PMI
POROSITY & PERMEABILITY TESTING

Permeametry

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OUTLINE

- Gas Permeability
- Envelope Surface Area, Average Particle Size and Average Fiber Diameter by Gas Permeability
- Average Fiber Diameter by Gas Permeability
- High Flow Gas Permeability
- Diffusion Permeability
- Water Vapor Transmission Analysis
- Gas Transmission Analysis
- Liquid Permeability
- Differential Gas Diffusion Porometry
- Membrane distillation
- Conclusions

GAS PERMEABILITY: BASIC PRINCIPLE

- Permeability defined by Darcy's law:

  v = linear flow rate
  k = *specific permeability* or simply *permeability*
  μ = viscosity of the fluid
  P = pressure
  x = displacement in the direction of flow

$$v = -\left(\frac{k}{\mu}\right) \cdot \frac{dP}{dx}$$

- Unit of Permeability:

  CGS unit: cm^2 ; 1 Darcy: $9.87 \times 10^{-9}\ cm^2$
  Many other units also used

GAS PERMEABILITY: BASIC PRINCIPLE

- Permeability in terms of gas flow rate in volume at STP:

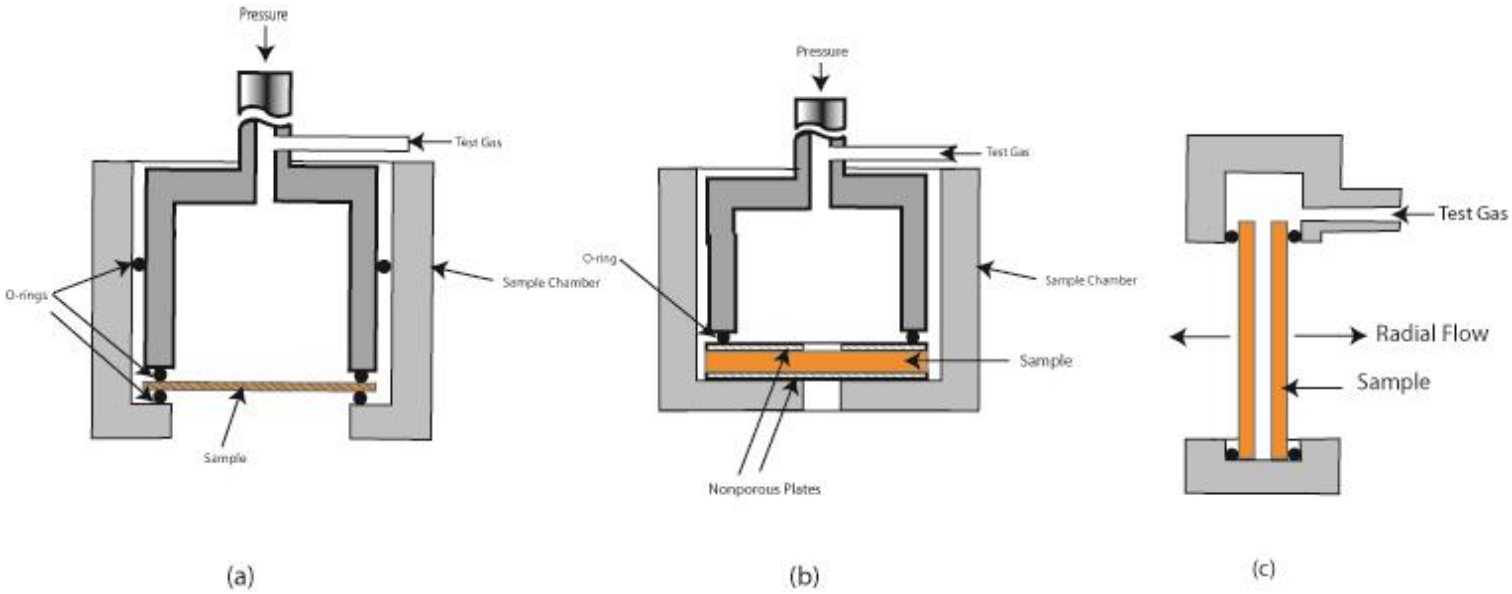
$$F = \left[\frac{P}{P_s}\right] \cdot \left[\frac{T_s}{T}\right] \cdot \left[-\left(\frac{k \cdot A}{\mu}\right) \cdot \frac{dP}{dx}\right]$$

F = gas flow rate in volume at standard pressure, P_s, and standard temperature, T_s
P = test pressure
A = cross-sectional area of the porous material
T = test temperature in K

This relation is used to compute permeability

TECHNOLOGY

- Sample sealed in sample chamber
- Flow restricted to direction in which permeability is desired;
  z-direction, x-y plane, Radial direction, etc.



(a) z-direction permeability of a disc sample
(b) x-y plane permeability of a disc sample
(c) Radial permeability of a hollow cylindrical sample

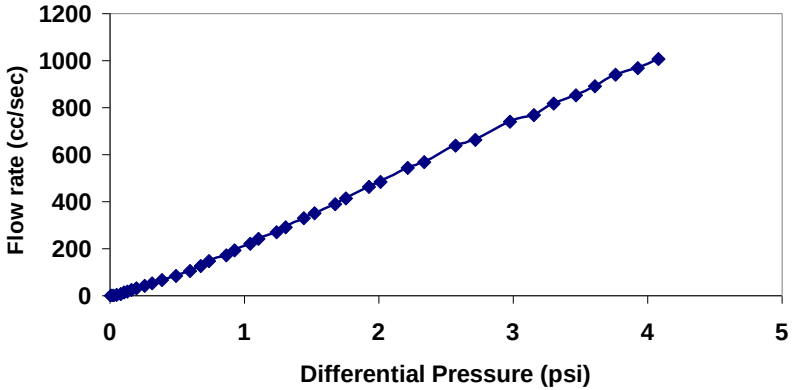
- Pressure of test gas increased on sample in sample chamber
- Differential pressure & gas flow rate measured with increasing differential pressure
- Test temperature can be up to 800˚C

MEASUREMENT CAPABILITY

PERMEABILITY IN THE THICKNESS DIRECTION

- Flow of air through a filter material in z-direction.
- For such experimental conditions Darcy's Law reduces to the following for computation of permeability

$$F = \left[\frac{P}{P_s}\right] \cdot \left[\frac{T_s}{T}\right] \cdot \left[\frac{-k \cdot A}{\mu}\right] \cdot \frac{dP}{dx}$$



$$F = k\left(\frac{A}{2 \cdot \mu \cdot l \cdot P_s}\right) \cdot \left(\frac{T_s}{T}\right) \cdot \left(P_i + P_o\right) \cdot \left(P_i - P_o\right)$$

l = thickness of sample
p_i = inlet pressure
p_o = outlet pressure

MEASUREMENT CAPABILITY

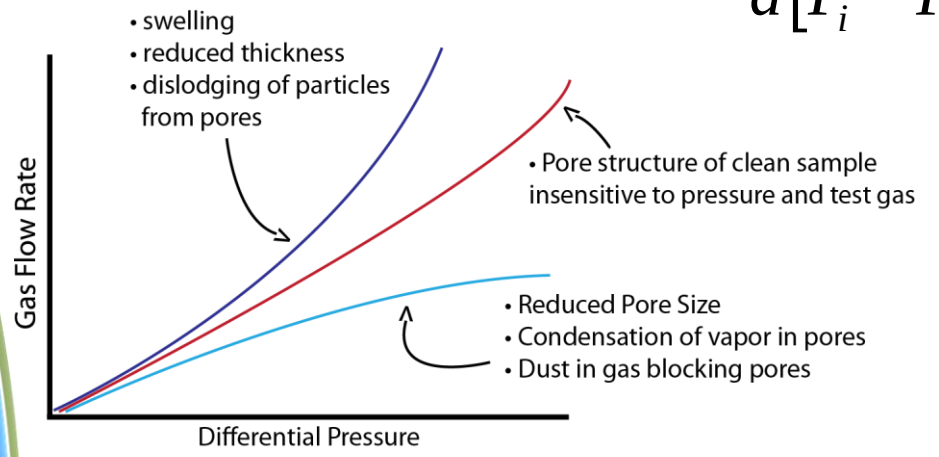
PERMEABILITY IN THE THICKNESS DIRECTION

Calculation of permeability						
For the data shown in Figure 2:						
	Sample radius	=	2.25 cm			
	Sample thickness	=	0.2 cm			
	Viscosity of air	=	0.019cp	=	0.000,19 dynes-s/cm^2	
	Flow rate	=	103.53 cm^3/s			
	At differential pressure, ($p_i - p_0$)	=	0.59786 psi			
	Standard pressure, p_s	=	p_0= 14.7 psi			
	Inlet pressure, p_i	=	$p_0 + (p_i - p_0)$	=	14.7 + 0.59786	
		=	15.29786 psi			
	1 psi	=	6.894,76×10^4 dynes/cm^2			
	(T_s / T)	≈	1			
Substituting in Equation 4:						
K	=	[103.53]/[π(2.25)^2/2×0.00019×0.2] [6.89476×10^4{(15.29786)^2 –(14.7)^2}/14.7] × [1]				
	=	5.881×10^{-9} cm^2				
	=	(5.881×10^{-9}) / (9.87×10^{-9})	=	0.5959 Darcies		

VARIATION OF PERMEABILITY

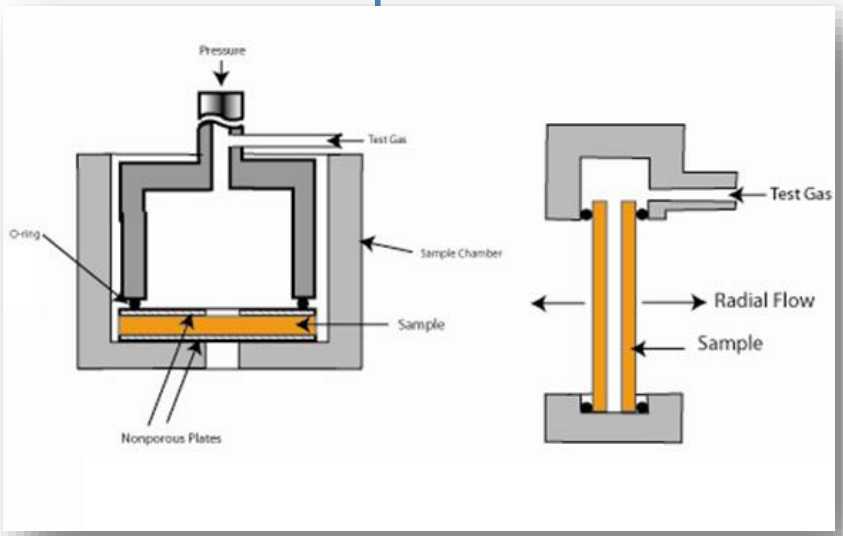
- If pore structure is insensitive to pressure, rate of increase of flow rate with differential pressure is proportional to pressure, P_i
- Permeability can also change because of the following factors:
  - Change of thickness, pore size, pore distribution with pressure
  - Interaction of test gas/vapor with sample: Swelling, Removal of Dirt , condensation, blocking of pores etc

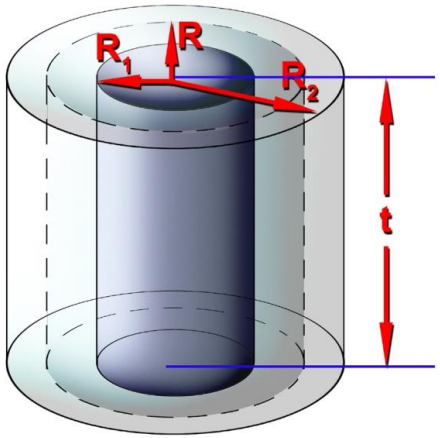
$$\frac{dF}{d\left[P_i - P_o\right]} = k \cdot \left(\frac{A}{\mu \cdot l \cdot P_s}\right) \cdot \left(\frac{T_s}{T}\right) \cdot P_i$$



PERMEABILITY IN THE RADIAL DIRECTION OF A HOLLOW CYLINDER

- Radial gas flow rates measured with increasing differential pressure





- Darcy's Law for computation of permeability ;

$$F = \left[\frac{P}{P_s}\right] \cdot \left[\frac{T_s}{T}\right] \cdot \left[\frac{-k \cdot A}{\mu}\right] \cdot \frac{dP}{dx}$$

$$F = k \cdot \left[\frac{\pi \cdot t \cdot T_s}{\mu \cdot T \cdot P_s \cdot \ln\left(\frac{R_2}{R_1}\right)}\right] \cdot \left(P_i^2 - P_o^2\right)$$

GURLEY PERMEABILITY

The **time (seconds)**

for **flow of 100 cm^3** of air

through one **square inch** of sample

at a differential pressure of **125 mm water**

(4.921 inches of water or 0.178 psi)

GURLEY PERMEABILITY = 100 CM^3 / $F(P_i)$

- **$F(P_i)$ =** volume of air in cm^3 at P_i and test temperature, T, flowing through one square inch section of sample per second under a pressure gradient of 0.178 psi

- **Assuming linear variation of flow with pressure:**

$$F(P_i) = F \cdot \left[\frac{P_s}{P_o + 0.178}\right] \cdot \left[\frac{T}{T_s}\right] \cdot \left[\frac{1}{\text{sample area in } in^2}\right] \cdot \left[\frac{0.178}{P_i - P_o}\right]$$

- Instrument can also be designed to directly measure **$F(P_i)$** at the low ΔP of 0.178 psi

FRAZIER PERMEABILITY

- Cubic feet of air with 55% humidity at 23°C
- Passing one square foot of sample/minute
- At a pressure gradient of 0.5 inch of water (0.5 inch of water = 0.01806 psi)

FRAZIER PERMEABILITY

- 1 cubic feet per minute = 471.947 cm^3/s
- Assuming linear variation of flow with pressure

$$\text{Frazier Permeability} = \left[\frac{F}{471.947}\right] \cdot \left[\frac{1}{\text{Sample Area in } ft^2}\right] \cdot \left[\frac{0.01806}{P_i - P_o}\right] \cdot \left[\frac{296.15}{273.15}\right]$$

- Instrument can also be designed to directly measure F at the low ΔP of 0.01806 psi

AIR FLOW RESISTANCE

- Important for acoustical materials
- Characteristics of acoustical materials defined by ASTM
- Data from flow Porometer in ASTM recommended ranges yield resistance characteristics

  - Example: Specific Air Flow Resistance

$$R = \left[\frac{\Delta P\,(\mathrm{Pa})}{v\,(\mathrm{m/s})} \right] \text{rayls}$$

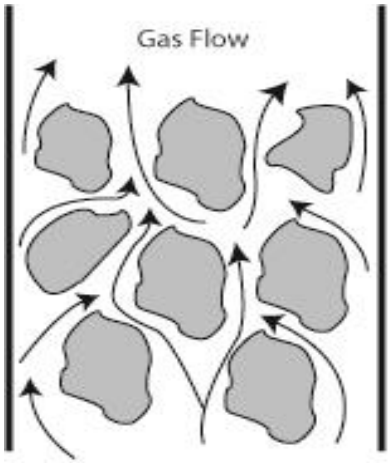
ΔP (Pa) = ΔP x 6894.7
ΔP = differential pressure, psi
v(m/s) = (Flow at P_s & 22°C) / (Sample area)

$$= \left[\frac{F \cdot \left(\frac{295.15}{273.15} \right) \cdot 10^{-2}}{\pi \cdot R^2} \right]$$

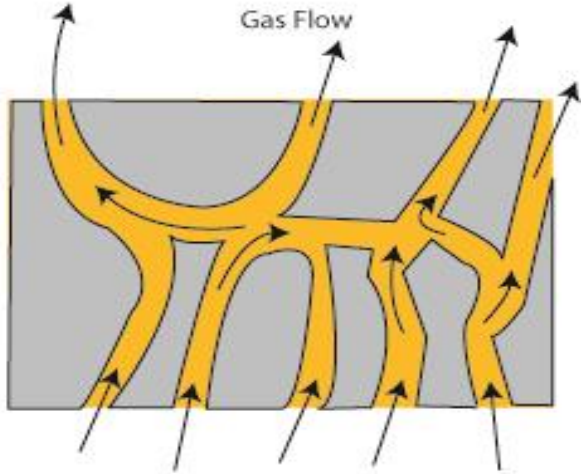
F = flow rate in cm^3/s at STP
R = radius of sample

ENVELOPE SURFACE AREA & AVERAGE PARTICLE SIZE BY GAS PERMEAMETRY

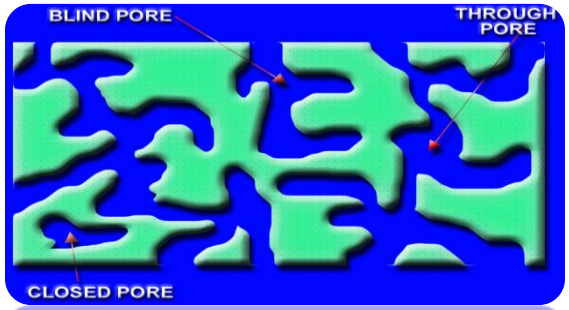
Envelope surface area is the surface area of pores which permit flow (through pores, pores between particles).



Throughpore in a Powderbed



Throughpore in a Consolidated Material

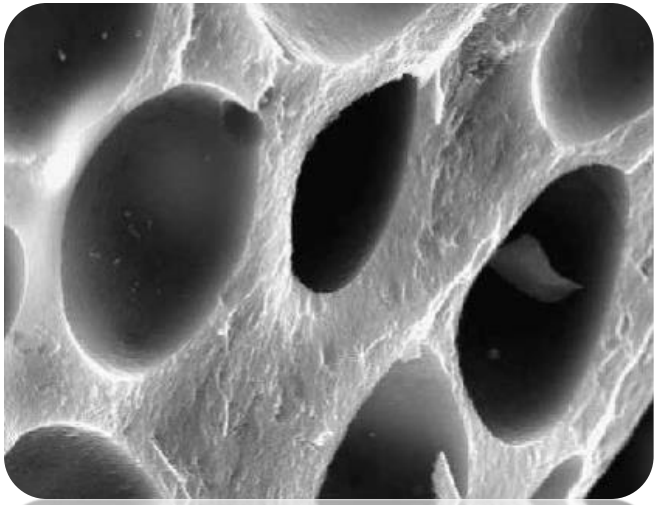


The Envelope Surface Area Analyzer

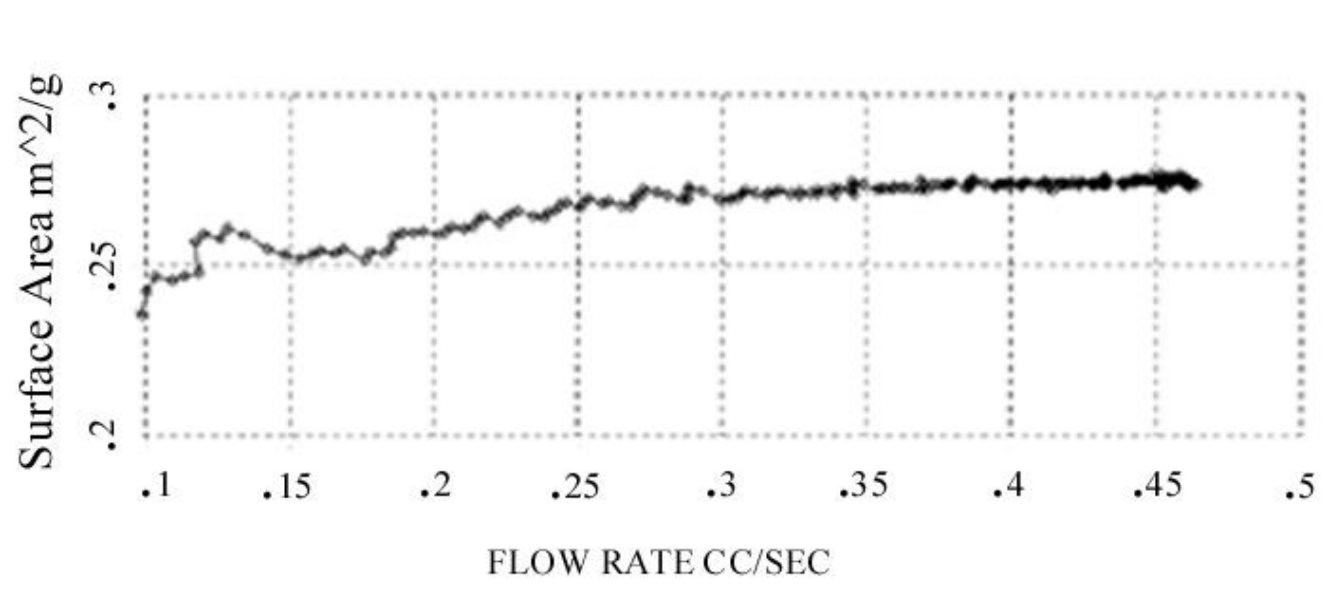
Pore surface area computed using Kozeny-Carman equation:

$$\left[\frac{\underline{F}\cdot l}{p_{diff}\cdot A}\right]=\left[\frac{P^3}{K\cdot(1-P)^2\cdot S^2\cdot\mu}\right]+\left[\frac{Z\cdot P^2\cdot\pi}{(1-P)\cdot S\cdot(2\pi\cdot\overline{p}\cdot\rho)^{1/2}}\right]$$

$\underline{F}$	=	flow rate at average pressure P
l	=	thickness of sample
p_{diff}	=	differential pressure
$\overline{p}$	=	average pressure
A	=	area of sample
P	=	porosity
S	=	through pore surface area per unit volume of solid
ρ	=	density of gas at average pressure,
μ	=	viscosity
K	=	a constant. 5 is used for most media
Z	=	a constant. (48 / 13 π)



OUTPUT OF THE ENVELOPE SURFACE AREA ANALYZER



THE ENVELOPE SURFACE AREA ANALYZER

COMPARISON WITH BET

Materials with limited blind pores

	Surface area, m2/g	
Material	BET	ESA
Magnesium Stearate Powder – A	12.16	11.13
Magnesium Stearate Powder –B	7.13	6.97
Glass Bubbles – A	0.92	0.89
Glass Bubbles – B	1.91	1.76
Polyethylene and Polytetrafluoroethylene Powder	1.86	1.69
Lead Monoxide Powder	0.11	0.25
Fibrous Battery Separator	0.52	0.52

- Excellent agreement: BET and ESA
- For the lead monoxide sample, sample quantity was not enough for accurate BET calculations

THE ENVELOPE SURFACE AREA ANALYZER

Table 2. Comparison between ESA and BET techniques

		ESA	BET
1.	Surface area	Through-pore	Through-pore & Blind-pore
2.	Low surface area sample	Large sample not required	Large sample required
3.	High surface area * sample	Not high accuracy	High accuracy
4.	Test temperature	Room temperature	Liquid nitrogen
5.	Sample preparation	None	Evacuation & baking
6.	Test gas	Non-reacting	Non-reacting & highly pure
7.	Test time	Fast	Slow
8.	Expense	Inexpensive	Expensive
9.	Test operation	Simple	Involved

THE ENVELOPE SURFACE AREA ANALYZER

AVERAGE PARTICLE SIZE AND AVERAGE FIBER DIAMETER

- Average particle size of powders computed assuming spherical particles of uniform size

$$D_p = 6 / (S_m \ \rho_p)$$

D_p = average particle size
S_m = the surface area per unit mass
ρ_p = the density of particles

- Average fiber diameter, D_f computed assume cylindrical fibers of uniform diameter and length

$$D_f = 4 / (S_m \rho_f)$$

ρ_f is the density of the fiber.

THE ENVELOPE SURFACE AREA ANALYZER

Average Particle size

Sample ID	Particle Size, μm	BET Particle Size, μm	Mercury Intrusion Particle Size, μm
Magnesium stearate A	0.43	0.39	–
Magnesium stearate B	0.69	0.67	–
Glass bubbles A	14.8	14.4	–
Glass bubbles B	22.3	20.5	–
Alumina #54	79	–	76
Alumina #180	32	–	29

THE AVERAGE FIBER DIAMETER ANALYZER

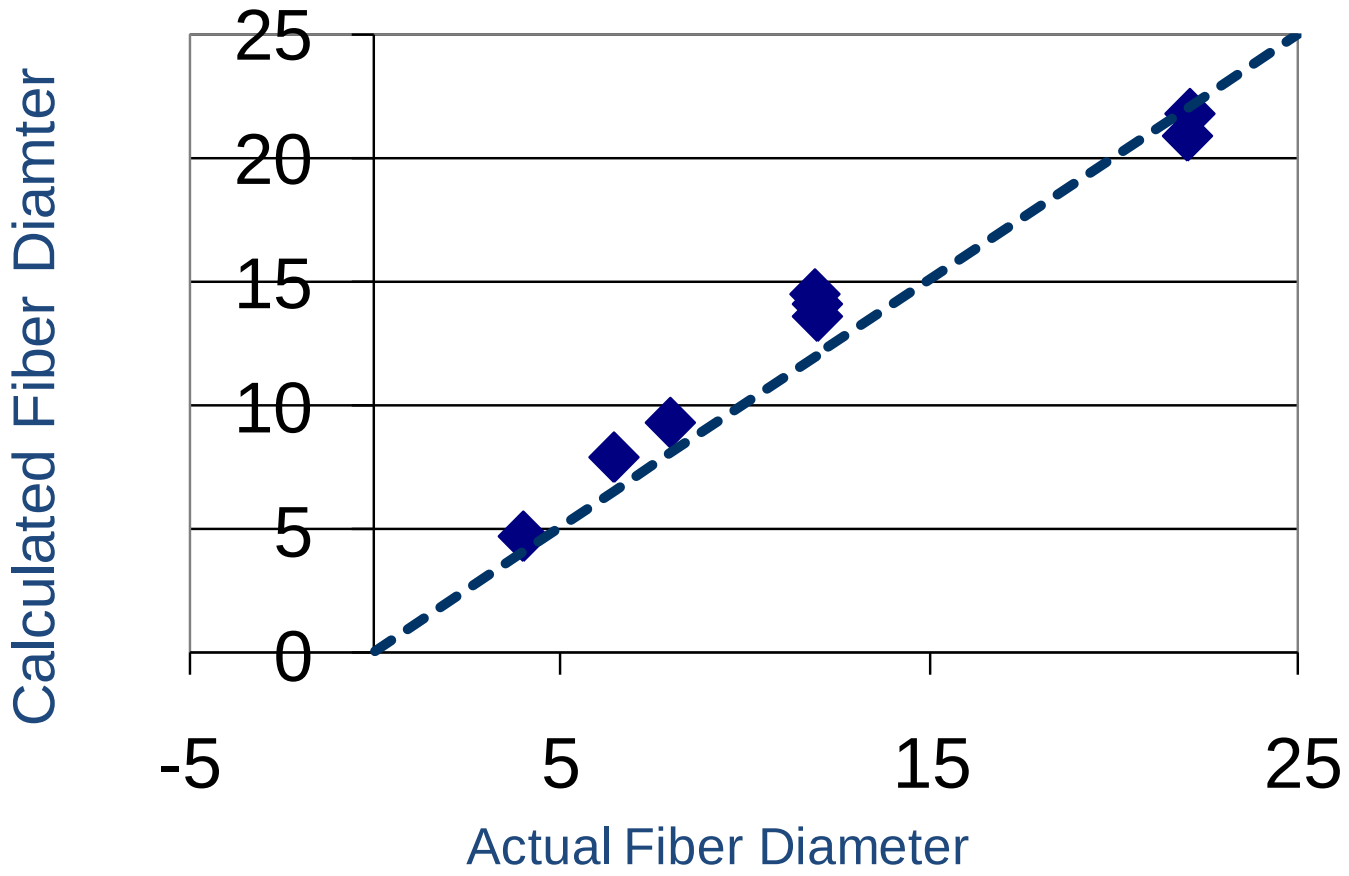
- Davies used the measurements made on a wide variety of fibrous materials and their average fiber diameters
- Experimental results of Davies lead to the following relationship:

$$\frac{4 \cdot \Delta P \cdot A \cdot R^2}{\mu \cdot \underline{F} \cdot l} = 64 \cdot c^{1.5} \cdot \left(1 + 52 \cdot c^3\right)$$

C=(1-P), P=Porosity, ≈ 0.7 - 0.99

- This is used to compute average fiber diameter

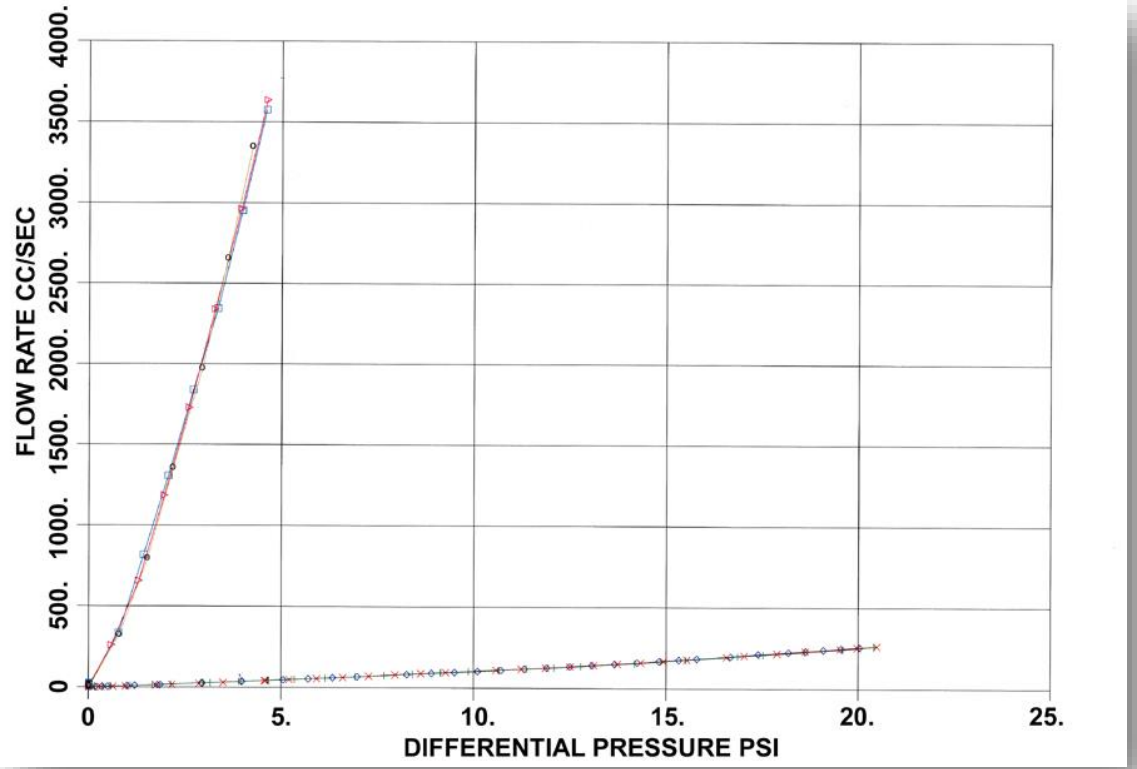
THE AVERAGE FIBER DIAMETER ANALYZER



- The reproducibility of the results was better than ± 3 %.
- The measured values are within 20 % of the actual values.

HIGH FLOW GAS PERMEABILITY

Permeability measured in the High Flow Porometer using a ceramic cartridge & in the Capillary Flow Porometer using a small sample



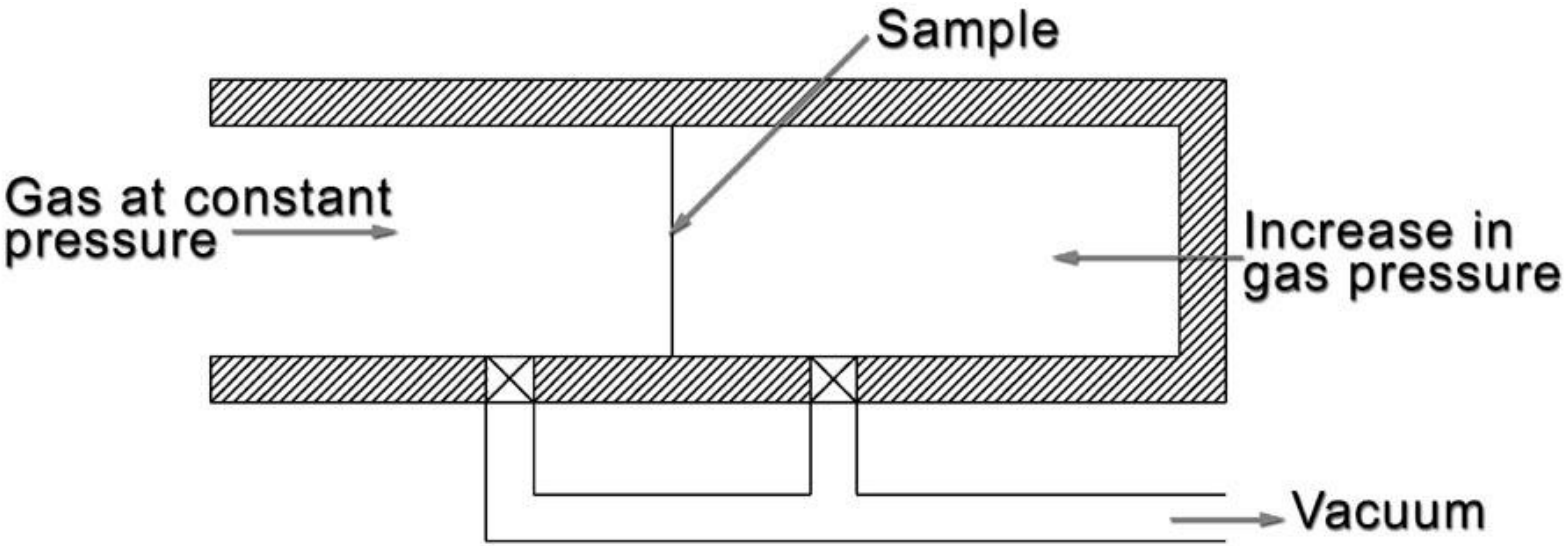
Instrument	Permeability, darcies
Capillary Flow Porometer	0.0447 ± 0.0021
High Flow Porometer	0.0424 ± 0.0020

DIFFUSION PERMEABILITY

For samples showing very low permeability

Principle:

Flow rate computed from rate of increase of pressure in the outlet side



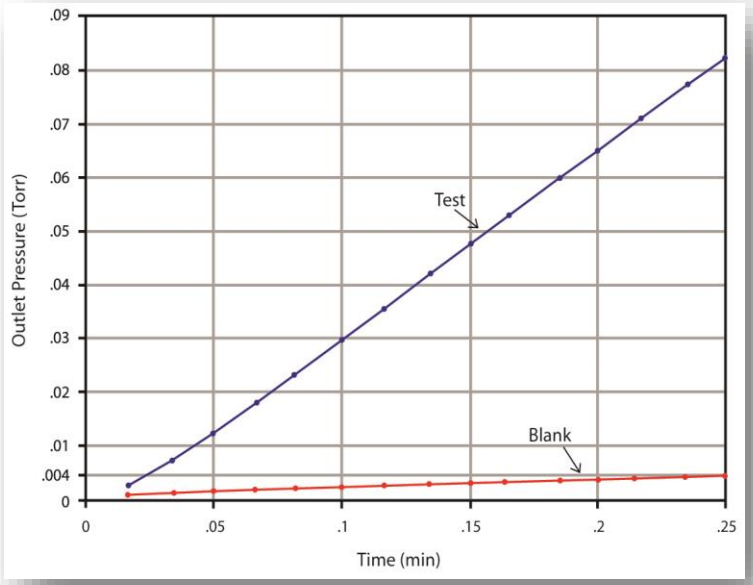
DIFFUSION PERMEABILITY: TYPICAL RESULTS

- Flow rate computed from outlet pressure

p= outlet gas pressure
t = time
Vo = volume of outlet chamber
T, Ts = test & standard temperature in K
Ps= standard pressure

$$F = \left[\frac{V_o \cdot T_s}{P_s \cdot T} \right] \cdot \frac{dP}{dt}$$

- The test data shown are corrected using data from blank run



Change of outlet gas pressure with time in the test and in the blank run

THE INSTRUMENT

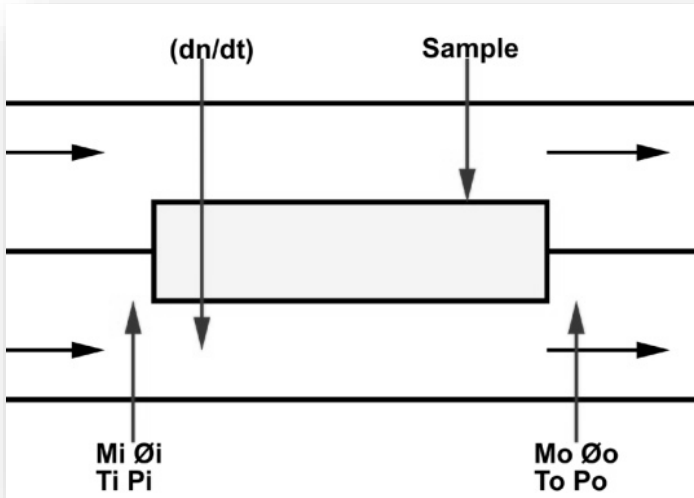
- Can measure flow rate as low as 10^{-4} cm^3/s
- Pressures up to 200 psi,
- Temperatures up to 200 °C
- Many gases including
  H_2, CO_2, & NH_3
- Transmission rates of vapors can also be measured

WATER VAPOR TRANSMISSION ANALYSIS (ASTM F-2298)

Principle

Vapor transport rate computed from known T, P, ϕ and M.

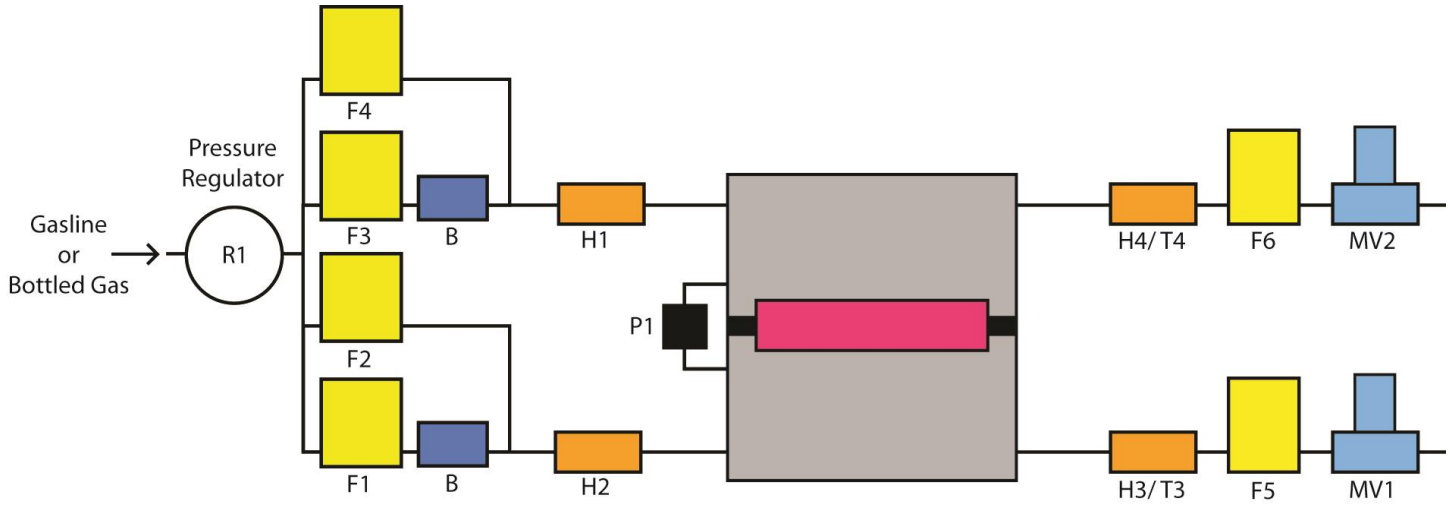
$$\left[\frac{dn}{dt}\right] + \left[\frac{P_{e,i\phi_i}}{P_i} + M_i\right] = \left[\frac{P_{e,o\phi_o}}{P_o} + M_o\right]$$



dn/dt = rate of vapor transport in moles
P_e = equilibrium vapor pressure at temperature, T, and total pressure, P.
ϕ = humidity = (P_v/P_e)
P_v = partial pressure of vapor in unsaturated gas
M = rate of gas flow in moles
I = incoming flow
o = outgoing flow

WATER VAPOR TRANSMISSION ANALYSIS

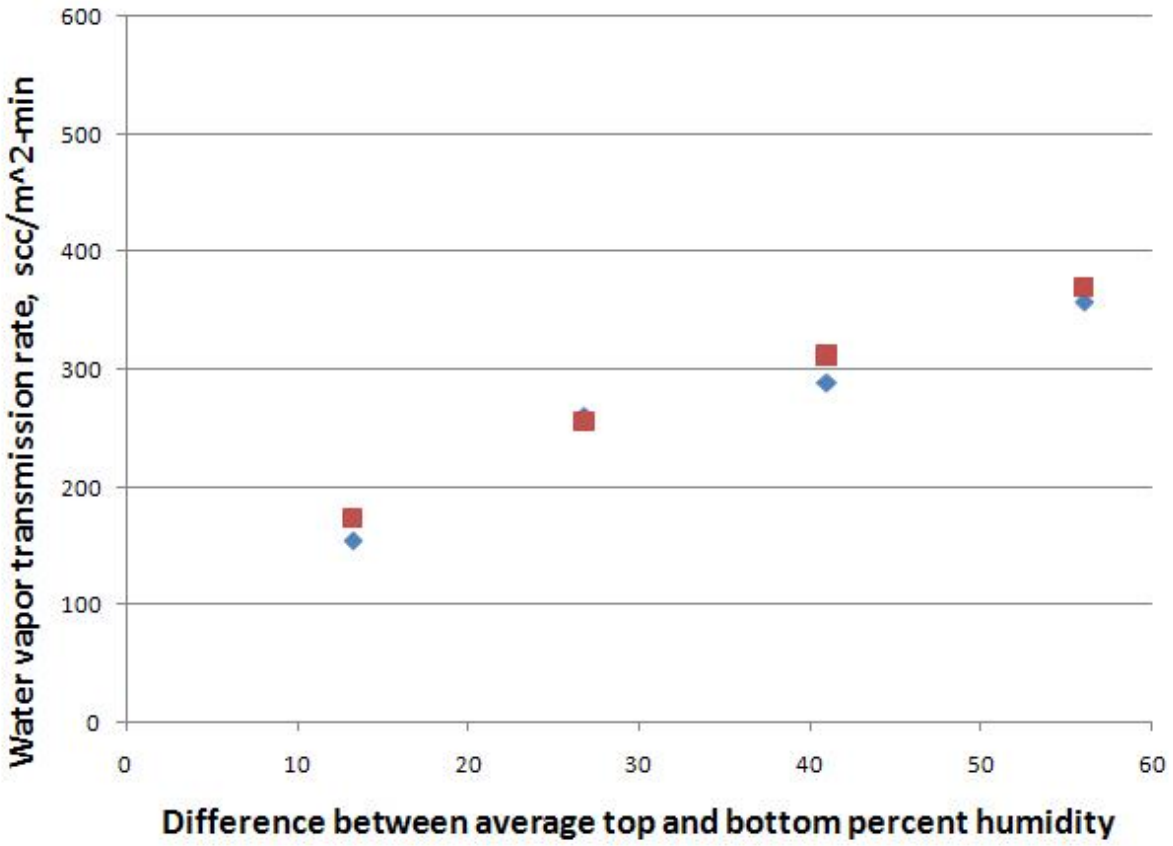
- Humidity on each side is independently maintained
- Pressure kept near one atmosphere and temperature is kept constant
- Humidity, flow rate, temperature, and differential pressure are measured



F = Flow Controller / Flow meter
B = Bubbler
H = Humidity Sensor
MV = Valves
P1 = Differential Pressure Gauge
T = Temperature Sensor

WATER VAPOR TRANSMISSION ANALYSIS

VAPOR CONCENTRATION: 5 TO 95 % HUMIDITY



Two repeated tests show excellent repeatability

ADVANCED WATER VAPOR TRANSMISSION ANALYSIS

MEASUREMENTS IN TEMPERATURE GRADIENT

Temperature: -5° to 90°C

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	Temperature ˚C	Humidity %
Side 1	18	10.4
Side 2	5.8	90.5

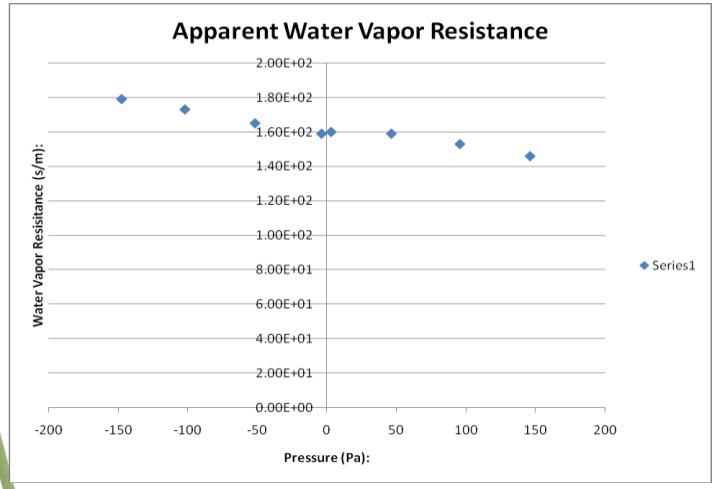
Transmission Rate = 7.44 Kg/m^2-day

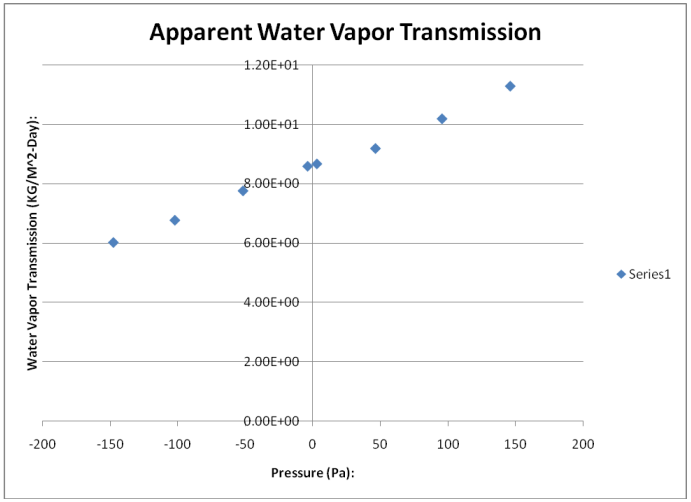
INSERT Correction: side 1=30.3 C, 87.7 %, side 2=5.5C, 36 %

ADVANCED WATER VAPOR TRANSMISSION ANALYSIS

MEASUREMENTS IN PRESSUREGRADIENT

Pressure drop: Several hundred pascals



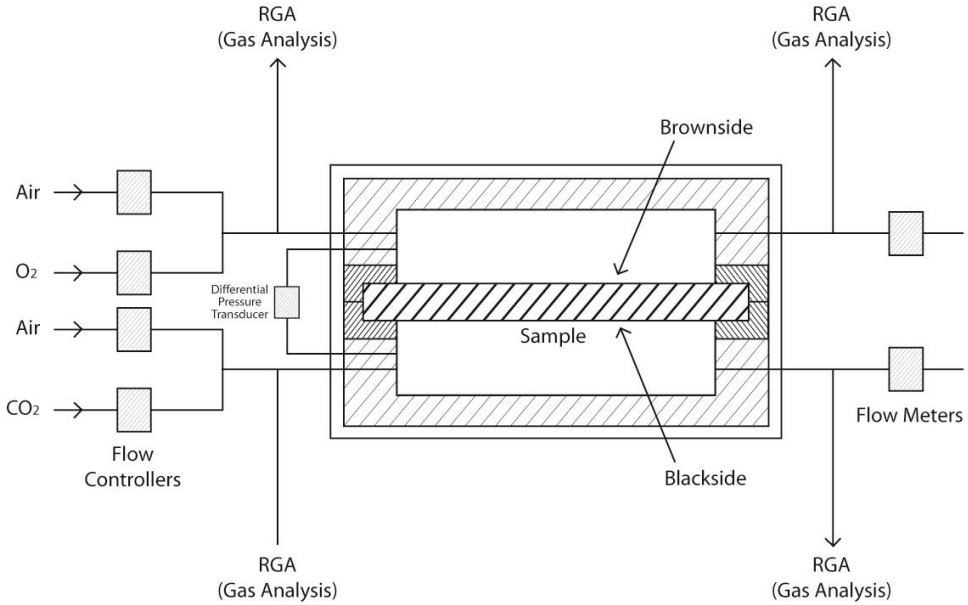


GAS TRANSMISSION ANALYSIS

- Transmission of a gas at the same total pressure
  - Due to its concentration gradient
  - Over a range of temperatures
  - Over a range of humidity
- Important for many fabric applications such as:
  - Breathability
  - Comfort
- Important for storage materials

GAS TRANSMISSION ANALYZER

- Gas containing the test gas flows over one side of sample
- Gas containing the test gas flows over the other side of sample
- Differential pressure kept at zero
- Flow rates measured
- Test gas concentrations measured at the four entry and exit points



GAS TRANSMISSION ANALYSIS

Results

Transmission rate, R: $R = (Fo - Fi) / A$

R= test gas transmission rate per unit area from high concentration side to low concentration side
Fo = test gas flow rate at the output on the low concentration side
Fi = test gas flow rate at the input on the low concentration side
A = area of the sample permitting flow

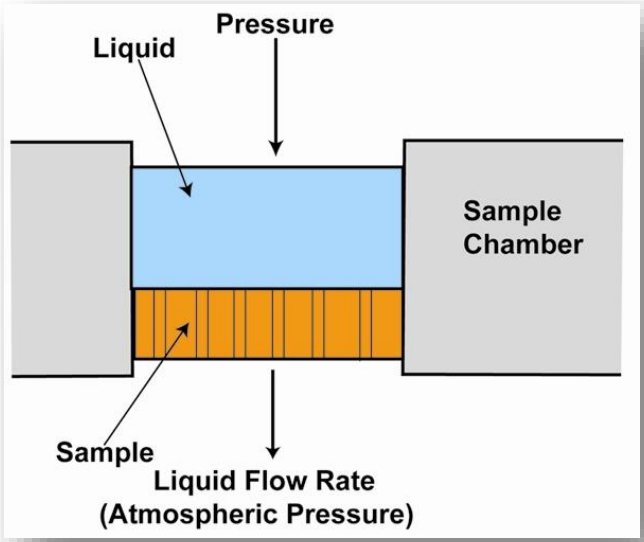
	CO_2		O_2	
Sample #	Transfer Rate sccm/cm^2	Difference in concentration %	Transfer Rate sccm/cm^2	Difference in concentration %
1	0.1227	2.2017	0.2008	1.8479
2	0.1196	2.1342	0.1990	1.8559
3	0.1177	2.0976	0.1851	1.9398
4	0.1449	1.9434	0.2042	1.7374

LIQUID PERMEABILITY PRINCIPLE

Darcy's Law in the following form is used

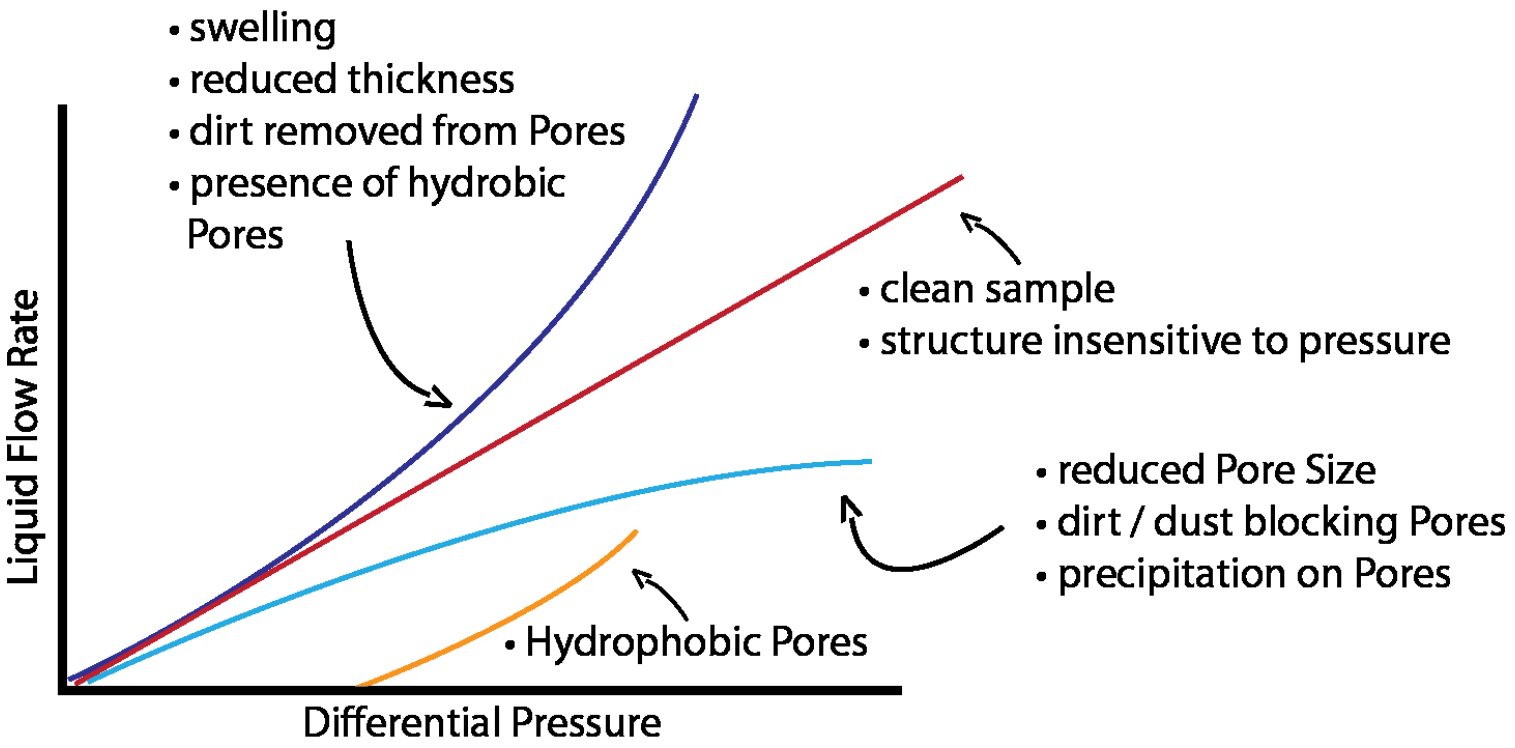
$$\underline{F} = k \cdot \left(\frac{A}{\mu \cdot l} \right) \cdot \left(P_i - P_o \right)$$

l = thickness of porous material
P_i = inlet pressure
P_o = outlet pressure
$\underline{F}$ = volume flow at average pressure



LIQUID PERMEABILITY

Variation of Flow rate with Differential Pressure



MICROFLOW LIQUID PERMEABILITY

- A sensitive weighing balance is used to measure the liquid flowing out of the sample

- Water permeability of three commercial samples:

Sample Fabric #	Permeability	
	cc/min-cm^2-psi	darcy
#1	0.22×10^{-3}	1.1×10^{-5}
#2	0.29×10^{-3}	1.2×10^{-5}
#3	0.57×10^{-3}	2.6×10^{-5}

CUSTOM LIQUID PERMEAMETERS

- Permeability measurable from Radial or In-Plane (x-y plane) Flow Using the following relation:

$$\underline{F} = \left[\frac{k \cdot 2\pi \cdot t}{\mu \cdot \ln\left(\frac{R_2}{R_1}\right)} \right] \cdot \left(P_i - P_o\right)$$

- Permeability at High Temperatures up to 120˚C
- Permeability at High Pressure (Several hundred psi)
- Permeability through Samples under Compression
- Odd shaped samples
- Recirculation of hot liquid

CUSTOM LIQUID PERMEAMETERS

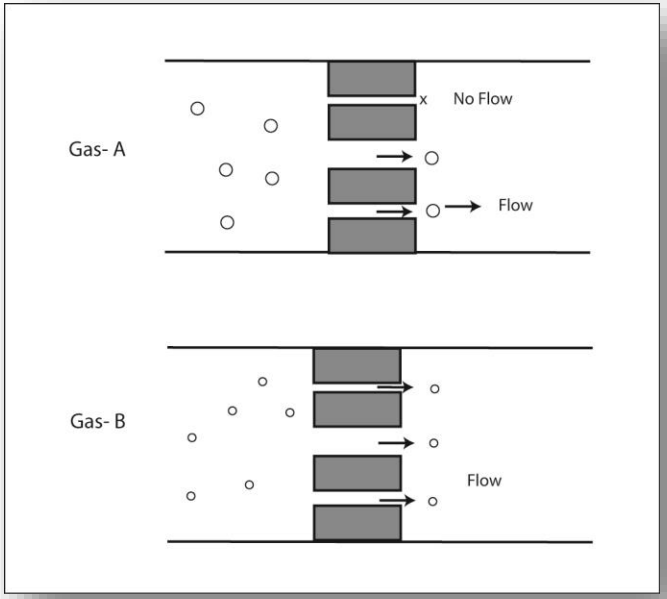
The PMI Liquid Permeameter capable of measurements:

- At high-pressure
- At high-flow rates
- At elevated temperatures
- Using heated and recirculating oil

DIFFERENTIAL GAS DIFFUSION POROMETER

PRINCIPLE:

- The flow rate of a gas through the sample is measured as a function of differential pressure.



- Time rate of pressure increase in outlet chamber is measured to compute flow rate.

Gas flow through pores having diameter larger than the molecular size of the gas

MEASURABLE PORE STRUCTURE CHARACTERISTICS

- Normally mean free path > Pore diameter, D
  - For 27˚C, 5 Torr pressure, & 5 Å molecular diameter
    Mean free path 0.06 μm
  - Flow through pore of diameter, D, is **Molecular**

$$F = \left(\frac{T_s}{T}\right) \cdot \left(\frac{1}{6 \cdot \tau \cdot P_s}\right) \cdot \sqrt{\frac{2\pi \cdot R \cdot T}{M}} \cdot \left(\frac{\Delta P}{l}\right) \cdot \left(D^3\right)$$

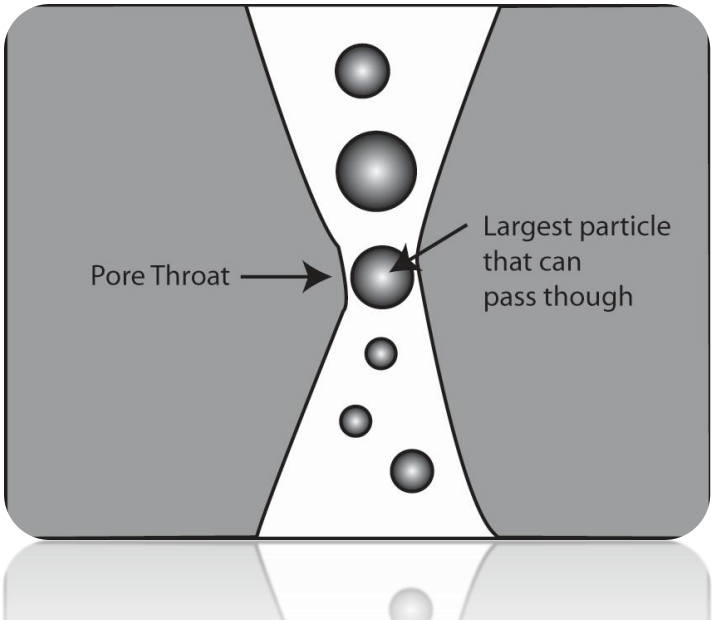
F	= flow rate in volume at STP (T_s & P_s) per unit time
T	= test temperature
τ	= tortuosity
M	= molecular weight of gas
ΔP	= pressure drop
l	= thickness

PORE-THROAT DIAMETER

- Gas flows through all pores having throat diameter
  - molecular diameter
- Flow rate through all such pores assuming $\tau = 1$ and $T_s = T$:

$$\left[\frac{F\left(M^{1/2}\right)}{\Delta P}\right] = \left[\frac{1}{6 \cdot P_s \cdot l}\right] \cdot \sqrt{2\pi \cdot R \cdot T} \cdot \sum D^3$$

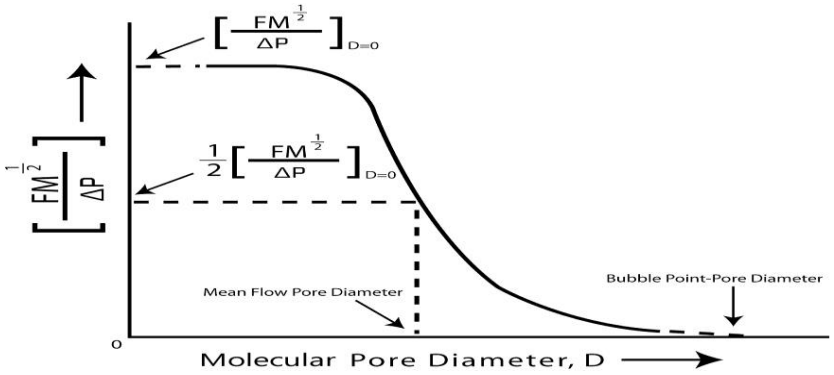
D = pore throat diameter
Σ = summed over all pores of diameter greater than the molecular diameter of the gas

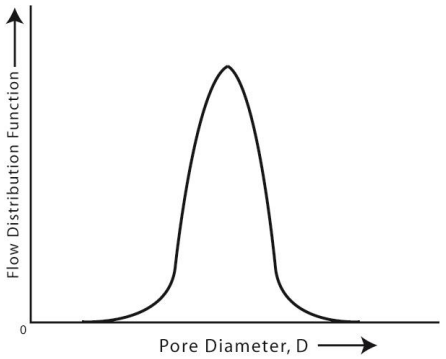


Gas flows through pores having throat diameter greater than the size of the gas molecule

CHANGE IN FLOW RATE WITH CHANGE IN MOLECULAR SIZE

Very large molecular diameter	No flow
Decreasing molecular size	Increasing gas flow
Very small molecular size	High flow
As D $\rightarrow$ o	No flow increase with decrease in size
Distribution function, f:	$f = -\frac{dF'}{dD}$



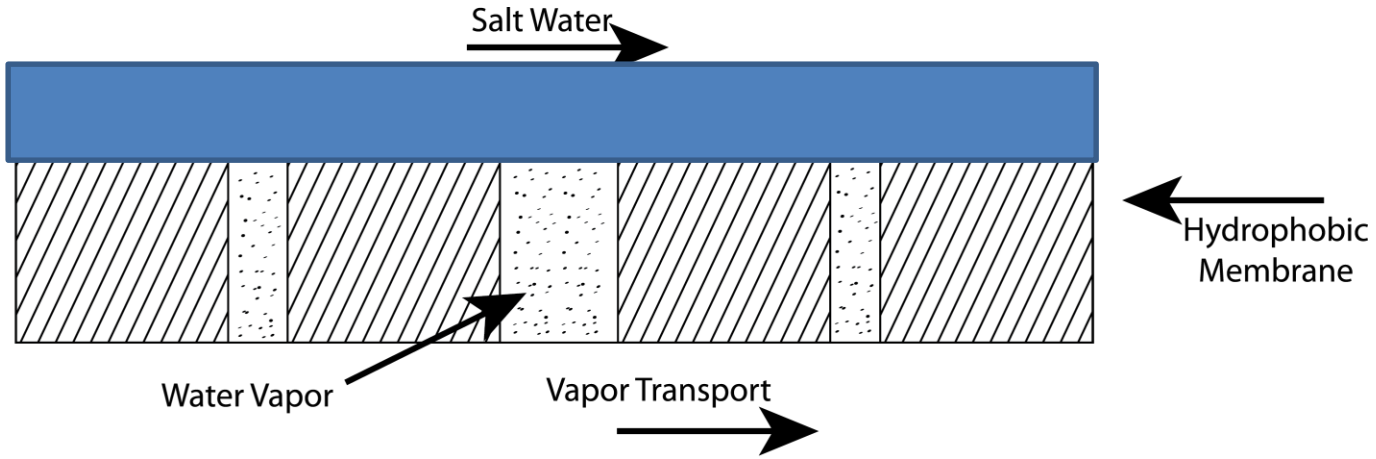


Variation of flow function, $[F(M)^{1/2} / \Delta p]$, with molecular diameter of the gas

MEMBRANE DISTILLATION

Principle

- Salt water flows on top of hydrophobic membrane
- Water doesn't enter membrane, but vapor fills pores
- Vapor removed from other side of membrane by flowing cold water, flowing air, or Vacuum
- Vapor migrates through pores



Removal of Vapor by Flow of Cold Water, Vacuum, & Air Flow.

INSTRUMENT

- Three sample chambers for water, vacuum & air
- Pressure, temperature and flow on both sides independently controlled
- Penetrometers measure change in water volume
- Conductivity meters measure change in salt content
- Measured humidity changes yield transfer rate
- Flat sheet and hollow fiber membranes can be tested
- Fully automated

PMI Water vapor transmission analyzer for membrane distillation

MEMBRANE MAKING MACHINE

- These machines can be used to make membranes of desired characteristics
- Compact & manageable machines
- Both hollow fiber and flat sheet membranes can be made

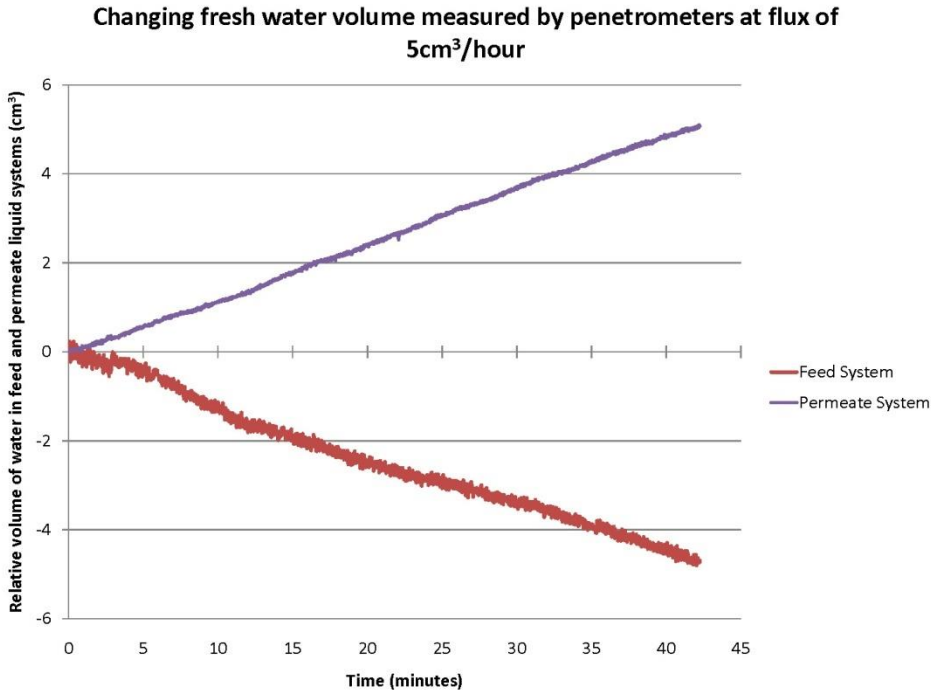
Hollow Fiber Membrane Machine

Flat Sheet Membrane Machine

TYPICAL RESULTS

Water-Water system

- With increase in time volume on the feed side decreases & volume on the permeate side increases
- The magnitudes of the changes are identical



CONCLUSIONS

- Development of a number of permeameters have been discussed
- The wide range of applicability of these instruments has also been considered
- Continuous update of instruments is one of our primary goals at PMI as we attempt to meet the changing needs of our customers.

Thank You!