

# Commercial helium permeation leak standards: Their properties and reliability

P. J. Abbott<sup>a)</sup> and S. A. Tison

*Thermophysics Division, Chemical Science and Technology Laboratory,  
National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

(Received 11 October 1995; accepted 12 February 1996)

Standard leaks or leak artifacts are used extensively in industrial and research environments, typically for the calibration of helium leak detectors. The most commonly used leak is the helium permeation type, which uses a glass, quartz, or polymer barrier to restrict the flow of helium via diffusion. Physical leaks, on the other hand, use a physically restrictive element to limit the flow. This article will discuss the properties and reliability of helium permeation standard leaks, based on eight years of accumulated calibration data. Physical helium leaks will not be discussed since relatively few have been calibrated at the National Institute of Standards and Technology.

## I. INTRODUCTION

The National Institute of Standards and Technology (NIST) Pressure and Vacuum Group calibrates commercially available helium leaks between  $10^{-14}$  mol/s and  $10^{-6}$  mol/s, which are frequently used as secondary standards in industrial and research environments. Most of these leaks are used to calibrate helium leak detectors, which can then be used to quantify leak rates of closed structures. In general, leaks consist of a gas reservoir, a leak element, and a fitting to attach the leak to the system of interest. The leaks are classified as either physical or permeation, depending on the characteristics of the leak element. A physical leak relies on a physical restriction such as a small diameter tube to limit the flow of gas from the reservoir. A permeation leak establishes its flow by a diffusion process across a barrier composed of a material which is permeable to the gas of interest.

During the past eight years, NIST has performed over 100 customer leak calibrations; 92% of these were helium permeation leak calibrations. This paper will focus on helium permeation leak properties based on NIST calibration experience. Further information on physical leaks may be found in the literature.<sup>1</sup>

The molar leak rate of a permeation leak has been found empirically to obey the following relationship,

$$Q = ATe^{-B/T}, \quad (1)$$

where  $Q$  is the molar leak rate (mol/s),  $A$  is a constant that depends on the solubility, diffusivity, area, and thickness of the leak element ( $\text{mol s}^{-1} \text{K}^{-1}$ ),  $T$  is the absolute temperature of the leak (K), and  $B$  is a constant (usually called the temperature coefficient) that is equal to the activation energy of the leak element material divided by the universal gas constant. Both  $A$  and  $B$  are independent of the absolute temperature for the temperature range investigated here (0 °C to 50 °C). Calibration of permeation leaks involves determining the constants  $A$  and  $B$ .

There are advantages and disadvantages associated with using permeation leaks. Among the advantages are the fol-

lowing: (1) a permeation leak tends to purify the gas as it diffuses through the leak element, because most impurities are not capable of diffusing through the leak element material; (2) by choosing the proper leak element dimensions and reservoir fill pressure, it is possible to produce very low leak rates, e.g.,  $10^{-14}$  mol/s; (3) if properly cared for, permeation leaks tend to be very stable over time, as the data presented later will show. Disadvantages of permeation leaks include: (1) the leak rate has a strong temperature dependence, as shown in Eq. 1; (2) the leak element, typically made of glass, is fragile; (3) the buildup of gas that occurs when the vacuum valve (if one is present) is closed produces changes in the helium concentration gradient across the leak element and hence instabilities in the leak rate; (4) the leak rate can require an hour or longer to equilibrate to changes in temperature; (5) one is limited to using gases for which permeating materials are available.

## II. CALIBRATION APPARATUS

NIST uses two systems for calibrating leaks; one is the NIST Primary Leak Standard (PLS), and the other is the NIST Leak Comparison System (LCS). The two systems are briefly described below.

The PLS, shown in Fig. 1, consists of three major parts: a leak manifold, a constant pressure flowmeter, and a vacuum chamber. The flowmeter is described in the literature in detail.<sup>2,3</sup> The vacuum chamber is composed of an upper and a lower chamber separated by a 1 cm diameter orifice. A  $500 \text{ } \ell \text{ s}^{-1}$  turbomolecular pump attached to the lower chamber is used to achieve a high vacuum. Two or more quadrupole mass spectrometers are connected to the upper chamber for partial pressure measurements, as well as several ion gauges for total pressure measurements. Flow from the flowmeter or the leak manifold can be valved into either the upper or lower chamber.

An unknown leak rate is measured as follows. The leak is attached to the leak manifold and the entire system is evacu-

<sup>a)</sup>Electronic mail: pja@tiber.nist.gov

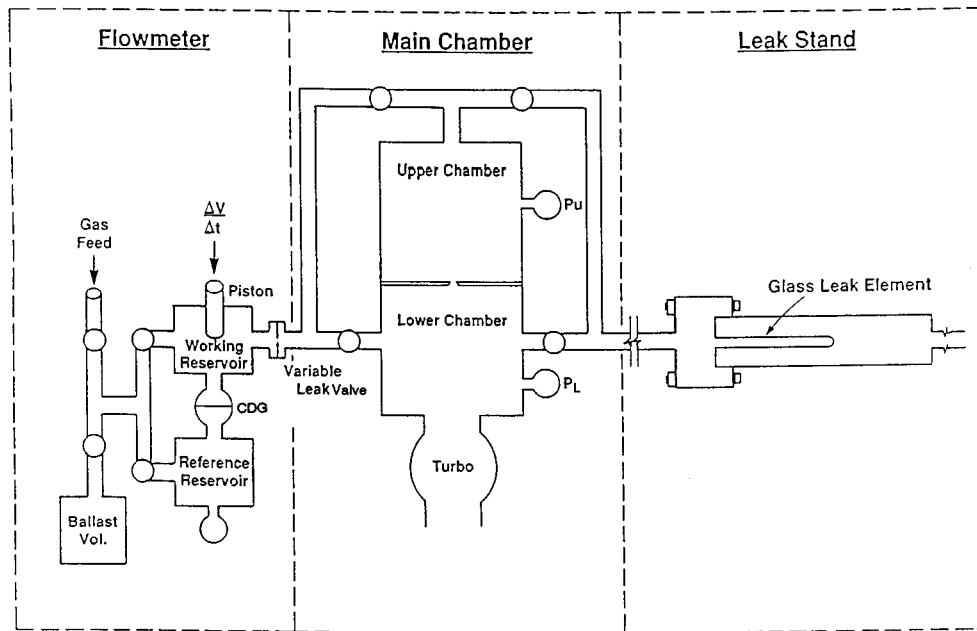


FIG. 1. Schematic of the NIST Primary Leak Standard (PLS) used for primary calibration of helium permeation leaks.

ated. Gas emitted from the leak is valved into the vacuum chamber, flows through the orifice, and is evacuated by the pump. After the gas flow and upper and lower chamber pressures reach equilibrium, the upper chamber gas partial pressure indication, as measured using one or more mass spectrometers tuned to helium, is recorded. The leak is then isolated from the system and the flowmeter is valved into the system. The flowmeter is pressurized with helium and the resulting flow is adjusted so that upon stabilization, the upper chamber partial pressure of helium as measured with the mass spectrometer(s) is the same as that recorded when the leak was valved into the system. The flowrate is then measured using the constant pressure flowmeter. The flowmeter is able to measure flow rates between  $10^{-6}$  mol/s and  $10^{-12}$  mol/s. To measure flow rates lower than  $10^{-12}$  mol/s, a flow division technique is used that allows extension of the lower limit of the flowmeter down to  $2 \times 10^{-14}$  mol/s.

The two-standard-deviation relative uncertainty in the measured flow rate of the constant pressure flowmeter varies from a few tenths of 1% at  $10^{-6}$  mol/s to about 5% at  $10^{-14}$  mol/s. The majority of leaks calibrated at NIST are in the range of  $10^{-12}$  mol/s to  $10^{-10}$  mol/s, and the typical two-standard-deviation relative uncertainties for these are between 1% and 3%. The PLS is used to determine the leak rate of the unknown near 23 °C. Once the temperature coefficient of the leak ( $B$  in Eq. 1) has been determined using the Leak Comparison System described below, the PLS data can be used to calculate the  $A$  coefficient in Eq. 1.

The NIST Leak Comparison System<sup>3</sup> (LCS) compares the flow of an unknown leak at a constant temperature with the flow from a calibrated reference leak maintained at 23 °C. The LCS consists of two independent manifolds, one for calibrated reference leaks and one for unknown leaks, that

can be separately valved into a quadrupole mass spectrometer that is tuned to helium. The quadrupole is evacuated with a  $50 \text{ } \ell \text{ s}^{-1}$  turbomolecular pump to achieve high vacuum. The reference and unknown leaks are pumped on continuously (when not valved into the quadrupole) by a  $10 \text{ } \ell \text{ s}^{-1}$  turbomolecular pump.

The LCS measures an unknown leak rate in the following way. The unknown leak is installed on the unknown leak manifold, and a reference leak having approximately the same leak rate is installed on the reference leak manifold. The leaks are pumped on until the leak rates reach equilibrium, usually within 24 h. The reference and unknown leaks are then alternately and independently valved into the quadrupole and their respective helium partial pressures are recorded. The leak rate of the unknown leak is then calculated based upon the ratio of these helium partial pressures and the known leak rate of the reference leak. The calibrated reference leak is chosen such that its leak rate at 23 °C is within a factor of 10 of the unknown leak rate at 23 °C. This is done so as to minimize the uncertainty due to nonlinearity of the quadrupole response over a wide range of leak rates. Typical two-standard-deviation relative uncertainties for the LCS are about 1% greater than the relative uncertainty associated with a primary calibration, and about 2% to 4% for leak rates in the range of  $10^{-12}$  mol/s to  $10^{-10}$  mol/s.

The LCS is used to calibrate a leak as a function of temperature (both  $A$  and  $B$  in Eq. 1 are determined) or to determine the temperature coefficient ( $B$  only in Eq. 1) of the unknown leak as part of a primary calibration using the PLS. In either case, the unknown leak rate must be measured as a function of temperature. To do this, the unknown leak is covered by an insulated metal can that is connected to a temperature bath. A target temperature is set and temperature

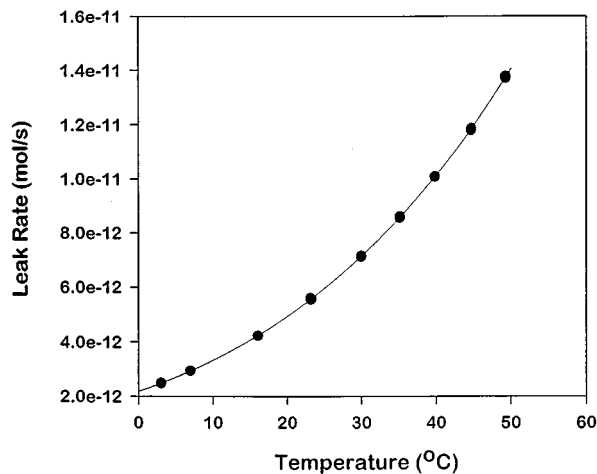


FIG. 2. Plot of measured leak rate of unknown leak vs temperature for a calibration done on the NIST Leak Comparison System (LCS). The dependence of leak rate on temperature is described by Eq. 1.

measurements of the unknown leak are made at regular time intervals. At the same time, the quadrupole monitors the signal generated by the unknown leak and a computer subroutine determines when stability has been achieved, usually between 30 min and 60 min after the target temperature has been set. The unknown leak is then compared to the reference leak which is maintained at 23 °C, as described above. A typical LCS calibration consists of comparing the unknown leak rate to the reference leak rate at a series of temperatures between 0 °C and 50 °C. Example calibration results are shown in Fig. 2. From these data the temperature coefficient  $B$  is calculated using a nonlinear curve fitting routine. The LCS is fully automated and is controlled by a personal computer running BASIC software written at NIST.

### III. HELIUM GLASS PERMEATION LEAKS CALIBRATED AT NIST

#### A. Temperature coefficients

As of this writing, NIST has performed 106 leak calibrations on several types of different commercially available leaks made by seven different manufacturers; 97 of these calibrations have been performed on 42 different helium permeation leaks, the others being physical leaks. Of these 42 permeation leaks, 25 have been calibrated more than once. As shown in the histogram in Fig. 3, the range of helium permeation leaks calibrated extends from  $10^{-13}$  mol/s to about  $5 \times 10^{-9}$  mol/s, with over 80% in the range of  $10^{-12}$  mol/s to  $10^{-10}$  mol/s. The distribution of measured temperature coefficients of helium permeation leaks calibrated at NIST is shown in Fig 4. The temperature coefficient is proportional to the activation energy for helium in the leak element material through the relationship

$$E_{act} = BR, \quad (2)$$

where  $E_{act}$  is the activation energy ( $\text{J mol}^{-1}$ ),  $B$  is the temperature coefficient (K), and  $R$  is the universal gas constant

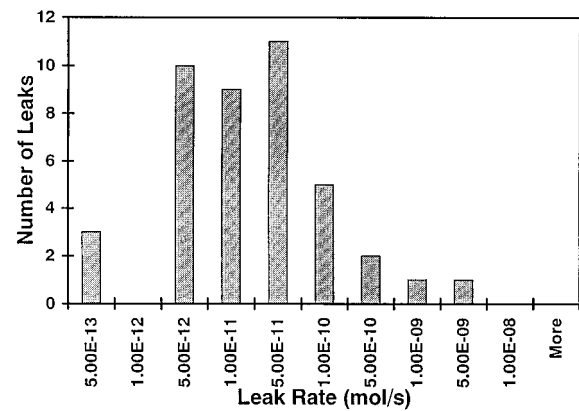


FIG. 3. Histogram showing the distribution by leak rate of the 42 different helium permeation leaks calibrated at NIST. The vertical bar on each histogram "bin" indicates the number of leaks falling between that bin and the next lowest bin.

( $\text{J mol}^{-1} \text{K}^{-1}$ ). Differing structures and compositions of glasses used as leak elements result in a wide distribution of helium activation energies. Therefore, it is possible to distinguish the type of glass used for the leak element by looking at the temperature coefficient of the leak.<sup>4</sup> The temperature coefficient vs leak rate data plotted in Fig. 5 show that about 80% of the leaks calibrated have a temperature coefficient close to 3000 K. In addition, two leaks have temperature coefficients of about 3600 K, two leaks have coefficients just below 2900 K, and five of the leaks have a temperature coefficient of 2500 K or less. Most commercial leak elements manufactured today use Pyrex 7740 for the leak element, which is sometimes stated on the label on the leak. Before 1980 some manufacturers used borosilicate glasses as leak elements. Other element materials such as Corning 7052 borosilicate and quartz are used today for special applications. Unfortunately the type of glass used in the element is not usually indicated on the leak or known by the customer requesting its calibration, but it can be deduced from its tem-

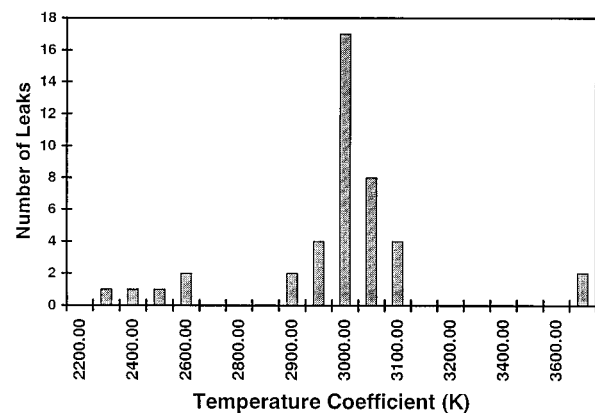


FIG. 4. Histogram showing the distribution by temperature coefficient of the 42 different helium permeation leaks calibrated at NIST. The vertical bar on each histogram "bin" indicates the number of leaks falling between that bin and the next lowest bin.

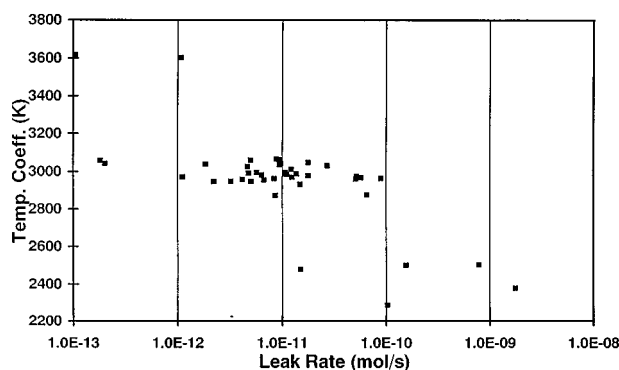


FIG. 5. Plot of the temperature coefficient vs leak rate for the 42 different helium permeation leaks calibrated at NIST. Note that most leaks have a temperature coefficient of about 3000 K.

perature coefficient or obtained from the manufacturer. Based upon the previously measured activation energies of helium in various types of glass<sup>5</sup> and the relative differences between activation energies of various glasses, we infer the probable glass types which correspond to the measured activation energies,<sup>6</sup> shown in Table I.

Figure 5 shows that most leaks are made from Pyrex 7740, with  $B$  approximately equal to 3000 K. Artifacts with a higher leak rate ( $\geq 10^{-10}$  mol/s) tend to be made from a material with a lower temperature coefficient. This may indicate that the material has a greater helium diffusivity and thus would require a lower reservoir helium concentration (fill pressure) to achieve a given leak rate in comparison with Pyrex 7740. Similarly, smaller leaks made from a relatively high temperature coefficient material such as Corning 7052 ( $B \approx 3600$  K) may indicate a smaller helium diffusivity and would require a higher fill pressure than if Pyrex 7740 were used.

## B. Stability

The leak rate of a helium permeation leak depends on the composition and construction of the leak element as well as the reservoir helium concentration behind the leak element. As helium flows out of the leak element, the reservoir helium concentration decreases and hence so does the leak rate. If

TABLE I. Correlation between NIST measured temperature coefficients<sup>a</sup> and probable glass types for helium permeation leaks.

NIST measured temperature coefficient (K)	NIST measured activation energy ( $\text{J mol}^{-1}$ )	Activation energy (published) ( $\text{J mol}^{-1}$ )	Probable glass type
$\leq 2500$	$2.3 \times 10^4$	$2.3 \times 10^4$	Borosilicate
2700	None calibrated	$2.6 \times 10^4$	Fused silica
3000	$2.7 \times 10^4$	$2.7 \times 10^4$	Pyrex 7740
3600	$3.2 \times 10^4$	b	Corning 7052

<sup>a</sup>For the purpose of comparison with the data in Ref. 5, activation energies corresponding to the temperature coefficients measured at NIST were calculated assuming no pre-exponential factor of  $T$  in Eq. 1.

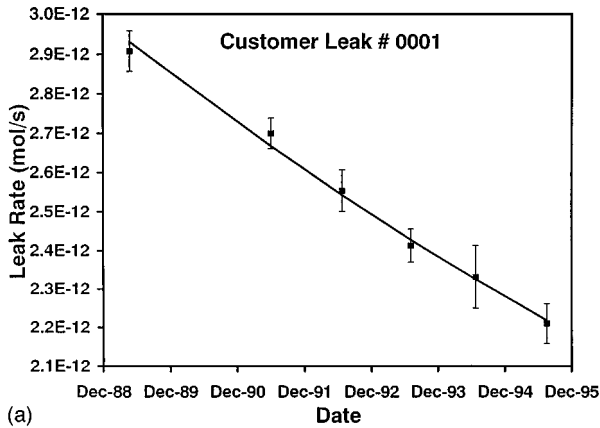
<sup>b</sup>Activation energy not available; glass type obtained from leak manufacturer.

the leak is maintained at a constant temperature, the decay rate will have an exponential time dependence.

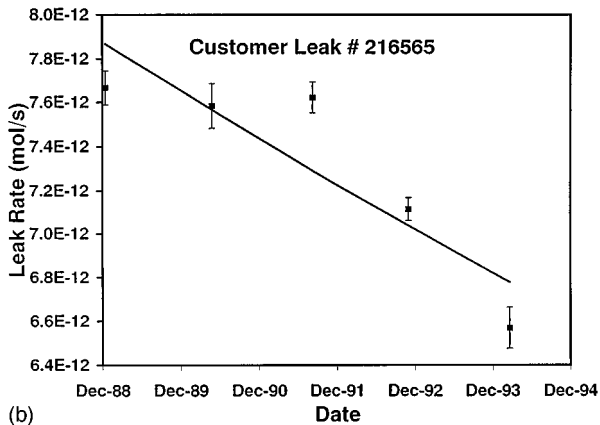
In practice it is important to know the decay rate of the leak, since it may be on the order of several percent per year and may cause changes that are greater than the uncertainty of the calibration. However, the decay rate may vary considerably depending on how the leak is constructed, how it is used, and how it is stored when it is not in use. Many helium permeation leaks have valves after the leak element that allow the flow of helium to be shut off. Closing this valve for a long period of time, e.g., months, will change the helium concentration gradient across the leak element and thus alter the natural decay rate; this could lead to a greater uncertainty in the leak rate than if the shut-off valve remains open. Some permeation leaks also have a fill valve on the helium reservoir; if gas escapes through or around this valve, the overall leak rate will decay more rapidly than normal. Furthermore, microcracks in the leak element would cause an abnormally high decay rate. Since the leak rate is highly temperature dependent, using or storing a leak at a higher or lower temperature than the calibration temperature (23 °C) will greatly alter the natural decay rate of the leak.

NIST has performed repeat calibrations on 25 helium permeation leaks; 15 of these have been calibrated three times or more over the past eight years. In general, NIST has no knowledge of the usage or storage conditions of the leak at the customer site. For this discussion, the working criterion for good stability is a predictable decay rate over a period of several years. Figure 6 shows examples of some repeat calibrations, one showing good stability and one showing poor stability. It should be noted that the overlapping error bars representing the two-standard-deviation uncertainty in the data in Fig. 6b point more to a constant leak rate between the second and third calibrations (as would occur if the vacuum valve were closed) than an apparent increase in the leak rate. Poor stability may be due to one or more of the reasons discussed above. The lines in Figs. 6a and 6b correspond to an exponential fit to the data, but a linear fit may be used without making a significant error since the decay rates are small; the decay rates for the present analysis were calculated based on linear fits to the leak rate vs time data.

Figure 7 is a summary of the decay rate vs leak rate data for all the repeat calibrations. Six of the repeat leaks were not used because of obvious instabilities and two were disqualified because of decay rates greater than 10% per year (one of the two leaks exhibiting a decay rate greater than 10% per year was found to have a leak at the reservoir fill valve due to incorrect installation of the valve). Of the leaks exhibiting good stability, the decay rates vary between 1% and 5% per year, the average being 2.6% per year. This is in good agreement with previously published decay rate values for this type of leak.<sup>1</sup> As mentioned above, NIST typically has no knowledge of the way a leak is handled between calibrations, but for many of the leaks that exhibited poor stability, it appears that the shut-off valve was closed for some period of time between calibrations. Based on those leaks that exhibited good stability, it seems reasonable for one to expect a



(a)



(b)

FIG. 6. Leak rate vs time data for two different helium permeation leaks calibrated at NIST. The error bars represent the two standard deviation uncertainty. (a) Leak 0001 shows a stable decay rate of approximately 3.9% per year over a six year period. (b) Leak 216565 shows unstable behavior. The vacuum valve may have been closed between the second and third calibrations (May 1990 to August 1991).

decay rate of between 1% and 5% per year for a commercially available helium permeation leak if the leak is maintained at or near room temperature (23°C), and any shut-off valve is left open.

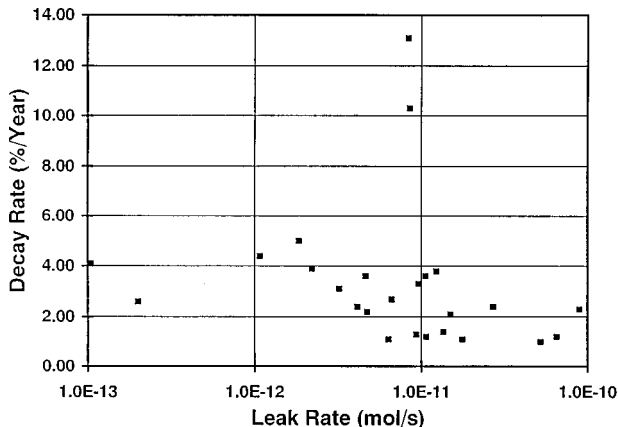


FIG. 7. Plot of the decay rate vs leak rate for the 25 helium permeation leaks that have been calibrated more than once at NIST. Most leaks have a decay rate between 1% and 5% per year.

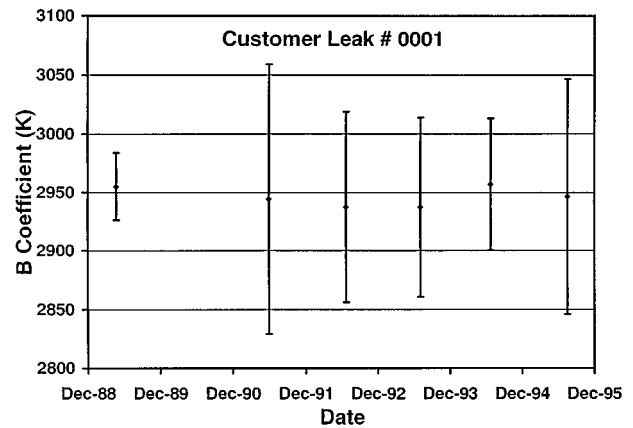


FIG. 8. Plot showing the temperature coefficient stability of helium permeation leak 0001. The average value of the temperature coefficient is 2946 K. The error bars represent the two standard deviation uncertainty.

It has been our experience that a helium permeation leak will have a relatively constant temperature coefficient as long as it is not mistreated. The measured temperature coefficient for helium permeation leak 0001 is shown in Fig. 8. These data show that the temperature coefficient has remained constant to within the uncertainty of the measurement over a period of about six years. This result is typical for all the leaks that exhibit good leak rate stability.

#### IV. CONCLUSION

The stability and properties of helium glass permeation leaks have been evaluated based upon NIST calibrations over a period of eight years. In general, helium glass permeation leaks in the range of  $10^{-12}$  mol/s to  $10^{-10}$  mol/s were found to have decay rates ranging from 1% to 5% with an average of 2.6%. The temperature dependence of the leak rate for helium glass permeation leaks, described by Eq. 1 was found to be highly correlated with the type of glass used in the leak element. The average temperature coefficient,  $B$  in Eq. 1, for the most commonly used glass leak element (Pyrex 7740), was determined to be approximately 3000 K, which corresponds to about a 4% change in leak rate per °C. While the leak rate of closed reservoir glass permeation leaks decay with time, the temperature coefficients are found to remain constant.

#### ACKNOWLEDGMENTS

The authors wish to thank Rich Kayser, Charles Ehrlich, and Scott Wight for useful discussions and suggestion regarding this work.

<sup>1</sup>C. D. Ehrlich and J. A. Basford, *J. Vac. Sci. Technol. A* **10**, 1 (1992).

<sup>2</sup>K. E. McCulloh, C. R. Tilford, C. D. Ehrlich, and F. G. Long, *J. Vac. Sci. Technol. A* **5**, 376 (1987).

<sup>3</sup>C. D. Ehrlich and S. A. Tison, NIST (U.S.) Special Publication No. 250-38, 1992.

<sup>4</sup>J. E. Shelby, **54**, 125 (1971).

<sup>5</sup>R. H. Doremus, *Glass Science* (Wiley, New York, 1973), p. 138.