PROCEEDINGS OF THE INTERNATIONAL
CONFERENCE HELD AT GATLINBURG
TENNESSEE, OCTOBER 1-3, 1975

Sponsored By

OAK RIDGE NATIONAL LABORATORY

UNITED STATES ENERGY RESEARCH
AND DEVELOPMENT ADMINISTRATION

AMERICAN NUCLEAR SOCIETY

NUCLEAR METALLURGY COMMITTEE
OF AIME

RADIATION EFFECTS *and* TRITIUM TECHNOLOGY *for* FUSION REACTORS

Editors

J. S. WATSON
F. W. WIFFEN

Compiling Editors

JULIA L. BISHOP
BRENDA K. BREEDEN
OAK RIDGE NATIONAL LABORATORY

MARCH, 1976

HYDROGEN ISOTOPE PERMEATION IN ELASTOMERIC MATERIALS

R. H. Steinmeyer
J. D. Braun

Monsanto Research Corporation, Mound Laboratory

ABSTRACT

The permeabilities of elastomeric and polymeric
materials to hydrogen isotopes were measured at room
temperature. The technique for measuring permea-
tion rates is based on the following constant-volume
method: a fixed pressure of gas is applied to one
side of the specimen to be studied and the permeabil-
ity constant is determined from the observed rate of
pressure increase in an initially evacuated volume
on the other side of the specimen. Permeability
constants for hydrogen, deuterium, and tritium were
measured for Mylar, Teflon, Kapton, Saran, Buna-N,
and latex rubber. Results were compared with litera-
ture values for hydrogen and deuterium where avail-
able and showed excellent agreement.

Application of existing tritium technology to fusion
reactors requires careful evaluation of a variety of materials
commonly used in containment systems with respect to tritium
permeation and stability in a radiation environment. One
class of materials of great importance in the fabrication
and assembly of any tritium containment system is elastomers.
There are many types required in assembling even simple sys-
tems: for example glovebox gauntlets of various types of
rubber, gasket materials of a variety of elastomeric mate-
rials, sealing tapes of Teflon, plastic films for trash stor-
age, and plastic tents required for maintenance. Figure 1
shows a typical inert-atmosphere glovebox system in a labora-
tory where the effects of tritium on mechanical properties of
materials are measured. The extensive use of elastomers
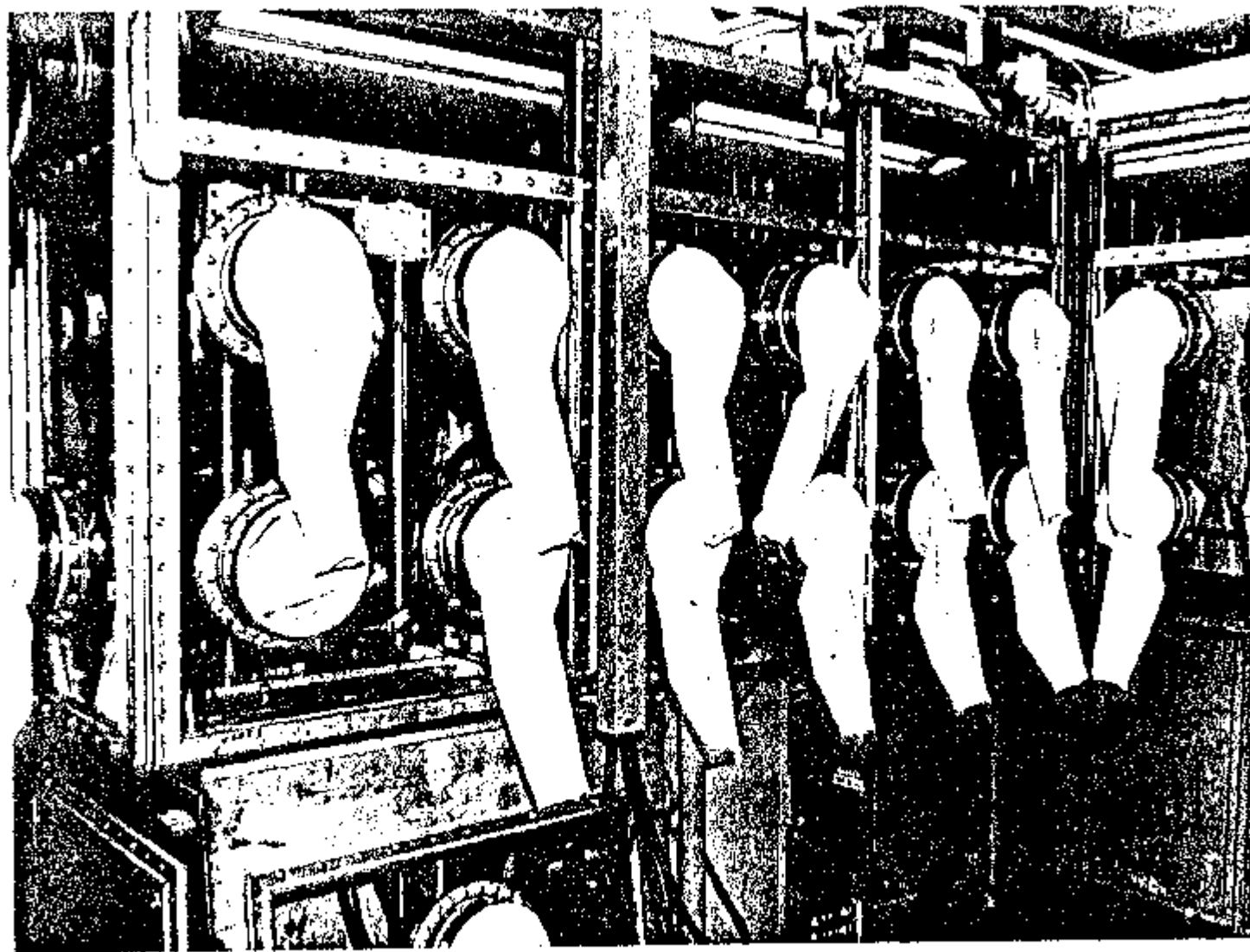is evident in this photograph.

Fig. 1. Photograph of Typical Glovebox System Showing Extensive Use of Elastomeric Materials.

Information in the literature on the permeation of hydrogen isotopes through this class of materials is widely scattered and generally reported for hydrogen only. Some information is available for deuterium; however, information on tritium is necessary both for design applications (choosing the proper material for each system application) and also for evaluation of effects of radiation or exchange reactions on the materials. For these reasons we have initiated a study of hydrogen isotope permeation in common elastomeric materials.

The initial experimental work was conducted with hydrogen and deuterium for design of the apparatus and evaluation of the experimental techniques. The majority of our current work is now devoted to the measurement of tritium permeation through these materials and evaluation of the effects of tritium on the properties of these materials. As designs for specific systems related to fusion technology are completed, additional materials will be studied to provide the necessary data for choosing materials of fabrication.

The process of permeation in elastomers generally is one of solution of the gas molecules on one surface of the material, followed by diffusion through the elastomer to the other side where the gas evaporates. The quantity of dissolved gas in the elastomer is proportional to the pressure, following Henry's law $(S = kp)$, while Fick's law, $\frac{(dC)}{dt} = D \frac{d^2C}{dx^2}$, applied to the actual process of diffusion. On this assumption the quantity of permeating gas, q, is determined by $q = DhA[(p_1-p_2)/d]t$ where

    D = diffusivity,
    h = solubility,
    A = area of the membrane,
    d = thickness of the membrane,
    p_1 and p_2 = pressures on both sides of the membrane, and
    t = time.

If unit values are taken for the difference in p_1-p_2, area A, thickness d, and time t, then Q = Dh, where Q stands for the permeability.

The technique used for measuring permeation in this experimental work was based on the constant-volume method. In this method a fixed pressure of gas is applied to one side of the specimen to be studied, and the increase in pressure from the permeation of the gas into an initially evacuated chamber, separated from the fixed pressure side by the specimen, is measured. The permeability constant Q can then be determined from the observed rate of pressure increase and other parameters related to the permeability apparatus and the specimen according to the following relationship:

$$Q = \frac{(\Delta p)(V)(d)273}{(\Delta t)(p)(A)(T)}$$

where

    Δp = pressure increase,
    Δt = time interval of measurement,
     p = fixed gas pressure applied to one side of specimen,
     V = volume of initially evacuated chamber,
     d = thickness of specimen,
     A = exposed area of specimen, and
     T = average temperature of the volume.

The apparatus used to determine Q is similar in principle to that used by several previous investigators such as van Amerongen[1] and consists of the following major components: (1) a permeation cell, (2) a manifold to supply gas and vacuum service, and (3) a pressure sensor to measure pressure change. The permeability cell (Figure 2) was a high-pressure membrane filter holder (Millipore Filter Corp.). The specimen to be studied, consisting of a thin disc cut to fit the cell, was mounted so that a seal was formed separating the apparatus into two chambers. The chamber volumes were calibrated by PVT determinations.

Inlet Tubing

Hold-down Bolts (6)

O-ring Seals

Top Assembly

Specimen

Specimen Support Screens

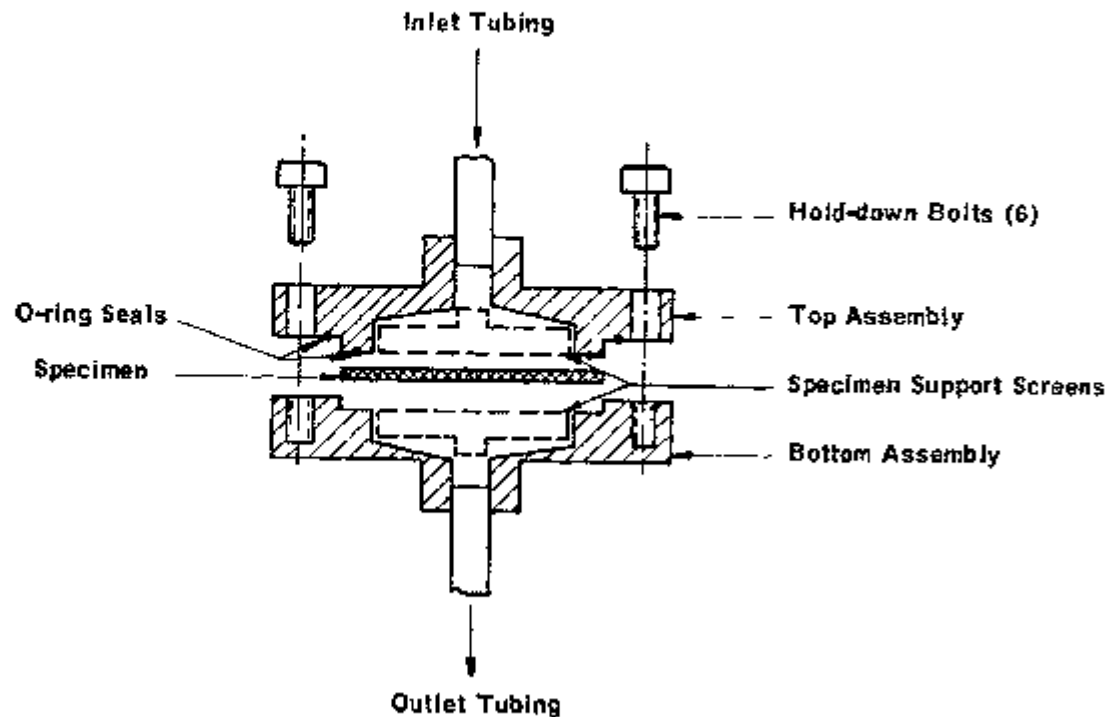Bottom Assembly

Outlet Tubing

Fig. 2   Permeation Cell.

Figure 3 shows the complete permeability apparatus located within an inert-atmosphere glovebox line, and Figure 4 shows a schematic drawing of the apparatus. A permeation experiment was conducted by initially evacuating both sections of the apparatus, isolating the sections from each other and the pumping system, and introducing the hydrogen isotope into the largest volume which is the fixed pressure side (Volume A), usually at 1 atm. The elastomer specimen was supported in the cell on a screen to prevent rupture due to the pressure differential between the two volumes. The increase in pressure in the smaller volume (Volume B) was measured as a function of time.
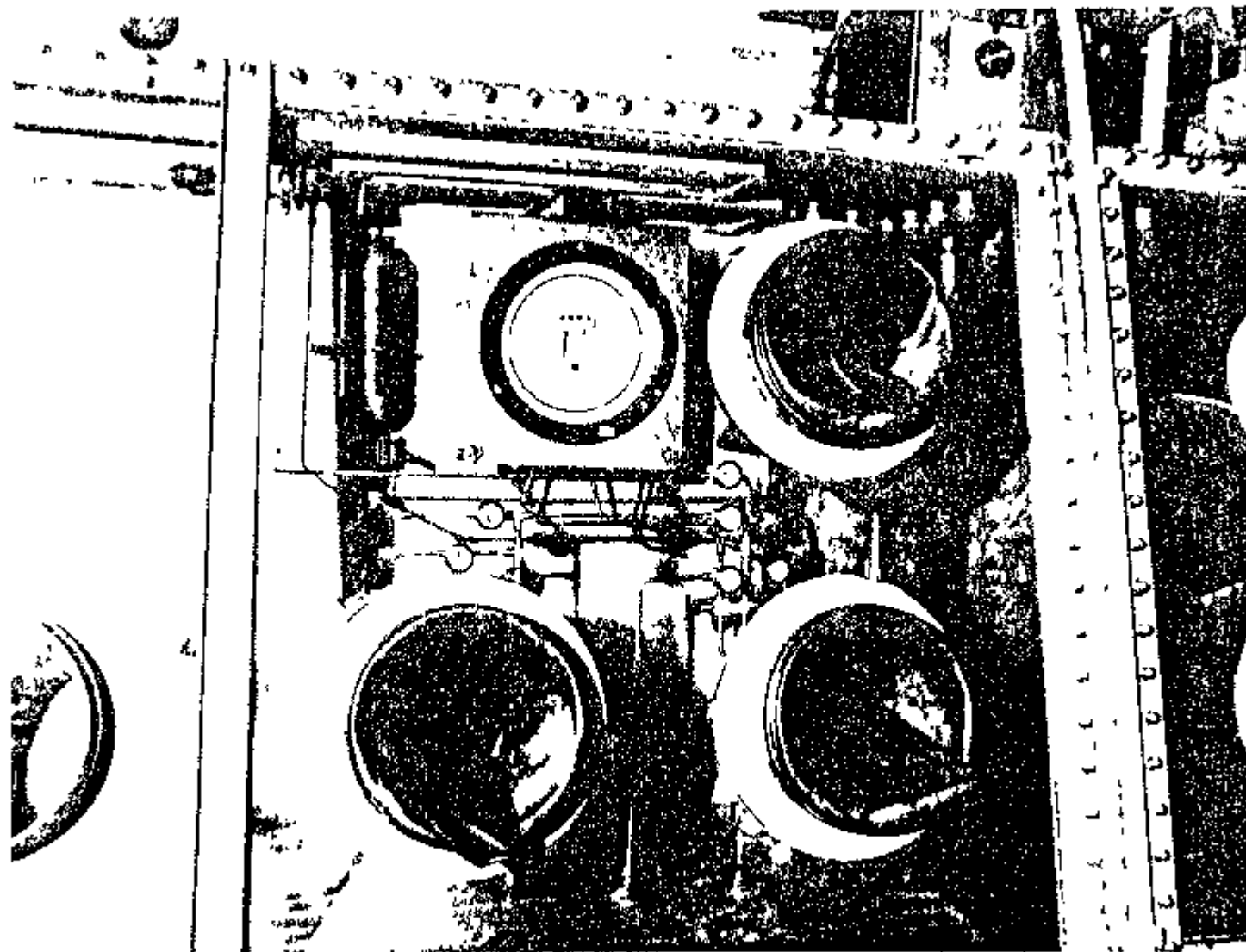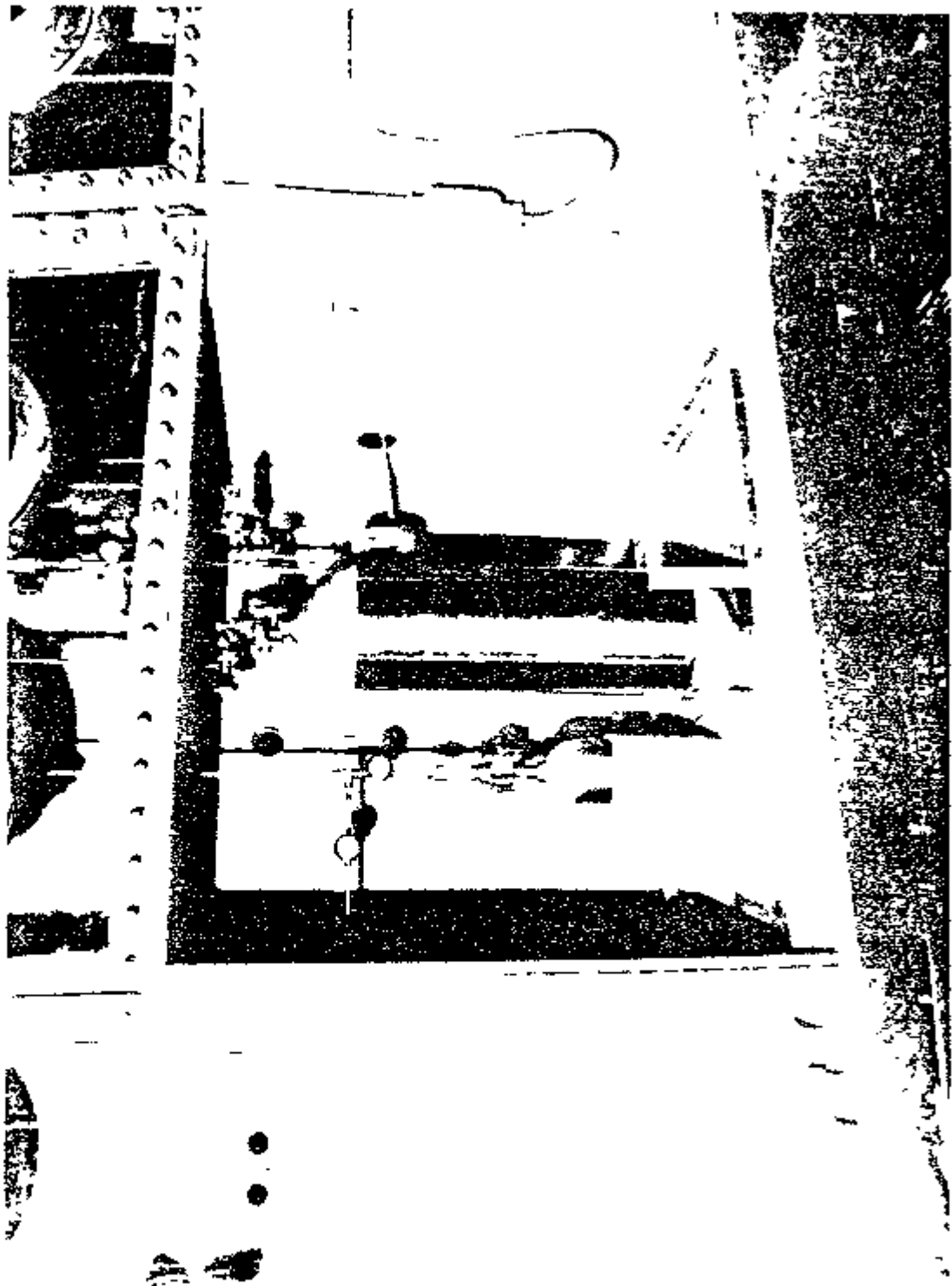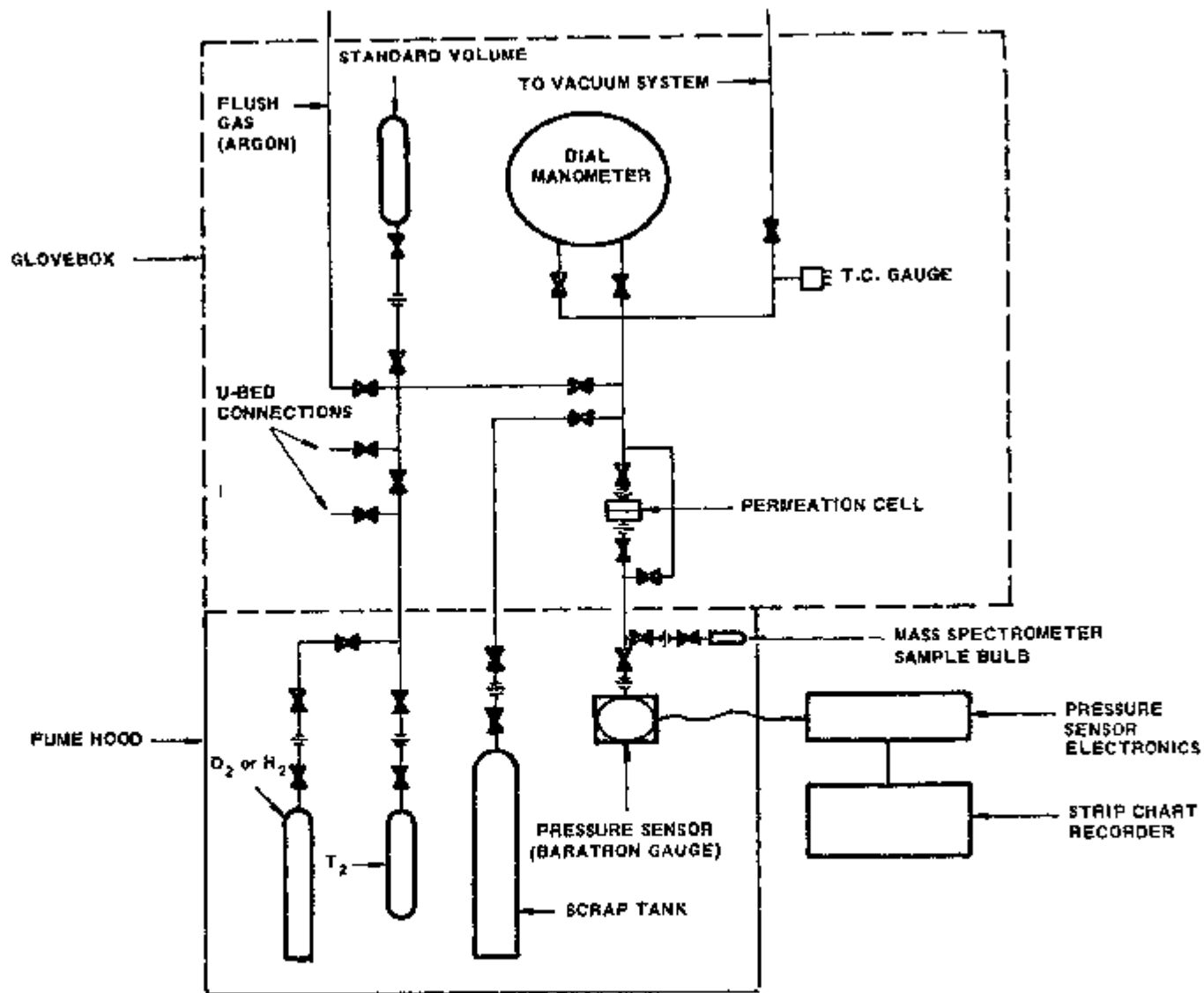
Fig. 3. Permeability Apparatus Located Within the Inert
Atmosphere Glovebox Line.

Fig. 3. Permeability Apparatus Located Within the Inert Atmosphere Glovebox Line.

Fig. 4. Schematic Drawing of Permeation Apparatus.

A capacitance manometer (Baratron Instrument Corp.) was used to detect the pressure increase in the smaller volume (Volume B). The pressure was continuously plotted on a strip chart recorder providing a permanent record of pressure-time data and permitting immediate determination of steady-state permeation. The permeation apparatus was constructed so that the ratio between Volume A and Volume B was large enough to prevent a significant pressure drop in Volume A during the course of a permeation determination. Temperature during the experiments was ambient, averaging 24.8°C ± 1°C. The accuracies in determining the volumes of the permeation apparatus and the pressure in the smaller volume (Volume B) were ± 0.4 and ± 0.15% respectively. The specimen thickness was determined by checking several locations with a caliper micrometer. An average of these determinations was then computed. In general, the variation in measurements on a given specimen was 8-10% because of irregularities in the material as well as its resiliency. This measurement, being the least accurate, limited the overall accuracy of the experimental determinations.

The hydrogen isotope permeabilities of a number of readily available elastomeric and polymeric materials were measured and compared with values obtained from literature sources (where available). These experimental results and the literature comparisons are shown in Table 1. The agreement was good in most cases. The largest deviation occurred for very thin specimens where inaccuracies in thickness measurements or uncertainties as to the exact nature of the particular specimen was greatest. The permeation ratios of H/D/T as shown in the table do not follow the ratio of the square root of the mass as many isotope-effect results on other diffusion studies have. In the case of elastomers, the size of the molecules may have more significance in explaining the permeation ratios. In any case this points up the

Table 1   Permeability Constants of Hydrogen Isotopes
Through Various Elastomeric and Polymeric Materials

Material	Specimen Thickness (cm)	Isotope	Permeability Constant (Q) (cm^2/sec-atm)[a]	
			Measured Value	Literature Value
Latex (natural rubber)	0.018	H	3.5×10^{-7}	3.9×10^{-7}[b]
Latex	0.018	D	3.0×10^{-7}	
	0.023	T	2.58×10^{-7}	
Buna-N (nitrite butadiene rubber)	0.025	D	5.6×10^{-8}	9.77×10^{-7}[a]
	0.032	T	4.4×10^{-8}	
Mylar (polyethylene teraphthalate)	0.005	H	4.5×10^{-9}	4.4×10^{-9}[c]
Mylar	0.005	D	4.1×10^{-9}	
Teflon (polytetra-fluroethylene)	0.007	H	6.1×10^{-8}	
	0.007	D	0.98×10^{-7}	1.25×10^{-7}[e]
	0.007	T	$1.01 \times 10^{+7}$	
Kapton (polyimide)	0.005	H	1.3×10^{-8}	
Kapton	0.005	D	1.3×10^{-8}	
	0.009	T	1.96×10^{-8}	
Saran (vinylidene chloride)	0.001	H	3.6×10^{-8}	3.1×10^{-7}[d]
Saran	0.001	D	2.3×10^{-8}	

[a]All measurements were made at room temperature (approx. 25°C)
[b]Reference 1
[c]Reference 2
[d]Reference 3
[e]Reference 4

need for direct experimental measurement of the permeation
of tritium through materials rather than predictions based on
theoretical assumptions.

REFERENCES

1. G. J. van Amerongen, J. Appl. Phys., _17_, 972-85 (1946).

2. S. B. Tuwiner, _Diffusion and Membrane Technology_, Reinhold
    Publishing Corp., New York, N. Y., 1962.

3. T. W. Sarge, Anal. Chem., _19:6_, 396-400 (1947).

4. R. G. Derrick and M. R. Louthan, Jr., _J. Chem. Eng. Data_,
    _19:1_, 48-51 (1974).