Vacuum Envelope Penetration

Removing the ambient air from a vacuum chamber and keeping it that way describes vacuum technology at its most basic level. Although vacuum technology requires the blending of a number of complex and stringent measures to ensure a successful process, nothing else will matter unless there's a chamber with sufficient integrity to allow the chamber's pressure to be reduced to the process dictated level. As the pressure within the chamber is reduced, the pressure differential between the chamber and its surroundings will cause ambient gas to flow through any possible channel. Gas vectors that can penetrate a vacuum vessel break down to two separate categories: leaks and permeation.

A semantic problem lurks within the leak category because there are two distinct types of gas loads represented by the term. Pockets of gas trapped within the confines of the vacuum chamber are usually referred to as virtual leaks, but this term is used only because they can easily be mistaken for real leaks. Real leaks are actual openings or voids in the vacuum envelope that allow gas to pass from the atmosphere into the envelope. Every vacuum practitioner will have already spent countless hours finding, fixing, and generally avoiding leaks. They need no introduction, but they do need definition. In its simplest form, a leak can be pictured mentally as a "point source" leak. Good examples are a radial scratch on an O-ring-sealed flange or a hair lying across an O-ring. These simple leaks are called point source because the leaking gas enters from a single point that is almost like a classic pinhole. Diffuse leaks are a little more difficult to picture because the inleaking gas will enter from an area instead of a single point. A good example would be a slightly dirty O-ring that forces the gas into a number of small leak paths and enters the chamber from around the circumference of the entire O-ring. Most leaks, found in practical process systems, will fall into these two categories.

A leak is usually suspected whenever a system fails to achieve its usual ultimate pressure. The question that should immediately arise is whether it's a single leak or a collection of small leaks. Since gas loads are additive, the resultant total gas load that shows up as a higher pressure reading on a vacuum gauge will be the same in either case. Although an apparent leak that suddenly appears in a system that's already in use and has a known history will probably be a single leak, there's no guarantee that it isn't a collection of small leaks. Porosity is a good example to consider. Many vacuum envelopes can be porous in that they contain a large

number of tiny pathways through the envelope. In short; pores. Any one of these pores would be too small to allow a measurable amount of gas to pass through into the vacuum, but taken together, they can provide a total measurable gas load to the system. Porous materials might be a poorly sintered piece of ceramic or a weld that wasn't fused completely. Porous materials might or might not actually leak in that they can be easily clogged with grease, condensed gases such as water vapor, or frozen liquids. Leaks, caused by porosity, might suddenly appear as the clogging material clears the pores through vaporization and appear to be a single leak. Baking a system can cause vaporization of the clogging material. The reverse can also happen when leak checking with a solvent that will clog either a single leak or pores as it cools during the expansion of the solvent vapor as it passes through the envelope into the vacuum chamber.

There is one common attribute to any sort of leakage, and that it that gases passing through will obey the dynamic gas laws. This means that light gases will penetrate a leak at a higher rate than a heavier gas. The amount of gas passing through a leak will then be governed by the conductance of the leak and the molecular weight of the gas. This is true for any leak from a simple pinhole to a long labyrinthine passage such as might be found with a poor weld. This attribute has helped give rise to a particular piece of technological folklore that helium (He) is used as a probe gas for leak detection because it is a small molecule and more able to pass through a leak. It is true that He has the smallest diameter of all molecules, but the amount of He that will flow through a leak in the molecular flow regime is only 2.7 times that of air. In fact, in a large viscous flow leak, the ratio is actually less than 1. A higher flow rate through a leak is useful, but the actual increase isn't all that important.

He is used as a probe gas because it is more suitable than any other gas when we consider that a magnetic-sector mass spectrometer is used as the most common sensor in leak detection. Hydrogen (H_2) with a molecular weight of 2 would be a better choice than He with a molecular weight of 4 if flow rate were the most important parameter. H_2 would flow through at a higher rate than He even though its diameter is bigger than He. H_2 is larger due to the fact that it's a diatomic molecule. More important, then, is the fact that no other gases fragment, during ionization, into any ion species that have a mass of 4, while H^+ and H_2^+ ions are commonly produced by fragmentation of water vapor and hydrocarbons. These fragments would be detected by a mass spectrometer tuned to mass 1 or 2 and be mistaken for inleaking H_2 probe gas. He also has the advantages of being inert so that it won't sorb easily to the inner surfaces of chambers and is present in the atmosphere at only 5 ppm.

Permeation is the other category of vacuum envelope penetration to be considered. Permeation can be easily mistaken for a leak, but it occurs through an entirely different mechanism. A leak is free, although sometimes torturous, passage through the vacuum wall. Permeation, on the other hand, is a three-step process which includes sorption on the external surface, diffusion through the material, and re-

sorption on the inside surface before it can desorb into the vacuum space. The most commonly encountered permeation problem by vacuum practitioners is the permeation of O-rings by atmospheric gases. Gases will permeate the elastomeric material at an entirely different rate than would be encountered with a real leak.

In a simple experiment, a Viton-sealed flange pair was shrouded and sealed by a metal housing that had been thoroughly flushed out with He on a system containing a residual gas analyzer (RGA). After a few minutes, He was detected on the RGA and the signal increased steadily as the He permeated through the O-ring. At first, the He signal increased fairly rapidly, but its rate-of-increase declined with time. It took almost 48 hours for the signal to totally stabilize. When the He-filled housing was removed, a roughly mirror image decrease in signal occurred. The relative rates of increase and decrease with time are exemplary of the many possible diffusion paths through the material. The gas was required to pass through spaces between long, intertwined, and cross-linked molecules of material that is not totally homogeneous. This meant that the He penetrated quickest through the most open paths, but that it took a much longer period to totally pass through the longer or smaller paths. The permeation rate of a particular gas is partially a function of the partial pressure gradient of the across the material. When leak checking an O-ring-sealed system, this effect can be irritating. If the He probe gas is sprayed too slowly over an area when looking for small single leaks or porosity, it can begin to permeate an O-ring and produce a leak detector signal that is easily mistaken for a real leak.
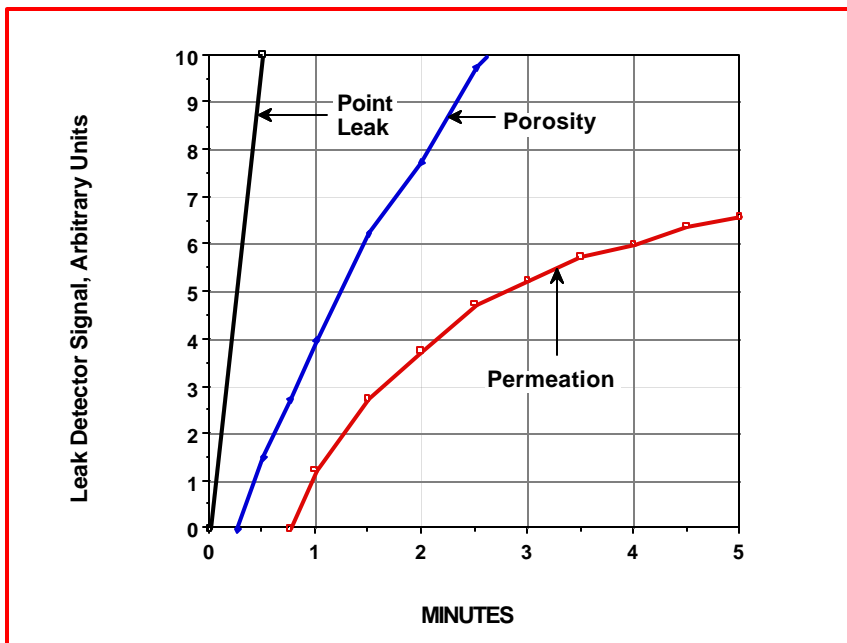
Helium probe gas is sprayed on an area at 0 minutes, and the differences between a point leak, porosity, and O-ring permeation can be seen by the length of time required for a response and the rate of response.

Permeation is differentiated from real leaks by the fact that the rates are not controlled by the molecular weight of the gas as is found with real leaks. There is a much more complex mechanism at work. If we form a mental picture of the internal diffusion pathway through an O-ring as a capillary tube that's hundreds of meters long and crumpled into a ball, we can easily see that the permeating

gases will not follow the net flow picture of a flow vector from atmosphere through the bulk and into the vacuum space. In addition to the convoluted pathway, each specific gas species will interact with the O-ring material. The capillary tube picture allows us to see the surfaces of the elastomer's molecules as the walls of the tube, and the electronic properties of both the specific gases and the elastomer will allow either faster or slower mobility of the gas through the tube and the molecular weight of the gas does not control the rate. Water vapor at 18 amu might have a greater permeation rate than He at 4 amu. There is no reasonable correlation of the permeation rates of various gases between various elastomers. The rates for each material and each gas must be ascertained. The rates are also temperature dependent, and a gas with the lowest permeation rate at room temperature might well have the highest rate at a higher temperature.

Glasses and metals that are commonly used for the construction of vacuum vessels are also permeable. Glasses of various types all allow He to permeate through the material at rates dependent upon the actual type of glass. Metals will allow H_2 permeation, and this is a problem for ultrahigh-vacuum applications. Permeation through glasses depends upon the microstructure of the glass itself in terms of providing a pathway for the gas and the diameter of the permeating gas molecule. This explains why He, having the smallest molecular diameter, has the highest permeation rate. Metals, on the other hand, require that the gases dissolve in the material. H_2, for example, dissociates from the diatomic H_2 to H when it adsorbs on the outer surface and dissolves in the metal before emerging on the vacuum side. The permeability of glasses and metals can be used to provide a controlled gas source that functions as a combination of purifier/leak valve where the permeation rate is controlled by temperature. A quartz barrier can be used for He while palladium alloys can be used for H_2 and silver for oxygen.

Penetration of the vacuum envelope is a problem and concern for all vacuum applications. An example is any static sealed-off device such as a cryogenic dewar that will be exposed to possible penetration of gases without the luxury of dynamic pumping to deal with the penetrant gas load. Although the various processes will be sensitive to varying degrees of penetration along with all the other possible gas loads, it is important to understand and appreciate the amount of gas involved and to understand the difference between a real leak and atmospheric permeation when either developing a new process or system or attempting to trouble-shoot or improve an existing one. Leaks and permeation are not the same phenomena, and they should never be confused.

O-ring Material Permeation Constants

Selected from the literature for room temperature comparison, Units are stdCC/sec./cm^2/torr x 10^{-10}

	He	N_2	CO_2	H_2O
Buna-N	1.0	0.024	0.75	100
Viton	1.2-2.3	0.03-0.07	0.3-0.8	5.2
Kalrez	11.2	0.3	2.5	--
Chemraz	14.3	0.88	--	--
silicone	31-33	10-16	60-300	400-1,000
Teflon	6.8	0.14-0.32	1.2	3.6

Permeation rates vary widely between gases and o-ring materials. Comparing the permeation constants can supply relative and practical numbers for material selection. Compiled by Phil Danielson