Corrections to Graham's Law of Effusion for Predicting Leak Rates Through Hermetic Seals

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***Abstract*— Graham's law of effusion has been used for decades to facilitate the prediction of the flow rates of gases penetrating into hermetically sealed devices. Typically, a trace gas such as He is used as a measure of gas flow into or out of a device. He flow is then related via Graham's law to the flow of an unwanted gas, and this in turn is used to predict the service lifetime of the device based on the maximum allowable leak rate. As hermetically sealed devices become smaller and lower leak rates are required, there is evidence to suggest that Graham's law is inaccurate. We evaluate Graham's law by measuring the flow rates of noble gases (He, Kr, and Xe) and diatomic gases (D_2 and N_2) through realistic leaks. Our findings indicate that Graham's law is not always accurate, and the incorporation of a relative tangential momentum accommodation coefficient into Graham's law leads to improved correlation between different gases and thus improved predictions of service lifetime.**

***Index Terms*— Graham's law of effusion, tangential momentum accommodation coefficient (TMAC).**

I. Introduction

WHEN electronic devices require high levels of reliability, hermetic packaging is often employed to protect sensitive components from environmental degradation. For implantable biomedical devices in particular, moisture ingress is of particular interest due to the device's operational location in the human body and moisture's ability to, when condensed, interact with solutes to then initiate and sustain corrosion [1]. Similar concerns also apply to the packaging of integrated circuits. The ingress of noncondensable gases may also be a concern: microelectromechanical systems (MEMS) can incorporate components such as resonators operating in a vacuum that are highly sensitive to changes in pressure in the encapsulation [2]. One application for these resonators is in real-time clocks, where precise timing may be needed for data acquisition or transfer.

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Tests have been developed to predict the leak rate of arbitrary gases into a device. The most commonly used of these is the fine helium leak test described in MIL-STD 883H and used to predict leak rates across hermetic seals for both noncondensable gases, as in MIL-STD 883H, and also water vapor [1]–[3]. This test uses the Howl–Mann equation, and the version used to predict the leak rate of air has been reproduced in

$$R_1 = \frac{LP_E}{P_O}\left(\frac{M_A}{M}\right)^{\frac{1}{2}} \times \left\{1 - e^{-\left[\frac{Lt_1}{VP_O}\left(\frac{M_A}{M}\right)^{\frac{1}{2}}\right]}\right\} \times e^{-\left[\frac{Lt_2}{VP_O}\left(\frac{M_A}{M}\right)^{\frac{1}{2}}\right]} \quad (1)$$

where R_1 is the measured leak rate of the tracer gas (typically helium), L is the air leak rate, P_E is the bombing pressure, P_O is the atmospheric pressure, M_A and M are the molecular masses of air and the tracer gas, respectively, t_1 is the bombing time, t_2 is the dwell time, and V is the internal volume of the device.

As a more general case, the leak rate of a small molecular mass (and thus fast leaking) trace gas such as He may be measured using a mass spectrometer. The flow of He is then used to predict the air leak rate through Graham's law of effusion as described in

$$\dot{m}_1 = \dot{m}_2\sqrt{M_2/M_1} \quad (2)$$

where $\dot{m}$ is the mass flow rate and M is the molecular mass.

Graham's law may be clearly seen several times in the Howl–Mann equation, in particular where the flow rate of the tracer gas must be converted into the flow rate of air.

In the case of implantable biomedical devices, the maximum acceptable amount of water inside the package before corrosion-based failure can occur is determined. By then using Graham's law or the Howl–Mann equation, the leak rate of a tracer gas may then be used to predict the leak rate of water and hence predict the lifetime of a hermetically sealed device.

If predictions using Graham's law are incorrect, then the device may fail unexpectedly. In the case of implantable biomedical devices, there may be a risk to the patient's health due to cessation of operation if the device is life sustaining (e.g., pacemakers) and a further risk in the form of the surgery needed to replace the device. Leakage of any gas into a cavity containing a MEMS resonator will dampen the movement of the resonator, leading to a loss in accuracy.

Despite its widespread use, there is evidence against using Graham's law for predicting water leak rates at the levels

required by modern hermetically sealed devices in the fine leak range ($<10^{-6}$ atm·cm^3/s). Graham's law has been used under the assumption that water flows through a leak channel purely as a vapor in the molecular flow regime [1], [4], [5]; however, it has been demonstrated that water leak rates are greater than what is predicted from air leak rates [6]. It is also known that water vapor is a condensable gas and the presence of liquid water on the channel surfaces may result in faster or slower transport than expected from Graham's law [6]–[8].

There is also some experimental evidence to suggest that Graham's law is not accurate even for noncondensable gases [9], although Romenesko and Ely came to the opposite conclusion.

There is also an objection to the use of Graham's law on a theoretical basis. Graham's law is related to Knudsen's equation for molecular flow

$$\dot{m} = \frac{4\sqrt{2\pi}}{3} r^3 \sqrt{\frac{p_{\text{avg}}}{\rho_{\text{avg}}}} \frac{\Delta p}{L} \tag{3}$$

where $\dot{m}$ is the mass flow rate, r is the channel radius, p_{avg} and ρ_{avg} are the average pressures and densities across the channel length (taken by averaging the inlet and outlet pressures and densities), respectively, Δp is the difference between the inlet and outlet pressures, and L is the channel length [10].

By realizing this relationship to Knudsen's equation, a limitation to Graham's law becomes apparent. An underlying assumption of Knudsen's equation is that any molecules striking the channel wall will be reflected in a diffuse manner. It is, however, well documented that some proportion of reflections are specular [11]–[15]. This observation was first put forward by Maxwell, who described the tangential momentum accommodation coefficient (TMAC) α as the proportion of diffuse reflections. A TMAC of 1 indicates that all reflections are diffuse and a TMAC of 0 indicates that all reflections are specular. Given that a lower TMAC results in the retention of more momentum in the gas flow's direction of travel through the channel, the net result is a greater flow rate.

A common definition of TMAC is provided in

$$\alpha = \frac{\tau_i - \tau_r}{\tau_i} \tag{4}$$

where τ_i is the tangential momentum of the incident gas molecule and τ_r is the tangential momentum of the reflected gas molecule.

Due to the presence of TMAC, a year after Knudsen published his equation [10], a modified version was put forward by Smoluchowski [16]

$$\dot{m} = \frac{2-\alpha}{\alpha} \frac{4\sqrt{2\pi}}{3} r^3 \sqrt{\frac{p_{avg}}{\rho_{avg}}} \frac{\Delta p}{L}. \tag{5}$$

The most prominent reason for favoring Knudsen's original version over Smoluchowski's modified version is the uncertainty and difficulty in determining TMAC for a given set of conditions. However, the TMAC of a given gas/surface combination is not always at unity as Knudsen assumed or near it. Instead, it may be substantially less than unity as shown in Fig. 1. The effect of this may be seen using different values of α in (5), where a reduction of α from 1.0 to 0.9 results in a 22% increase in flow. As may be seen in the literature, factors that influence TMAC include the gas and surface compositions, surface roughness, adsorbed layers, gas velocity, and pressure [11]–[15]. A selection of reported TMAC for noble gases is provided in Fig. 1 to demonstrate the variance in observations. Despite this variance, the relationship between TMAC and molecular mass appears to be monotonic, even if different researchers have reported different magnitudes and directions in those trends. The causes of these differences are difficult to ascertain and some properties such as channel surface roughness are difficult to measure and sometimes not reported, while some properties are dependent on other variables, e.g., the presence and thickness of an adsorbed gas layer are dependent on gas type, pressure, and temperature. This may also extend to the experimental setup: if the TMAC is calculated using pressure-driven flow through a channel, then the gas velocity is dependent on the pressure. In contrast, a spinning rotor gauge decouples the two factors, but at the expense of being unable to evaluate a Knudsen number ($Kn = \lambda/d$, where λ is the mean free path and d is a characteristic dimension) that is directly comparable to that used when describing flow through a channel.

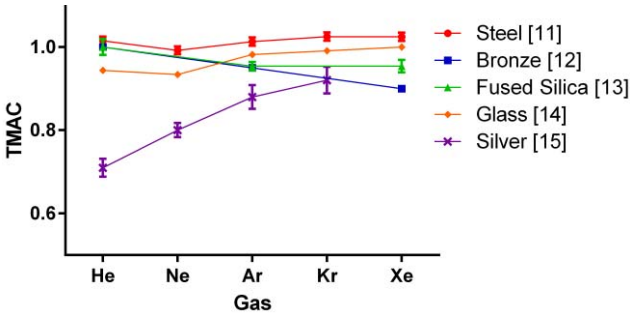

Fig. 1. Examples of different TMACs of noble gases in the transitional or molecular flow regimes as measured using channels formed from the materials given in the legend. This demonstrates that Knudsen's assumption of purely diffuse reflections is incorrect and also that channel material and gas type both play a role in determining TMAC.

Given the relationship between Graham's law and Knudsen's equation and that Smoluchowski's equation is a more refined version of Knudsen's equation, it stands to reason that a similar derivation may be performed to obtain a more general version of Graham's law that incorporates TMAC. The result is given in

$$\dot{m}_1 = \dot{m}_2 \left(\frac{(2-\alpha_1)\alpha_2}{(2-\alpha_2)\alpha_1} \right) \sqrt{\frac{M_2}{M_1}}. \tag{6}$$

While the actual TMACs of a leak channel of unknown geometry are impossible to measure, we hypothesize that through the flow rate measurements of two gases, one may determine what we describe as the relative TMAC. Here, we assume an arbitrary TMAC for one gas and then calculate a relative TMAC for the other gas using (6). In comparison, Graham's law assumes a TMAC of 1 for both gases and thus also assumes that the TMAC ratio is 1. Therefore, while we are still making an assumption, it is a more realistic one than

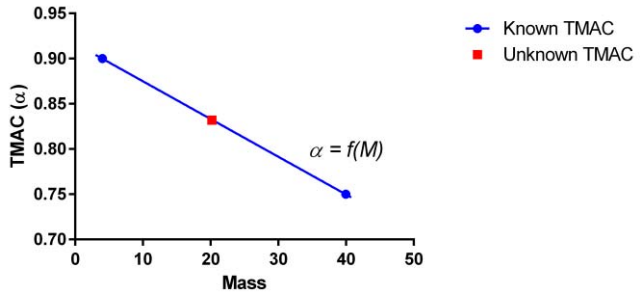

Fig. 2. Proposed use of (6), where if the relationship $\alpha = F(M)$ is known (in this example, it is assumed to be linear for simplicity), then by finding the TMAC of two gases, the TMAC of a third unmeasured gas may be interpolated. This predicted TMAC may then be used in (6) to generate a more accurate prediction of the flow rate of the unknown gas.

what occurs in Graham's law. Furthermore, a literature review for values of TMAC may be of value in selecting an assumed TMAC that may be close to the true value. As described in Fig. 2, if we can approximate the relationship between TMAC and molecular mass, then by knowing the molecular mass and relative TMAC of two gases, we may interpolate the relative TMAC of a third gas that has an unknown flow rate, provided that it possesses a molecular mass between those of the first two gases. For example, Fig. 2 describes a situation where the relative TMAC of He (mass: 4.00) and Ar (mass: 39.95) are known, and we assume that the relationship between TMAC and molecular mass, $\alpha = F(M)$, is linear. Then by knowing the mass of Ne (20.18), we may then interpolate to predict the relative TMAC of Ne. It should be noted at this point, however, that the accuracy of this method will depend on the accuracy of $\alpha = F(M)$. While using (6) and assuming a linear relationship should provide better results than using Graham's law alone, further improvements will be seen if the relationship between TMAC and molecular mass can be more accurately described.

II. Experimental Setup

A. Equipment

To demonstrate the utility of (6), flow rates through soldered samples were measured using a two-chamber constant volume technique [17]–[19], as shown in Fig. 3. The volumes of both chambers were made to be large relative to the volume of the leak channels tested in order to minimize the effects of pressure variations over the course of the experiments.

The larger upper chamber (designated chamber 1) was filled with a predetermined quantity of gas. The gas would then flow through the sample mounted on a CF flange and into chamber 2.

The samples used were 25-mm-diameter, 1-mm-thick 96% polycrystalline Al_2O_3 discs (Kerafol, Germany) soldered to copper annuli with inner diameters of 6 mm using S-Bond 220 solder (S-Bond Technologies, USA). All samples were manufactured in a nominally identical fashion. Of importance here were the leak channels present in these samples, predominantly where the solder met the copper or alumina.

The flow rates of five gases through these samples were measured to test Graham's law. He, Kr, and Xe were used

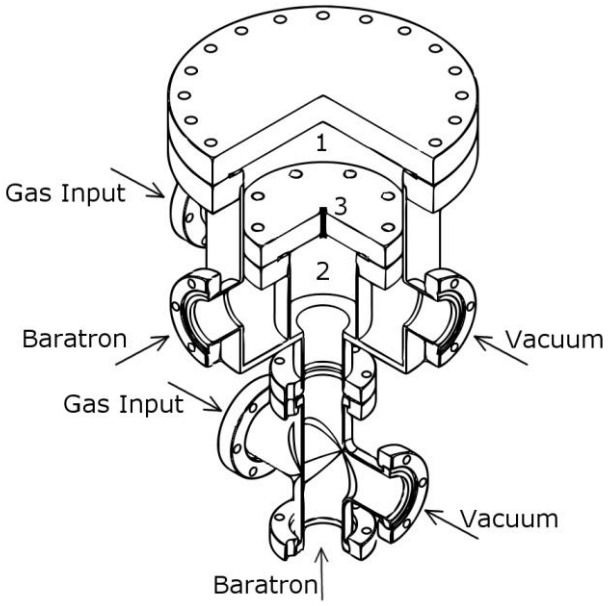

Fig. 3. Experimental apparatus. 1: chamber 1. 2: chamber 2. 3: sample mount.

due to their status as simple monatomic gases. Furthermore, as He is commonly used as the tracer gas in leak rate tests, its inclusion was of great importance. The diatomic gases D_2 and N_2 were also tested, the former because it possessed a very similar molecular mass to He while also possessing a different geometry, and the latter because of its prevalence in air.

Pressures in both chambers were measured using "Baratron" capacitance manometers manufactured by MKS Instruments Inc., where the maximum operational pressures for the manometers were 1000, 100, 10, and 1 torr. The pressures used were dependent on the leak rates of the individual samples: too high a leak rate would cause the pressure in chamber 2 to traverse the full range of the capacitance manometer too quickly for the pressure change to be recorded. Other measurements encountered the reverse problem: even with the highest measurable pressures, the flow rate was extremely low, necessitating an extremely long measurement time. Due to these concerns, the time at which pressures in both chambers were measured ranged from 15 min to approximately three days. The specific times were chosen so that the pressure in chamber 2 would change by at least 10% of the capacitance manometer's usable range.

Four alumina samples soldered to copper annuli were tested using the procedure described above. Using the measured leak rates, we were able to evaluate the accuracy of Graham's law.

B. Calibration and Uncertainty

The volume in chamber 2 was measured to be 447.6234 mL $\pm$ 0.0098 mL using a known volume reference.

The manometers were compared to each other and to the 100-torr manometer, which was factory calibrated, meeting the ISO/IEC 17025:2000 requirements. Based on these comparisons, a linear equation to convert the gauge output voltage (V) into pressure (Pa) was formed (7), where P is the pressure,

TABLE I
MANOMETER CALIBRATION COEFFICIENTS

Manometer	a	b
1000 torr	99.998	-5.7889
100 torr	10.000	0.0000
10 torr	1.0021	0.1231
1 torr	0.0977	0.1110

and a and b are constants as given in Table I. The final constant then converts the pressure from torr to pascal

$$P = (V \times a + b) \times 133.3224. \tag{7}$$

To determine experimental uncertainty, the method described by Ewart *et al.* [18] was used. Isothermal conditions were assumed and the uncertainty was therefore related to the specifications of chamber 2, where the ideal gas law applies

$$PV = mk_BT. \tag{8}$$

where P and V are the pressure and volume of chamber 2, respectively, m is the molecular mass of the gas in chamber 2, k_B is the Boltzmann constant, and T is the temperature of the system.

Taking the chamber volume to be constant, we can write that

$$\frac{dP}{P} = \frac{dm}{m} + \frac{dT}{T}. \tag{9}$$

The division of (9) by dt yields an expression for the mass flow rate as follows:

$$\frac{dm}{dt} = \frac{V}{k_BT}\frac{dP}{dt}(1-\delta) \tag{10}$$

where $\delta = (dT/T)/(dP/P)$.

If $\delta \ll 1$, then it may be neglected [18]. The maximum temperature variation over the course of our experiments was 0.1 °K at 293.15 °K, as measured by a precision mercury thermometer. The smallest pressure variation in chamber 2 and hence largest value of δ came from an increase in pressure from 112.143 to 113.969 Pa. This yielded a worst case scenario of $\delta = 2.095 \times 10^{-2}$. Therefore, the expression for the mass flow rate may be taken as

$$\frac{dm}{dt} = \frac{V}{k_BT}\frac{dP}{dt}. \tag{11}$$

For the experiments performed, as the change in pressure is small compared to the initial pressures, *dP/dt* may be expressed as a linear function.

The total fractional uncertainty may thus be described as in

$$\frac{\Delta\dot{m}}{\dot{m}} = \frac{\Delta V}{V} + \frac{\Delta T}{T} + \frac{\Delta a}{a} \tag{12}$$

where Δ indicates the absolute uncertainty and a is the slope of the function *dP/dt*.

TABLE II
SAMPLE INFORMATION

Sample Description	Input Pressure	Output Pressure	He Flow Rate (atm.cm^3/sec)
a) Sample 1	78 kPa	110 Pa	2.31 x 10^{-6}
b) Sample 2, Pressure 1	76 Pa	35 Pa	1.99 x 10^{-5}
c) Sample 2, Pressure 2	315 Pa	115 Pa	8.69 x 10^{-5}
d) Sample 3, Pressure 1	1020 Pa	113 Pa	5.61 x 10^{-8}
e) Sample 3, Pressure 2	79 kPa	105 Pa	1.37 x 10^{-7}
f) Sample 4, Pressure 1	9100 Pa	113 Pa	2.43 x 10^{-7}
g) Sample 4, Pressure 2	80 kPa	112 Pa	2.60 x 10^{-7}

III. RESULTS AND DISCUSSION

A. Data Analysis

To ensure that our use of (6) is valid, the conditions required to use (5) were reviewed. Given the channel dimensions and pressures used, we were satisfied that the channel length was much greater than the average channel radius, that the pressure gradient along the length of the tube was sufficiently small, and that the experiments were being performed in the molecular flow regime.

Information on the initial pressures used to test the flow rates of all gases through particular samples is provided in Table II. The He flow rates at those pressures are also provided to demonstrate the variability in the samples. We attempted to keep the pressures in chamber 2 constant at 110–115 Pa, the exception was sample 2, which had a very high flow rate, necessitating a reduction of the pressure in chamber 2. The pressures in chamber 1 were chosen based on the pressure ranges of the capacitance manometers used and their calibration.

The flow rates predicted by Graham's law are compared to the measured flow rates in Fig. 4. The highest uncertainty of a measurement over the course of the experiments was 2.23% of the readings. While Samples 1 and 2 appeared to follow Graham's law, Samples 3 and 4 showed clear deviations, where the observed flow rates of some gases could be more than double the flow rate predicted by Graham's law.

As stated previously, the true TMAC of the leak channels in a given sample is impossible to determine as we do not know the channel geometry. However, if the proposed corrections to Graham's law (6) were applied to these results and by assuming that helium had a TMAC of 0.9, we may calculate a relative TMAC of the other gases using He as a reference. The results are as in Fig. 5. The TMAC of 0.9 for He was chosen based on the review of TMAC in Fig. 1, and also for convenience so that the relative TMAC values of other gases lie in the range 0 to 1.

The decreasing trend in TMAC has been previously reported in [12] and [13], as per Fig. 1. We believe that the extremely low TMAC seen in samples is a function of the small channel diameters, which should be orders of magnitude lower than

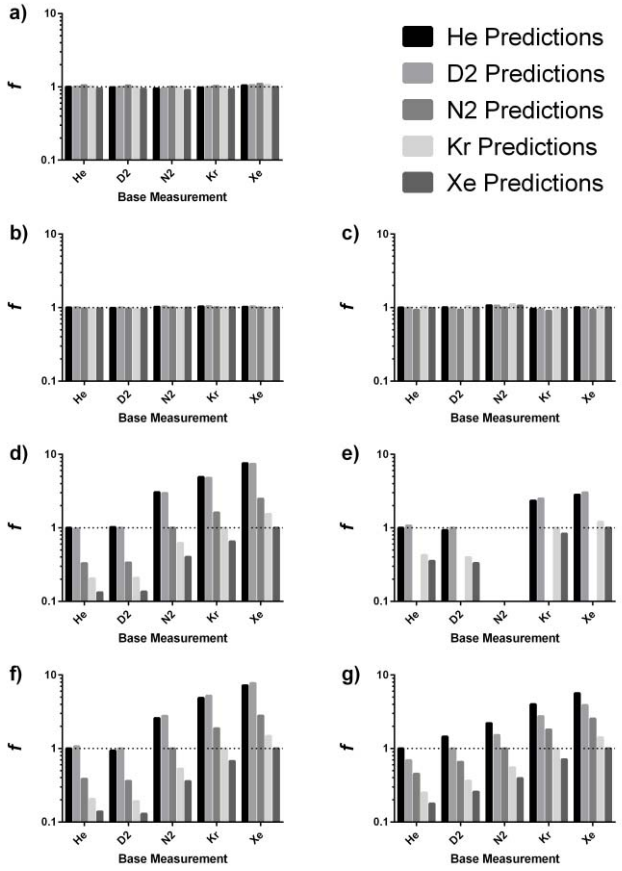

Fig. 4. Accuracy of using Graham's law in predicting flow rates, showing that Samples (a) 1 and (b) and (c) 2 follow Graham's law, while Samples (d) and (e) 3 and (f) and (g) 4 do not. This comparison is performed by taking the flow rates predicted using Graham's law as a fraction of the measured flow (f), shown on a logarithmic scale. Samples (a)–(g) in Table II correspond to those of (a)–(g). For each set of five base measurements, there is one prediction that must be correct and have an f of 1 (e.g., the prediction of He from the known He flow rate must be accurate), while the other predictions may vary considerably. The N_2 readings in (e) are absent due to the sample breaking during that test and causing an extremely high flow rate. If Graham's law were tested using this flow rate, the prediction of He from the N_2 flow rate would be 5.81×10^6 times the measured He flow rate.

those used to determine the TMAC in Fig. 1. This would multiply the number of times a gas molecule collides with a wall and result in a stronger effect.

These results demonstrate that the TMAC should be considered when attempting to predict the flow rates of gases through leak channels like those found in hermetically sealed devices. More specifically, these results serve as a warning that if the flow rate of a lighter gas is used with Graham's law to predict the flow rate of a heavier gas, that prediction may underestimate the real flow rate. Given the ubiquity of the fine helium leak test, this category of heavier gases may include the vast majority of known gases.

The inclusion of TMAC may take place through the use of the modified version of Graham's law, which requires the prediction of the TMAC of an unknown gas using two known flow rates. One gas of known flow rate should have a molecular mass higher than the unknown gas and the second gas should have a lower molecular mass. The closer the masses of the

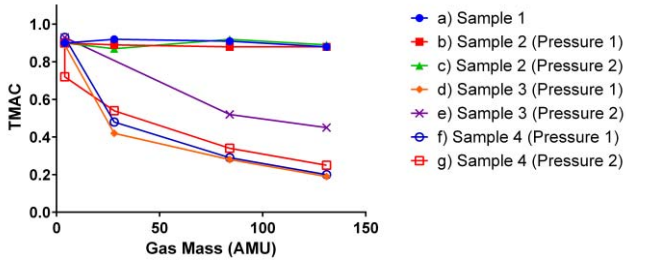

Fig. 5. Relative TMAC as calculated using (6). Sample descriptions correspond to those in Table II.

known gases are to that of the unknown gas, the more accurate are the predictions.

While the channel geometries inside a sample remain constant irrespective of the gas being tested, due to the uniqueness of the channel geometries, the set of relative TMACs generated for one sample is unlikely to be applicable to other samples.

As an example, let us take the results from sample 4 at high pressures, as described in Fig. 4(g), and an attempt to predict the flow rate of Kr from N_2 and Xe. Using (6), the relative TMACs of N_2 and Xe are 0.54 and 0.25, respectively. Due to a lack of further information about how TMAC varies with respect to molecular mass, we will use linear interpolation to predict the TMAC for Kr, yielding a value of 0.383. After the relative TMAC is known, (6) may be used to predict the flow rate of Kr from both N_2 and Xe. The predicted flow rates from these two gases are 86.3% and 84.9% of the measured flow rate of Kr. In comparison, using Graham's law alone (2), the predictions are 55.3% and 140.9% of the measured flow rate. Of particular note is how the difference between the predictions made using (6) and the measured flow rate are similar in magnitude and have the same sign. In comparison, the difference between the predictions made using Graham's law and the measured flow rate are not only larger, but differ in sign.

The results of using the above method to predict the flow rates of N_2 and Kr for all samples are as shown in Fig. 6. A general improvement in accuracy can be seen, and no adverse consequences are shown when using (6) if Graham's law is already accurate, as demonstrated by the results for Samples 1 and 2. If we take the differences in predictions from all four samples, the root-mean-square error when Graham's law is used is 140.4% of the measured values, while if our modified law is used, the overall error is only 23.5%. It should be noted that in both cases, the majority of the error came from Samples 3 and 4, being those that did not conform to Graham's law.

The accuracy of (6) is dependent on the accuracy of the method used to calculate the relative TMAC. This may be seen in Fig. 6(d), (f), and (g), where the N_2 flow rate predictions were consistently less accurate than the Kr predictions. This was due to the less accurate TMAC predictions, e.g., in Fig. 6(g), the predicted relative TMAC for N_2 was 135.5% of the measured TMAC, but for Kr it was only 112.8%. This is attributed to our assumption that the relationship between TMAC and molecular mass is linear. This assumption was made due to its simplicity, but as demonstrated in

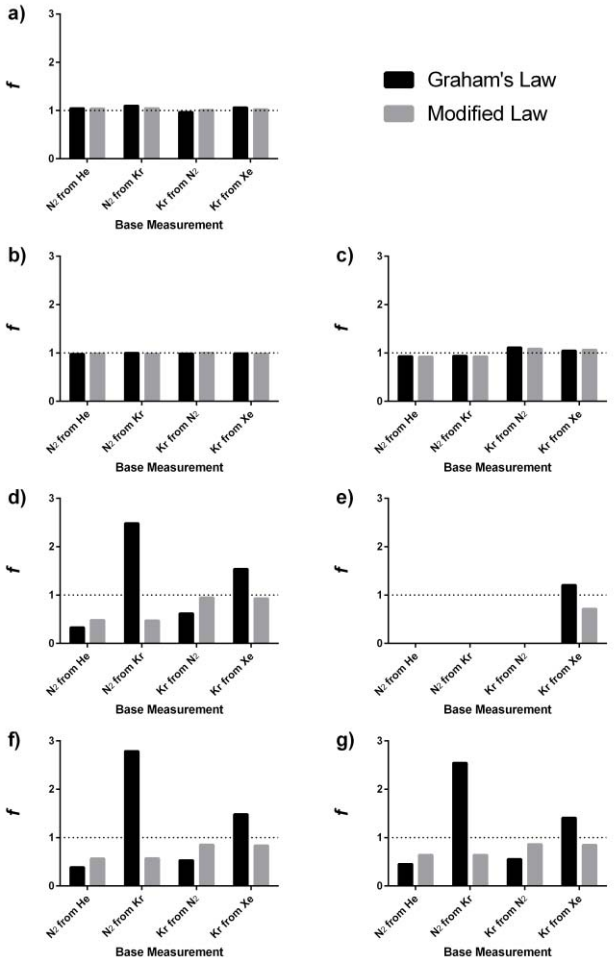

Fig. 6. Predicted flow as a fraction of the measured flow (f), where the flow rates of N_2 and Kr are predicted using both Graham's law (1) and our modified law (6). Results requiring N_2 in (e) are absent due to the sample breaking during that test, as previously noted in Fig. 4. The modified law shows better agreement with the observation. Samples (a)–(g) in Table II correspond to those of (a)–(g).

Figs. 1 and 5, better fits may be obtained. An improved understanding of how TMAC and molecular mass are related will result in improved flow rate predictions.

B. Comparison to the Literature

In addition to our own analysis, it is instructive to compare these results to those obtained by Romenesko and Ely [9], who performed fine leak tests using both He and Kr and concluded that the use of molecular weight scaling (Graham's law) was supported by the data. Forty-one samples were tested. However, results were excluded from further analysis if the measured leaks were at the upper or lower limits of detection for either of the He or Kr leak rate tests, resulting in less than half of the data points being used. While a large number of these samples showed no detectable leak rate of either He or Kr, seven excluded samples had measurable He leak rates but a Kr leak rate lower than the detection limit, while many of the samples that were used by Romenesko and Ely [9] to support Graham's law possessed similar He leak rates to those that were excluded (between 1×10^{-5} and 3×10^{-8} atm·cm^3/s). We believe that the presence of such a large group cannot simply be excluded in this way without further investigation, in particular if there was an experimental or handling issue that caused a blockage, or whether these samples do indicate a deviation from Graham's law. Furthermore, some of the data points that were retained also showed large deviations from Graham's law: when both Kr and He leak rates were converted into equivalent air leak rates, three samples deviated from predictions by up to an order of magnitude.

A comparison of our results to those of Romenesko and Ely [9] shows that in both sets of results, there appear to be two types of samples: those with flow rates that conform to Graham's law and those that vary substantially. However, the direction of the deviation is different: Romenesko and Ely's [9] results indicate a lower Kr leak rate than one would expect from the He leak rate, while in ours the opposite is true. This may be attributable to different trends in TMAC, as may be seen in Fig. 1, where different authors describe the TMAC as increasing or decreasing with respect to mass. No conclusive reason has been given. However, simulations previously performed by the authors indicate that these contradictory trends may be due to the TMAC of entrapped gas molecules on the channel surface that are later released when they gain enough energy from free gas molecules that impact the surface [20].

As such, we believe that Romenesko and Ely's [9] results do not, in fact, support the use of Graham's law, but instead demonstrate the need for a modification to account for TMAC, which, as we have shown previously, produces more accurate predictions.

C. Implications and Implementation

Given the use of Graham's law in the Howl–Mann equation itself described in MIL-STD 883H, we may conclude that using the Howl–Mann equation may result in an underestimation of the true leak rate of air, leading to out-of-specification devices and the potential for premature device failure.

To demonstrate the effect that this may have, let us imagine a sealed package with an internal volume of 0.1 cm^3 and a resonator that is initially held at a pressure of 10 kPa. The frequency of this resonator changes at a rate of 20 Hz/kPa and is considered to be unusable when the frequency has changed by 40 Hz, i.e., an internal pressure change of 2 kPa. We wish for the device to have a lifetime of ten years.

We may use the following equation and industry standard units to calculate the maximum acceptable leak rate:

$$L = -\frac{V}{t}\left[\ln\left(1 - \frac{Q_{inP}}{\Delta p_i}\right)\right] \tag{13}$$

where L is the leak rate in atm·cm^3/s, V is the internal volume of the chamber in cubic centimeters, t is the lifetime of the device in seconds, Q_{inP} is the pressure change that arises from the amount of gas that has leaked in over the time t in atm, and Δp_i is the initial partial pressure difference of the gas between the inside and outside of the device in atm [1].

Using the above information, the maximum allowable leak rate of air is 7.02E-12 atm·cm^3/s. If a package was measured to have a He leak rate of 1.00E-11 atm·cm^3/s, then using

Graham's law and taking the molecular masses of air and He to be 28.7 and 4, respectively (as per MIL-STD 883H), the predicted air leak rate would be 3.73E-12 atm·cm^3/s, satisfying our requirements.

If, however, using our proposed method, we find out that the relative TMACs of He and air for this package are 0.9 and 0.54, respectively (similar to sample *g* as described in Table II and Figs. 4 and 5), we will find that our air leak rate is actually 8.26E-12 atm·cm^3/s. This is above our acceptable threshold, and will result in an undesirable lifetime of only 8.5 years.

From this example, we may see that the modified version of Graham's law that we propose in (6) has the potential to be used in hermeticity testing to provide more accurate results than are currently obtained. Doing so would be more complex than the current helium leak test as described in MIL-STD 883H. However, the need for accuracy cannot be overstated, given the importance of hermeticity testing for devices involved in biomedical and aerospace applications, to name two examples.

In theory, the method used for the helium leak test as described in MIL-STD 883H could be duplicated for a second gas. However, we advocate backfilling the package [1], [21] to avoid complications that may arise from bombing. The sealed device may then be placed in a vacuum chamber and an appropriately tuned mass spectrometer may then be used to measure the leak rates of both gases out of the package. Given the size of the leak channels, we expect to be in the molecular flow regime and therefore the flow of one gas should not affect the flow of the second gas.

Despite these more accurate predictions, it should also be noted that the modification of Graham's law, as with the original version, is only applicable to noncondensable gases, such as He and N_2. If the flow rate of water or other condensable gases is to be accurately measured, the movements of both water vapor and condensed water must be taken into account, as described in [22].

IV. Conclusion

We have demonstrated that Graham's law can produce significant inaccuracies in its prediction of flow if the TMAC is not accounted for. These inaccuracies may result in incorrect lifetime predictions for hermetically sealed devices. We proposed a modification of Graham's law that accounts for the TMAC and improves the correlation between the predicted and measured gas flow rates.

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