Critical Review

Recommended practices for the calibration and use of leaks

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This document is the consensus view of the Calibrated Leak Subcommittee of the Recommended Practices Committee of the American Vacuum Society. It is divided into four main sections: Description, Calibration, Proper Usage, and Recommended Documentation of Leaks. Included in Sec. II are discussions of types of leaks, temperature effects, depletion rates, and units of leakage rate measurement. Section III addresses primary and secondary techniques for leak calibration, including uncertainties. Section IV addresses the proper handling and usage of leaks to achieve optimum results, recommendations of standardization of connections, and safety. The documentation to accompany and to be attached to each calibrated leak, recommended in Sec. V, is intended to provide the user with sufficient information about the leak for accurate and safe use. The appendices contain a glossary and a discussion of the use of throughput and flow rate units and conversions.

I. INTRODUCTION

Leaks are used to provide controlled delivery of gases at relatively low flow rates for a variety of applications, including gas transfer and calibrations of mass spectrometers and leak detectors. A leak consists of a gas source, a flow restricting element, and a means of attachment to a system. Common terms used to describe leaks are calibrated leaks, standard leaks, or leak artifacts. Flow rates from leaks discussed here are less than 10^{-6} mol s^{-1} (2×10^{-2} atm cm^3 s^{-1} at 0 °C or 2×10^{-3} Pa m^3 s^{-1} at 0 °C). A schematic diagram illustrating the important components of a leak is shown in Fig. 1.

With the advent of tighter quality control constraints for many industrial goods and processes and with greater public awareness of environmental and other safety issues, the quantification and control of leakage rates is becoming an increasingly important matter, placing increased demands on the understanding of leak behavior and on the accurate measurement of leakage rates. The Calibrated Leak Subcommittee of the American Vacuum Society (AVS) Recommended Practices Committee was formed with its major goal being to provide a document in which the manufacturers, calibrators, and users of leaks could find or be directed to the best techniques and practices to fit their requirements. The Subcommittee, made up of representatives from manufacturers, calibrators, and users, has held many meetings in which the relevant issues were discussed and debated. This document contains the best technical judgement of the Subcommittee members, tempered by practical considerations. It is intended to be the AVS primary source for critically evaluated information on leaks. However, this document is not intended to be comprehensive or exhaustive concerning experimental and other detail, and selected references are provided in the Bibliography to enable further study.

This document contains four key sections. Section II discusses the various types of leaks that are in use and provides information to enable a user to select the type best suited to meet the requirements. Temperature effects and depletion rates are considered. This section briefly describes the concepts of leakage rate, of pressure–volume and throughput units to describe leakage rate, and the confusion that frequently ensues when this is done. The recommendation of the use of moles per second (mol s^{-1}) as the unit of leakage rate measurement is fully discussed. A discussion of several methods of calibration of leaks and related uncertainties appears in Sec. III. Section IV only briefly addresses proper handling procedures, standard connections to vacuum systems, and safety, because these topics are well covered in other sources.[1] Section V contains recommendations on information to be included on the label attached to each leak and on the document accompanying each leak. A selected bibliography is included, covering leak uses, calibrations, and practices. The Appendices include a glossary which extends and modifies the American Vacuum Society Dictio-
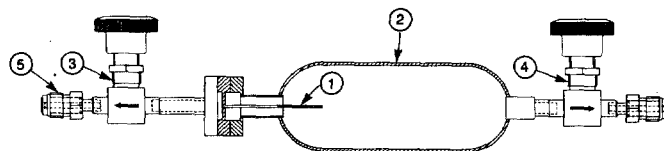

FIG. 1. Schematic diagram illustrating the major components of a leak. (1) leak element, (2) reservoir, (3) leak valve, (4) fill valve, (5) process connection.

nary as applied to leaks and a discussion of conversion between units and of flow rate and throughput.

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II. DESCRIPTION OF LEAKS

A. Types of leaks

While it would be difficult to describe in detail the wide variety of leaks that are commercially available, there are some features that all have in common. In its most basic form, a leak is divided into three components: (i) the leak element, (ii) the gas supply, and (iii) the gas outlet. Figure 1 shows schematically the arrangement of these components. The housing for the leak element allows the introduction of gas at relatively high pressure to one side of the element, usually from a pressurized reservoir, and presents the gas that passes through the element to the process apparatus attached to the other side. Volatile liquids and solids can also be used in leaks.

The leak element can be anything compatible with the system that limits the flow of gas to the desired level in a safe, stable, reproducible fashion. Additional design requirements include ruggedness, durability, low susceptibility to clogging and contamination, and the ability to pass only one gas species. Permeation leak elements, which allow gas to permeate through the element, have been made of glass, plastics, elastomers, metals, and other materials. Examples are helium and hydrogen which permeate glass and palladium, respectively. Physical leak elements, which use physically restrictive construction designs to effect the desired pressure drop, include capillary tubing, drawn glass capillaries, crimped tubing, sintered materials, and orifices. While physical leaks allow the flow of many fluids, permeation elements generally allow the flow of only one or a few species, thus also acting to purify the permeating gas. Table I lists some characteristics of various leak elements.

TABLE I. Some characteristics of leak element types.

Leak element	Gases	Temperature coefficient, %/°C	Flow rate range, mol s^{-1}
Permeation			
Glass	Helium	2–7	10^{-15}–10^{-9}
Paladium	Hydrogen	3–7	
Plastic	Water SO$_2$, NO$_2$	10–20	10^{-13}–10^{-8}
Physical	Any[a]		10^{-12}–$>10^{-6}$
Capillary		<0.5	
Crimped tube		<0.3	
Sintered			
Orifice		<0.3	

[a] Must not coat or react with the leak element.

While it is desirable to have a good theoretical understanding and experimental measurements of the flow rate through each leak element as a function of pressure, temperature, and gas species, this is usually not available. Experimental data for other leak elements of the same class can frequently be used to estimate the first two dependencies. Species dependence should always be determined for each type of leak element.

Design requirements for leaks may include fast time response to changes in temperature and partial pressure (or concentration) differential, portability, and ease of use. For leaks in which the gas is supplied from a fixed reservoir, sufficient gas should be available to prevent large changes of the leakage rate with time.

The leak should also be designed with process connections suitable to the equipment under test and able to minimize leakage to or from the environment. For leaks for which the process connection side is a vacuum system, the leak should also be designed with vacuum-compatible materials and valves that are free of virtual leaks and outgassing sources. While there is no single type of leak that meets all of these design criteria, the choice of what type of leak to use in a particular situation depends heavily on which of the criteria are most critical to the application. Also, since it is usually economically desirable to maintain a small inventory of leaks, the use of a design which facilitates the widest range of needs, or can be adequately modeled[2] over a range of flow rates and gases, can be highly advantageous. A discussion of the various aspects of leak design can be found in Ref. 1.

There are several kinds of leak reservoirs. In its simplest form, an air leak can use the atmosphere as its reservoir. Relatively stable pressures and compositions are thus available for extended periods. A collapsing reservoir, such as a plastic bag filled with the gas of interest, provides nearly constant pressures but a limited supply of gas. Fixed volume reservoirs of metal or glass can be used as the source of high purity gases or mixtures. They have a valve or crimpable tubing which is closed after evacuation and backfilled to pressures from 10^2 to 10^7 Pa (10^{-3} to 10^2 atm). Large metal reservoirs filled to high pressures are useful for leaks with larger leakage rates to minimize the decay of the leakage rate, thus giving nearly constant flow rates for extended periods. The high densities of liquids and solids allow use of much smaller reservoir volumes.

A brief survey of several of the more common types of leak elements will further emphasize the relative advantages and disadvantages of the various designs.

1. Permeation leaks

The leak element in a permeation leak is made from a material which permits diffusion of one or more species of gas through it. The most commonly used element is the helium permeation type, which takes advantage of the relatively high, selective helium permeability of most types of glass. Typically, helium permeation leaks have either sealed or refillable reservoirs supplying helium to one side of a glass element, which is exposed on the other side to the vacuum system of a helium leak detector, mass spectrometer, or pro-

cess. The behavior of these leaks depends upon the permeation rate of the element, which is found experimentally to be an exponential function of the form[3]

$$Q_m = ATe^{-E/RT}, \tag{1}$$

where Q_m is the molar leakage rate (in mol s^{-1}), A is a constant incorporating the solubility, diffusivity, area, and thickness of the leak element, T is the absolute temperature, E is the diffusivity activation energy, and R is the ideal gas constant. The constants A and E are normally determined empirically during calibration. However, once established, this equation can be applied over a broad range of temperatures.[3,4]

Frequently, a linear approximation to Eq. (1) is used:

$$Q_m = Q_{cal}[1 + \alpha(T - T_{cal})], \tag{2}$$

where Q_m is the molar leakage rate at temperature of usage T, Q_{cal} is the molar leakage rate at the calibration temperature T_{cal}, and the temperature coefficient α is calculated from values of Q_m obtained over a suitable temperature range. It is recommended that α be calculated from a linear least-squares fitting routine, using leakage rate versus temperature data that are evenly distributed over the temperature range of interest. This correction is adequate over a very limited range of temperatures, as can be seen in Fig. 2, where the fitted data for an exponential function and two linear approximations are plotted. One approximation is a linear least squares fit of the data from 288 to 308 K while the other is drawn through the point at 298 K with a slope of 3% K^{-1}. Figure 3 shows that the errors associated with these linear approximations can be very large, particularly when the leak temperature lies outside the temperature range of calibration. These linear temperature approximations, however, give much more accurate flow rate estimates than no temperature correction, as shown by the solid line in Fig. 3. Therefore, it is recommended that linear corrections be limited to temperature ranges that keep errors below 10%. Any extrapolation beyond the temperature range over which the leak was calibrated should be avoided.
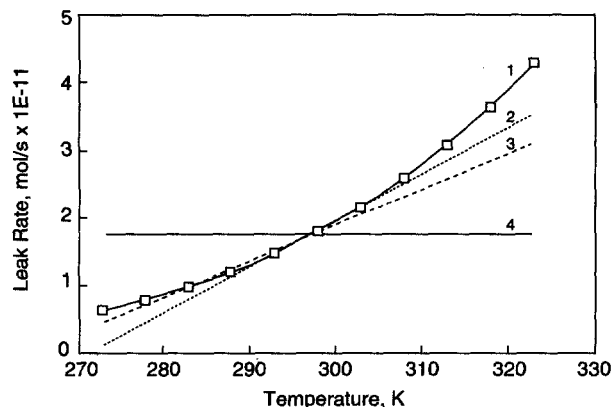
FIG. 2. Temperature dependence of leakage rate from a helium permeation leak. The solid line shows that experimental data □ are well described by Eq. (1). The straight dotted line is a linear least squares fit of data from 288 to 308 K, with slope $\alpha = 0.0684$ K^{-1}. The straight dashed line, with the commonly used assumption of $\alpha = 0.03$ K^{-1}, passes through the 298 K point.
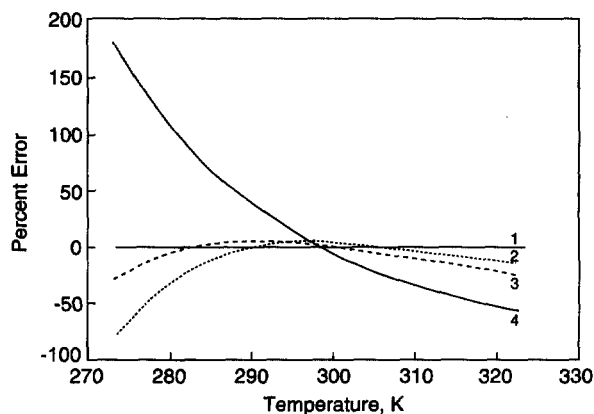
FIG. 3. Errors encountered with temperature dependence of a permeation leak. The dotted line represents the error from using a linear least squares fit from 288 to 308 K. The dashed line shows the error encountered in using $\alpha = 0.03$ K^{-1}. The solid curve demonstrates the very large errors introduced by using no temperature correction.

As an example, using Eq. (2) and the data for Fig. 2, the linear temperature coefficient is 3.7% K^{-1} (or °C^{-1}), and the reference temperature for calibration (i.e., the temperature of the leak when it was calibrated) is 293.0 K (19.8 °C). To determine the leakage rate at an operating temperature of 25.0 °C we use Eq. (2), with the leakage rate value of 1.46×10^{-11} mol s^{-1} (3.27×10^{-7} atm cm^3 s^{-1} at 0 °C) for the leak at the reference temperature as follows:

$$Q_m(T = 293.0 \text{ K}) = 1.46 \times 10^{-11}$$
$$\times [1 + 0.037(25.0 - 19.8)]$$
$$= 1.74 \times 10^{-11} \text{ mol s}^{-1}. \tag{3}$$

The use of this correction yields a leakage rate value that is within 2.2% of the value that would be achieved by using the exponential correction. Considering the relative accuracy of leakage rate and temperature measurements achieved in normal usage environments, this linear approximation of the temperature correction results in an error of leakage rate measurement that is acceptable for the majority of applications.

An additional factor which must be considered in making careful leakage rate measurements, but which is frequently overlooked, is that of the thermal time constant of the leak. The amount of gas per unit time permeating through the leak element is proportional to the surface area, concentration (or density) differential, and permeation constant, and is inversely proportional to wall thickness.[4,5] For most permeation leaks, the time required to attain a steady state flow rate after a temperature change is on the order of hours, which corresponds to the time required for the leak element to achieve thermal equilibrium, the permeation rate being a strong function of temperature. Consequently, the temperature must be stabilized prior to calibration and use to assure that the gas flow rate is stable before accumulating data. It is worth noting here that the permeation rate at a given temperature is proportional to the concentration differential, which *is not* a function of temperature in a closed-reservoir

leak, as opposed to the pressure differential, which *is* a function of temperature. This explains why, when a permeation leak is first filled with helium, several days are required to equilibrate the flow rate (the helium concentration in the reservoir is changed), while attainment of a stable leakage rate from a leak which has undergone a temperature change is much faster (the helium concentration in the reservoir is not changed).

There are several advantages of permeation leaks. The leakage rates are not very susceptible to contaminants in the fill gas or from atmospheric exposure, since the sealed element acts as a filter, purifying the gas passing through. They are usually very stable over long periods. Provided the construction conforms with good vacuum practice, leaks emitting very low flow rates of purified gases can be manufactured.

There are some disadvantages which must be overcome that require proper laboratory technique to assure accurate calibration and usage. The permeation rate is very temperature dependent and correction must be made for use at temperatures other than the original calibration temperature. Glass elements are fragile and consequently will not withstand a mechanical shock such as a drop on the floor. In addition, when the leak valve is closed for even moderate periods of time, the ensuing buildup of gas begins to saturate the permeation element so that, when opened, a considerable response time is experienced until steady-state flow rates are attained. Up to several days may be required for equilibrium, corresponding to the time constant for establishment of a new concentration gradient in the leak element. For this reason, it is recommended that permeation leaks with leak valves should be either stored with the valves open or that sufficient time be allowed after attaching the leak to the vacuum system so that steady state flow rates are achieved (i.e., > 24 h). Similarly, a temperature change of the leak also requires an equilibration period, usually on the order of hours, corresponding to the time required for the temperature of the leak element to reequilibrate. Permeation leaks, though sometimes less expensive than physical leaks, are restricted to those gases for which permeating materials are available.

Use of liquids and solids in permeation leak reservoirs introduces an additional temperature dependence. The equilibrium pressure above the condensed phase, and thus the concentration presented to the permeation leak element, is found from the Clausius–Clapeyron equation[6]

$$\ln P = [- \Delta H_{vap}/RT] + C, \qquad (4)$$

where ΔH_{vap} is the heat of vaporization, R is the gas constant, T is the absolute temperature, and C is a constant. For some materials, this vapor pressure dependence on temperature is much larger than that of the leak element, requiring much tighter temperature control and longer stabilization times.

2. Physical leaks

Physical leaks are those in which the leak element provides a physically restricted flow path between the reservoir and the process connection. Among the restrictions that have been used are capillary tubing, drawn glass capillary, crimped tubing, sintered powders, and micro orifices.

Because all of the constituents of the reservoir gas pass through physical leak elements, pure gases or well-characterized mixtures must be used to ensure the required composition of gas emitted by the leak. The purity of the gas emitted by the leak can be no higher than that of the gas in the reservoir, although the partial flow rates will in general be different from the partial pressures in the reservoir, depending on the relative conductances of the leak element for the different gas species. The user should be aware that some calibration methods give only total flow rates. If it is required, the flow rate of the gas of interest must be obtained by employing an analysis of the emitted gas or by using a calibration method that gives the required partial flow rate.

Because the flow regime in physical leak elements is usually not known, it is recommended that corrections for pressure dependence be established by means of calibration. In physical leaks, changes in temperature result in changes in the physical dimensions of the leak element, the reservoir pressure, and the gas viscosity, all of which affect the leakage rate. In addition, irreversible dimensional changes in the leak element will change the leakage rate, requiring periodic recalibration. Although temperature changes usually have a much smaller effect on the leakage rates of physical leaks than of permeation leaks, it is recommended that the temperature dependence be established empirically by means of calibration, and that temperature be included as a calibration parameter. For leaks with liquids or solids, the temperature dependence of vapor pressure, given by Eq. (4), is much larger than those of other effects. Another precaution to take when using physical leaks with fixed reservoirs is to avoid conditions where significant amounts of unwanted gas may "back-diffuse" through the leak element into the reservoir. This can happen if a large concentration of the unwanted gas is introduced to the downstream side of the leak element, or if the leak element is simply exposed to the atmosphere.

Physical leaks, especially those with small restrictive cross-sectional areas, can become plugged from exposure to particulates, and from condensation of vapors of oils, water, and other contaminants. For this reason, it is important that uncontaminated gases or mixtures be used to fill these leaks. A mechanical pump, even when protected by a molecular sieve trap, should not be used to evacuate physical leaks below the limit of the viscous flow regime. Filters are sometimes incorporated into physical leaks to minimize plugging hazards. Shutoff valves on physical leaks are a must and should be closed during venting and transportation to prevent plugging. The valve may also be used to limit the depletion of gas from the reservoir for larger leaks. Unlike permeation leaks, establishing steady state leakage rates after opening the valve on a physical leak is rapid, typically on the order of seconds. Care should be taken, however, to minimize the effects of the burst of gas that may enter a vacuum system when the valve is opened.

a. Capillary leaks. Capillary tubing and drawn capillaries (i.e., reduced diameter) are used to create leak elements for use with pure gases or mixtures. The most common usage is that of capillaries constructed with glass or metal tubing,

either with a self-contained reservoir or a supplemental gas source.

The temperature correction for capillary leak elements is generally quite small, less than 0.5% K^{-1}, and, therefore, can often be neglected. However, if a high degree of accuracy is required, the actual temperature correction over a limited temperature range will have to be established by calibration, since adequate calculations of thermal effects are difficult. This is primarily because the internal cross sectional shapes and dimensions of the capillaries are not generally known in sufficient detail to apply corrections. The main sources of the temperature dependence are the viscosity of the gas, which is proportional to $T^{1/2}$, and the reservoir pressure for closed reservoir leaks, which is proportional to T. These offsetting dependencies lead to near-zero effect on flow rate. For leaks which operate in the molecular flow regime, the molecular weight of the gas becomes an important parameter.

The dependence of the molar leakage rate on pressure is either linear for molecular flow,[7]

$$Q_m \propto (1/MRT)^{1/2}(d^3/l)(P_1 - P_2),   (5)$$

or quadratic for laminar viscous flow,[7]

$$Q_m \propto (d^4/\eta l)(P_1^2 - P_2^2),   (6)$$

where Q_m is the flow rate in mol s^{-1}, M is the molecular weight, R is the gas constant, T is the absolute temperature, d and l are the diameter and the length of the capillary, P_1 and P_2 are the upstream and downstream pressures, and η is the viscosity of the gas. These expressions for the flow rates are based upon the assumptions that the capillaries have a circular cross section. The differences in the dependence of molar leakage rate on pressure, temperature, tube dimension, viscosity, and molecular weight in the viscous and molecular flow regimes are important. Transition flow is less tractable to calculation of conductance.[7] The corrections for pressure dependence should be determined empirically because the flow regime in the restriction may not be known.

In leak checking, many leaks with leakage rates less than about 10^{-6} mol s^{-1} (about 10^{-2} atm cm^3 s^{-1} at 0 °C) fall within transitional flow behavior,[7] and, because the dimensions of the leak are seldom, if ever, known, it is almost always impossible to calculate accurately the flow rate of one gas through a leak from data taken with another gas. Therefore, the widespread use of "air equivalent leakage rate" based upon helium leakage rate determinations is generally invalid and should be strongly discouraged. For leaks with flow rates of less than about 10^{-12} mol s^{-1}, the flow regime is usually molecular, giving the $M^{-1/2}$ dependence.

Drawn glass capillary leaks are built so that the gas flows through a tiny physical opening in the glass. The capillary is made by heating and then pulling glass tubing to a fine, almost hairlike strand leaving a very thin internal diameter tube with a long path length. Drawn glass capillary leaks, like glass permeation leaks, are fragile, requiring care in filling and handling. When using drawn glass capillary leaks with helium, care must be taken to account for the contribution of helium permeation to the leakage rate, which may affect both the time response and the temperature dependence.

b. *Crimped metal capillary leaks.* Crimped metal capillary leaks are of all-metal construction and utilize a crimped (pinched) metal, usually stainless steel, capillary tube element. Due to their construction they are bakeable, UHV compatible, and virtually unbreakable. The crimped capillary leak element also has a low temperature coefficient. As with drawn glass capillary leaks, plugging is possible for leak elements with the very small cross sectional areas required for very low flow rates. Gas fill purity must be maintained and exposure to substances such as water and oil vapors prevented. Vacuum baking of the all-metal crimped capillary leaks can sometimes unplug contaminated leak elements. The elements are usually demountable, allowing repair or replacement, but recalibration is necessary. Proper construction and processing during manufacture are required to ensure clean, stable gas flows.

c. *Sintered leaks.* Sintered leaks consist of a plug of sintered powdered material mounted into a supporting fixture. Sintered leaks have been made of stainless steel and silicon carbide mounted into stainless steel and glass tubing, respectively. They are available with or without a gas reservoir. Since the effective cross sections of the gas paths in these leaks are extremely small, they are very susceptible to contamination from condensation. A sintered filter is highly resistant to clogging from other particles. Like other physical leaks, they have a low temperature coefficient. Other advantages are their low cost, ruggedness, and repeatability at higher leakage rates. However, they cannot be easily cleaned, and are sometimes unstable at low leakage rates.[3]

d. *Orifice leaks.* Leak elements made from thin metal foils in which a single hole (orifice) is present have been described.[8] Typically, the orifices are made in the foil by first creating a thin region on a disk by mechanical drilling. Then the orifice is made in the thinned region through chemical etching or laser drilling. The foils can be mounted into high vacuum fittings for easy attachment to the vacuum system and reservoir. The behavior of the gas flow through the orifices usually approximates a short or tapered tube, depending on the technique used to make the hole. Usually the cross sectional area of the orifice can be measured, making calculation of approximate leakage rates possible for a variety of conditions of gas species, pressure, and temperature. The low temperature coefficients, approximately -0.3% °C^{-1} at a constant reservoir pressure, are due primarily to the temperature dependence of the gas viscosity. The prime advantage of orifice leaks is that they can be used with any nonreactive gas, including mixtures. The purity of the emitted gas is limited by the purity of the gas supply. A disadvantage is that all orifice-type leak elements are prone to plugging by small amounts of contaminants in vacuum systems, since orifice diameters usually range from 10^{-4} to 10^{-3} cm. Care must be taken to keep orifice leaks clean during storage and use (see Sec. IV).

3. Decay rate of closed-reservoir leaks

The flow rate of gas coming from a closed-reservoir leak is a function of several parameters, the most important being the properties of the leak element, the pressure (or concen-

tration) of the gas in the closed reservoir, and the temperature of the leak. While the temperature of the leak can be regulated or monitored, the pressure of the gas in the closed reservoir can usually only be surmised, based on the initial filling conditions and the history of the leak. The leakage rate from such a leak is not constant in time, but will decay at a rate that depends on the amount of gas in the reservoir and the leakage rate. For those leaks where the leakage rate is directly proportional to the amount of gas in the reservoir, the decay will be strictly exponential if the leak is maintained at a constant temperature. Without knowing the mechanical properties and geometry of the leak, the time constant for decay can be calculated from the initial quantity of gas in the reservoir $N(0)$ and the initial leakage rate $Q_m(0)$, according to

$$\tau = N(0)/Q_m(0). \tag{7}$$

$N(0)$ can be determined from the reservoir volume (V) and the initial fill pressure $P(0)$ and temperature $T(0)$ using the following ideal gas law:

$$N(0) = [P(0)V]/[RT(0)]. \tag{8}$$

$Q_m(0)$ can be measured after the leakage rate equilibrates after initial filling. Although physical leak elements stabilize very quickly, several days are required to obtain a stable leakage rate after filling a permeation leak. Note that τ is the amount of time that it takes for the leakage rate to decay by a factor of $[1 - (1/e)]$, or 63%. Many leak manufacturers state a value of decay of leakage rate in terms of percent/year, which is not to be confused with, but can be derived from, the value of τ.

As an example, for an initial leakage rate of 1×10^{-10} mol s^{-1} (2×10^{-6} atm cm^3 s^{-1} at 0 °C), a fill pressure of 1000 Torr at 23 °C, and a reservoir volume of 1 ℓ, the time constant τ [$= N(0)/Q_m(0)$] is

$$\tau = (1000 \text{ Torr})(1\ell)/[(62.4 \text{ Torr } \ell \text{ mol}^{-1} \text{ K}^{-1})$$
$$\times (296.2 \text{ K})$$
$$\times (1 \times 10^{-10} \text{ mol s}^{-1})]$$
$$= 5.41 \times 10^8 \text{ s} = 17.1 \text{ yr.} \tag{9}$$

In one year ($t = 3.16 \times 10^7$ s), the leakage rate will have decayed by an amount $(1 - e^{-t/\tau})$, or 5.7%. Most closed-reservoir leaks sold commercially have yearly decay rates of 10% or less, with some as low as 2% per year.

B. Flow rate and units of measure

Fundamental to understanding and measurement of the flow rate of gases is a clear definition of the system through which the gas is flowing, the forces, mechanical or otherwise, which cause the gas to flow, the equation of state of the gas under conditions of equilibrium, and the energy flow in the system. If the system through which the gas is flowing is not well defined, then some of the gas molecules may be moving into areas not accounted for, and the anticipated flow rate past a particular area of the system may differ from the actual flow rate. Note that by "gas flow rate" we mean the net number of atoms or molecules of a particular gas species

passing a specified region of the system per unit time. Thus the simplest units of gas flow rate are atoms per second or molecules per second. Frequently, however, it is not possible to count directly the number of atoms or molecules, and the equation of state of the gas under equilibrium conditions is relied upon to obtain this information. In almost all practical cases of interest, the equation of state is adequately represented by the ideal gas law, given in Eq. (8). Note that one mole of gas molecules is 6.022×10^{23} molecules (Avogadro's number). From Eq. (8) it is easily seen that the number of moles of gas atoms or molecules *for the gas at a given temperature T* is directly proportional to the product PV. It has accordingly become customary to sometimes express quantity of gas in so-called "PV units" or "throughput units." This custom leads to a good deal of confusion, however. Appendix B discusses the units issue in great detail, by way of analyzing a simple gas flow system, and presents a step-by-step discussion of how to convert between conventional flow rate and throughput units. An equivalence relationship is established in Appendix B between PV units and flow rate at temperature $T_i(K)$ as follows:

1 atm cm^3 s^{-1} at $T_i(K)$

$$= [273.15/T_i(K)]4.462 \times 10^{-5} \text{ mol s}^{-1}. \tag{10}$$

To move from T_i to T_j as the reference temperature in the unit:

1 atm cm^3 s^{-1} at $T_j(K) = T_i(K)/T_j(K)$ atm cm^3 s^{-1}

at $T_i(K)$. $\tag{11}$

Equation (11) forms the basis on which conversions to other PV units can be performed. For the most general conversion

$$A_j(Q_j \text{ at } T_j) = A_i(Q_i \text{ at } T_i), \tag{12}$$

where Q_i and Q_j are any two throughput units, related by the conversion factor $\mu_{j,i}$

$$Q_j = \mu_{j,i} Q_i, \tag{13}$$

then A_i is related to A_j according to:

$$A_i = A_j \mu_{j,i} T_i(K)/T_j(K). \tag{14}$$

Note that $\mu_{j,i}$ is independent of temperature. Examples are given in Appendix B.

Mass rate units such as kilograms per second, while fundamental, have the drawback that it is necessary to know the molecular weights. The unit *moles per second* (mol s^{-1}) was therefore chosen as the recommended unit for flow rate because it is unambiguous and applies to all gases without requiring molecular weight conversion factors.[9]

Table II[10] lists the factors needed to convert flow rates from one unit into another. The seven units in the upper left corner are throughput units and are separated by the heavy black line from the flow rate units contained in the rest of the table. The factors for use with throughput units are valid for a gas temperature of 0 °C (273.15 K), so that their use for other gas temperatures requires the factor of T/T_0, where T and T_0 are the gas temperature (in kelvins) and 273.15 K, respectively. For example, 1 mol/s of air equals $3.221\ 95 \times 10^7$ oz of air per year. To convert 1 mol/s to Torr ℓ/s at 23 °C the required factor is $1.703\ 45 \times 10^4 \times (296.15/273.15)$.

TABLE II. Leak rate conversion chart at $T = 0$ °C.

FROM \ TO	Pa M³/s	Pa l/s	mbar l/s	Torr l/s	Micron l/s	Micron ft³/s	Micron ft³/hr	AIR MOLECULES/s	AIR Oz/yr	AIR Kg/yr	AIR mg/s	@STP cm³/s	Kg Moles/s	Moles/s
Pa M³/s	1	1.0E3	1.0E1	7.50062	7.50062 E3	2.64882 E2	9.53574 E5	2.65162 E20	1.41869 E4	4.02191 E2	1.27534 E1	9.86923	4.40319 E-7	4.40319 E-4
Pa l/s	1.0E-3	1	1.0E-2	7.50062 E-3	7.50062	2.64882 E-1	9.53574 E2	2.65162 E17	1.41869 E1	4.02191 E-1	1.27534 E-2	9.86923 E-3	4.40319 E-10	4.40319 E-7
mbar l/s	1.0E-1	1.0E2	1	7.50062 E-1	7.50062 E2	2.64882 E1	9.53574 E4	2.65162 E19	1.41869 E3	4.02191 E1	1.27534	9.86923 E-1	4.40319 E-8	4.40319 E-5
Torr l/s	1.33322 E-1	1.33322 E2	1.33322	1	1.0E3	3.53147 E1	1.27133 E5	3.53520 E19	1.89143 E3	5.36211 E1	1.70031	1.31579	5.87044 E-8	5.87044 E-5
Micron l/s	1.33322 E-4	1.33322 E-1	1.33322 E-3	1.0E-3	1	3.53147 E-2	1.27133 E2	3.53520 E16	1.89143	5.36211 E-2	1.70031 E-3	1.31579 E-3	5.87044 E-11	5.87044 E-8
Micron ft³/s	3.77527 E-3	3.77527	3.77527 E-2	2.83168 E-2	2.83168 E1	1	3.600E3	1.00106 E18	5.35593 E1	1.51838	4.81475 E-2	3.72690 E-2	1.66232 E-9	1.66232 E-6
Micron ft³/hr	1.04869 E-6	1.04869 E-3	1.04869 E-5	7.86579 E-6	7.86579 E-3	2.77778 E-4	1	2.78072 E14	1.48776 E-2	4.21772 E-4	1.33743 E-5	1.03497 E-5	4.61756 E-13	4.61756 E-10
AIR MOLECULES/s	3.77128 E-21	3.77128 E-18	3.77128 E-20	2.82859 E-20	2.82859 E-17	9.98943 E-19	3.59619 E-15	1	5.35027 E-17	1.51676 E-18	4.80956 E-20	3.72196 E-20	1.66057 E-27	1.66057 E-24
AIR Oz/yr	7.04877 E-5	7.04877 E-2	7.04877 E-4	5.28701 E-4	5.28701 E-1	1.86709 E-2	6.72153 E1	1.86907 E16	1	2.83495 E-2	8.98957 E-4	6.95659 E-4	3.10371 E-8	3.10371 E-5
AIR Kg/yr	2.48638 E-3	2.48638	2.48638 E-2	1.86494 E-2	1.86494 E1	6.58597 E-1	2.37095 E3	6.59294 E17	3.52740 E1	1	3.17098 E-2	2.45357 E-2	1.09480 E-9	1.09480 E-6
AIR mg/s	7.84105 E-2	7.84105 E1	7.84105 E-1	5.88127 E-1	5.88127 E2	2.07695 E1	7.47702 E4	2.07915 E19	1.11240 E3	3.15360 E1	1	7.73851 E-1	3.45256 E-8	3.45256 E-5
AT STP cm³/s	1.01325 E-1	1.01325 E2	1.01325	7.60E-1	7.60E2	2.68391 E1	9.66209 E4	2.68675 E19	1.43749 E3	4.07520 E1	1.29224	1	4.46153 E-8	4.46153 E-5
Kg Moles/s	2.27108 E6	2.27108 E9	2.27108 E7	1.70345 E7	1.70345 E10	6.01566 E8	2.16564 E12	6.02205 E26	3.22195 E10	9.13409 E8	2.89640 E7	2.24138 E7	1	1.0E3
Moles/s	2.27108 E3	2.27108 E6	2.27108 E4	1.70345 E4	1.70345 E7	6.01566 E5	2.16564 E9	6.02205 E23	3.22195 E7	9.13409 E5	2.89640 E4	2.24138 E4	1.0E-3	1

* CONVERSION FACTOR IS EXACT, ALL SUBSEQUENT DIGITS ARE ZERO
† BY DEFINITION

WHERE: 1 YEAR (365 DAYS) = 3.153600 E7 SECONDS
1 OUNCE = 2.8349523125E-2 Kg
1 HOUR = 3600 SECONDS
MW(AIR) = 28.964 AMU
1 MOLE = 22.41383 l AT STP FOR AN IDEAL GAS
STP DEFINED AS: $T = 0$ °C
$P = 1$ atm
1 AMU = 1.6605655 E-27 Kg

III. CALIBRATION OF LEAKS

There are several techniques available for the calibration of leaks. The primary techniques depend on the measurement of the quantities mass, pressure, volume, temperature, and time. The secondary techniques use a leak of known leakage rate to generate a signal on an instrument which is then compared to the signal due to the gas emitted by the leak under test. The first seven techniques discussed in this section are primary methods while the eighth technique is a secondary method. All of the methods, except where a mass spectrometer is used to measure partial pressures, measure total leakage rates. The discussions presented here are not intended to be comprehensive or exhaustive, but to give the reader a general overview of the various techniques and provide appropriate references.

A. $V\Delta P$ leak calibration method

AVS Standard 2.2-1968[11] describes a technique and apparatus which can be used for the calibration of leaks using the pressure rise method. As gas from a leak initially enters an originally evacuated volume V, the pressure P in the volume rises linearly. Differentiation of the ideal gas law, Eq. (8), with respect to time at constant temperature yields an expression that may be used to evaluate the molar leakage rate.

$$Q_m = \frac{dN}{dt} = \left[P\left(\frac{dV}{dt}\right) + V\left(\frac{dP}{dt}\right) \right] \bigg/ [RT]. \tag{15}$$

With the volume held constant and the pressure allowed to change, the first term is zero and the leakage rate can be calculated using the second term. The values of the pressure P, the volume V, and the temperature T of the vessel must be known to accuracies commensurate with the desired accuracy of calibration. The contributions of outgassing, vacuum system leaks, and pressure transducer drift to the apparent pressure readings should be reduced as much as possible and must also be determined. The leakage rate Q_m can be calculated using the expression

$$Q_m = [(\Delta P_{avg}/\Delta t) - (\Delta P_0/\Delta t)] V/[RT], \tag{16}$$

where Δt is the time required for the pressure to rise over the pressure range ΔP_{avg}, and ΔP_0 is the measured pressure rise without the leak. Note that in order to use this technique successfully the time interval Δt must be small enough that the pressures rise linearly during the time interval.

The $V\Delta P$ total pressure rise technique has been employed to calibrate both permeation and physical leaks. However, close attention to error sources is essential to achieving successful results. One method of evaluating the errors associated with this technique is to calculate

$$\delta Q_m/Q_m = (\delta P/P) + (\delta V/V) + (\delta t/t) + (\delta T/T), \tag{17}$$

where δQ_m is the maximum uncertainty in the leakage rate due to δP, δV, δt, and δT, the errors in the pressure, volume, time and temperature, respectively. Additional elements contributing to the errors that are not included in Eq. (17) are those of the temperature and pressure coefficients for the leak elements. For permeation leak elements the most signif-

icant source of error will be that due to temperature. Isothermal conditions during calibration are essential to successful calibrations.

The total pressure rise method for leak calibration presents obstacles that may be overcome by special attention to details. A significant problem is that of outgassing of interior surfaces of the volume in which the pressure rise is being measured. If the internal surfaces of the volume have been cleaned by baking and/or other means, the initial influx of gas from the leak may adsorb to the clean surfaces, resulting in a condition of an initial pressure rise that yields a calculated value of leakage rate that is less than the true value. Conversely, if the internal surfaces are not clean, the resulting outgassing may lead to an initial unwanted partial pressure in the volume which, if not properly accounted for as in Eq. (16), will result in an apparent total pressure rise and calculated leakage rate that is larger than the actual. In either case, it follows that an initial stabilization period is required to allow the flows to or from the interior surfaces and the leak to equilibrate, resulting in a rate of pressure rise that is consistent with and indicative of the flow rate of the leak being calibrated. Note that if there is significant outgassing from the interior surfaces of the leak itself, then the use of Eq. (16) will still lead to erroneous results if this additional outgassing cannot be quantified. Also, if it is not possible to limit the outgassing rate to a level where the pressure rise due to outgassing remains linear during the leak rate measurement, it is necessary to delay the start of the timing interval until the partial pressure of the extraneous gas has been allowed to equilibrate, so that ΔP_0 in Eq. (16) is zero. However, the partial pressure of the gas flowing from the leak in the measurement volume must not reach such a high level that it significantly affects the flow rate of gas from the leak. Use of a partial pressure analyzer (PPA) to try to measure the partial pressure of only the gas of interest presents additional subtle difficulties, such as nonlinearity due to interactions with the background gas or to high total pressures. Multiple data sets and long time periods are encouraged to improve the confidence of measurements and the calibration of the PPA.

B. $P\Delta V$ leak calibration methods

Several variations of the constant-pressure, variable-volume flow rate measurement technique exist. In these, the fundamental relationship is that stated in Eq. (15), with the second term being zero. To calculate the leakage rate for the $P\Delta V$ technique Eq. (15) may be rewritten as

$$Q_m = P\Delta V/RT\Delta t, \tag{18}$$

where Q_m is the molar leakage rate, P is the gas pressure at the beginning and end of the time interval Δt, ΔV is the change in volume, and T is the absolute temperature of the gas.

One of the $P\Delta V$ methods of calibration[12] is initially similar to that of the $V\Delta P$ technique, in which gas from the leak is allowed to flow into a volume V_0 while monitoring the pressure in the volume. After the flow of gas from the leak has stabilized, with the pressure increasing linearly, a timer is started at the predetermined pressure P_1. A vessel of vol-

ume ΔV, preevacuated to a negligible pressure, is then added to the original volume by opening the valve between them. This additional volume causes a pressure reduction to P_2 in the combined volume due to the expansion of the gas. Moreover, the temperature change is negligible because the heat capacity of the vessel is large compared to the heat absorbed by the expansion of the gas. Thus,

$$P_1 V_0 = P_2 (V_0 + \Delta V). \tag{19}$$

The pressure in the combined volume then rises linearly, though at a slower rate, until P_1 is again reached and the timer stopped at t. The leakage rate is then calculated using Eq. (18), with $P = P_1$. One advantage of this technique is that the pressure gage need only be calibrated at the pressure P_1. Several other methods are derived from the $P \Delta V$ method, as follows.

Instead of increasing the volume of the system by opening a valve to an evacuated, fixed volume, the pressure can be maintained constant by increasing the volume using a variable volume. Either the volume increase at the end of a fixed time interval or the time interval after a fixed volume increase can be measured. Alternatively, the rate of change of volume could be determined in an apparatus which maintains constant pressure. Thornberg[13] varies the system volume by using a stepping motor to drive a piston for small, incremental volume increases, yielding improved precision with reduced calibration time for leaks between 10^{-6} and 10^{-11} mol s^{-1}. Substitution of values in Eq. (18) yields the leakage rate from the leak.

The $\Delta P \, \Delta V$ variation of the $P \, \Delta V$ technique[14] has been used to decrease calibration times and interference from outgassing while allowing multiplexing of the pressure gage. The timer is started when the leak valve is closed to begin the accumulation of gas. At time t_1, the pressure P_1 is measured and the valve to the evacuated volume is opened. Instead of waiting until the pressure again returns to P_1, the pressure is measured as P_2 at time t_2. The flow rate is

$$Q_m = P_1 P_2 V/RT(P_1 t_2 - P_2 t_1), \tag{20}$$

where V is the evacuated volume, R is the gas constant, and T the absolute temperature. One pressure transducer can be used to calibrate several leaks in rapid succession because the gas accumulations do not need to be monitored. Smaller flow rates can be measured because the surface area and measurement time are much smaller than those in the standard $P \Delta V$ technique, giving much smaller contributions from wall outgassing and pressure transducer drift. An error analysis showed the error to be $\pm 5\%$ between 10^{-7} and 10^{-9} mol s^{-1}.

These methods suffer similar limitations to those of the V ΔP approach. If Δt is sufficiently long (> 10 min) and P is sufficiently high ($> 10^{-2}$ Torr), the effects of gas adsorption and desorption to or from metal surfaces are small for leaks in the 10^{-10} to 10^{-7} mol s^{-1} (2×10^{-6} to 2×10^{-3} atm cm^3 s^{-1} at 0 °C) range. For smaller leaks, background corrections, due primarily to vessel surface outgassing, must be determined. Corrections to the calibration of the pressure transducer for gas composition must be made for those gages so affected. Background corrections, including thermal transpiration corrections for capacitance manometers, are required.

C. Direct comparison with a known (primary) gas flow

Direct comparison of a gas leakage rate with the gas flow rate from a primary flow rate standard, such as a constant pressure flowmeter, is used by national standards laboratories such as the National Institute of Standards and Technology (NIST)[3,15] and Physikalisch-Technische Bundesanstalt (PTB, Germany)[16] to perform primary leak calibrations. Use of the constant pressure flowmeter is, in effect, a $P\Delta V$ technique to calibrate leaks, where the flowmeter is set up to flow gas at approximately the same rate as that from the leak. The comparison is performed by alternately and separately flowing gas from the leak and from the flowmeter into a vacuum chamber equipped with a mass spectrometer tuned to the gas species being measured. In the constant pressure flowmeter, the pressure in a volume from which gas is escaping is kept constant by reducing the volume at the appropriate rate, either manually or with feedback circuitry. The equation which is used to calculate the leakage rate is then

$$Q_m = (H_L/H_F)(P/RT)(\Delta V/\Delta t), \tag{21}$$

where H_L and H_F are the indicated mass spectrometer readings when the leak and the flowmeter, respectively, are opened to the vacuum chamber, and ΔV is the total reduction in flowmeter volume during time interval Δt required to keep the flowmeter pressure constant at P.

Measurement accuracies of $\sim 0.5\%$ near 5×10^{-8} mol s^{-1} to $\sim 1\%$ at 2×10^{-10} mol s^{-1} and $\sim 5\%$ at 5×10^{-11} mol s^{-1} are reported by NIST.[15] PTB reports systematic uncertainties of 4.9% in the range 10^{-8}–10^{-13} mol s^{-1}.[16] The limitations of this technique lie in the capabilities of the flowmeter and the pressure transducer and in the time required for each leak calibration. McCulloh et al.[17] discuss a piston-type flowmeter design, application, and error analysis. Other references to flowmeters are listed in the Bibliography.

D. Accumulate dump technique

In the accumulate dump technique,[12] a mass spectrometer, tuned to the species of interest, is used to compare the partial pressures of the collected leak gas with a series of standards. The standards, obtained by expansion from a known pressure contained in a known volume, are dumped through a restriction into the mass spectrometer. The gas from the leak, collected for a time t, is dumped under identical conditions. The signals of the standards and the leak are compared and the partial pressure of the leak gas calculated. The leakage rate is obtained from the partial pressure, the volume, the temperature, and the collection time. The method is used to calibrate leaks from 10^{-8} to 10^{-12} mol s^{-1}

$(2 \times 10^{-4}$ to 2×10^{-8} atm cm^3 s^{-1} at 0 °C) with $\pm$ 5% uncertainty and from 10^{-12} to 2×10^{-14} mol s^{-1} $(2 \times 10^{-8}$ to 2×10^{-10} atm cm^3 s^{-1} at 0 °C) with $\pm$ 20% uncertainty.

A variation of the accumulate dump technique has been described.[14] A partial pressure p_S of gas is established in volume V_1 by flowing a constant source, from a flowmeter or dedicated leak, through a restricted conductance. The gas from a very small leak is accumulated in a volume V_2 for a period t which is estimated to be required to attain partial pressure p_L close to p_S. The difference $(p_S - p_L)$ is measured by the integrated, transient changes in the mass spectrometer signal when the valve between V_1 and V_2 is opened. The mass spectrometer calibration curve, shown to be linear, is established by filling V_2 to known partial pressures. The flow rate of the gas of interest at the measurement temperature T is

$$Q_m = p_S V_2 t_0^{-1} R^{-1} T^{-1}, \tag{22}$$

where t_0 is the accumulation time, obtained using the calibration curve, that would be required to make $p_L = p_S$. Flow rates of 10^{-14} mol s^{-1} $(2 \times 10^{-10}$ atm cm^3 s^{-1} at 0 °C) have been measured using a 10^{-10} mol s^{-1} $(2 \times 10^{-6}$ atm cm^3 s^{-1} at 0 °C) dedicated leak standard. Minimal accumulation times are required so that concentration profiles in permeation leak elements are not disturbed.

E. Matrix stripping technique

If a gas mixture is available which contains a well-established trace concentration of the gas of interest, stripping the major component (the matrix) of a sample can leave a very small, known quantity of the trace constituent. In an experiment,[18] a mixture certified by the Bureau of Mines to consist of 5139 $\pm$ 4 parts per billion of helium in nitrogen was used to create a small standard of 0.33 cm^3 at 0.500 Torr. At 25 °C, the quantity of helium N in this standard was

$$N = FPV/RT = 4.63 \times 10^{-14} \text{ mol}, \tag{23}$$

where F is the mole fraction of helium. The standard was then introduced into a closed, evacuated chamber equipped with a sensitive quadrupole mass spectrometer and a chemical getter which pumps nitrogen but not helium. As the pressure inside the chamber remained low, the mass spectrometer sensitivity S remained high and was calculated to be $S = I/N$, where I is the increase in ion current as a result of exposure to N moles of helium. Then the chamber was evacuated and reclosed. Helium from the leak being calibrated was introduced into the chamber and the time t to attain the same ion current I was measured. The leakage rate is then

$$Q_m = I/tS. \tag{24}$$

With this technique, leaks of 1×10^{-16} mol s^{-1} $(2 \times 10^{-12}$ atm cm^{-3} s^{-1} at 0 °C) can be calibrated in one hour with a stated uncertainty of $\pm$ 5%. While this technique has been applied only to mixtures of helium in nitrogen, other gases can be used for which chemical getters are available to remove all but the trace constituent of interest.

F. Weight loss calibration methods

Determination of the rate of loss of mass from a leak depends on the measurement of only weight and time and is thus the technique with the fewest derived quantities. However, this can be measured conveniently only under certain circumstances. To avoid weighing errors, the leak vessel should be much lighter than the source material and is, therefore, restricted to liquid- and solid-source leaks. This introduces the vapor pressure dependence on temperature in Eq. (4), requiring tighter temperature control than gas-source leaks. In addition, the rate of mass loss is usually so low that measurements must extend over many weeks to obtain sufficient accuracy. Despite all its inconveniences, this method is still preferred for the calibration of those leaks which interact strongly with vacuum system walls, such as water.

G. Alternate techniques and enhancements to commonly used techniques

The techniques described in Secs. III A–III F above are the most commonly used. However, there are other methods that have been suggested to calibrate leaks. For example, pressure measurement at a known pumping speed, utilizing the relationship $Q = PS$, where the pressure P is measured in a vacuum system with a pump having pumping speed S, could be used. When an orifice or other limited conductance is used to establish a known, stable pumping speed, it can be used to derive the flow rate of the leak Q_m. There are many problems associated with this approach that frequently limit its practical application.

Improvements to commonly used methods enhance their application. For all of the calibration methods, automation of the data acquisition would appear to be a valuable contribution as the effort required to perform calibrations is excessive in many instances.

H. Calibration by comparison methods

With a mass spectrometer type leak detector or a mass spectrometer with a vacuum system, a previously calibrated leak may be compared with a leak whose leakage rate is to be determined. The leakage rate using the comparison method is calculated using the relationship

$$(Q_m)_{unk} = (Q_m)_{std} [H_{unk} (1 + \alpha_{std} \Delta T_{std})]/$$
$$[H_{std} (1 + \alpha_{unk} \Delta T_{unk})], \tag{25}$$

where Q_m is the leakage rate, H is the mass spectrometer reading that corresponds to the amount of the gas from the leak present in the analyzer, α is the linear temperature coefficient of the leak, and ΔT is the departure of the temperature of the leak from the reference temperature, with the subscripts std and unk referring to the standard and unknown, respectively. The use of Eq. (25) assumes that the mass spectrometer gives a linear response to partial pressure changes. Note that, because of the uncertainties introduced from the use of the standard and the mass spectrometer, the use of the linear temperature approximation instead of the exponential form should not cause significant additional error.

The comparison may be accomplished in any fashion that

results in the comparative readings H being taken under known conditions of pressure, time, and temperature for all of the leaks. At least three reading cycles of standard, unknown, and background are recommended. Each reading must be obtained under steady-state flow conditions, which is best demonstrated by constant signals. For the most accurate results, it is usually necessary to have the two leaks register signals in the same decade of the measuring instrument because unsuspected nonlinearities and offsets frequently occur. The use of valves to select and isolate the leaks and the use of modern electronic meters will facilitate the comparison process. Analog meters and chart recorders can be used,

but with attendant increased chances for error. Digital meters which can perform a statistical analysis of the data are available, resulting in an improvement of precision and, possibly, accuracy. The readings should be sufficiently large in number (~ 100) and over a long enough period (~ 5 min) that statistical precision and reliable signals are obtained.

As in any uncertainty analysis, that for the comparison method must take into account both the random and systematic errors. Random errors are determined by repetitive comparisons of the leaks using the standard deviation of the mean of the data. Systematic errors are established by an error analysis of the contributing elements of the process:

$$\delta(Q_m)_{unk}/(Q_m)_{unk} = \delta(Q_m)_{std}/(Q_m)_{std} + \delta H_{std}/H_{std} + \delta H_{unk}/H_{unk} + (\alpha_{std}\delta\Delta T_{std})/(1 + \alpha_{std}\Delta T_{std})$$
$$+ (\alpha_{unk}\delta\Delta T_{unk})/(1 + \alpha_{unk}\Delta T_{unk}) + (\Delta T_{std}\delta\alpha_{std})/(1 + \alpha_{std}\Delta T_{std})$$
$$+ (\Delta T_{unk}\delta\alpha_{unk})/(1 + \alpha_{unk}\Delta T_{unk}), \tag{26}$$

where the δ terms are the systematic errors of the parameters $(Q_m)_{std}$, H_{std}, H_{unk}, ΔT_{std}, ΔT_{unk}, α_{std}, and α_{unk}, and Q_m, H, T, and α are the leakage rates, analyzer readings, temperatures, and leak temperature coefficients, respectively.

In practice, the major contributing source of error is the systematic error of the value of the leakage rate of the standard. However, the other error sources must be carefully controlled to minimize their effects. The temperature correction factors for the leak elements can be significant and should be established during the initial calibration. Temperature coefficients for permeation leaks are often quoted to be on the order of 2 to 7%/°C, but the values should be determined for each type of leak element over the temperature range expected in use. Random errors of the process are those accumulated during the comparisons of the leakage rates of the standard and the unknown leak. Errors contributed by using analog readings of the analyzer can be relatively large, so that the use of modern computing multimeters is recommended. If one is not available, the random errors may be computed manually using Eq. (25) for each reading according to

$$\delta R = \left\{ \sum_{i=1}^{n} [(Q_m)_i - (Q_m)_{ave}]^2/(n-1) \right\}^{1/2}, \tag{27}$$

where δR is the random error for an individual data set and $(Q_m)_i$ is the individual reading of the analyzer taken n times for one data set and then averaged to calculate the average $(Q_m)_{ave}$.

Because the technique is limited by the accuracy of the comparison standard, the comparison method will generally yield accuracies no better than $\pm 5\%$–7% in the range 10^{-9}–10^{-12} mol s^{-1} (2×10^{-5} to 2×10^{-8} atm cm^3 s^{-1} at 0 °C). If the random errors are between $\pm 3\%$ and 5%, the calibration accuracy will be about $\pm 10\%$, which is a reasonable level for many applications. The comparison method should not be used to calibrate leaks that are to be used as

standards, because the accumulation of errors will usually result in a calibration standard with an unacceptably large uncertainty.

IV. PROPER HANDLING AND USAGE OF LEAKS

A. Handling procedures

Once a leak has been carefully calibrated, great care must be taken to preserve the integrity of the calibration over time. This section discusses the many possible pitfalls which must be avoided to prevent unnecessary degradation of the calibration accuracy. For standard practices relating to general vacuum techniques and leak detectors which may have a bearing on the ultimate accuracy with which the leak may be used, the reader should refer to the standard literature, some of which is referenced in the Bibliography.

As discussed earlier, leaks are frequently damaged by inattention to cleanliness. Physical leak elements are very susceptible to clogging by any of several types of contaminants. These contaminants, often introduced into leak elements through exposure to ambient atmosphere or to oils backstreaming from mechanical pumps, migrate to the flow restricting part of the element, reducing the size of the opening available to gas flow. In general, the smaller the size of the opening, the smaller the leak and the more easily its flow rate can be affected. Although permeation elements are not as susceptible to clogging, gas flow rate can be altered with sufficient exposure. Proper handling of leaks, therefore, minimizes potential contamination. Use of a high vacuum pump, rather than a mechanical pump, is preferred to maintain the leaks in the best standby condition. The shutoff valve on the process side of the leak should be kept closed until all air and oils have been removed.

The leakage rate through permeation elements is dependent upon temperature and process side as well as reservoir side concentration. Accordingly, the temperature of permeation leaks must be maintained within limits defined by the required accuracy of flow rate. Reestablishment of

steady-state flow rates after a temperature change requires several hours. Likewise, if the leak valve on a permeation leak is kept closed for a significant period, the resulting increase in concentration of the leak gas on the process side changes the concentration gradient in the leak element. Upon reevacuation of the process side, the asymptotic approach to stable flow can require more than 24 h. Conversely, steady-state flow conditions are attained by leaks having physical leak elements within a very short time (typically a few seconds) after changing process-side pressures to new levels. The reestablishment of steady-state flow conditions for this type of leak tracks the reestablishment of the temperature of the leak after the leak is immersed in a new temperature environment.

Because fixed-reservoir leaks are usually operated in a manner such that the gas leaks continuously through the element, the amount of gas in the reservoir is depleted. If the initial quantity of gas in the reservoir and the leakage rate are known, the fractional change in pressure of the reservoir can be calculated as a function of time. As the leakage rate is a function of the reservoir pressure or concentration, the leakage rate will, likewise, decay in a predictable manner, provided that the thermal history of the leak is known or remains within certain tolerances. Data required to do this calculation (as discussed above in Sec. II A 3), which are to be included in the documentation accompanying each leak, are the reservoir fill pressure, fill date, volume, and initial leakage rate. Decay of reservoir pressures of 1–10%/y are common. It should be noted that reservoir pressure can also decrease through leaks in the reservoir and fill valve and by permeation of some gases through some kinds of materials of the reservoir or its valve. For example, if the fill valve has a permeable seat or stem packing and is installed in such a manner that the reservoir gas is directly exposed to these unwanted leakage paths, an unknown amount of gas will be lost from the reservoir, giving larger, unpredictable depletion rates than expected. For those leaks stored for extended periods with their shutoff valves closed, the decay rate is also affected by the back pressure on the leak element in the volume between the leak element and the valve seat, and the time over which the valve is closed. Calculations of decay rate are then more difficult. Leaks that incorporate a shutoff valve in the leak element structure, resulting in essentially zero accumulation volume, are available. The decay rates of these leaks are essentially zero when the valves are closed. These are particularly useful for leaks with large flow rates, as the calibration correction for decay is much smaller.

The materials of construction exposed to the vacuum system are also very important. While many applications, such as helium leak detector calibration, require only that the flow rate of the gas of interest be well known, others are more stringent on the gas composition requirements. Use of materials such as elastomers, sealants, fluxes, and glues, which are intrinsic outgassers or which allow permeation of air into the vacuum system, can cause difficulties. Construction techniques should ensure that the probability of leakage of gas from the reservoir via any means other than the leak element is very low. In this regard, valves installed on the reservoir should be in such orientation that the valve seat,

and not the valve packing, is exposed to gas in the reservoir, as mentioned above. Likewise, process gases can infiltrate into the leak, causing plugging of the element or preferential adsorption on, or chemical reaction with, certain kinds of materials of the leak. For example, the rates of moisture adsorption and desorption on glass are quite different from those on steel.

The fittings and valves on both the process and fill sides of leaks require correct handling in order to assure proper operation of the leak. The manufacturers of these components should be consulted for such parameters as the required torque needed to assure leak tightness without galling of sealing surfaces. Overtightening of valves and fittings distorts sealing surfaces, creating subsequent leakthrough conditions.

Because most leaks are used in applications that require that their leakage rates be known, calibration is usually necessary. The initial calibration can be used for only a finite time interval before recalibration is necessary, due to the uncertainties of flow rate introduced by both normal and abusive handling, leak element dimensional changes, reservoir leakage, and normal reservoir pressure decay. The decision of the normal recalibration interval must be made on the basis of the required accuracy of leakage rate and estimates of the effects of handling and reservoir pressure decreases. For leaks treated with care, recalibrations every year for permeation leaks and every three to six months for physical leaks are typically satisfactory. Unusual conditions of required accuracy and exposure may require shorter or may permit longer intervals.

The three main problems in shipping leaks are the fragility of some materials of construction, the high pressures used in some reservoirs, and the toxicity or reactivity of some gases. The incidence of breakage, with consequent release of the fill gas, may be decreased by the use of energy-absorbing packing materials and by closing the valve on the process side of the element. The United States Department of Transportation has established regulations for the shipment of pressurized containers and of hazardous materials. They are to be scrupulously followed.

B. Connections

Standardized process connections on calibrated leaks assist users and manufacturers in buying or making devices which are interchangeable and can be readily attached to leak calibration and process apparatuses. However, numerous types of process connections have been used that give less than optimum service, primarily because of the potential for introduction of air leaks or of contamination. The best type of connection for a given application depends on the needs of the user and calibrator and the test requirements, gas type and budget.

All-metal connections are generally required to reduce contamination effects to the lowest levels, and are strongly recommended. There are five basic types. Flare fittings are used in many applications requiring all-metal connections but are not commonly used as vacuum fittings because of their need for special tools and their sometimes unreliable

sealing when using stainless steel. Pipe-threaded and ferrule-sealed connections are often used in fluid flow applications but are not leak tight for high vacuum usage. The copper-gasketed sexless bolted flanges (Conflat® type), are the most widely used ultra high vacuum fittings. While they are quite acceptable for the connection of leaks, their use of bolts can make the routine interchange of leaks inconvenient. Metal gasketed, face-sealing fittings depend on the force of external screw threads to exert sufficient force for sealing. When properly torqued, they provide a high quality, all-metal attachment that is quickly made up with common-sized wrenches.

Many leaks are used with leak detectors that use elastomer o rings compressed onto the smooth tubing of the leak. These connections can be rapidly made and provide satisfactory sealing in many lower-accuracy applications. A potential drawback to elastomer seals is their propensity for absorbing and reemitting gases and for being permeable, particularly to helium. Therefore, proper care must be taken to allow sufficient time for adequate outgassing and equilibration, which can be a significant concern for helium leak rates below 10^{-11} mol s^{-1} (2×10^{-7} atm cm^3 s^{-1} at 0 °C).

The recommendation for the standard fitting on high-quality leaks for general use is either the metal-gasketed, face-sealing fitting, in the nominal 1/4 inch size, or the Conflat-type flange, whichever is most convenient. For less stringent applications, where the permeation and contamination qualities of elastomers are satisfactory to both the user and the calibrator, the use of smooth tubing is recommended. Use of other types of connections is discouraged unless an adapter fitting is included with the leak by the manufacturer.

C. Safety

Gas leaks have several potential hazards. For those with pressurized reservoirs, the dangers associated with pressurized gases, such as the ejection of high-velocity projectiles during failure, should be recognized. Materials of construction, pressure testing, filling procedures, and subsequent handling practices must follow established safety guidelines. Use of explosive, reactive, and/or toxic gases places an additional burden on the safe use of leaks. Fragile materials, such as glass permeation elements in helium leaks, can release large quantities of gas into systems not designed to accommodate super-ambient pressures. While the AVS Recommended Practices Committee on Calibrated Leaks has identified these general safety considerations, it is the responsibility of the shipper and the user to ensure that the proper handling procedures pertaining to the particular leak are followed and that shipping is in accordance with the relevant Department of Transportation and other applicable regulations.

V. DOCUMENTATION FOR LEAKS

One of the major goals of this Recommended Practice is to provide manufacturers, calibrators and users with a recommended common format for the reporting of leak calibration and usage data. This section of the Recommended Practice sets guidelines for providing these data on the label attached to each leak and on the accompanying calibration certificate. While compliance with these recommendations is, of course, voluntary, they represent the consensus view of a wide variety of manufacturers, calibrators and users, and are presented with the intent that improved communication pertaining to leaks will benefit the entire user community and that presentation in a common format reduces the chances for ambiguities. Each item listed as useful data is identified as being required for the label and calibration certificate, required for the calibration certificate only, or optional for either the label or certificate. Since a label must be brief, only the most important data which the user will need for field use of the leak have been recommended as required on the label. For subsequent calibrations, it is recommended that the same information be included to the extent possible.

In the discussion of the items that follow, the recommendations for including the data on the label attached to the leak, the accompanying hard-copy paper documentation, or both are abbreviated as label, paper, or both, respectively.

(1) The descriptive title of the document shall be included on both. For example, Argon Calibrated Leak in the case of a label and Calibration Certificate for Argon Calibrated Leak for the paper.

(2) The name of the manufacturer shall appear on both. The address of the manufacturer should appear on the paper.

(3) The manufacturer's model number of the leak shall be included on both.

(4) The manufacturer's serial number of the leak shall be included on both.

(5) The type of leak element (i.e., crimped tube, glass permeation, etc.) shall appear on both.

(6) The composition and the percent purity of the gas exiting the leak at the time of filling or last calibration shall appear on both. All constituents of a mixture shall be included if a pure gas is not used to fill the reservoir. This is important since some of the methods used for calibration measure only total flow rate and some leaks are manufactured with mixed gases for specific applications.

(7) The leakage rate of those leaks which have been calibrated shall appear on both, in the units of moles per second. Other units of leakage rate may also be included at the option of the manufacturer, provided that any such values are consistent with the reported value of moles per second.

(8) The temperature of the leak at the time when its leakage rate was measured shall be included on both.

(9) The estimated uncertainty of the calibration, expressed as a percentage uncertainty of the leakage rate, shall be given on both. This uncertainty must be derived by a thorough error analysis of the calibration system used. Traceability to a national standards laboratory, such as the National Institute of Standards and Technology, and the nature of that traceability may be included on the paper.

(10) The date on which the leakage rate calibration was last performed shall be included on both.

(11) A linear temperature coefficient associated with the leakage rate over a stated temperature range shall be reported on both. In addition, the equation which describes the true physical process, such as the exponential temperature

dependence of permeation through glass over a stated range, and a clear statement of the uncertainties involved in using the linear approximation, shall be reported on the paper.

(12) For leaks with a gas reservoir, the reservoir pressure at the time of filling, the date the reservoir was filled, and the calculated depletion rate of the reservoir (expressed in percent per year) shall be included on both. In addition, the volume of the reservoir occupied by the gas shall be stated on the paper for purposes of depletion rate calculations and gas inventories.

(13) All of the materials of construction exposed to the process system shall be clearly stated on the paper.

ACKNOWLEDGMENTS

APPENDIX A: GLOSSARY OF TERMS

The definitions in the *Dictionary of Terms for Areas of Science and Technology Served by the American Vacuum Society*, 2nd ed., (1984), except those listed below, are considered to be part of this Recommended Practice.

1. Calibrated leak

A leak which has a known, measured leakage rate for a specific gas under specific conditions, preferably with the calibration traceable to a primary standard.

2. Calibration temperature

The temperature of the *calibrated leak* at the time of calibration. For liquid and solid materials which are vaporized or sublimed, the temperature of the condensed phase (or the pressure above it) must be stated if different from the temperature of the leak element.

3. Depletion rate

The rate at which the reservoir pressure (concentration) of a leak decreases. Its value at any time depends on the quantity of gas in the reservoir and the leakage rate through the leak element. Different pure gases and different constituents of a mixture have differing depletion rates. For mixtures, this can lead to changing reservoir composition.

4. Equivalent leakage rate

(Use of this term is strongly discouraged.)

(a) The hypothetical, calculated leakage rate of one gas determined from the measured leakage rate of another gas through the same leak or leak element. Because the flow regime and dimensions of the gas passageway, required for the calculation, are seldom known, standard conversion factors are not applicable.

(b) Specifically, the leakage rate for helium multiplied by 0.37, which is the ratio $MW_{He}^{1/2}/MW_{air}^{1/2}$, where MW is the molecular weight. This factor applies only to conditions of molecular flow, which are generally inappropriate for leaks.

(c) The calculated leakage rate for air through a leak element, based on the measured leakage rate for some other gas. This is often called AIR EQUIVALENT LEAKAGE RATE. Calculations of flow rates of one gas from data for another are usually difficult due to the necessity of knowing the flow regime and dimensions of the gas passageway.

5. Fill pressure

The pressure to which the reservoir of a leak is initially filled on a given date.

6. Flow rate

The quantity (e.g., moles, grams, etc.) of gas which passes a specified region of a vacuum system per given time interval, divided by that time interval. The recommended unit is moles per second, $mol\ s^{-1}$. Other frequently used units include atm cm^3 s^{-1} at temperature T and Pa m^3 s^{-1} at temperature T.

Partial flow rate is the flow rate of a single, named constituent. Total flow rate is the sum of the partial flow rates of the constituents of a mixture.

7. Leak

(a) A small passage (hole, channel, etc.) or permeable element through which leakage may occur under the action of a pressure (concentration) difference across the passage or element. (b) A device used to house a leak element, which provides for gas at elevated pressure (concentration) on one side of the leak element and for connection of the other side to a vacuum system, sniffer probe or other process connection. (c) A calibrated leak, a leak artifact, a reference leak, or, less correctly, a standard leak.

8. Leak artifact

See Appendix A 7, definitions (b) and (c).

9. Leak calibration

The act of measuring and documenting the flow rate of gas emitted by a leak under specified conditions of gas species, reservoir pressure, temperature, technique, and date.

10. Leak element

The mechanical part of a leak that controls the leakage rate.

11. Leakage rate

The quantity (e.g., moles, grams, etc.) of pure gas which passes through a leak element per given time interval divided by that time interval.

Partial leakage rate refers to the leakage rate of a single, named constituent. The recommended unit is moles per second, $mol\ s^{-1}$, for each individual constituent. Other fre-

quently used units are atm cm^3 s^{-1} at temperature T and Pa m^3 s^{-1} at temperature T.

12. Permeation leak element

A leak element through which a gas or gases pass by permeation. For example, permeable elements have been made of glass, polyethylene, and palladium for use in helium, water, and hydrogen leaks, respectively.

13. Physical leak element

A leak element which uses mechanically restricting conductance, but not permeation, to limit the flow through it. Physical elements include capillary tubes, drawn glass capillaries, crimped tubes, orifices, and sintered porous plugs.

14. Primary calibration technique

Those calibration techniques involving measured quantities that are the base or derived units of time, pressure, length, temperature, volume, or mass, and which do not rely on direct intercomparisons of leakage rates.

15. Reservoir

The part of a leak which contains the gas, liquid, or solid from which the gas or vapor passes through the leak element. The atmosphere can also be the reservoir for air leaks.

16. Reservoir pressure (concentration)

The current pressure (concentration) in a leak reservoir.

17. Secondary or comparison calibration techniques

Those techniques in which the flow rate from a leak is determined by comparison with the flow rate from a leak which has been calibrated by a primary technique.

18. Standard leak or leak standard

Ambiguous terms sometimes used to mean calibrated leak.

19. Throughput

There are two popular definitions, having units with different dimensions. (a) Leakage rate or flow rate: when used in this context, the recommended unit is moles per second, mol s^{-1}. (b) The rate of change with time of the product of the pressure of a gas and the volume in which it is contained, under conditions where the gas is escaping from the volume in some controlled manner, such as through a leak element. Frequently used units for this definition are atm cm^3 s^{-1} and Pa m^3 s^{-1}.

APPENDIX B: USE AND CONVERSION OF UNITS OF FLOW RATE AND THROUGHPUT

To discuss the differences between flow rate and throughput units, consider the simple experimental apparatus in Fig. 4, where a cylindrical volume is divided by a plate with a small orifice in it, a tightly fitting piston is inserted in one end, and the other end is attached to a vacuum pump. While
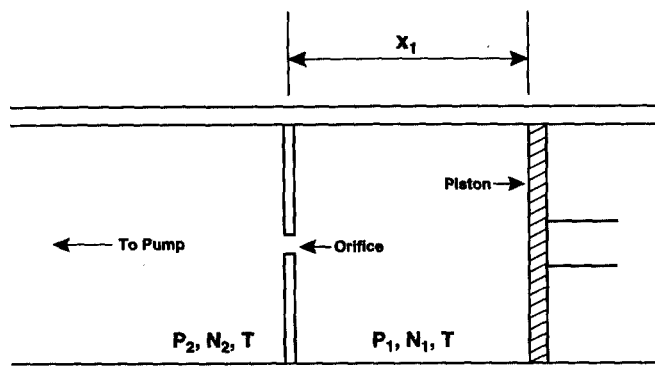
FIG. 4. Schematic cross-sectional diagram of a simple piston and cylinder device used to discuss flow rate and throughput units. Gas in region 1, at pressure P_1 and temperature T, effuses through the orifice into region 2. The distance X_1 between the orifice and the face of the piston changes at such a rate as to keep P_1 constant.

this system is quite simple, it can be used to discuss many of the factors that should be considered when performing gas flow rate measurements. Let an ideal gas at pressure P and temperature T fill the reservoir side of the cylinder. As gas effuses through the orifice and is pumped away, let the piston be moved at a rate that maintains the pressure in the reservoir at P. The equation of state of the gas at each instant of time is

$$PV = NRT, \tag{B1}$$

where N is the number of moles of gas contained in the volume V, and R is the universal gas constant (numerically equal to 8.314 41 J mol^{-1} K^{-1} or 82.057 atm cm^3 mol^{-1} K^{-1}). If dN moles of gas are passing through the orifice every dt seconds, giving the molar flow rate $Q_m \equiv dN/dt$, then, to keep P constant, the piston must be moved at a rate such that the volume change per unit time is given by

$$\frac{dV}{dt} = \left[\frac{(RT)}{P}\right]\left(\frac{dN}{dt}\right) \equiv \left[\frac{(RT)}{P}\right]Q_m. \tag{B2}$$

It is assumed that the process is slow enough and that the heat capacity of the cylinder walls is great enough that the process is isothermal. Equation (B2) can be rewritten as

$$Q_m \equiv \frac{dN}{dt} = \left[\frac{P}{(RT)}\right]\left(\frac{dV}{dt}\right) = \left[P\left(\frac{dV}{dt}\right)\right]/(RT)$$

$$\equiv \frac{Q}{(RT)}, \tag{B3}$$

where $Q[= P(dV/dt)]$ is frequently called the "throughput" of the gas. Thus while the number of moles of gas passing through the orifice per unit time (Q_m) is an explicit function of the gas temperature, the throughput (Q) is not.

For example, if the pressure P is equal to one atmosphere (1 atm) and the volume rate of change necessary to maintain that pressure is one cubic centimeter per second (1 cm^3 s^{-1}), then the gas throughput is equal to

$$Q = P\left(\frac{dV}{dt}\right) = (1 \text{ atm})(1 \text{ cm}^3 \text{ s}^{-1}) = 1 \text{ atm cm}^3 \text{ s}^{-1}, \tag{B4}$$

independent of the temperature of the gas. If the gas temperature is 273.15 K (0 °C), the molar flow rate of gas can be computed using Eq. (B3) as

$$Q_m = Q/(RT)$$
$$= (1 \text{ atm cm}^3 \text{ s}^{-1})/[(82.057 \text{ atm cm}^3 \text{ mol}^{-1} \text{ K}^{-1})$$
$$\times (273.15 \text{ K})]$$
$$= 4.462 \times 10^{-5} \text{ mol s}^{-1}. \tag{B5}$$

If the temperature of the gas is 296.15 K (23 °C), then the molar flow rate of gas can again be computed, using Eq. (B3), as

$$Q_m = Q/(RT)$$
$$= (1 \text{ atm cm}^3 \text{ s}^{-1})/[(82.057 \text{ atm cm}^3 \text{ mol}^{-1} \text{ K}^{-1})$$
$$\times (296.15 \text{ K})]$$
$$= 4.115 \times 10^{-5} \text{ mol s}^{-1}. \tag{B6}$$

Thus, while it is frequent practice to interchange the words throughput and "flow rate," this example illustrates clearly that, for the same throughput of 1 atm cm³ s⁻¹, the actual flow rate of gas will have different values, depending on the temperature of the gas.

If throughput and flow rate are not the same quantity, we may ask if throughput has any physical significance. From the example above, we see that the quantity Q called throughput is actually the amount of work per unit time (or power) that must be done by the piston on the gas to maintain constant pressure P in the reservoir as gas effuses through the orifice, and that this quantity is independent of temperature. For isothermal conditions, this energy is transported across the orifice in the form of kinetic energy of the gas molecules.

Dual usage of the word throughput, on the one hand defined by $Q = d(PV)/dt$, and on the other hand meant to be synonymous with leakage rate, has caused considerable confusion in the literature over the years, and has led to the use of the words "throughput units" or "PV units" when the word throughput is meant to be synonymous with gas flow rate. The way that PV units or throughput units are associated with flow rates can be seen using the example above. For the conditions used to compute the flow rate in Eq. (B5), the throughput is 1 atm cm³ s⁻¹, the temperature of the gas is 0 °C, and the flow rate is 4.462×10^{-5} mol s⁻¹. The PV unit or throughput unit that is associated with this flow is 1 atm cm³ s⁻¹ at 0 °C. Similarly, for the conditions used to compute the flow rate in Eq. (B6), the throughput is still 1 atm cm³ s⁻¹, the temperature of the gas is now 23 °C, and the flow rate is 4.115×10^{-5} mol s⁻¹. The PV unit or throughput unit that is associated with this flow is 1 atm cm³ s⁻¹ at 23 °C. It is important to note that PV units or throughput units are not really units at all, in the sense that on their own they do not have clear dimensions: they are merely expressions of convenience that are, in fact, *defined* by the flow rates with which they are associated. Thus, an equivalence relationship can be established

$$1 \text{ atm cm}^3 \text{ s}^{-1} \text{ at } 0\,°C = 4.462 \times 10^{-5} \text{ mol s}^{-1}. \tag{B7}$$

From Eqs. (B5) and (B6) it can be seen that this definition can be extended to other PV units or throughput units at arbitrary temperature according to

$$1 \text{ atm cm}^3 \text{ s}^{-1} \text{ at } T_1 (\text{K})$$
$$= [273.15/T_1 (K)] \cdot 4.462 \times 10^{-5} \text{ mol s}^{-1}. \tag{B8}$$

Generalizing even further, then, to move from one PV unit or throughput unit to another, Eq. (B8) can be used to derive the expression

$$1 \text{ atm cm}^3 \text{ s}^{-1} \text{ at } T_1 (\text{K})$$
$$= [T_2 (\text{K})/T_1 (\text{K})] \text{ atm cm}^3 \text{ s}^{-1} \text{ at } T_2 (\text{K}). \tag{B9}$$

Equations (B7), (B8), and (B9) then form the basis on which conversions to other PV units or throughput units, such as Pa m³ s⁻¹ at T_3 (K), atm cm³ s⁻¹ at T_4 (K), Torr ℓ s⁻¹ at T_5 (K), etc., can be performed. Table II lists conversion factors for various units.[10] The following example illustrates such a conversion.

Let us say that for the gas flow rate measured under the conditions corresponding to Eq. (B5), we would like to know the flow rate in terms of the PV/throughput unit Pa m³ s⁻¹ at T_3 (K). That is, we would like to find A_3 in

$$A_3 (\text{Pa m}^3 \text{ s}^{-1} \text{ at } T_3(\text{K})) = 1 \text{ atm cm}^3 \text{ s}^{-1} \text{ at } 0\,°C. \tag{B10}$$

The first step is to perform the conversion between atm cm³ s⁻¹ and Pa m³ s⁻¹ which, from Table II (Ref. 10), is

$$1 \text{ atm cm}^3 \text{ s}^{-1} = 0.101\,325 \text{ Pa m}^3 \text{ s}^{-1}. \tag{B11}$$

Note that Table II must be used with some caution. The units in the top left quadrant, which is highlighted with a heavy black line, are all throughput units, and the conversions between them are independent of temperature. Alternatively, the units outside of the top left quadrant are all flow rate units, but are also independent of temperature (except for "ATM STP cm³ s⁻¹," where the temperature is referred to in the unit). When the expression "at 0 °C" is added to the throughput units in the upper left quadrant, as the Table II caption indicates is intended, the throughput units can then be regarded as flow rate units, and conversion of flow rate units across the heavy black line is then allowed. Substitution of Eq. (B11) into Eq. (B10) then gives

$$A_3 [\text{Pa m}^3 \text{ s}^{-1} \text{ at } T_3(\text{K})]$$
$$= (0.101\,325 \text{ Pa m}^3 \text{ s}^{-1}) \text{ at } 0\,°C. \tag{B12}$$

The next step is to convert to the desired temperature T_3 (K) on the right-hand side of Eq. (B12), using Eq. (B9) in the more generalized form

$$Q \text{ at } T_1 (\text{K}) = [T_2 (\text{K})/T_1 (\text{K})]Q \text{ at } T_2 (\text{K}), \tag{B13}$$

where Q is any throughput unit, such as atm cm³ s⁻¹, Pa m³ s⁻¹, etc. We get

$$A_3 [\text{Pa m}^3 \text{ s}^{-1} \text{ at } T_3(\text{K})]$$
$$= (0.101\,325) \cdot [T_3 (\text{K})/273.15]$$
$$\cdot [\text{Pa m}^3 \text{ s}^{-1} \text{ at } T_3(\text{K})], \tag{B14}$$

so that A_3 is

$$A_3 = (0.101\ 325) \cdot [T_3(K)/273.15]. \tag{B15}$$

This example can then be taken one step further to handle the most general conversion from Q_4 at T_4, to Q_3 at T_3, that is

$$A_4(Q_4 \text{ at } T_4) = A_3(Q_3 \text{ at } T_3), \tag{B16}$$

where Q_3 and Q_4 are any two throughput units, related by the temperature-independent conversion factor $\mu_{4,3}$

$$Q_4 = \mu_{4,3} Q_3. \tag{B17}$$

We wish to find A_3 in terms of the other known parameters. Following steps virtually identical to Eqs. (B10)–(B15), we get

$$A_3 = A_4 \mu_{4,3} T_3(K)/T_4(K). \tag{B18}$$

For example, suppose we wish to convert 1×10^{-7} atm cm^3 s^{-1} at 0 °C to Torr ℓs^{-1} at 23 °C

$$1 \times 10^{-7} \text{ atm cm}^3 \text{ s}^{-1} \text{ at } 0°C = A_3 \text{ Torr } \ell\text{s}^{-1} \text{ at } 23\,°C. \tag{B19}$$

Then, in Eq. (B16), $A_4 = 1 \times 10^{-7}$, $Q_4 = $ atm cm^3 s^{-1}, $T_4 = 0\,°C = 273.15$ K, $Q_3 = $ Torr ℓs^{-1}, and $T_3 = 23\,°C = 296.15$ K. From Table II, the conversion factor in Eq. (B17) is 1 atm cm^3 s$^{-1} = (0.760)$ Torr ℓs^{-1}, so that $\mu_{4,3} = 0.760$. Using Eq. (B18) we obtain

$$A_3 = 1 \times 10^{-7} \cdot (0.76) \cdot 296.15/273.15 = 8.24 \times 10^{-8}, \tag{B20}$$

so that

$$1 \times 10^{-7} \text{ atm cm}^3 \text{ s}^{-1} \text{ at } 0\,°C$$
$$= 8.24 \times 10^{-8} \text{ Torr } \ell\text{s}^{-1} \text{ at } 23\,°C. \tag{B21}$$

From Eq. (B7), this is equivalent to 4.462×10^{-12} mol s^{-1}.

From this discussion it should be clear why a unit such as moles per second (mol s^{-1}) was chosen by the committee as the recommended unit for flow rate or leakage rate, as opposed to a throughput unit. Other possibilities, such as kilograms per second, were also considered, but have the drawback that in comparing flow rates from leaks emitting different gas species or mixtures, it is necessary to know the relative molecular weights. Another popular leakage rate unit is the standard atmosphere cm^3 s^{-1}. However, there is an opportunity for ambiguity in stating the standard conditions in temperature because of the availability of more than one accepted standard, with 0, 25, 20 °C, etc. in use. Since "standard atmosphere cm^3 s^{-1}" requires knowledge of the "standard" temperature, the calibration temperature and the usage temperature, further confusion is possible.[9] Therefore, the recommendation of use of the unit moles per second is further strengthened. This use reduces the problems of ambiguity and confusion, since the originator of the measurements must immediately incorporate knowledge of the temperature T into the appropriate equation to express the flow rate in mol s^{-1}. Likewise, the user of a leak, given the temperature dependence of the leakage rate in mol s^{-1}, can

readily convert data to the applicable units during use knowing the temperature of the measurement process.

APPENDIX C: BIBLIOGRAPHY

In addition to those cited in the text, the following references provide further information pertinent to the calibration and use of leaks. This bibliography is not intended to be exhaustive, and contributions will be welcomed by the Committee for inclusion in future versions.

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