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Research Laboratory

GAS PERMEATION THROUGH THE VACUUM ENVELOPE

by

F. J. Norton

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ABSTRACT

The relationships and available values for permeation rate, diffusion constant, and solubility of various gases and solids are discussed. Values are given for walls of glass and metal in differing external environments. Some generalizations can be formulated.

True permeation through the wall is due to solution and then diffusion in the wall material. Experiments to measure it must be carefully devised to distinguish its effects clearly from various other gas sources as real leaks, pump back-streaming, gas originally in and on the wall material, electrolysis in glass walls, or oxide dissociation effects. Criteria are given for making sure true permeation is being measured.

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GAS PERMEATION THROUGH THE VACUUM ENVELOPE *

F.J. Norton

INTRODUCTION

The gases which spoil the attainment of ultrahigh vacuum may come in, on, or through the envelope wall material, or through very small actual holes. The flow rate through the holes, when their size is small compared to the gas mean free path in the external atmosphere, is proportional to $(T/M)^{1/2}$, T being absolute temperature, and M molecular weight of the gas.

The laws governing permeation through the initially degassed wall material are more complicated, and several steps are involved (Fig. 1). The gas is first adsorbed, then dissolved in the external surface layer. It then slides down the concentration gradient, according to Fick's law, and diffuses on to the vacuum side where it is desorbed and escapes. The whole permeation process is an exponential function of the temperature. This is because it is a process involving an activation energy for the molecular solid structure through which gas permeation occurs. The process depends in a specific manner on the particular solid and gas involved.

In some cases of diffusion when the concentration in the solid is high, the diffusion coefficient D varies with concentration.

For the cases here considered, the solubility S is very low and D is, in general, constant. There is then the relationship at constant temperature:

$$P = D \times S$$

where P is the permeation rate.

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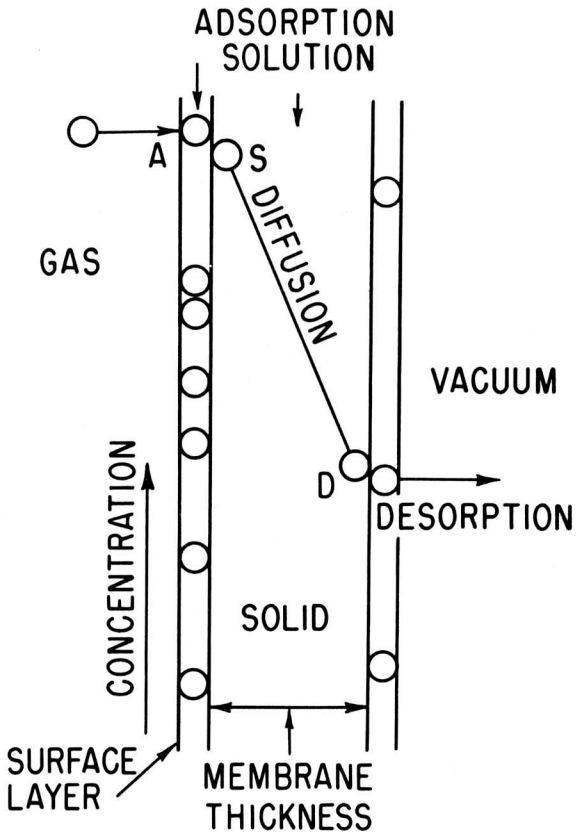

Fig. 1 Diagram of the permeation process.

The permeation rate is easiest to determine experimentally. A cell with a low- and high-pressure side is divided by a membrane of the material studied, with known area, thickness, and temperature. The low-pressure side leads to a device for measuring the rate and for analyzing the permeating gas. A mass spectrometer is ideal for the purpose. It measures the rate continuously and directly, rather than integrating over a time period as must be done with collection methods. On the high-pressure side, there can be applied either a vacuum for degassing, or known pressures of the specific gas under study.

CRITERIA FOR PERMEATION

Certain criteria must be fulfilled to distinguish, unambiguously, true permeation from gases flowing through an actual hole, and gases derived from the walls of the envelope.

1. The membrane must be thoroughly degassed by a good vacuum applied on each side.

2. The particular gas whose permeation rate is being measured is applied at known pressure to the high side.

3. The slow rise in rate of that particular gas is observed, to a steady-state rate.

4. Analysis should be made as completely as possible, of all the other gases appearing on the low-pressure side.

5. The gas on the high-pressure side should be removed, and the rate of that particular gas must be shown to go slowly down to zero.

These five steps must be carried out to be absolutely sure true permeation is being measured.

The effect of a hole can be distinguished from true permeation in two ways. Very rapid rise of the particular gas on the low side after application to the high side may indicate a hole. Variation of the rate with $(T/M)^{1/2}$ is shown by testing with gases of differing molecular weight.[1] Variation following this law shows that a hole exists.

The diffusion constant, when independent of concentration, is most conveniently measured by the time lag method of Daynes[2] and Barrer.[3] In this, the effective time lag L in seconds to attain steady-state flow through a membrane of thickness d in cm is related to the diffusion constant:

$$D = d^2/6\ L.$$

Mathematical details and recent applications are given by Van Wieringen and Warmoltz[4] and by Swets, Lee, and Frank.[5] Here again, to measure the diffusion constant involved in true permeation, the time lag method should start with the membrane completely degassed, and the time lags on and off should be symmetrical and long compared to pump-out times in the rest of the vacuum system. Conversely, knowing the diffusion constant, the time lag can be computed. The diffusion constant depends on the wall thickness and temperature, but not on gas pressure or surface area. The permeation rate involves all these factors.

PERMEATION THROUGH GLASSES

There are many published data on helium.[5-8] Figure 2 shows the helium permeation rate as a function of temperature for a variety

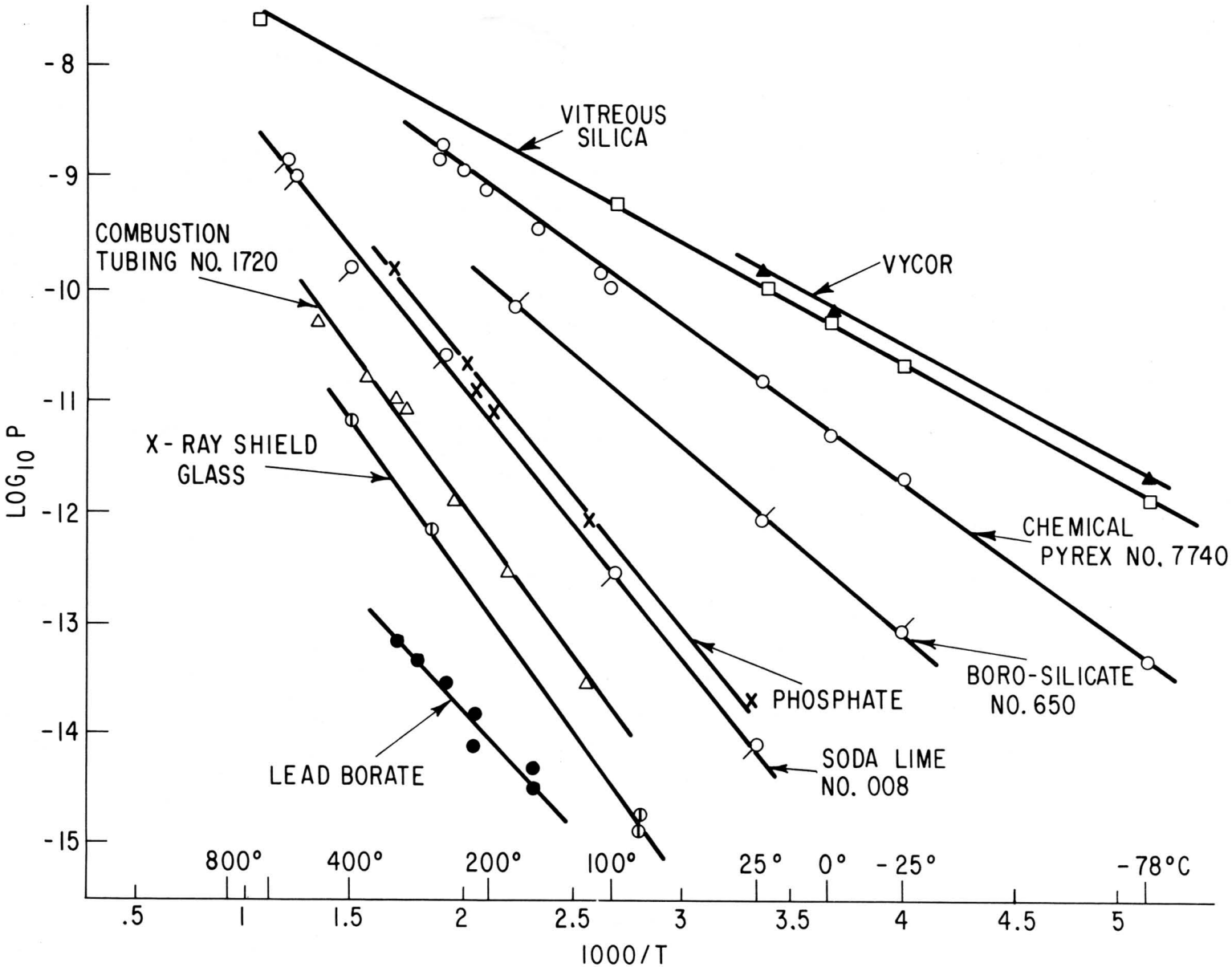

Fig. 2 Helium permeation rate P through various glasses. Units of P: cm^3 gas (STP) per second for 1 mm thick per cm^2 area per cm gas pressure difference. Plot is $Log_{10}P$ vs 1000/T.

of different kinds of glasses. Helium is fastest through vitreous silica and Vycor. As the glass formers SiO_2 and B_2O_3 are replaced by non-glass formers, the rate goes down sharply by many orders of magnitude.[8]

In addition, I have recently measured the permeation rates, P, for argon and oxygen diffusing through vitreous silica. These are presented in the following Table I. The diffusion constants, D, were determined at the same time by the lag method. This enables a calculation of the solubility, S, to be made, since P is the product of D and S.

TABLE I

Argon Through Vitreous Silica

	Permeation Rate		Diffusion Constant		Solubility
C°	P	Log P	D	Log D	(S)
800	2.3×10^{-14}	$\overline{14}.36$			
900	8.4×10^{-14}	$\overline{14}.92$			
1000	2.5×10^{-13}	$\overline{13}.40$			
1050	4.0×10^{-13}	$\overline{13}.60$	1.1×10^{-9}	$\overline{9}.04$	0.003
1100	6.8×10^{-13}	$\overline{13}.83$			

Gaseous Oxygen Through Vitreous Silica

	Permeation Rate		Diffusion Constant		Solubility
C°	P	Log P	D	Log D	(S)
700	2.1×10^{-15}	$\overline{15}.32$			
800	1.6×10^{-13}	$\overline{13}.20$			
900	5.5×10^{-13}	$\overline{13}.74$	2.65×10^{-9}	$\overline{9}.42$	0.0017
1000	1.6×10^{-12}	$\overline{12}.20$	6.6×10^{-9}	$\overline{9}.82$	0.0019
1100	3.8×10^{-12}	$\overline{12}.58$	1.45×10^{-8}	$\overline{8}.16$	0.0020

The units used are:

P, permeation rate in cm^3 gas (STP) per second for 1-mm-thick wall, 1 cm^2 area, per 1 cm gas pressure difference.

D, diffusion constant, in cm^2/sec.

S, solubility, cm^3 gas (STP) per cm^3 solid, for 76 cm gas pressure applied. For these units, S = 7.6 P/D.

Note that the wall thickness is expressed in centimeters for determinations of diffusion constant by the lag method, but is in millimeters for permeation rate P.

The experimental points are plotted in Figs. 3 and 4, and from these tabulated values were obtained. Both argon and oxygen give the usual straight line on the log P or log D against 1/T plot.

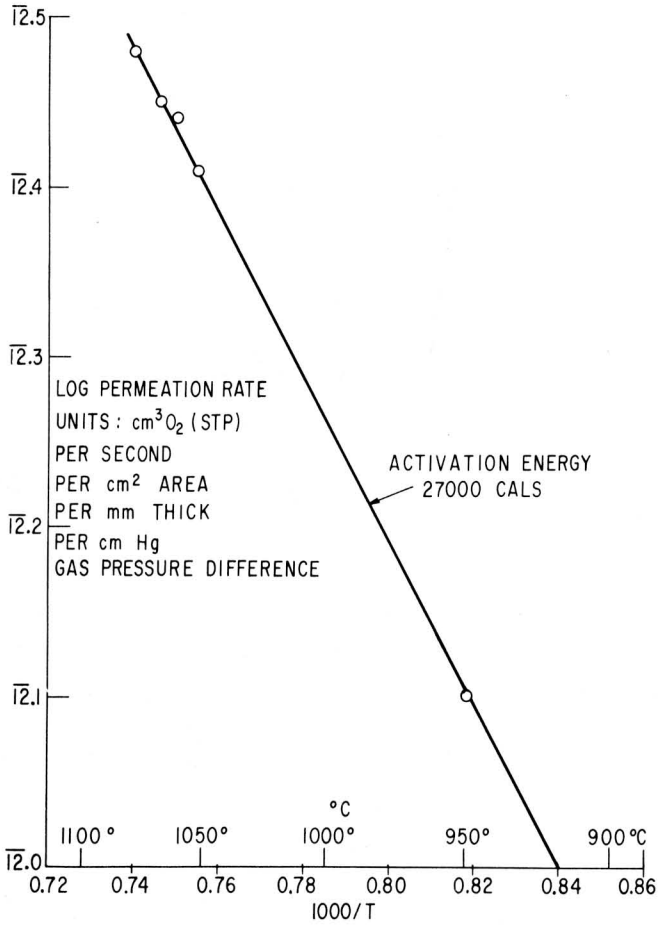

Fig. 3 Permeation of gaseous oxygen through vitreous silica. P in usual units, as in Fig. 2. $Log_{10}P$ vs 1000/T.

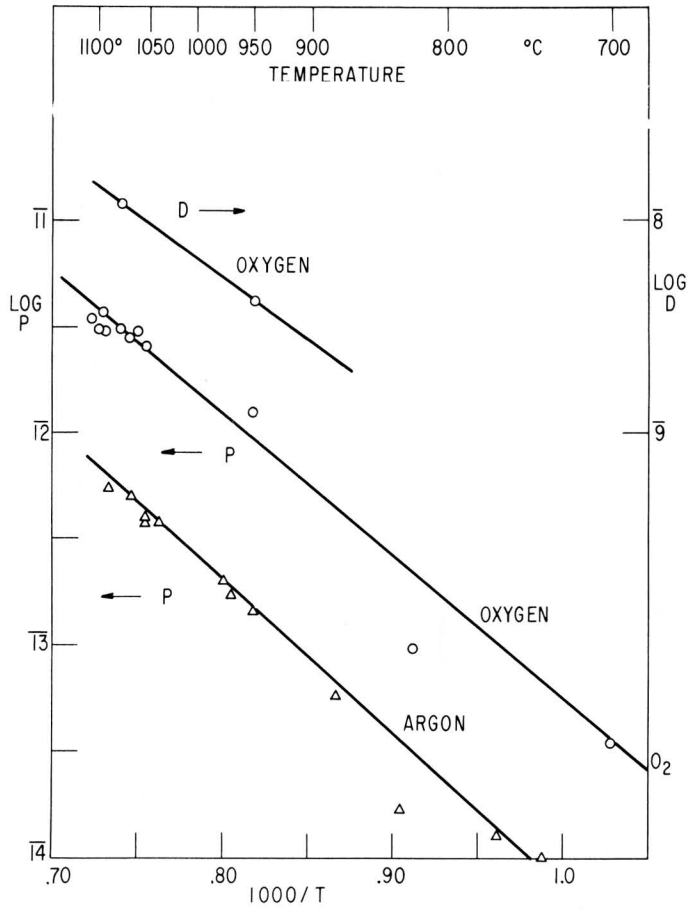

Fig. 4 Oxygen and argon through vitreous silica. P in usual units, as Fig. 2. D in cm^2/sec. Log_{10} of P and D vs 1000/T.

Since oxygen ions are a constituent of the silica lattice, it was of especial interest to find out if gaseous oxygen applied to the high side diffused through in the molecular form. The flow rate in cm^3/sec for 1 mm thickness, 1 cm^2 area, was found to be proportional to the first power of the pressure. This indicates the diffusing species is the O_2 molecule. The experimental data are shown in Fig. 5.

The high activation energy of 27,000 cals/mole was found for O_2 through SiO_2. This leads to a very low extrapolated value for the permeation rate of O_2 through vitreous silica, of the order of 10^{-28} at 25°C.

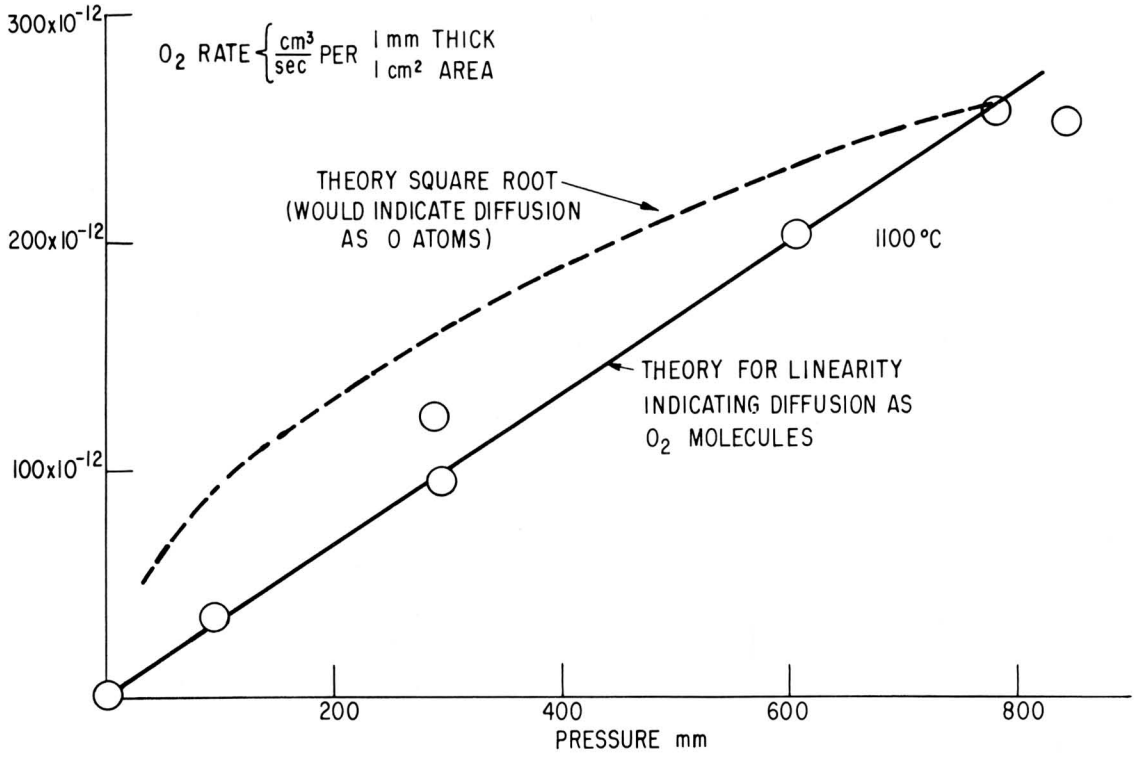

Fig. 5 Dependence of O_2 flow rate (cm^3/sec for 1 mm thick, 1 cm^2 area) through vitreous silica at 1100°C as a function of pressure in mm.

INFLOW FROM THE ATMOSPHERE

To visualize the importance of the inflow of atmospheric gases through the walls of a vacuum device, consider a bulb of vitreous silica at 25°C with walls 1 mm thick, surface area 100 cm^2 and volume 330 cm^3. Three assumptions will be made: (1) the walls have been completely degassed; (2) steady-state flow has just been established at 25°C; and (3) the initial pressure is 10^{-16} mm equivalent to 3.4 gas atoms per cm^3.

The gases in the atmosphere have the abundances[9] shown in Table II. Some values for the permeation rate extrapolated to 25°C are given in Table III. In Table IV, the abundance (expressed as cm pressure) times the permeation rate gives the order of inflow of the atmospheric gases. It is seen that the gases of low abundance show the highest inflow, and the order of accumulation in the silica bulb is: (1) helium, (2) neon, and (3) hydrogen. A big difference separates the succeeding gases oxygen, nitrogen, and argon.

TABLE II

Atmospheric Abundances

	% By Volume	Partial Pressure (in millimeters)
N_2	78.08	5.95×10^{2}
O_2	20.95	1.59×10^{2}
Ar	0.93	7.05
CO_2	.033	2.5×10^{-1}
Ne	1.8×10^{-3}	1.4×10^{-2}
He	5.24×10^{-4}	4.0×10^{-3}
Kr	1.1×10^{-4}	8.4×10^{-4}
H_2	5.0×10^{-5}	3.8×10^{-4}
Xe	8.7×10^{-6}	6.6×10^{-5}
H_2O	1.57	1.19×10^{1}
{50 %RH, 25°C}		
CH_4	2×10^{-4}	1.5×10^{-3}
O_3	7×10^{-6}	5.3×10^{-5}
N_2O	5×10^{-5}	3.8×10^{-4}

Compendium of Meteorology, page 6,
American Meteorological Society,
Boston, 1951.

TABLE III

Vitreous SiO_2, 25°C

		Gas Permeation Rate Per cm Pressure	Diffusion Constant, D
	He	5×10^{-11}	2×10^{-8}
	Ne	2.0×10^{-15}	5×10^{-12}
	H_2	2.8×10^{-14}	5×10^{-12}
Estimated	O_2	1×10^{-28}	1×10^{-24}
Estimated	Ar	2×10^{-29}	2×10^{-25}
Estimated	N_2	2×10^{-29}	2×10^{-25}

TABLE IV

Order of Flow of Atmosphere into SiO_2 Bulb at 25°C
(for 1 mm thick, 1 cm^2 area)

	Atmospheric Abundance, C $\left(\frac{cm}{\text{Partial Pressure}}\right)$	Permeation Rate, P	C x P = Inflow (cm^3/sec)	Order of Inflow	Atoms Per Sec
N_2	5.95×10^{1}	2.0×10^{-29}	1.2×10^{-27}	5	
O_2	1.59×10^{1}	1.0×10^{-28}	1.6×10^{-27}	4	
Ar	7.05×10^{-1}	2.0×10^{-29}	1.4×10^{-29}	6	
Ne	1.8×10^{-2}	2.0×10^{-15}	3.6×10^{-17}	2	900
He	4.0×10^{-4}	5.0×10^{-11}	2.0×10^{-14}	1	500,000
H_2	3.8×10^{-5}	2.8×10^{-14}	1.0×10^{-18}	3	25

The rate of gas accumulation with time is shown in Fig. 6. For a vitreous silica bulb, the gases and pressures at the end of one year in air at 25°C would be: 10^{-4} mm He, 10^{-7} mm Ne, and 10^{-8} mm H_2. Only a few molecules of O_2 would have permeated even after 100 years.

The increase in pressure in bulbs of silica and other glasses is shown in Fig. 7 for helium permeating from the atmosphere. To reach a helium pressure of 10^{-6} (starting with 10^{-16}) requires the following times with bulbs of different glasses; at 25°C: silica, 3 days; Pyrex 7740, a month; soda lime glass, about 100 years, and 1720 hard combustion glass, about 1000 years. From this, it is evident that if we are concerned with vacua in the pressure range of 10^{-9} mm, it is necessary to make the envelope of a glass of low permeability or surround it by a subsidiary evacuated chamber.

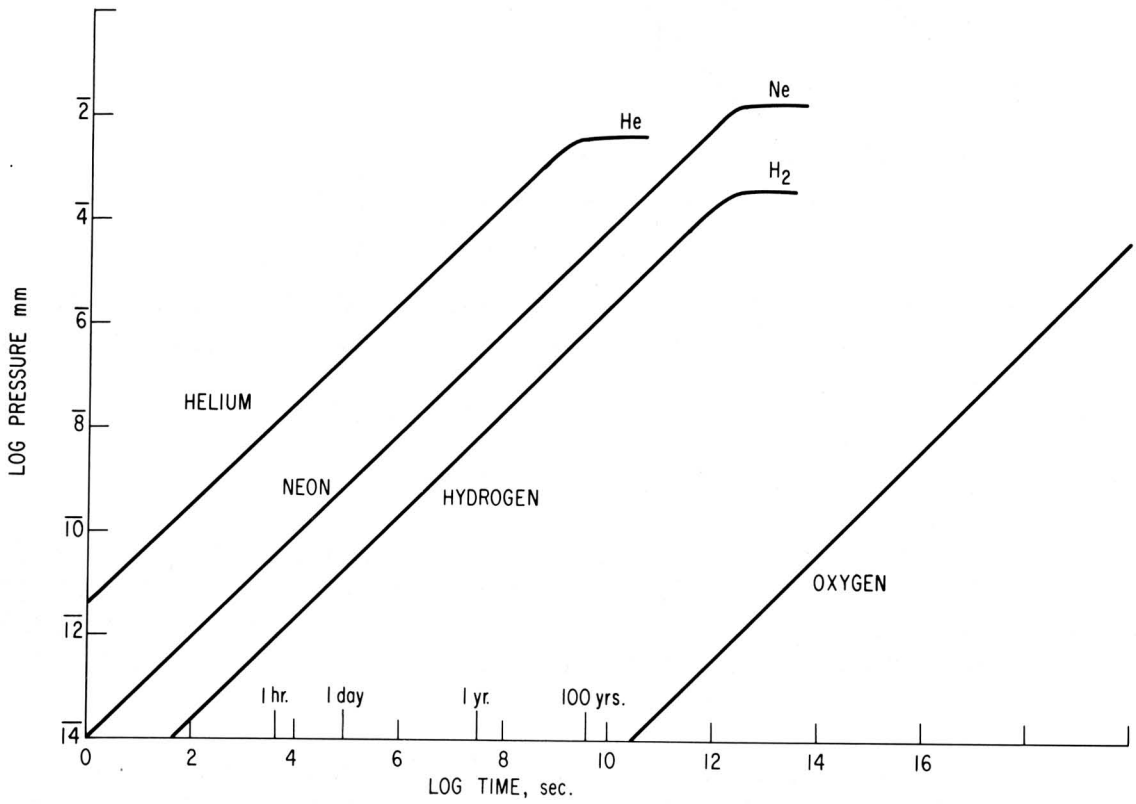

Fig. 6 Atmospheric gas accumulation, 25°C, in a silica bulb, 330 cm^3 volume, 100 cm^2 area, 1 mm wall thickness. Log_{10} pressure (in mm) vs Log_{10} time (sec).

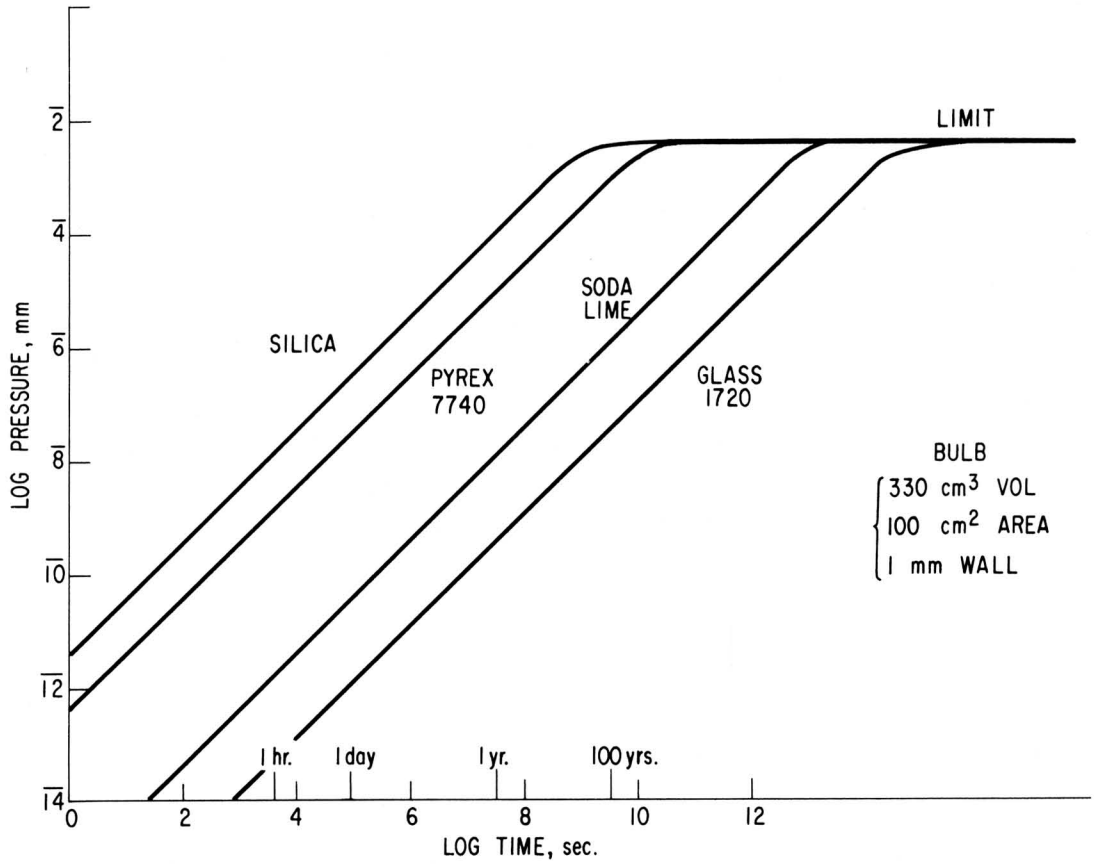

Fig. 7 Helium accumulation from the atmosphere in bulbs of different glasses, 25°C. Log_{10} pressure, (mm) vs Log_{10} time (sec).

GAS PERMEATION, METAL ENVELOPE

The permeation of atmospheric gases through sound metal walls does not involve helium or other inert gases, since no rare gas permeates metal at any temperature, under purely thermal activation. Helium permeation, however, has been measured through the semiconductors, silicon and germanium.(4)

Hydrogen is the main gas to be considered, particularly for steel walls. Its concentration in the atmosphere is under 0.5 parts per million, about 0.4 micron partial pressure. If the steel is unoxidized on the surface, the gaseous hydrogen rate is a maximum.(10) An oxidized surface cuts the rate, and the rate through chrome steels is lower by a factor of 10 to 100.

The permeation of gaseous hydrogen through steel and other metals varies as the square root of the pressure, indicating dissociation to atoms and passage as such through the solid. Recombination occurs on desorption and hydrogen molecules appear on the low side. With glasses and polymers, the gas permeation is proportional to the first power of the pressure for hydrogen and oxygen,[11] showing these are permeating in the molecular form.

However, there are many other mechanisms than atmospheric hydrogen permeation which produce hydrogen on the interior of the vacuum chamber. If the external wall rusts, this produces hydrogen, some of which permeates to the interior,[12] and on to the vacuum side. The abundance of bound hydrogen, as water in the atmosphere, is about 10^5 times that of free hydrogen. Hence, reaction of steel exterior walls with water is probably a much greater source of hydrogen on the interior than the very small amount of gaseous hydrogen in the air. Abrasion on the high side, in a damp atmosphere, sends H_2 through.[13] Acid pickling, caustic attack, and enameling all can cause hydrogen to permeate. Electrolysis may produce a hydrogen permeation rate equivalent to thousands of atmospheres gaseous pressure.

The permeation of hydrogen to the interior resulting from water cooling a plain steel wall to the interior vacuum space can be largely prevented by adding a small percentage of sodium chromate to the cooling water. This cuts down rusting, and hydrogen passage to the vacuum interior is cut down by many factors of 10. Chrome steels accomplish the same purpose.

Oxygen on the high side of steel is consumed in oxidizing the surface. However, silver and oxygen present an unusual case. Oxygen dissolves in it and passes through readily. A heated silver tube may be used purposely to admit oxygen to the vacuum.[14] Silver solder exposed to air should be avoided in ultrahigh vacuum systems for this reason. Oxygen through platinum has been shown to have an extremely low rate.[15]

In general, however, in metal systems, the gases other than hydrogen appearing on the vacuum side are far more apt to come from incompletely degassed metal than from permeation from the external atmosphere.

The data for gaseous hydrogen permeation through various metals are given in Fig. 8. The permeation rate for these, expressed here as K, is usually per atmosphere of applied pressure. The rest of the permeation rate unit is the same: cm^3 gas (STP) per second for 1 mm thick per cm^2 area.

The data for hydrogen permeation rate through Pd, Fe, and SiO_2 are presented in Fig. 9. This rate K is for 1 atm pressure difference. Neon, argon, and O_2 are also given. Note the great decrease in silica permeation rate going from neon to argon and oxygen. I have found nitrogen to have nearly the same low rate as argon. The permeation rate of hydrogen through metals varies as the square root of the pressure, but through vitreous silica as the first power of the pressure.

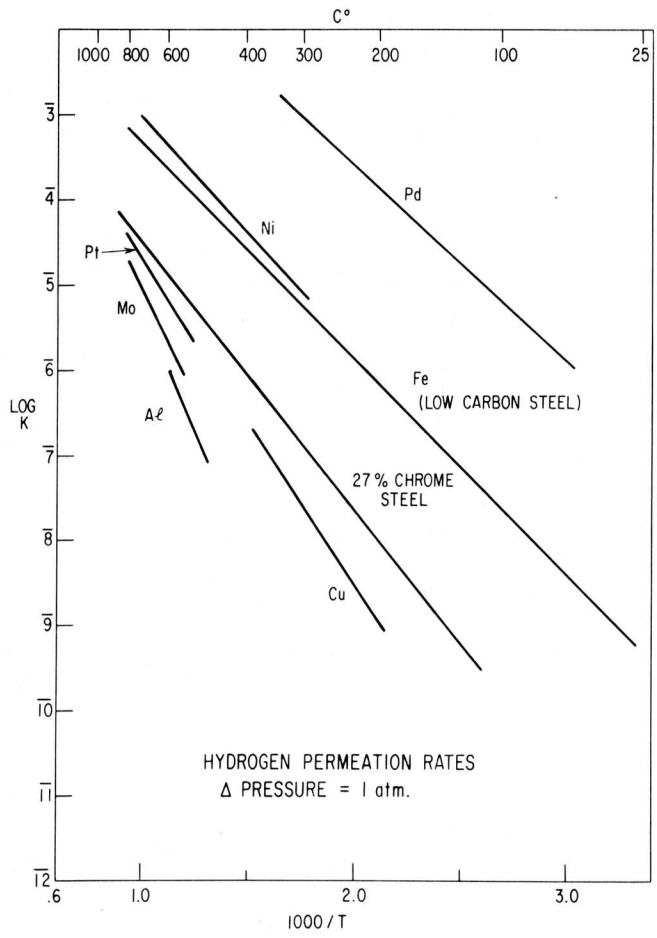

Fig. 8 Permeation rate K, per 1 atm gas pressure difference for H_2 through various metals, for 1 mm thick, 1 cm^2 area. $Log_{10}K$ plotted vs 1000/T.

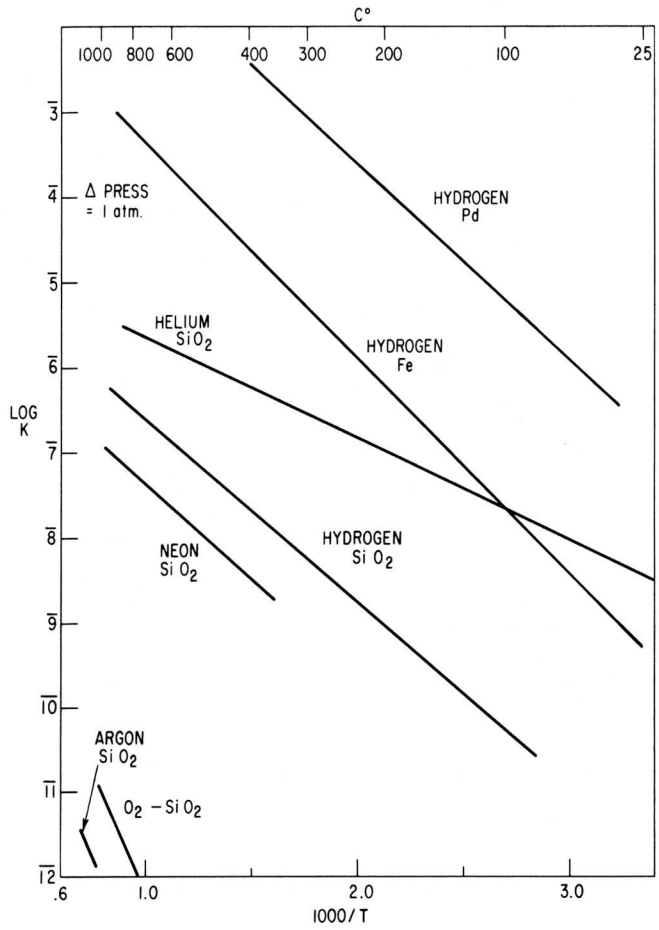

Fig. 9 Permeation rate K, per 1 atm gas pressure difference, for various gases through SiO_2, Fe, and Pd, for 1 mm thick 1 cm^2 area. $Log_{10}K$ plotted vs 1000/T.

Diffusion through the envelope walls has been shown to be most serious for helium through glass and hydrogen through metals. High pressures of these gases surrounding the envelope are to be avoided. There are two other sources of gas, often unsuspected, expecially in ceramic wall materials.

OTHER SOURCES OF GAS

If the device is to be operated at a high temperature (300° to 600°C) the oxides of iron or copper can dissociate to give appreciable and long-lasting oxygen pressure. Figures 10 and 11 show some of the values. At 600°C, CuO furnishes about 10^{-3} mm and Fe_2O_3 10^{-11} mm oxygen pressure.

When glass or ceramic is electrolyzed, especially at higher temperatures, the negative oxygen ion in the glass structure is

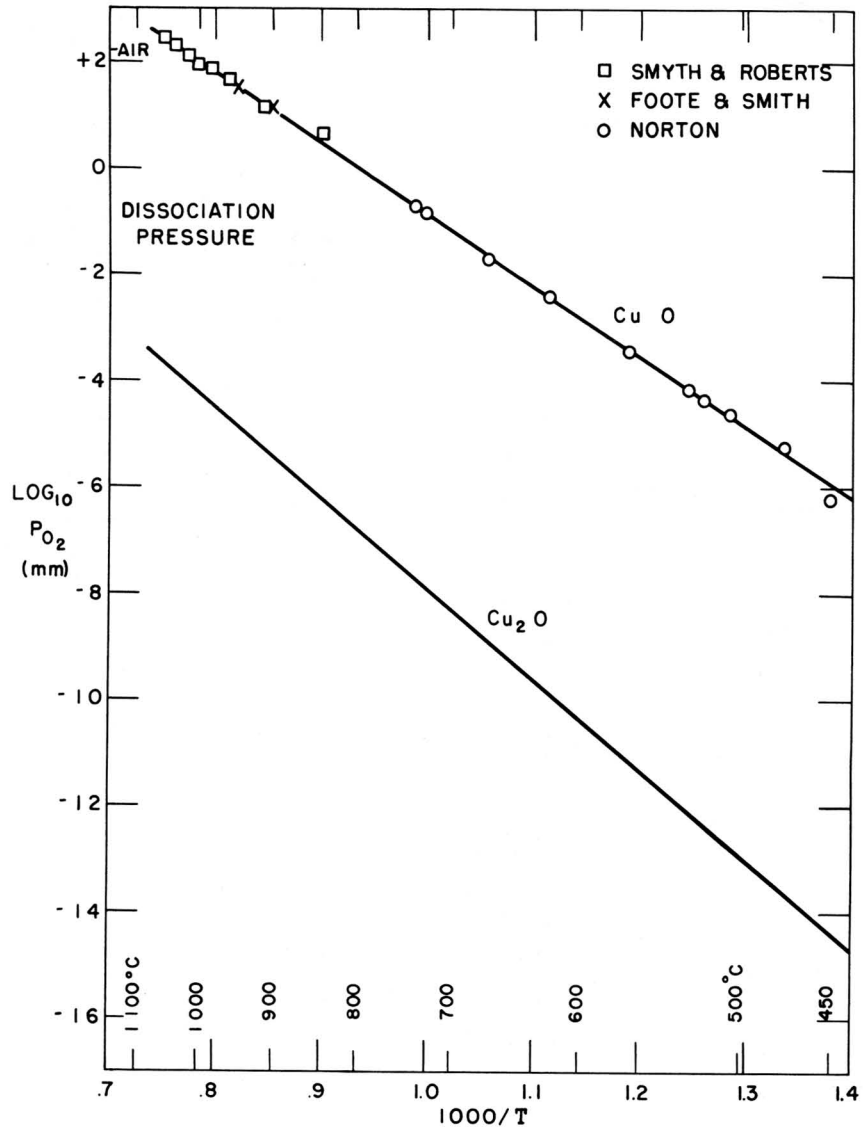

Fig. 10 Dissociation pressure of the copper oxides. Log_{10} pressure in mm vs 1000/T.

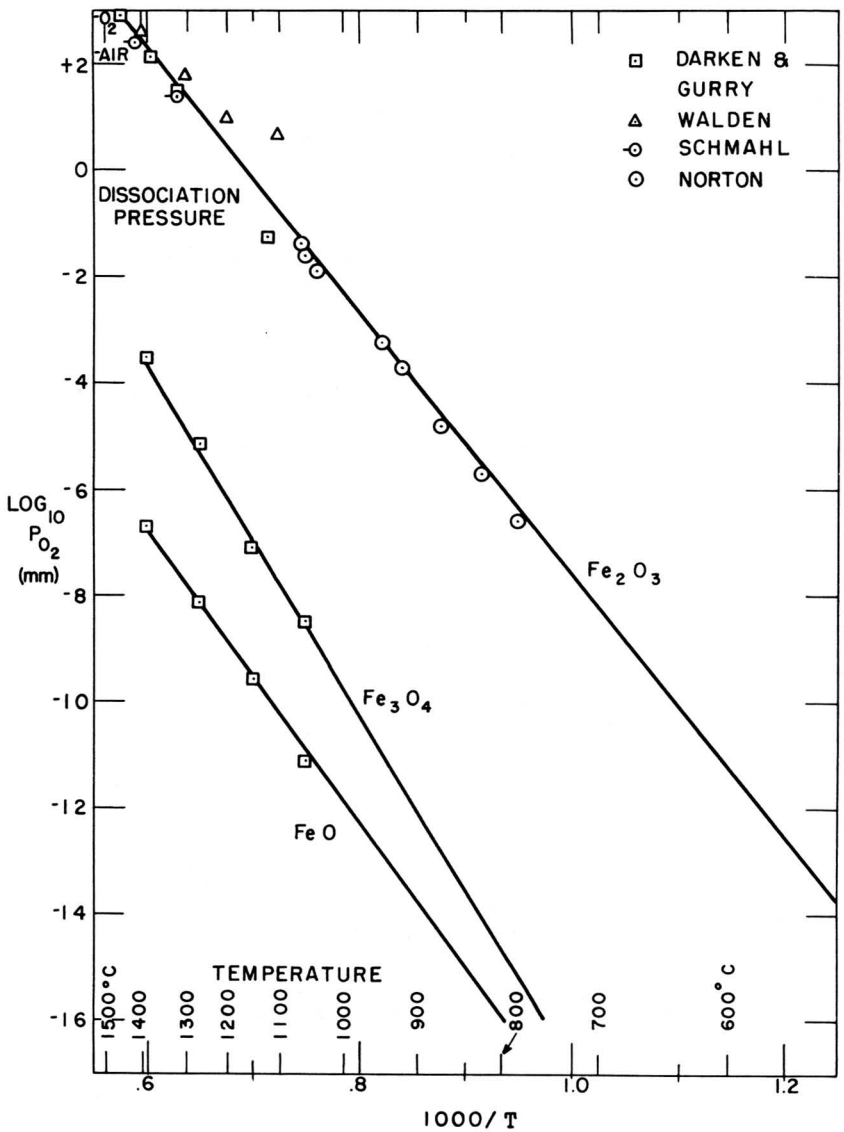

Fig. 11 Dissociation pressure of the iron oxides. Log_{10} pressure in mm vs 1000/T.

transported to the positive pole and evolved as gaseous O_2 molecules.(16) This requires only a few volts.

The appearance of molecular oxygen on electrolysis of various materials in a vacuum at elevated temperatures is shown in Table V.

A tabulated summary (Table VI) concludes this report with the main generalizations for gas permeation through solids.

TABLE V

Temperature of Gaseous Oxygen Evolution on Electrolysis

Material	With Voltage (C°)	Without Voltage (C°)
Pyrex 7740	355	None at 600
TiO_2-ZrO_2	435	800
TiO_2	540	None at 1000
GeO_2	550	875
ThO_2-Y_2O_3	730	1500
Alsimag 243	890	1220
ThO_2	940	None at 1550
Forsterite	950	1220

TABLE VI

Gas Permeation Through:

Glasses	Metals	Semi-Conductors	Polymers
He, H_2, D_2 Ne, Ar, O_2 measurable through SiO_2	No rare gas through any metal	He and H_2 through Ge and Si	All gases permeate all polymers
Vitreous silica fastest	H_2 permeates most, especially Fe	Ne, Ar not measurable	Water rate apt to be high
	O_2 permeates Ag		Many specificities
	H_2 through Fe by corrosion, electrolysis, etc.		
All rates vary as pressure directly	Rates vary as $\sqrt{\text{pressure}}$	H_2 rate varies as $\sqrt{\text{pressure}}$	All rates vary as pressure directly

In all, rate an exponential function of temperature for true permeation.

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True permeation through the wall is due to solution and then diffusion in the wall material. Experiments to measure it must be carefully devised to distinguish its effects clearly from various other gas sources as real leaks, pump back-streaming, gas originally in and on the wall material, electrolysis in glass walls, or oxide dissociation effects. Criteria are given for making sure true permeation is being measured.

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