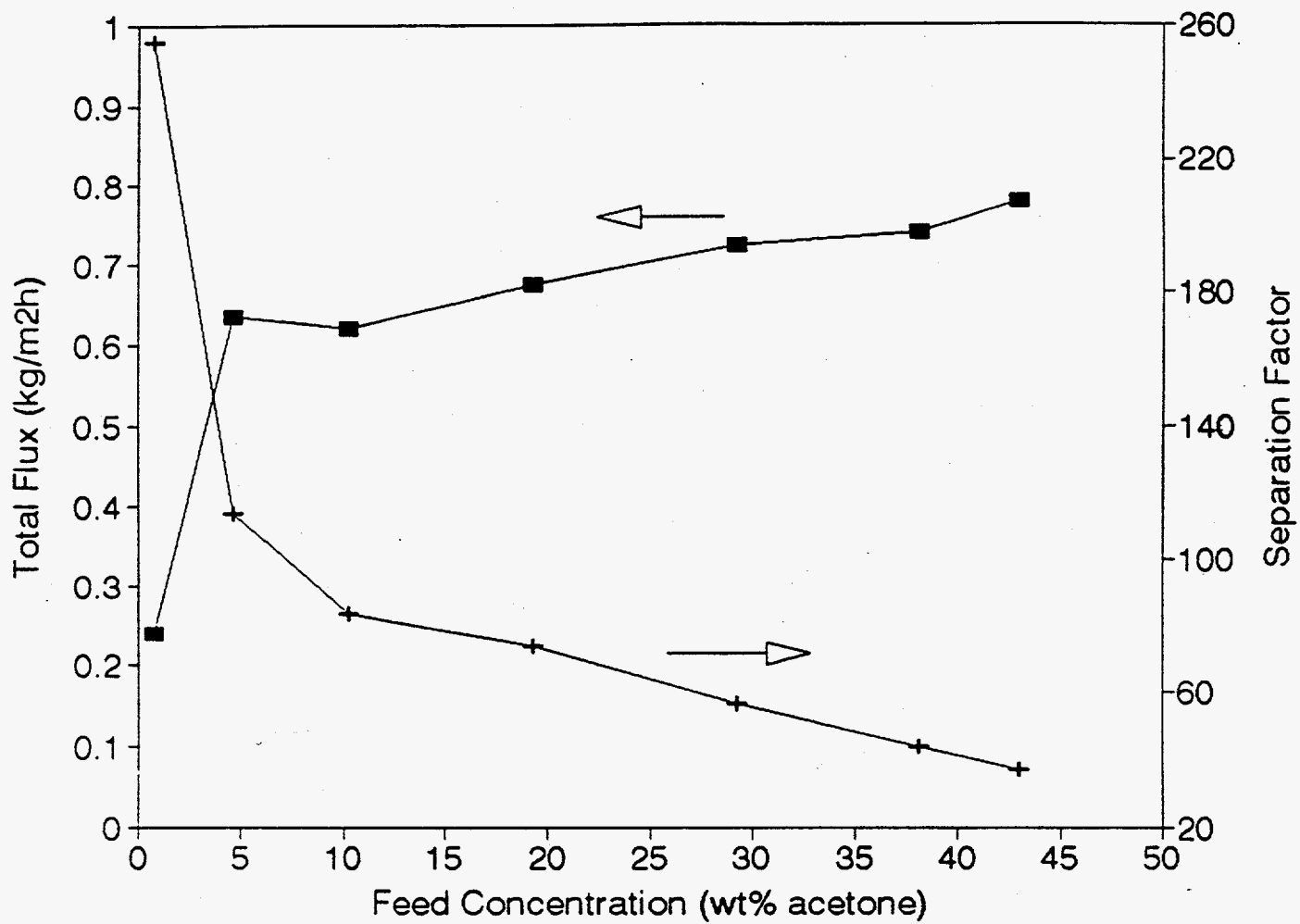


Figure 2: Effect of Concentration on Flux and Separation Factor

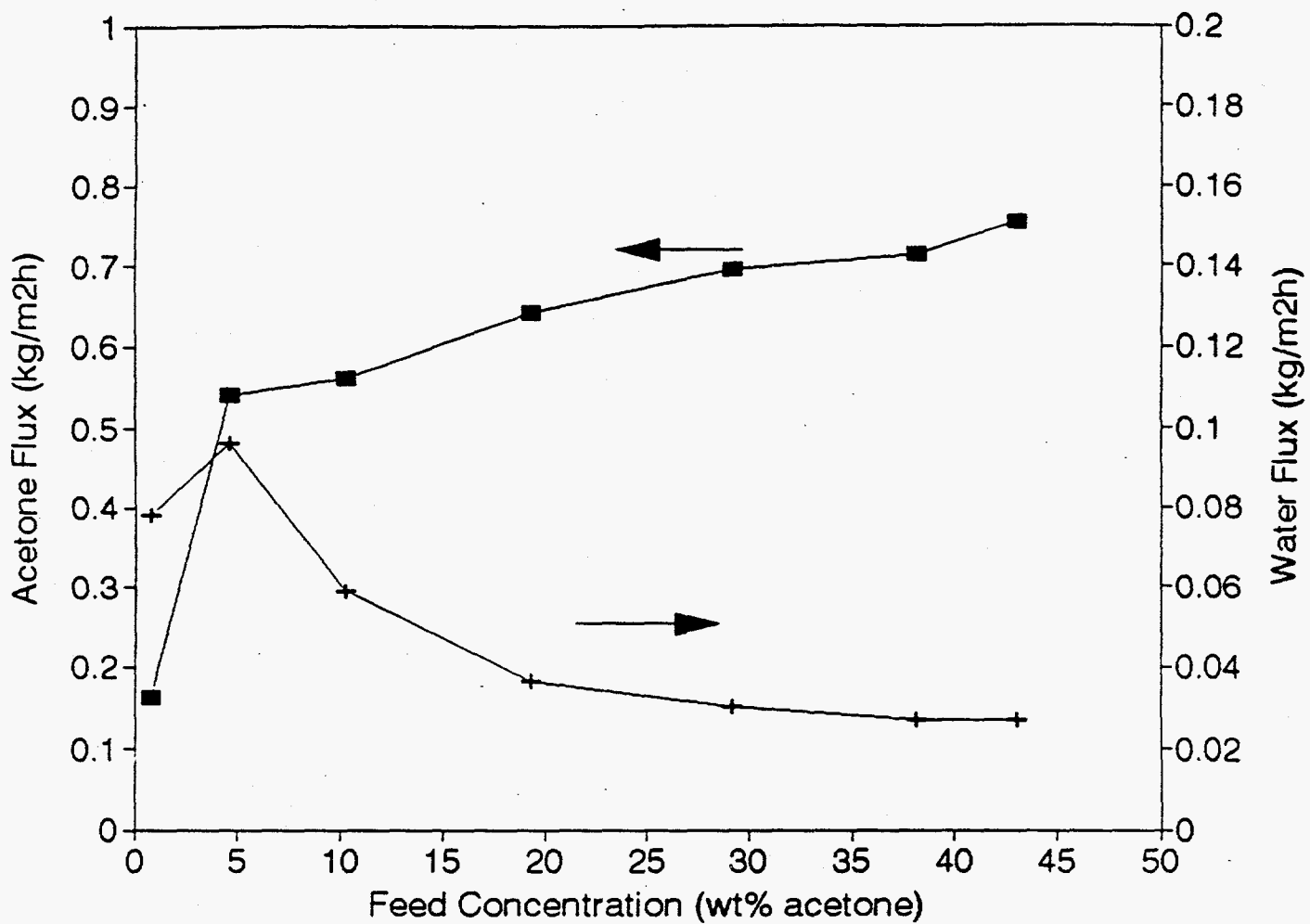


Figure 3: Effect of Concentration on Species Flux

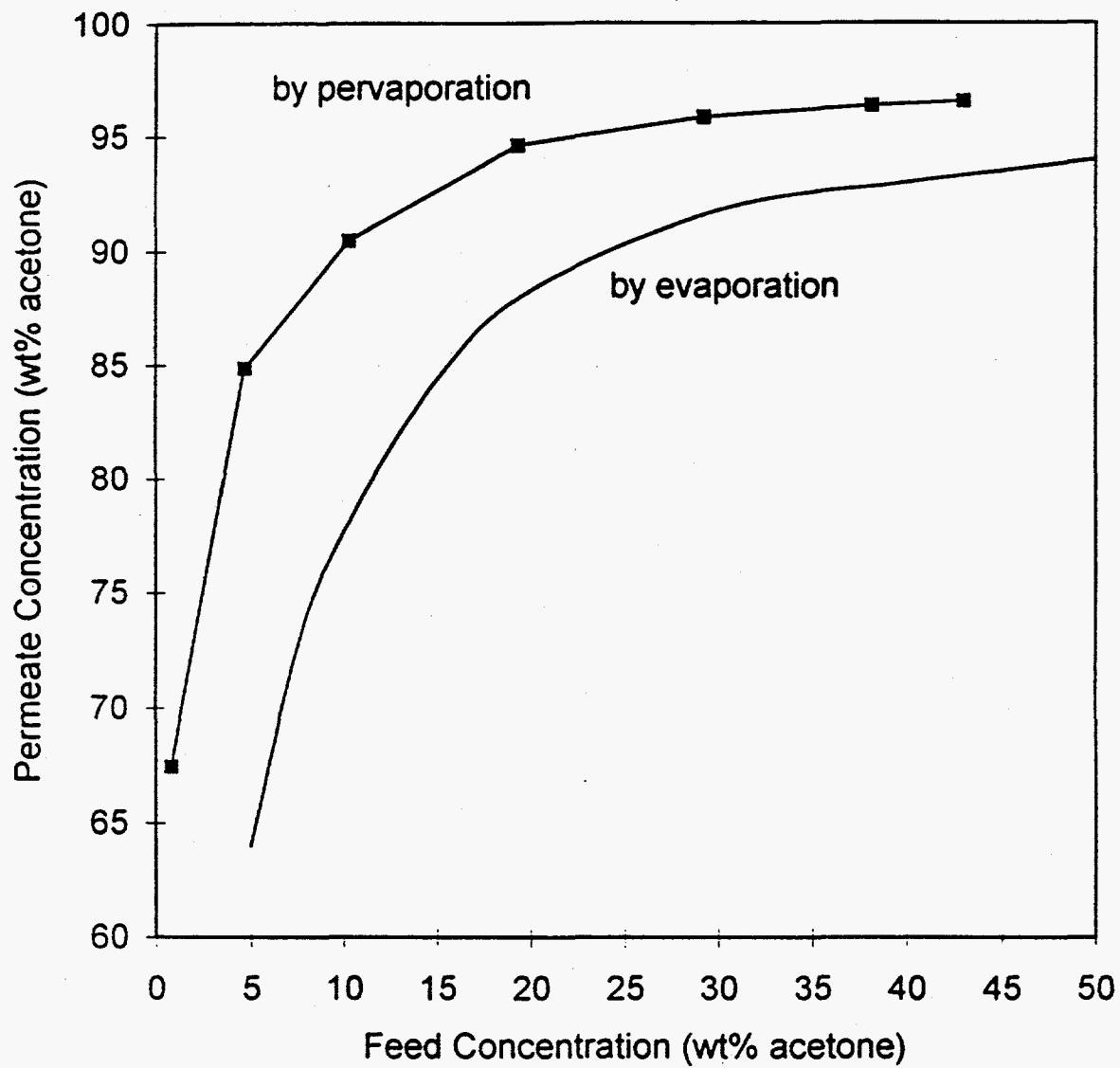


Figure 4: Comparison of Permeate Concentration Obtained by Two Methods

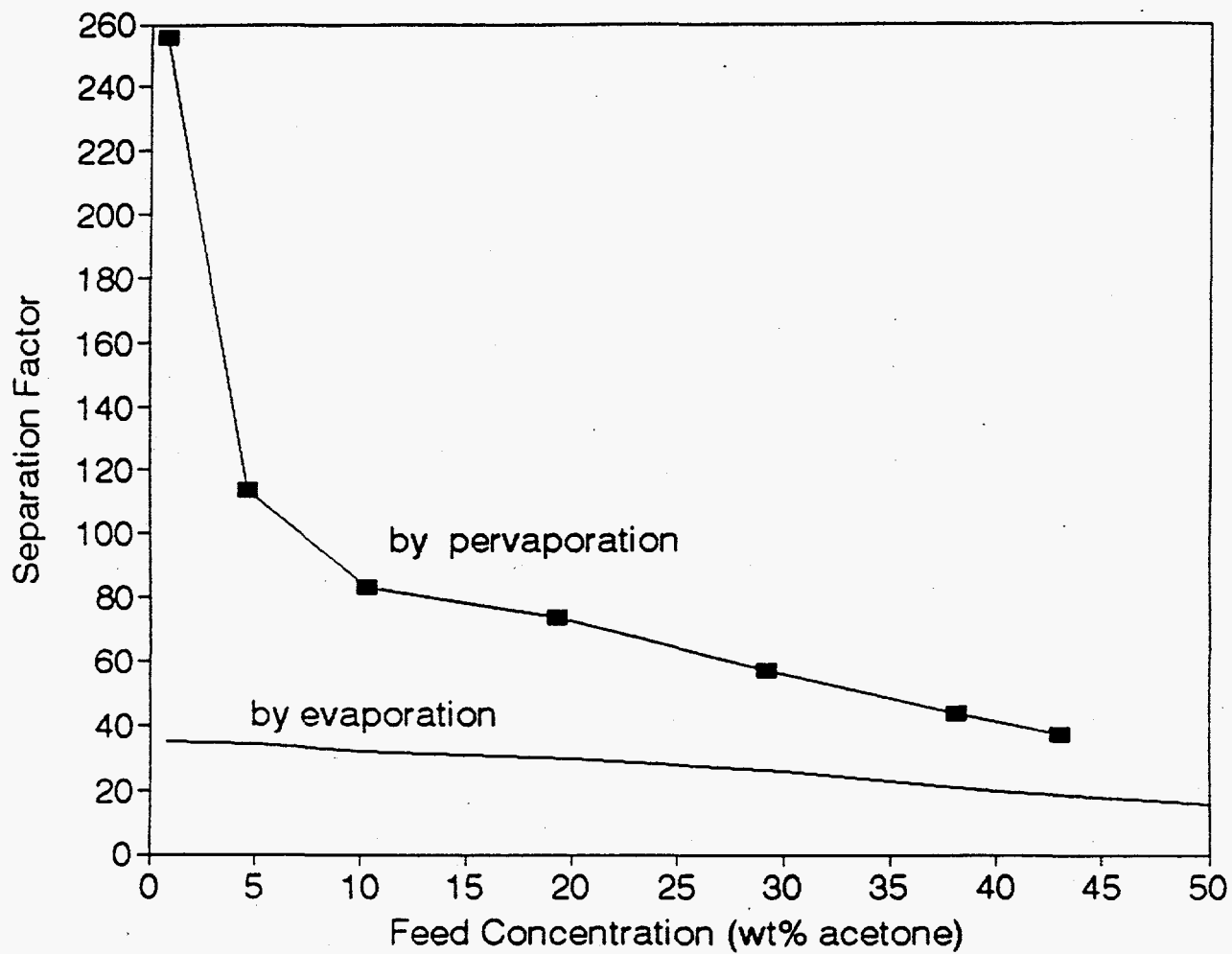


Figure 5: Comparison of Separation Factors Obtained by Two Methods

Figure 6
Single Gas Permeances (Silicalite -1)

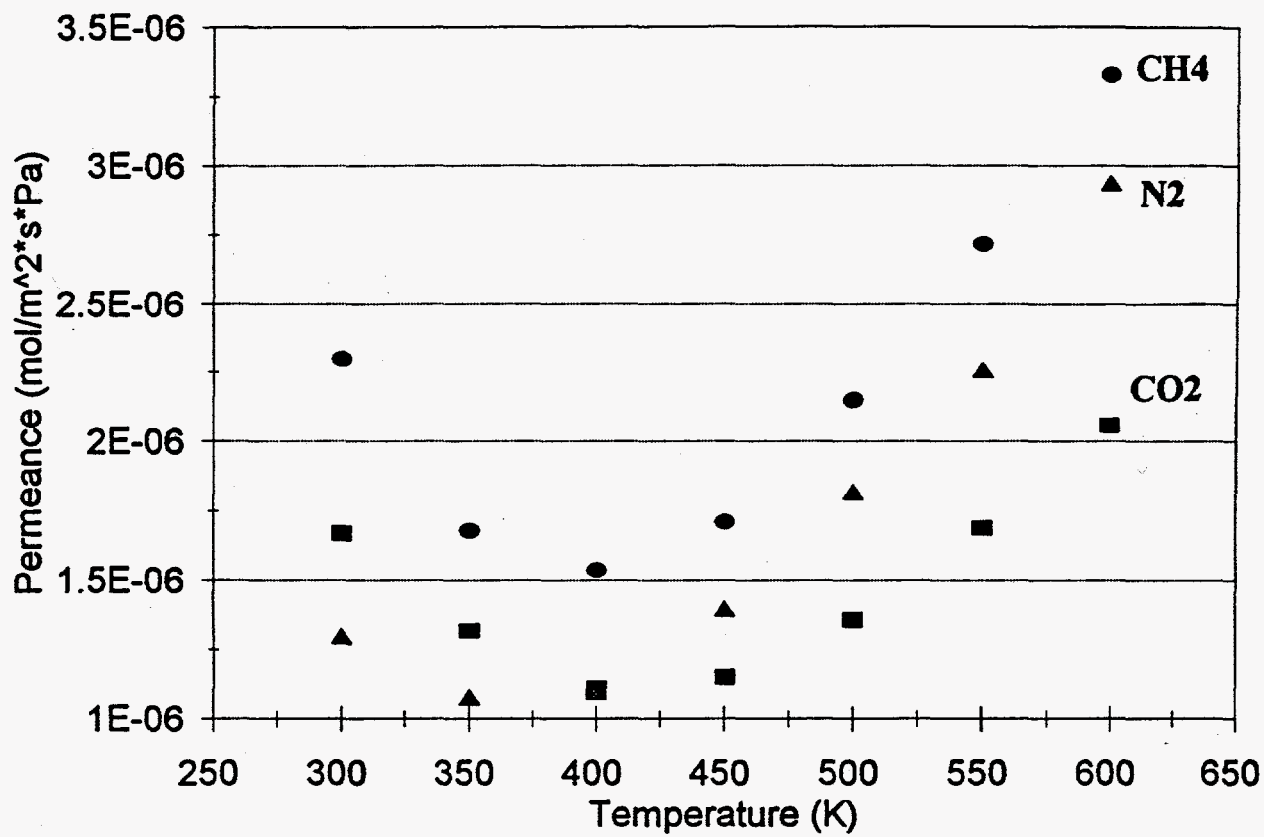


Figure 7
Single Gas Permeances on Silicalite-1

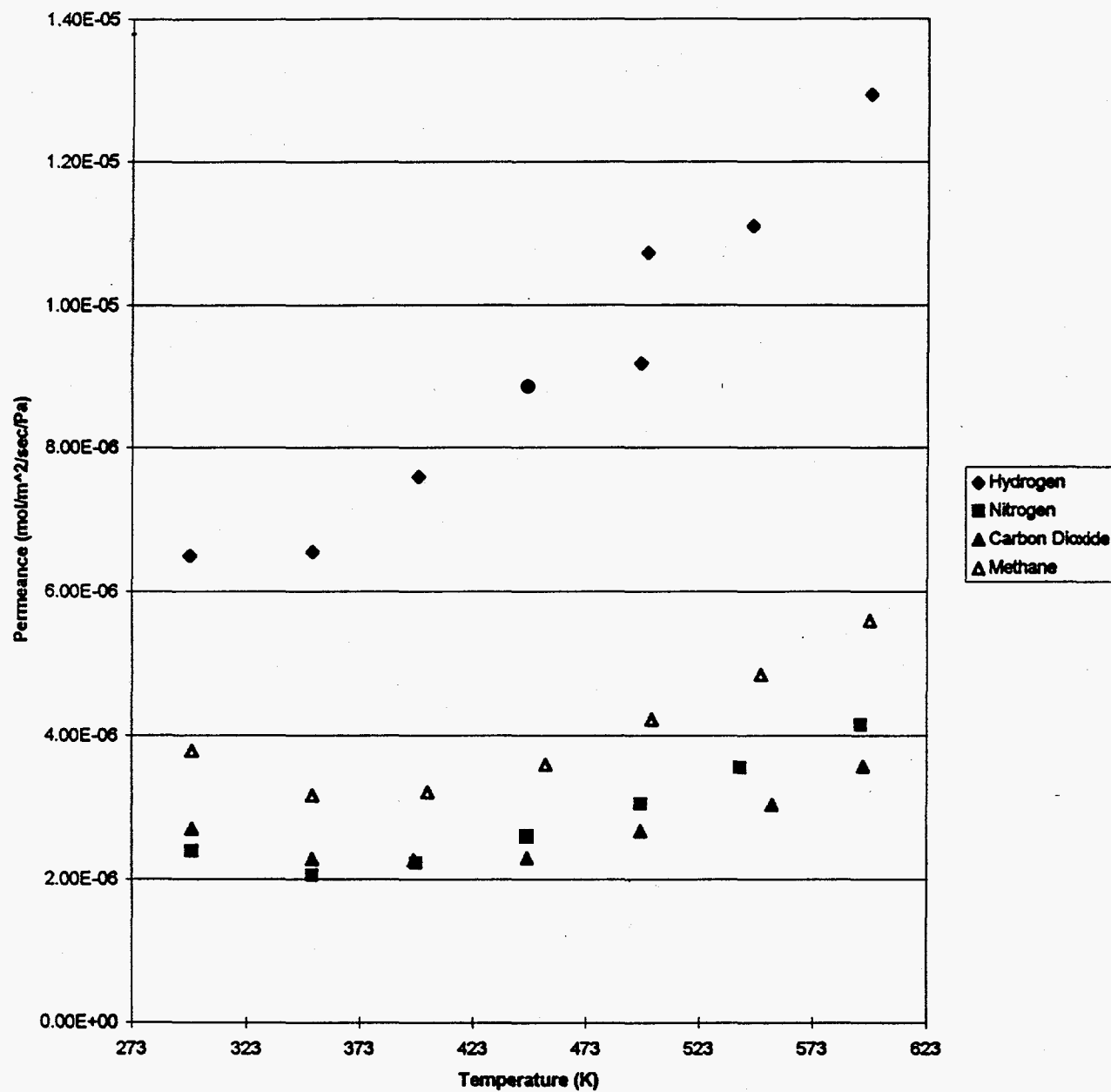


Figure 8
Total Permeance for H₂/CO₂ Mixture

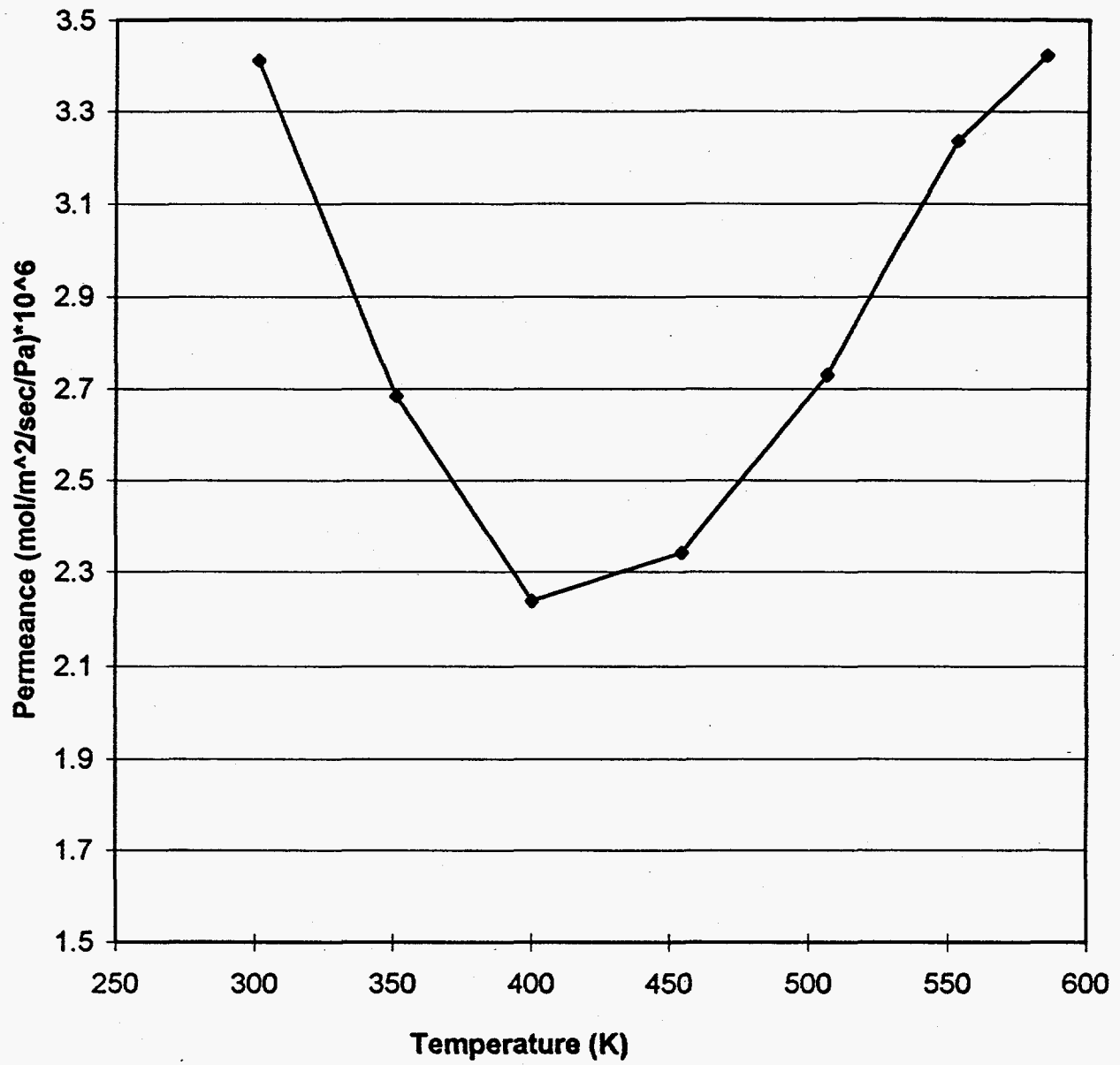


Figure 9
Permeances (using regular pressure values)

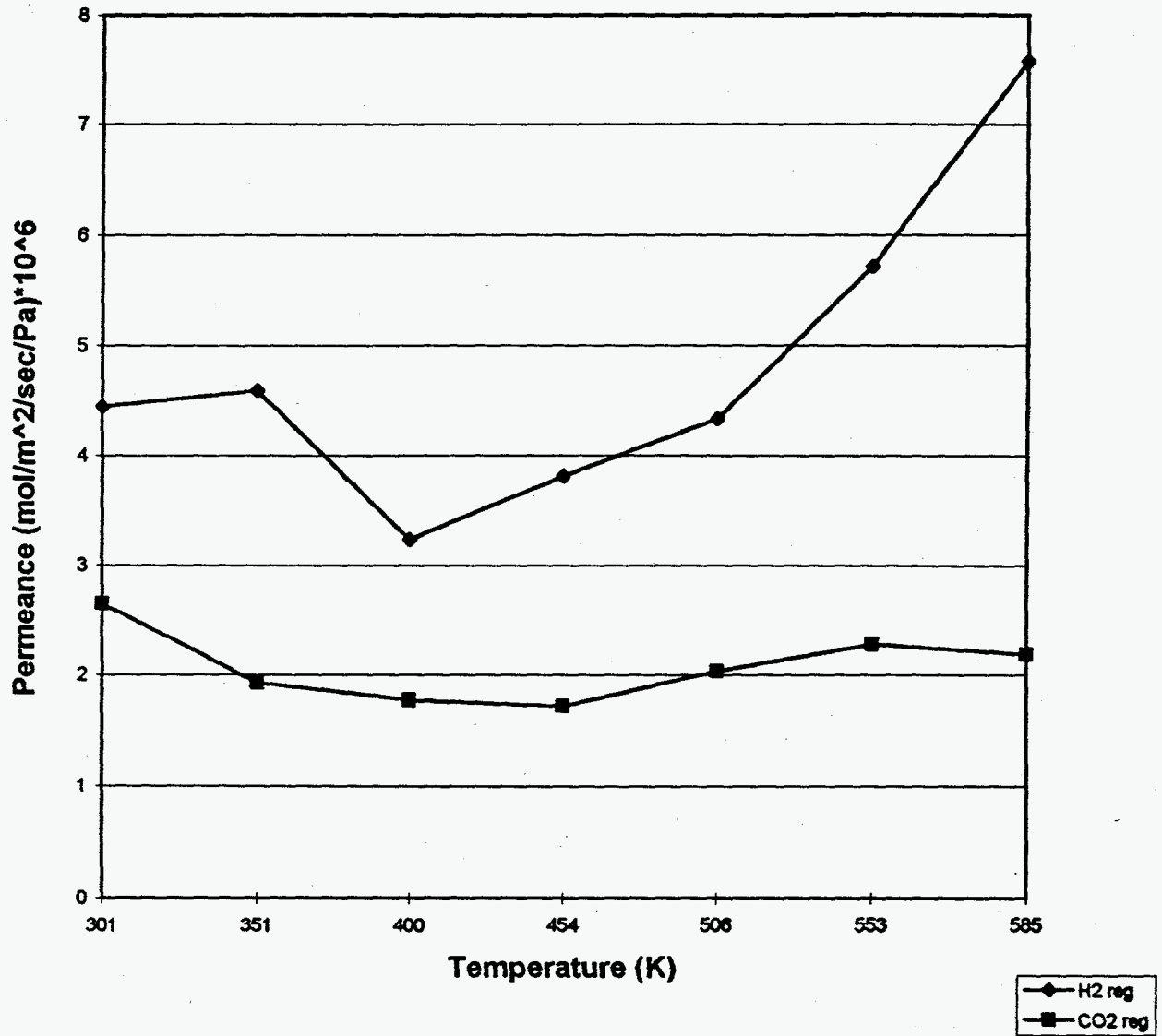


Figure 10
Permeances (using log mean pressure)

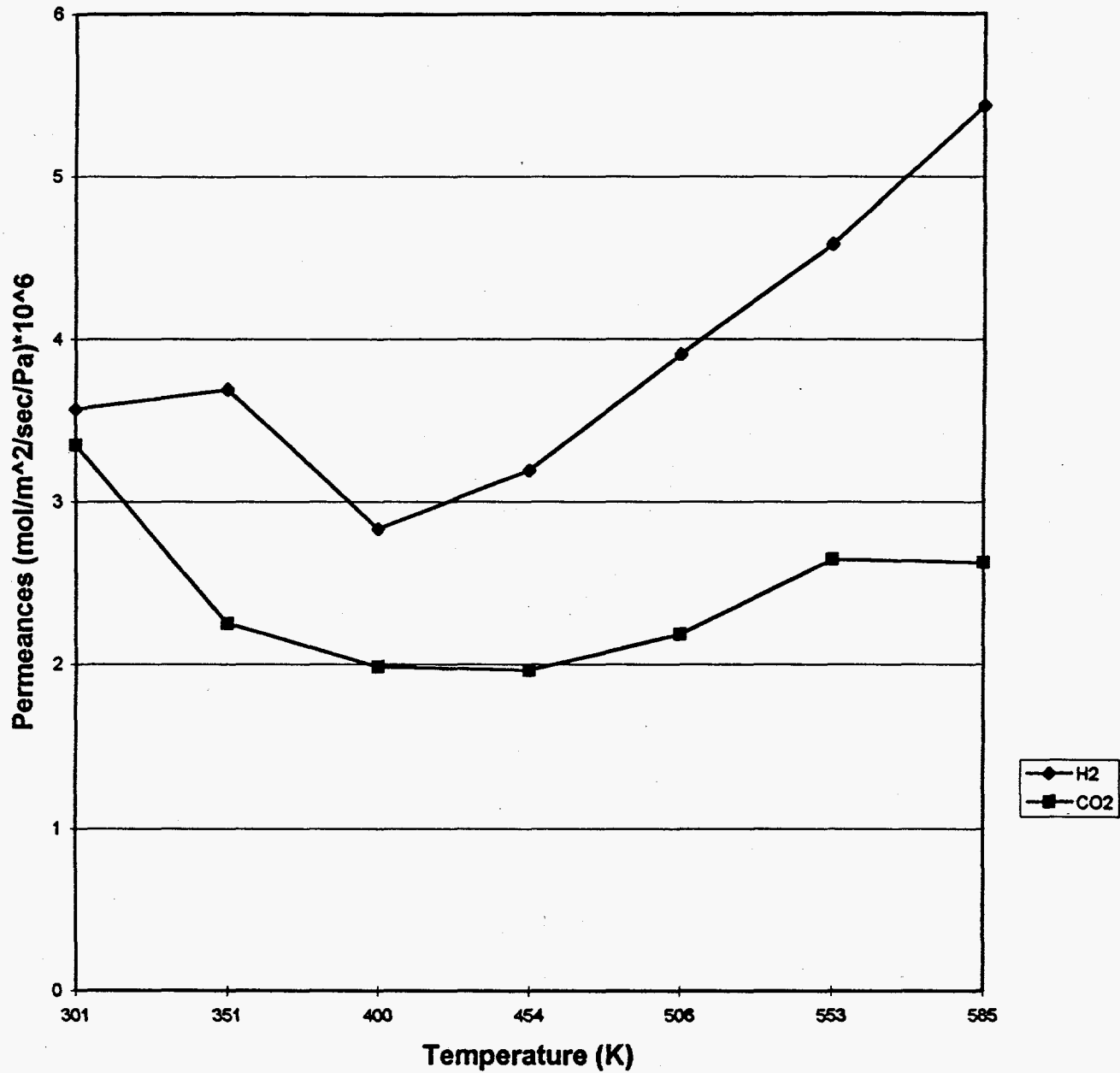


Figure 11
H₂/CO₂ Selectivity

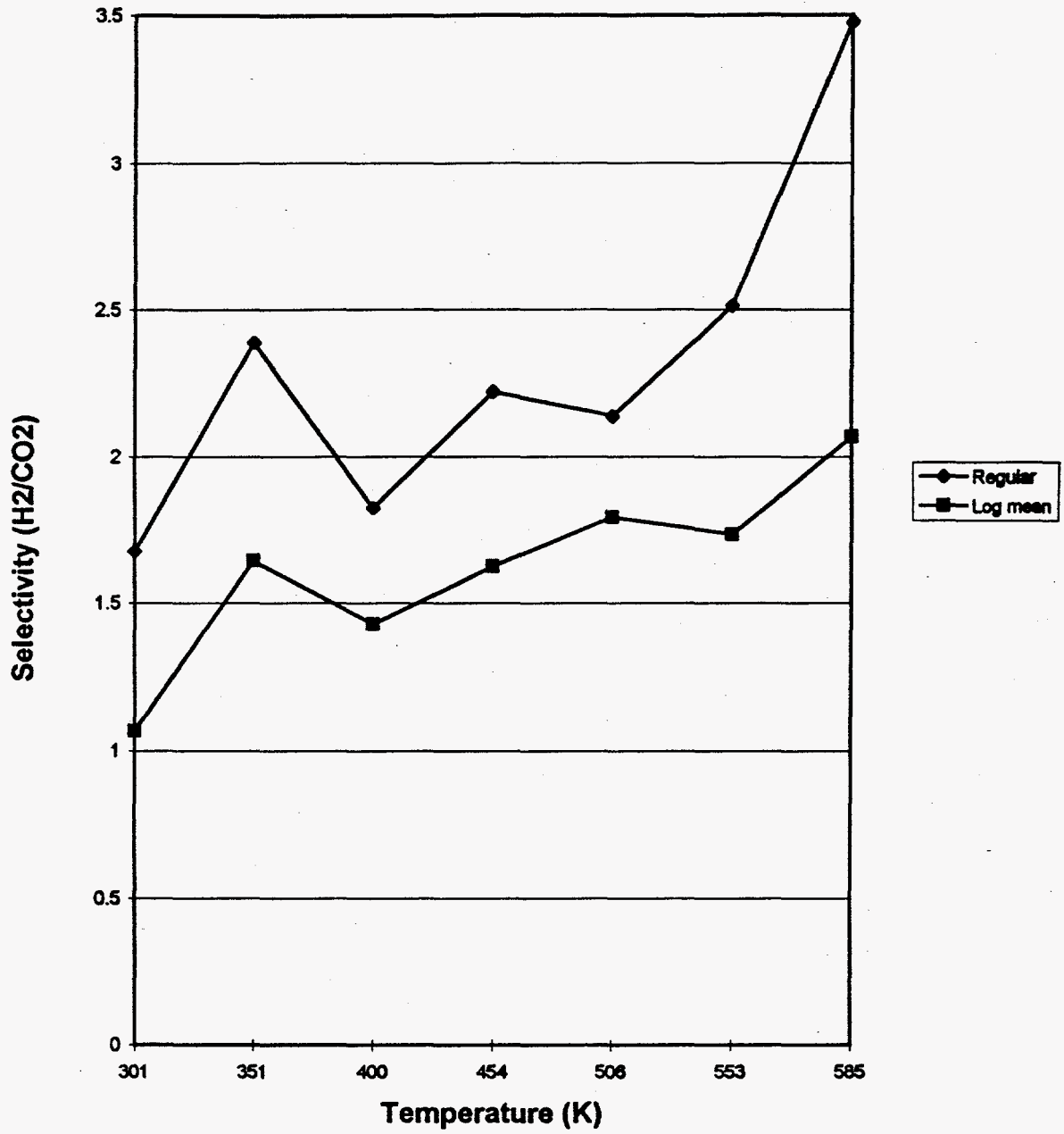
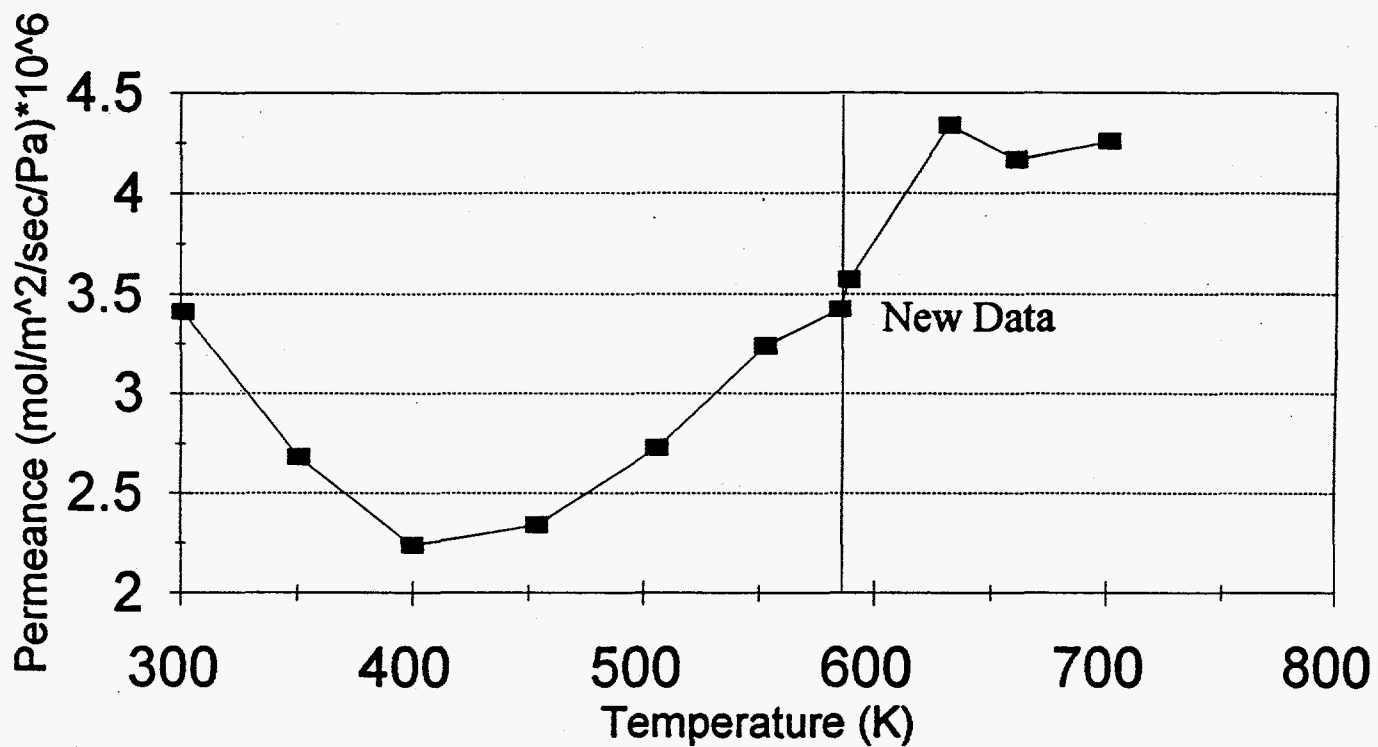


Figure 12
H₂/CO₂ binary gas on silicalite-1



■ Total Gas Permeance

Figure 13
H₂/CO₂ binary gas on silicalite-1

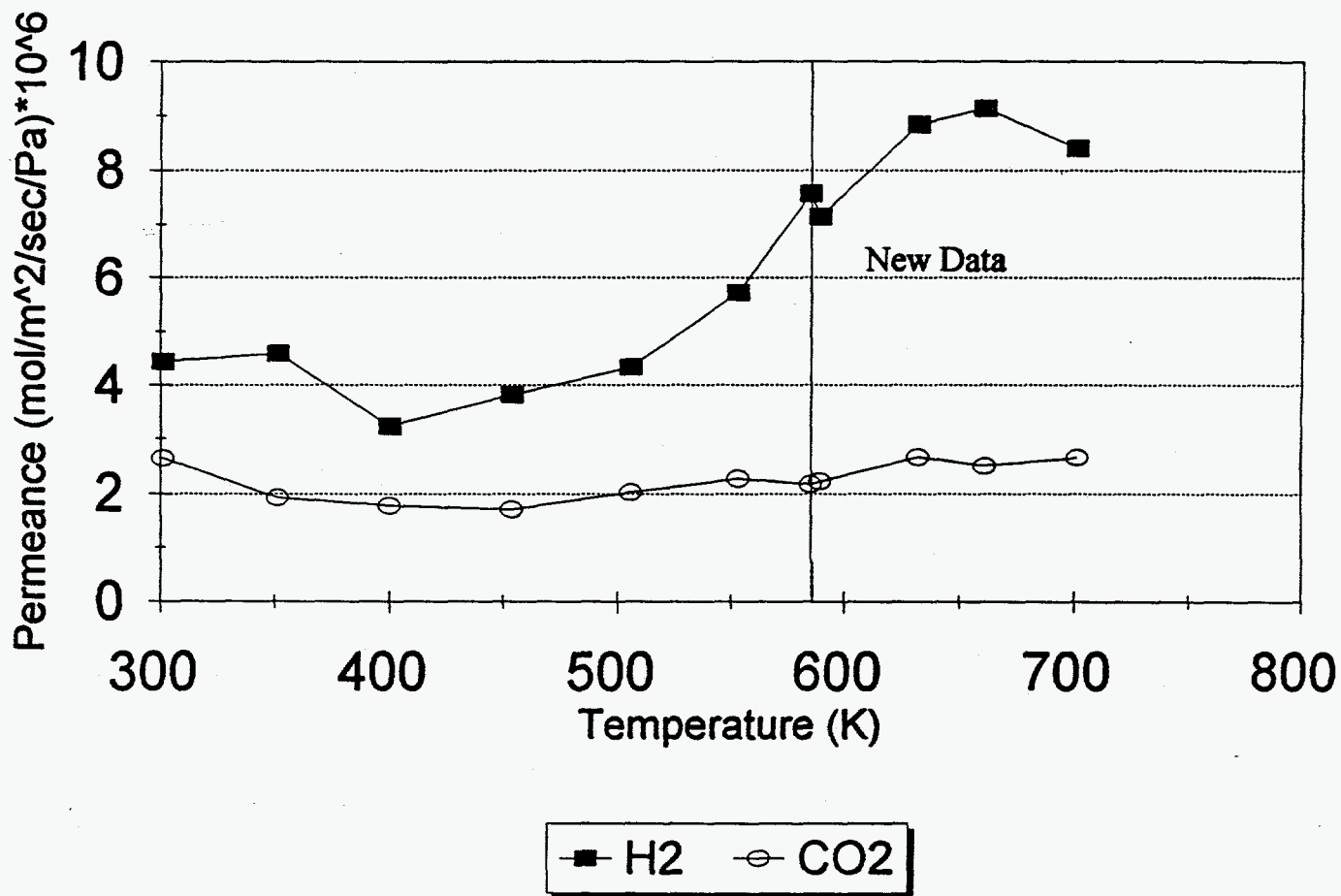


Figure 14
H₂/CO₂ binary gas on silicalite-1

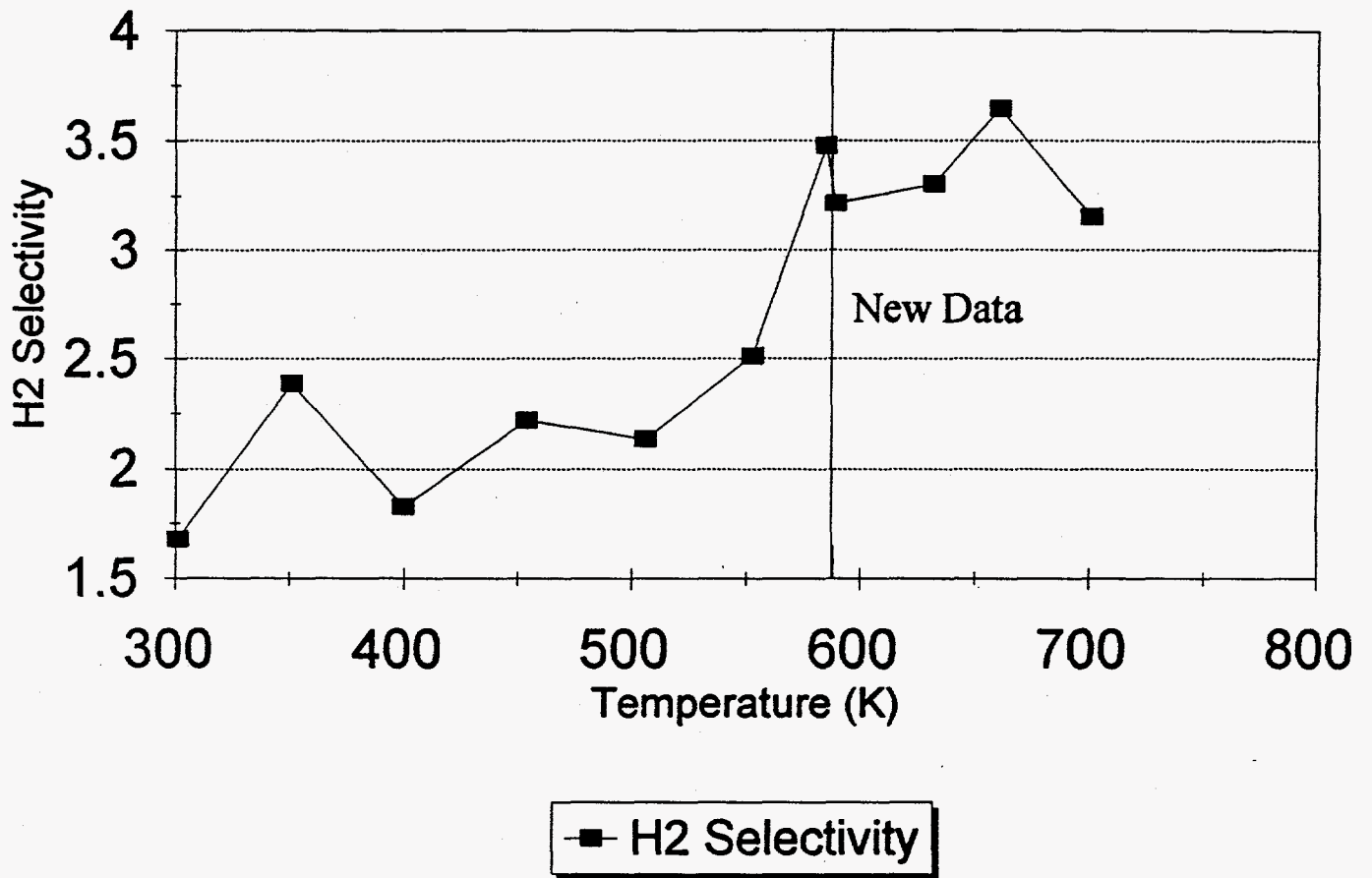
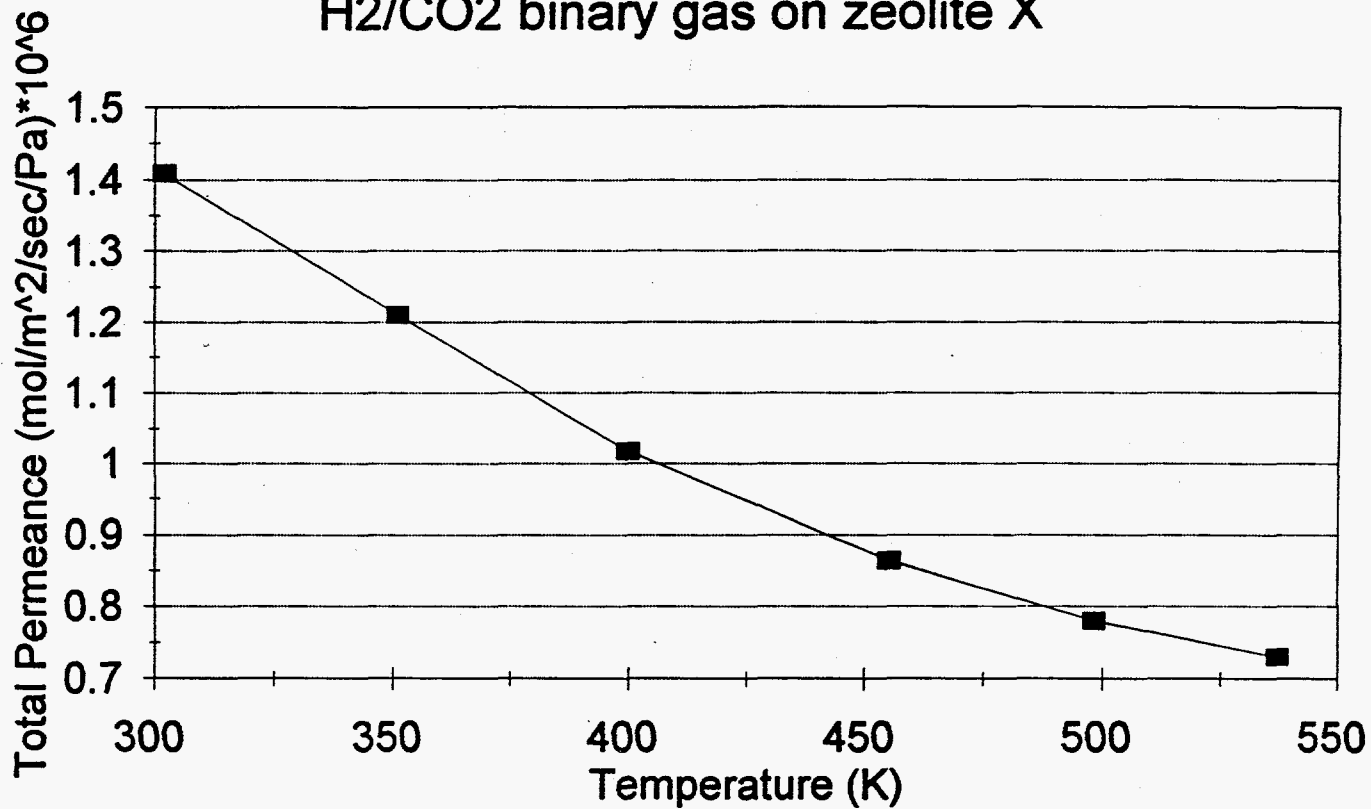


Figure 15

H₂/CO₂ binary gas on zeolite X



■ Total Gas Permeance

Figure 16
H₂/CO₂ binary gas on zeolite X

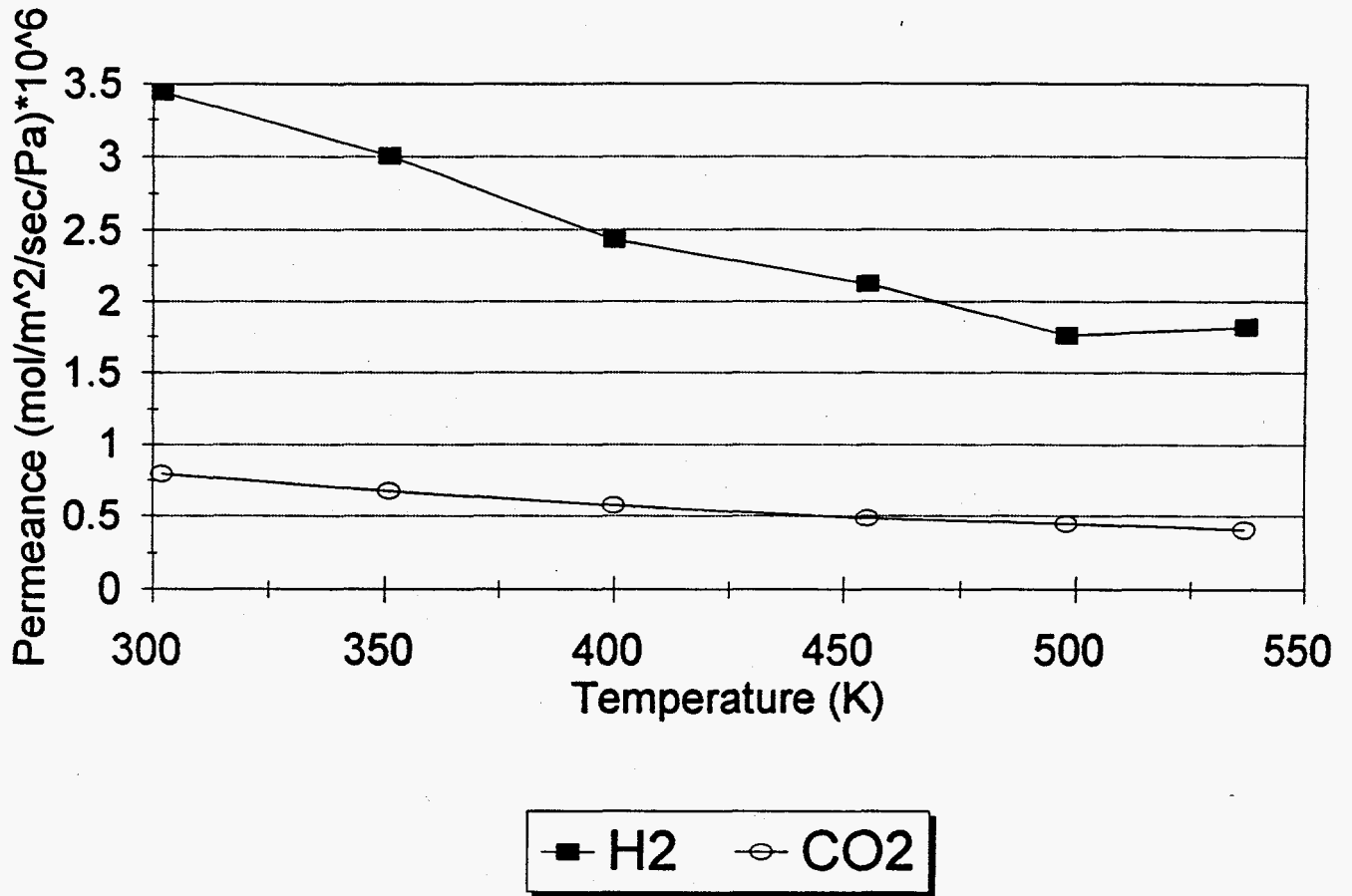


Figure 17
H₂/CO₂ binary gas on zeolite X

