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On the Use of Test Gases of Various Radii to Investigate Molecular Sieving in Leak Channels

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Abstract— **Evidence of the effect of molecule size (molecular sieving) was discovered in leak channels similar to those found in hermetically sealed implantable bionics. A range of test gases of different molecular sizes was used to investigate the relative leak rates of several different samples. A contemporary model of molecular sieving is shown to be in partial agreement with our data.**

I. INTRODUCTION

When high levels of reliability are required in electronic devices such as biomedical implants, sensitive components are often hermetically packaged to protect the electronics from environmental degradation. Moisture ingress is of primary concern due to its ability, when condensed, to interact with solutes and initiate corrosion that may eventually compromise device function [1, 2]. When long-term device integrity is required, these packages are typically manufactured from metals and ceramics. In these packages fluid flow may occur in discrete leak channels through the bulk of the material, or at the interface of where two components are joined together. An understanding of how leak channels function is important when designing and manufacturing packages to have a specified service lifetime, and also when measuring leak rates to ensure that the interpretation and extrapolation of said data is valid.

The study of the flow of ideal gases through uniform channels of well-specified shapes has enabled the quantitative prediction of flow rates over a wide range of pressures and channel sizes [1, 3, 4, 5, 6]. The regime of flow is described by the Knudsen number (Kn), which is the ratio of the mean free path to the channel diameter [3]. In the molecular flow regime ($Kn > 1$), Graham's Law can be used to predict the ratio of the flow rates $\dot{m}_1$ and $\dot{m}_2$ of two different ideal gases [1, 7]. For gases of molecular weights M_1 and M_2 the ratio of the mass flow rates is given by the square root of the inverse mass ratio.

$$\dot{m}_1 = \dot{m}_2 \sqrt{M_2 / M_1} \tag{1}$$

Knudsen's equation for molecular flow incorporates Graham's Law [3], as does the Howl-Mann equation used in MIL-STD 883H Method 1014.12 [8] for predicting the leak rate of air from the measured leak rate of helium. Similar effects can also be seen in other equations [4, 6], however Graham's Law only applies to ideal gases flowing in a uniform channel of a diameter significantly greater than the dimensions of the relevant gas. If the channel's diameter is smaller than the molecule's there will be a cutoff in flow [1, 7], and as the difference in the two diameters approaches zero the flow rate will be reduced. This effect is known as molecular sieving. Graham's law is also not applicable to surface flow, as may occur in cases regarding water vapor.

Evidence of molecular sieving has been found by measuring the permeance of He, O_2, CO_2 and SF_6 through nanoporous membranes containing highly uniform channels [9, 10]. The ratio of the flow rates, the separation ratio (α), of the heavier gases relative to helium was sometimes higher than the ratio expected from Knudsen flow. The manner in which the separation ratio changes has been studied by Fain et al., who developed a Hard Sphere Model (HSM) for highly uniform nanoporous membranes. This describes how the separation ratio is influenced not only by Graham's Law, but also by the difference between the pore diameter (d_p) and the gas molecule diameters (σ_1 and σ_2) [11].

$$\alpha = \sqrt{M_2 / M_1} \times \left[(d_p - \sigma_1)^3 / (d_p - \sigma_2)^3 \right] \tag{2}$$

A full transport model is also available that may be more accurate, but it has limited usefulness as it requires the measurement of gas adsorption and surface flow for each gas and material used [11]. The HSM has been used by Fain and Bischoff to calculate the pore size of a membrane through the flow of different gases with some success [9, 10].

In contrast to discrete leak channels flow may also occur through permeation. This is typically the case in polymers, although it also occurs for certain combinations of fluids and materials such as H_2 and Pd [12]. Permeance is a product of the fluid's solubility when it is sorbed on and into the material, and its diffusivity as it travels through the bulk of the material [7]. Molecular sieving may also affect this mode of flow depending on the material's atomic geometry.

These equations do not take into account tortuosity and constrictions in 'real' leak channels, however they have often been used to predict flow rates with some success. Davy also established a qualitative description that allows 'real' leak channels with non-ideal geometries to be simplified in order to predict their flow rates [13]. Other models do not attempt to simplify the leak channels present in a package as Davy did, but instead view the leaky area as a porous medium and

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assume that the channel dimensions follow a fractal distribution [14, 15].

Despite these efforts, the limitations of Davy's work and other equations predicting molecular flow do not appear to have been fully addressed, especially when molecular sieving comes into effect. The view of a number of researchers appears to be that molecular sieving does not occur in these ‘real’ leak channels, given the prevalence of Graham’s Law in equations used to predict flow [1, 7, 8, 13, 16]; although Greenhouse describes the conditions under which flow will cease completely [1], and Costello & Desmulliez note that Graham’s Law is not applicable when molecular sieving takes place [7].

There is evidence that the flow of ideal gases through ‘real’ leak channels can deviate from Graham’s Law and that molecular sieving does occur, however such evidence is often inconclusive. Romenesko’s comparisons between the results of He and ^{85}Kr leak tests [17] showed a number of samples with low but visible He leak rates, yet ^{85}Kr leak rates at or below the limit of detection, and also below those predicted by Graham’s Law. These samples were excluded from Romenesko’s analysis, however the authors propose that they demonstrate that Graham’s Law forms an upper limit for the leak rate ratio rather than a trend line, and that the excluded samples demonstrate molecular sieving.

The authors hypothesize that molecular sieving occurs in seals like those commonly found in hermetically sealed packages such as implantable bionics. It is also hypothesized that there is a link between molecular dimensions and flow rates that may provide a convenient way of assessing the physical dimensions of ‘real’ leak channels.

II. Materials and Methods

To test the above hypotheses the flow rates of a variety of gases through different samples were measured.

Sample materials were selected based on their expected leak modes. A 25 mm diameter sample made from polyether ether ketone (PEEK) film (APTIV Film, Victrex, UK) was used as an example of a homogeneous material with single molecule sized diffusive pathways. This was mounted onto a drilled copper disc to fit a 2.75” Conflat flange using Torr Seal epoxy (Varian Inc., USA), creating the assembly described in Fig. 1a. Samples with ‘real’ leak channels were formed from 25 mm Ti or 96% polycrystalline Al_2O_3 (Keralfol, Germany) and mounted onto the copper discs using S-Bond 220 solder (S-Bond Technologies, USA).

He, Kr and Xe were chosen as test gases for their wide range of molecular weights and sizes and their uniform geometry. He is also commonly used in leak rate testing. D_2 was chosen because it has the same molecular weight as He but a different morphology.

Leak rate testing for the above samples was performed using the experimental setup described in Fig. 1b. Sample assemblies were mounted between two 2.75” Conflat flanges to which 1/4” Swagelok VCR fittings were welded. The flanges were then connected to the gas chromatograph interface inlet of a DSQ II Series mass spectrometer (Thermo Fisher Scientific, USA) and gas/vacuum sources as per the diagram. A calibrated D_2 leak with a leak rate of 1.80E-7 atm.cm^3/sec (Vacuum Technology Inc., USA) was also connected as a reference to compensate for variation in the mass spectrometer’s sensitivity. An HP 6890 series gas chromatography (GC) oven (Agilent Technologies, USA) housed the flanges to maintain a temperature of 25°C +/- 0.5°C during measurements, and to facilitate removal of volatile contaminants by vacuum baking from the system whenever it had been exposed to atmosphere. Diaphragm valves (Swagelok, USA) were chosen for valves V4 and V5 because of their extremely low leak rates both when closed and also through the body of the valve; important factors as both valves were connected directly to the mass spectrometer. The space between valve V3 and the sample was designated chamber 1, while the space between the sample and valve V4 was designated chamber 2. A vacuum to 30 psi compound pressure gauge (Swagelok, USA) was mounted at the intersection of valves V1-V3 to measure the pressure in chamber 1.

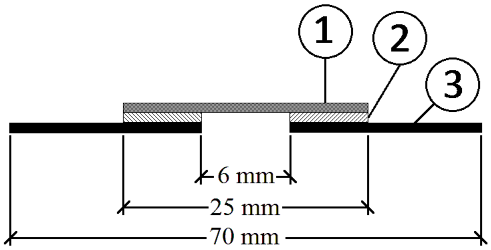

Figure 1a: Sample Assembly. 1: Sample (PEEK, Ti or Al2O3). 2: Joining material (Torr Seal or S-Bond 220). 3: Cu gasket.

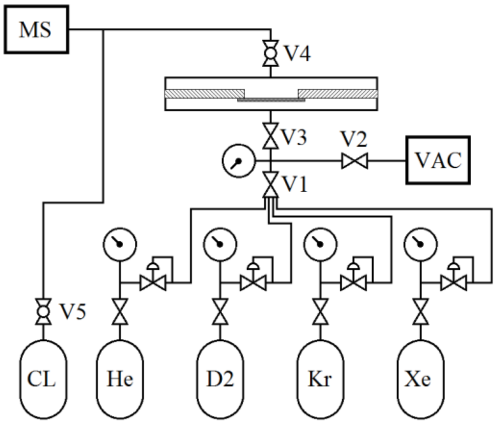

Figure 1b: Experimental Apparatus. MS: Mass Spectrometer. VAC: Vacuum source. CL: Calibrated Leak. He: Helium source. D2: Deuterium source. Kr: Krypton source. Xe: Xenon source. V1-V3: Ball valves. V4 & V5: Diaphragm valves. Gas sources are depicted with pressure regulators and gauges.

In addition to the above samples a fused silica capillary was used as an example of ideal flow through a well-defined channel, but required a modified setup due to its tendency to clog with particulate matter from the gas sources or other fittings after short periods of time. The output of valve V3 was fed into a 0.5 µm inline filter (Upchurch Scientific, Inc., USA), which led to a 40 mm section of 1.7 µm diameter (2 µm nominal) fused silica capillary (Polymicro Technologies, USA) which was used as the sample. The capillary output was connected to valve V4. This assembly, like the Conflat flanges, was housed in the GC oven for temperature control.

The test protocol was as follows: (1) A sample was mounted, chambers 1 and 2 evacuated, and the GC oven was set to 65°C overnight in order to remove volatile contaminants. (2) The following morning (typically a period of 12-14 hours) valve V4 was closed and valve V5 opened to feed the calibrated D_2 leak into the mass spectrometer as a reference signal. Once the mass spectrometer's signal had stabilized its magnitude was recorded for two minutes. (3) Valve V5 was closed, valve V4 was opened, and the test gas introduced into chamber 1 at 20 kPa. The resultant test signal was measured in the same way as the reference signal. (4) The gas pressure was increased and the signal recorded again. This increment was typically 20 kPa although concessions had to be made due to time constraints. After a series of pressures for one gas had been tested steps 1-4 were repeated with the next test gas.

The signal magnitude readings were then integrated to find their average and standard deviation. To compensate for drift in the mass spectrometer all readings were normalized to the signal obtained from the calibrated D_2 leak.

To convert the D_2 signal magnitudes into meaningful units (atm.cm^3/sec) the readings were compared directly with the D_2 reference. For He a calibrated 1.66E-7 atm.cm^3/sec He leak (Vacuum Technology Inc., USA) was mounted to the input of valve V4. Both the He and D_2 calibrated leaks were measured individually following the aforementioned test protocol to determine the mass spectrometer's relative sensitivity to He and D_2.

III. RESULTS

The D_2:He leak rate ratios are shown in Fig. 2, and the Kr:He and Xe:He signal ratios in Fig. 3. Results from the two Ti samples are omitted as no test gases could be detected, regardless of pressure or type. As the lowest He leak rate detected was 3.6E-10 atm.cm^3/sec it is expected that the Ti samples had a lower leak rate at 200 kPa, the highest pressure at which they were tested.

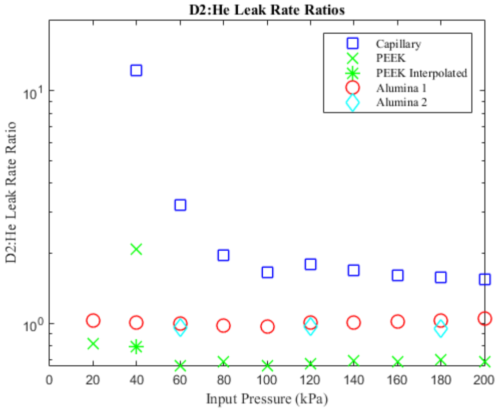

Figure 2: D_2:He Leak rate ratios as a function of the pressure difference across the sample. Leak rate ratios were calculated by using leaks traceable to calibrated standards.

IV. DISCUSSION

The leak rate ratios depicted in Fig. 2 demonstrate existing theory in some aspects, notably that both Al_2O_3 samples have a leak rate ratio of D_2:He very close to 1, indicating compliance with Graham's Law and that flow through the samples follows the molecular flow regime. The D_2:He ratio was lower in the PEEK sample, where solubility and bulk diffusion are both expected to affect the rate of flow, producing a lower ratio. Lower still were the flow rates of Kr and Xe, where neither gas could be detected at any pressure tested. This may be attributed either to lower solubility of these gases, or to reduced diffusion rates.

The Kr:He signal ratios for the two different Al_2O_3 samples were notably different, in contrast to Graham's Law, which predicts that the leak rate ratio for Kr:He should remain constant, even if the leak rates themselves vary.

The experimentally determined ratio for PEEK at 40 kPa was inconsistent with other data for this sample due to an unusually low He leak rate. We were unable to repeat the measurement, as the experimental apparatus had been disassembled at the time this outlier was first noted. In the absence of a repeat measurement, a datapoint based upon interpolation has been plotted along with the experimentally obtained datapoint.

The authors believe that these data demonstrate the existence of molecular sieving in at least one of the alumina samples and that these results can be explained using the

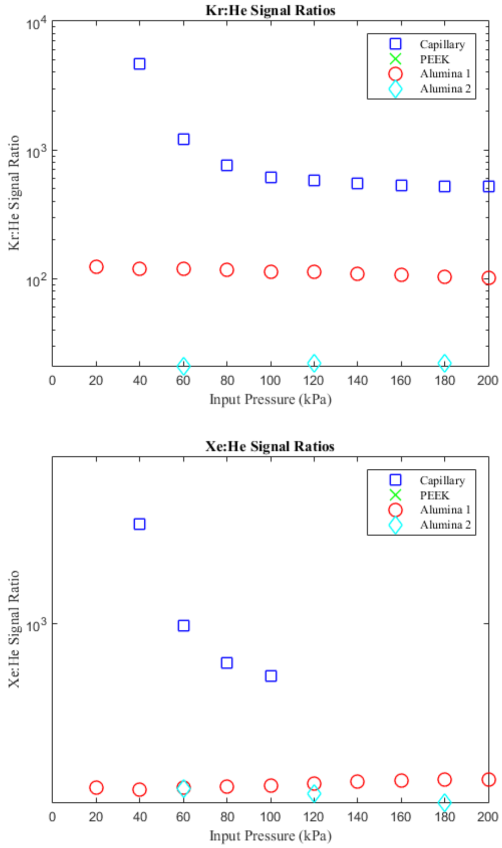

Figure 3: Kr:He and Xe:He mass spectrometer signal ratios as a function of the pressure difference across the sample.

TABLE I. ATOMIC RADII OF GASES

Radius Type (pm)	H/D	He	Kr	Xe
Covalent radius [18]	32	46	117	131
Van der Waals radius [19]	120	140	202	216

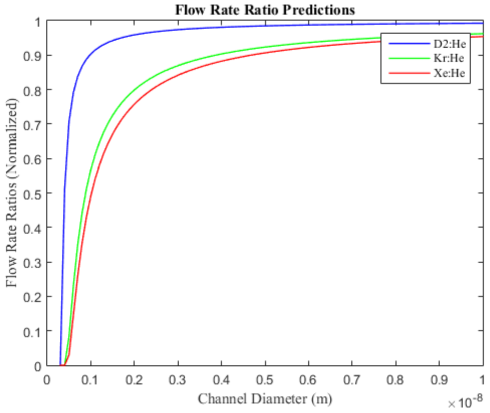

Figure 4: The flow rate ratios predicted by the HSM. Values on the y-axis are normalized to more clearly illustrate how the D_2:He ratios may remain similar over a range of diameters while the Kr:He and Xe:He ratios change by a larger amount.

HSM. Fig. 4 shows the results when the HSM is used to model flow rate ratios through single capillaries of varying diameters. The van der Waals radii in Table 1 were used to determine the diameters of the noble gases, while the 'diameter' of D_2, as a diatomic gas, was taken as the sum of twice the covalent radius and twice the van der Waals radius.

In this model two capillaries of differing diameters may have similar D_2:He ratios but Kr:He ratios that vary significantly, in agreement with our findings. The similarities in the Xe:He ratio, however, are not predicted, rather a significant difference should still be present due to Kr and Xe having similar atomic dimensions. The authors believe that this is due to surface flow and the large numbers of leak channels present, and that the distribution of leak channel dimensions plays a role in altering the separation ratios.

Of interest is why the separation ratios for capillary flow vary so much in comparison to the other samples tested, as the work by Lei & McKenzie [5] indicates that over the pressures tested the D_2:He ratio should have gradually risen from 1.01 to 1.09. Further investigation showed that while the measured flow rate for D_2 matched with theory, the flow rate of He was less than predicted. This difference may be due to Lei & McKenzie's use of N_2, a diatomic gas, while a monatomic gas may behave differently due to its geometry.

V. CONCLUSIONS

We have experimental evidence that molecular sieving occurs in hermetically sealed joints. If molecular sieving can be measured then it should be possible to infer the average leak channel size using a model such as Fain's HSM. This should aid in the prediction of flow rates from the channel and gas properties, rather than by comparison with other gases that behave differently, such as when helium is used to predict the leak rate of water vapor in implantable devices.

A further implication is that leak rate testing using ^{85}Kr and other larger-than-air tracer gases could underestimate the leak rate of smaller gases into hermetically sealed packages.

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