Chapter 2

PRESSURE AND VACUUM MEASUREMENTS

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1 INTRODUCTION

The art and science of pressure measurement can be fairly said to date from the middle of the seventeenth century. Evangelisti Torricelli is generally credited with the discovery that a glass tube filled with mercury can be used to measure atmospheric pressure. Torricelli's discovery was quickly put to use in a number of significant scientific investigations, but widespread use awaited the Industrial Revolution. During that time a variety of pressure measurement techniques, most of them for "high" pressures, were developed, along with the harnessing of steam power and the emergence of the science of thermodynamics. Their scope was further broadened at the beginning of this century to support the development of the light bulb and the vacuum tube amplifier. The post-World War II surge in research and high-technology manufacturing spurred a rapid increase in the volume and variety of pressure measurements, particularly for very low pressures or vacuum where the availability of new technologies stimulated the rapid development of entirely new industries.

Modern society depends on a diverse complex of sophisticated manufacturing processes and research activities, most of which require pressure and/or vacuum measurements. The accuracy of these measurements can have major effects on the validity of results, product quality, energy efficiency, and, in many cases, the safe operation of a process. Present-day industrial processes require pressure measurements over about 17 decades; research and development projects extend this range two or more decades higher and lower. The applications, accuracy requirements, limitations on the measurement process, and available instrumentation vary widely over this range. At the upper end of the range the pressures that can be generated and measured are limited by the ultimate strengths of materials, while at the lower end they are limited by surface interactions and the release of gas from vacuum chamber walls. Around atmospheric pressure the state-of-the-art accuracy is a few parts per million (ppm). At the high- and low-pressure extremes it is a factor of 2 or 3; indeed, in some cases one must be satisfied to know which decade the pressure is in. Around atmospheric pressure a wide variety of commercial instrumentation, with various strengths and weaknesses, is available. As the pressure becomes higher and lower, the choices are more limited and eventually the measurement becomes a major experiment in itself. For these reasons this discussion is of necessity somewhat limited. It is confined to the *industrial pressure* range, 10^{-8}–10^{9} Pa (10^{-10} torr to 150,000 psi). In all cases the accuracy obtained depends not only on the instrumentation and calibration protocols used, but also on the operator's level of understanding of the measurement process. Therefore, although much of this discussion concerns instrumentation, there is also an emphasis on problems generic to all measurements rather than those that are specific to certain instruments. Only static measurements are discussed; dynamic or time-varying pressure measurements present increasingly severe problems as the frequency range increases, and are well beyond the scope of this discussion. An attempt is made to provide guidelines to the range of accuracies that can be obtained at different pressures, and the basic operating principles are described for many of the available gauges and electromechanical pressure transducers. However, it is not possible to provide detailed performance data for the large variety of available commercial pressure instrumentation. The discussion of the higher pressure measurements includes the primary standards that are maintained in many industrial laboratories and often used for calibration or end-use measurements. As the pressure decreases into the vacuum area, primary standards become increasingly complex, to the point that they are maintained almost exclusively in national standards laboratories. The discussion in this portion of the range focuses more on the end-use instrumentation. The extent of the discussion is biased toward the low-pressure end because of the rapid expansion of vacuum technology over the past few decades and the consequent need for improved vacuum measurements.

As noted, the performance of instrumentation is only one of the factors that affect measurement accuracy. This is particularly true for vacuum measurements. As the pressure is reduced three or more orders of magnitude below atmospheric, pressure uniformity is increasingly difficult to maintain. At very low pressures order of magnitude pressure differences can exist in laboratory-scale systems, local pressures may be largely determined by chemical reactions or adsorption–desorption phenomena, measuring instrumentation can significantly perturb the pressure, and most instruments are sensitive to the gas species. Obtaining accurate measurements in these cases requires that we understand the entire apparatus, and steps must be taken to ensure that the gauge is measuring the pressure of interest.

2 DEFINITIONS

2.1 Pressure and Related Quantities

Hydrostatic pressure, P is generally defined as force F per unit area A. This is thermodynamically equivalent to the negative volume derivative of the Helmholtz free energy E at constant temperature T

$$P = F/A \tag{1}$$

or

$$P = -(\partial E/\partial V)_T \tag{2}$$

These definitions illustrate an important point: Pressure is a mechanical quantity and the basic limitations of the devices that measure pressure are mechanical. Although electrical measurement techniques, many of them quite sophisticated, can be used to enhance the mechanical measurements required and greatly improve the ease of the measurement, the basic limitations of the measurement process, such as response time, susceptibility to environmental changes, and instability or failure modes, are largely determined by the mechanical portion of the instrument.

In solids or high-viscosity liquids significant shear forces can exist and the pressure will be neither isotropic nor hydrostatic. This situation is very much the norm at the higher pressures that lie beyond the range of this chapter. In these situations the pressure is more properly defined as the negative average of the diagonal components of the stress tensor and it can vary significantly over volumes of interest.

At the other extreme, very low pressures, density or molecular flux is generally of more relevance than the pressure, although measurements are usually made in terms of pressure units. For a rarefied gas in thermal equilibrium the pressure and density n are related by the ideal gas law

$$P = nkT \tag{3}$$

where k is Boltzmann's constant, T is the absolute temperature, and n is the density in molecules per unit volume. Similarly, if v_i is the flux of molecules with mass m_i striking a surface of unit area per unit time

$$P_i = \sqrt{2\pi m_i kT}\, v_i \tag{4}$$

where P_i is the partial pressure due to molecules with a mass m_i. For mixtures the total pressure would be the sum of the contributions from different molecular species.

As can be the case with very high pressures, very low pressures may not be isotropic, in which case it is necessary to speak of directional dependent molecular fluxes or pressures. The density, molecular flux, and molecular velocities can also have large spatial variations in a laboratory-size vacuum system, particularly near pumps and heated or cooled parts of the apparatus, for example, near hot filaments or cryogenic shrouds. Under these conditions special techniques must be used to measure the molecular flux as a function of direction and location, or the apparatus must be designed to minimize these variations so that the pressure or density measured by the vacuum gauge is characteristic of the region where it is desirable to know these quantities.

The thermodynamic definition of pressure is that of the absolute pressure, with which this discussion is primarily concerned. The measurement techniques discussed here, however, are also applicable to differential pressure, or the difference between two absolute pressures. Differential pressure measurements are often required in industrial process control, most notably in flow measurements. As the absolute or *line* pressure increases in comparison to the differential pressure, unique problems can arise. A special case of differential measurement is gauge pressures. These are differential measurements referred to atmospheric pressure, and many lower accuracy *quasiabsolute* measurements are actually gauge measurements. In fact, it may well be argued that more gauge measurements are made than any other kind. The variability of atmospheric pressure can limit the accuracy of these measurements if they are used to determine absolute pressures.

2.2 Pressure Ranges

In this discussion reference is made to somewhat arbitrarily defined pressure ranges:

Range	*Pressure* (Pa)	*Conventional Units*
Very high pressure	10^8–10^{11}	1–1000 kbar
High pressure	10^5–10^8	15–15,000 psi
Atmospheric	10^2–10^5	1 torr–1 atm
Low vacuum	10^{-1}–10^2	10^{-3}–1 torr
High vacuum (HV)	10^{-4}–10^{-1}	10^{-6}–10^{-3} torr
Very high vacuum	10^{-7}–10^{-4}	10^{-9}–10^{-6} torr
Ultrahigh vacuum (UHV)	10^{-10}–10^{-7}	10^{-12}–10^{-9} torr

Several of these terms can have common usages that differ somewhat from those defined above; for example, high vacuum is often used for all pressures below 10^{-1} Pa. Reference is also often made to the *transition* regime or range. For most systems this is the higher pressure end of the high-vacuum range and the bottom to middle of the low-vacuum range (10^{-2}–10 Pa). Over this range the mean free path of molecules is comparable to the dimensions of laboratory apparatus, and the molecular dynamics are in a transition from domination by molecule–wall collisions (molecular flow) at the lower pressures, to domination by molecule–molecule collisions (viscous flow) at higher pressures. This range is of special interest because in this range the change in molecular dynamics complicates the design and operation of both primary standards and vacuum gauges, a notable complication being the thermal transpiration effect discussed in Section 6.3. These complications are of some concern since many important industrial processes, for example, sputtering and freeze drying, take place in this pressure range.

2.3 Measurement Accuracy

Pressure measurements, as with all measurements, have a meaning only to the extent that the accuracy of the measurement can be evaluated. A difficult task in any case, accuracy evaluation or error estimation is made all the more difficult by the prevalence of ambiguous or contradictory definitions of the terms used. The same terms are often used in specifications for commercial instruments, where an even wider range of definitions and a sometimes suspicious vagueness can be found. Several common terms are defined below. These definitions are not unique; the Compilation of ASTM Standard Definitions [1] alone lists 17 different definitions for *accuracy*. The definitions presented here, however, are in general accord with those found in [1] and common metrology usage.

Accuracy. The closeness of agreement between a measured value and the "true" or "accepted" value. Since the true value can never be known exactly, accuracy in this sense can only be estimated. When using accuracy most users specify the error or uncertainty; for example, if a measured value is 99% of the accepted value, it is said to have an accuracy of 1%. Accuracy is often specified for a measuring instrument, in which case it refers to the uncertainty of the measurements made with that instrument.

Confidence Level. The probability that the error of a measurement will not exceed the specified uncertainty. It may be specified as a percentage or as a multiple of sigma or standard deviations. As an example, if the errors are assumed to be normally distributed and the uncertainty is specified as "2% at the 3 sigma level," this means that there is a 99.7% probability that the measured value is within 2% of the true value. Unfortunately, confidence levels are often not specified and there is no accepted standard confidence level. Some workers or manufacturers may state uncertainties at the 1 sigma level, others at 2, 3, or some other multiplier. Still others may believe or imply that errors can never exceed the specified bounds.

Error. The difference between a measured value and the true or accepted value. Since the true value is never known exactly, the error in this sense can only be estimated.

Linearity. More properly termed *nonlinearity*, linearity is the deviation of an instrument output from a linear dependence on the input stimulus. It is often equivalent to the maximum deviation of the output from a linear function determined by the outputs at minimum and maximum values of the input.

Precision. The degree of agreement among independent measurements of a quantity. In some cases this term is used for the standard deviation of repeated measurements, in which cases it should be more properly called *imprecision*.

Random Error. The unpredictable variation of repeated measurements of a quantity. It is often characterized by an imprecision or standard deviation.

Repeatability. The closeness of agreement of measurements made under the same conditions. It typically implies the measurements were taken over a short period of time, although *long-term repeatability* may be specified.

Reproducibility. The closeness of agreement of measurements taken under different conditions. The conditions may include different environments, laboratories, operators, or apparatus. Reproducibility may also imply measurements that are repeated over long periods of time.

Sensitivity. The minimum detectable change in a measured quantity, or, the change in output divided by the change in input. Generally, but not always, the context will make apparent which of these two different meanings is intended.

Traceability. The documentation of the relationship between the accuracy or uncertainty of an instrument or measurement and a recognized standard. For example, "Traceable to NBS" implies that the specified uncertainty or accuracy has been established by documented comparisons or calibrations relative to standards maintained by the National Bureau of Standards (now the National Institute of Standards and Technology). Although this term is often used in contractual or legal documents the rigor of its implementation varies widely from one case to another.

Uncertainty. The estimated bounds of the error of a measurement. Uncertainty may also be ascribed to the instrument making the measurements. It should include a specified confidence level, but it often does not.

3 PRESSURE UNITS

The seemingly innocuous subject of units is actually the cause of significant pressure measurement errors in a surprising number of instances. Not only are a large number of pressure units found in regular use, but many of them are defined in an incomplete or ambiguous manner; subtle conditions that are part of the definition are not specified or are misunderstood. The force-per-unit-area pressure units, of which the pascal or newton per square meter (Pa or N/m^2) is the internationally accepted unit (the SI unit or Système International d'Unités), and the pound per square inch (psi) is a non-SI but widely used example, are unambiguously defined. Other units, such as the torr, bar, or atmosphere, are now effectively defined in terms of the pascal, although, in the case of the atmosphere, there are at least two different definitions of the atmosphere, *normal* and *technical*, in common use. Also, it should be noted that "standard conditions," implying a standard pressure and temperature, are not uniquely defined. The pressure is generally 1 atmosphere, although which atmosphere is usually not specified; and various standard temperatures, ranging from 0°C to "room temperature," are used. What is standard is that almost every user of this term is quite confident that his temperature and pressure are the "standard" and that other workers understand this.

Major pressure measurement problems are caused by the widespread use of pressure units expressed in terms of manometer liquid-column lengths, such as *millimeters of mercury*, *microns* (micrometers of mercury), and *inches of water*. Unfortunately, to derive a pressure from the height of a manometer column, or to convert from a "manometer" pressure unit to a true thermodynamic pressure unit, the density of the manometer liquid and the acceleration of gravity must be known. For example, to convert inches of mercury to pascals or pounds per square inch requires that the acceleration of gravity, the temperature, and the pressure of the mercury all be specified (the density of mercury depends on both the temperature and the pressure). However, while it is fairly uniform to assume "standard" gravity (9.80665 m/s^2), there is no standard or convention for the density of the fluid. Thus, we find inches of mercury commonly used to refer to a pressure unit assuming the density of mercury at 32°F, as well as to a different unit assuming the density of mercury at 60°F. A misunderstanding as to which definition is being used will introduce an error of 0.28%, significant for even routine industrial measurements. Smaller errors can be caused by a failure to specify the pressure of the mercury. For example, because of the compressibility of mercury, the pressure equivalence of 1 in. of mercury will change by 4 ppm if the ambient pressure of the mercury is alternately assumed to be 0 or 101 kPa. The possibilities for confusion are compounded when different temperature scales, discussed in Section 4.1.3, are considered. Because of changes in scales, the density of mercury at 20°C also depends on which temperature scale the 20°C is determined.

The conversion factors presented in Table 2.1 for mercury manometer units, and the related torr, are calculated using mercury density values at 1 atm, based on the International Practical Temperature Scale of 1968. Because of the ambiguities in the definition and use of these units, the conversion factors have been deliberately truncated to the number of digits presented, and they should *not* be changed to allow for different temperature scales, as this will only greatly increase the already ample confusion. Similarly, units based on a column of water are uncertain because of ambiguities in the density value used. Additional conversion factors for a variety of units can be found in [2, 3]. To avoid difficulties with units the user is strongly encouraged to use force-per-unit-area units, or, at a minimum, specify clearly the definition and conversion factor to pascals if "manometer" units are used.

Table 2.1 Conversions Factors to Pascals[a]

Unit	*Conversion Factor*
1 psi	6.894757×10^3
1 normal atmosphere	1.013250×10^5
1 technical atmosphere	9.806650×10^4
1 torr	1.33322×10^2
1 bar	1 (exact) $\times 10^5$
1 mm Hg (0°C)	1.33322×10^2
1 in. Hg (32°F)	3.38638×10^3
1 in. H_2O (39.2°F)	2.49082×10^2

[a] To convert the specified units to pascals multiply by the conversion factors.

4 PRESSURE STANDARDS

Measurement standards are of two different types: primary and secondary. Primary standards are those that permit a measurement of a quantity in terms of other known measurement units with a predictable uncertainty. Primary standards are not calibrated against another standard of the same unit, although parts of a primary standard may be calibrated against standards of other units; for example, a primary pressure standard is not calibrated against another pressure standard, but component parts may require calibration against standards of length and temperature. The design of a primary standard must be based on well-established physical laws relating the quantity to be measured to the component measurements; for example, the relationship must be known between the pressure applied to a standard and the measured quantities: length, temperature, mass, time, and so on. The uncertainty analysis of a primary standard requires a thorough understanding of the operation of the standard, including its susceptibility to environmental influences and a knowledge of the uncertainties of the component measurements. Common examples of primary pressure standards are liquid column manometers, piston gauges, and McLeod gauges.

Secondary or transfer standards are calibrated against a primary standard of the same unit and depend on a predictable stability to maintain their accuracy. In theory, any instrument with a well-evaluated stability can serve as a transfer standard; in practice, the term is generally reserved for instruments of exceptional stability. The uncertainty of a secondary standard will always be greater than that of the primary standard against which it is calibrated, the difference being due to the random errors of the calibration; the short-term random errors of the secondary standard; and the instabilities caused by time, environmental parameters, or operator technique. Some instrument types may be used as either primary or secondary standards, for example, piston gauges. The operating theory of other types may not be well enough understood to permit their use as primary standards, but they may possess the stability required for a transfer standard. It is neither impossible nor uncommon for some transfer standards to have a stability superior to the primary standards against which they are calibrated. In these cases the transfer standard can be used to check the stability of the primary standard. Repeated calibrations of the transfer or check standard are monitored to determine whether the differences between the primary and check standard are within expected bounds. If excessive changes are detected, this may indicate a malfunction of the primary and/or check standards, an undetected environmental perturbation, or an underestimation of the inherent instability of either standard.

Discussed below are commonly used pressure or vacuum primary standards: liquid-column manometers, piston gauges, McLeod gauges, volume or Knudsen expansion systems, and orifice-flow vacuum standards. Liquid-column manometers and piston gauges are discussed in more detail because of their widespread use.

4.1 Liquid-Column Manometers

Liquid-column manometers are widely used as primary standards for the calibration of other instruments and also for many end-use measurements. They are capable of the most accurate measurements, and can be the cheapest and simplest pressure measurement device to construct. Unfortunately, these two attributes are not found in the same instrument. The basic principle is illustrated in Figure 2.1. A pressure P applied to the right-hand liquid surface displaces the liquid, which generates a differential pressure ΔP determined by the liquid density ρ, the displaced height h, and the gravitational acceleration g. When the applied pressure and the displaced liquid are in equilibrium, allowing for a nonzero reference pressure P_{ref} on the left column, the absolute pressure P is given by

$$P = \rho g h + P_{\text{ref}} \tag{5}$$

Manometers are widely used for the measurement of atmospheric pressure and the calibration of other instruments, such as aircraft altimeters that are used for this same purpose. Therefore, a great many manometers have a full-scale range of about 100 kPa, although lower range instruments are not uncommon and commercial manometers with ranges up to 350 kPa are found in many

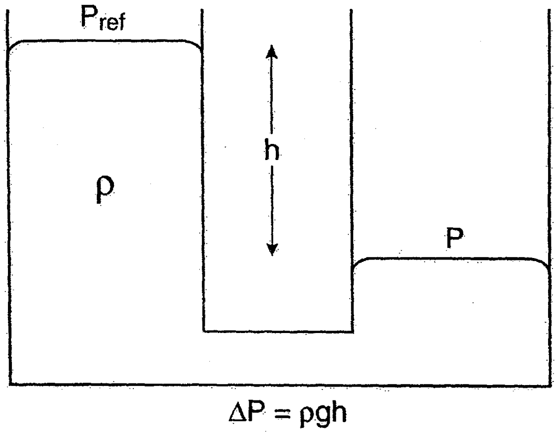

Figure 2.1 Schematic representation of a basic liquid column manometer. The height h is measured along the vertical, ρ is the average density of the liquid in all nonhorizontal parts of the manometer, and g is the local acceleration due to gravity; P_{ref} is the reference pressure and for absolute pressures it should be "zero"; otherwise, the measured pressure will be a differential pressure with respect to P_{ref}.

industrial standards laboratories. Special purpose manometers have been built for higher pressures [4, 5], although generally piston gauges, discussed in Section 4.2, are used for the higher pressure measurements. Manometers are used for both differential and absolute measurements. For absolute measurements the higher quality instruments use a vacuum pump, generally a two-stage mechanical pump, to maintain a "zero" reference pressure. However, large numbers of barometers, used exclusively to measure atmospheric pressure, rely on a vacuum sealed in the closed manometer tube at the time it was filled with mercury.

Manometers may be as simple as a plastic U tube mounted next to a vertical ruler. However, as the desired accuracy increases so does the complexity and cost, although the complexity and cost of some commercial instruments may be due as much or more to a desire for measurement convenience as to an effort to secure measurement accuracy. The differences between various types of manometers arise largely in the techniques used to determine the location of the liquid surfaces and to measure the differential height between them. This is particularly true in the low-range instruments used for vacuum or small differential measurements where the useful range of the manometer may be limited by the resolution of the height measurement. However, the accuracy of state-of-the-art instruments near atmospheric pressure, and the resolution of state-of-the-art low-range instruments is probably constrained as much by the stability and knowledge of the liquid temperature as by any other factor. High-accuracy manometers of the type found in national standards laboratories have been reviewed by Guildner and Terrien [6] and low-range manometers for use in low vacuum and differential measurements have been reviewed by Rüthberg [7] and Peggs [8].

Manometers utilize a variety of liquids, but most manometers with any pretext to high accuracy use mercury. Mercury is readily purified, is chemically stable, has a highly reproducible density with a small temperature coefficient (for a liquid), and possesses a modest vapor pressure. Many of the properties of mercury are discussed in a very comprehensive review by Wilkinson [9]. For very low pressure measurements, low-vapor pressure, low-density (compared to mercury) oils can be used to minimize the reference pressure and obtain an improved pressure resolution. However, the density of some oils may vary by several percent, depending on composition, and the density of even highly purified oils may vary more than 0.01% from lot to lot [10]. The appreciable amount of gas absorbed in oils can hinder the attainment of low reference pressures.

Overall, good commercial mercury manometry can attain uncertainties as low as 25–30 ppm of the measured pressure near atmospheric pressure. Attempts are being made to produce commercial instruments with uncertainties as low as 10 ppm, and the specialized manometers in national standards laboratories are designed to attain uncertainties as low as a few parts per million [6]. Manometers used for low-range vacuum measurements are designed to optimize length resolution. Commercial versions of a low-range instrument [11] using precision micrometer screws for the length measurements can achieve a length imprecision of about 10^{-3} mm, depending on the skill of the operator. Figure 2.2 shows a low-range calibration system that includes two manometers of this type, one employing mercury, the other oil. Full-scale range of the mercury manometer is 13 kPa. The lower density and vapor pressure of the oil allows a better lower pressure limit than can be achieved by the mercury manometer. Specialized instruments using optical [12, 13] or ultrasonic [14, 15] length measurement techniques can achieve a length imprecision of about 10^{-5} mm, further reducing the low-pressure limit. However, most manometers have much larger uncertainties and the accuracy of results obtained with a given type of manometer will vary widely with environmental conditions, maintenance of the instrument, and, in many cases, the skill of the operator. Some appreciation of the factors limiting accuracy can be gained by considering the individual terms in (5): gravity, height, density, and reference pressure.

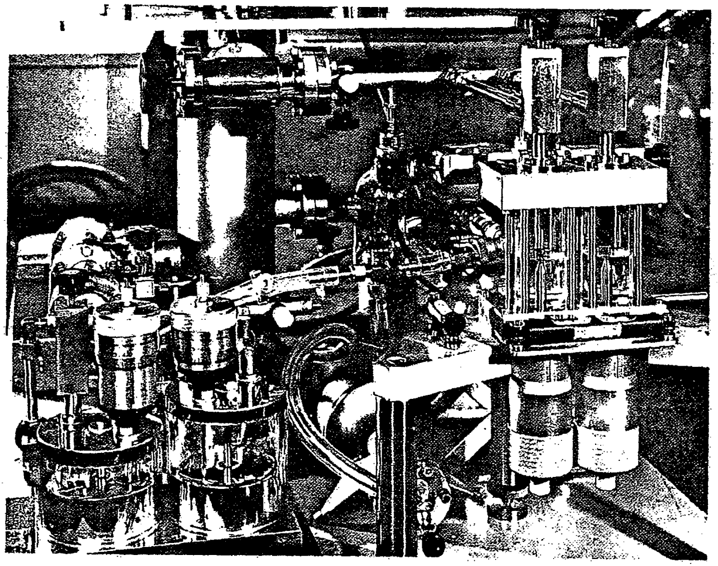

Figure 2.2 Calibration system employing two low-range liquid-column manometers that use micrometer screws to measure the displaced height. The manometer on the left is filled with mercury and the one on the right is filled with a low-vapor pressure oil. The ends of the micrometer screws are sharpened to a point and the liquid surfaces are located by adjusting the screws until the points just "dimple" the surface.

4.1.1 Gravity

The local acceleration of gravity at the site of the instrument g has nothing to do with so-called *standard* gravity. Without going to geographic extremes, g can vary by 0.1% within the continental United States. The acceleration of gravity, in meters per seconds squared (m/s^2), can be calculated from a theoretical formula [16] based on an ellipsoid approximating the earth's shape. Corrected for local deviations from the ellipsoid, the acceleration g is given by

$$g = 9.78032(1 + 5.2789 \times 10^{-3} \sin^2 \phi + 2.35 \times 10^{-5} \sin^4 \phi) - 3.086 \times 10^{-6} h + 1.19 \times 10^{-6} h' \quad (6)$$

where ϕ is the latitude, h is the elevation in meters above mean sea level, and h' is the difference in elevation in meters from the average terrain elevation for the surrounding 100-km radius area. The uncertainty in g, calculated from this equation, will typically vary between 10 and 100 ppm depending on the extent of local geophysical anomalies. Improved accuracies can be provided by interpolating between measured reference points,[†] typical uncertainties being a few parts per million. Measured values can be obtained with uncertainties less than 0.1 ppm, although account must be taken of tidal variations at the 0.3-ppm level. Many institutions, such as national geodetic surveys, petroleum exploration firms, and geophysical research organizations, have the capability to make gravity measurements at field locations.

4.1.2 Height

The diversity of techniques used to locate and measure the heights of the liquid surfaces is too great for a comprehensive discussion. The most common techniques involve a visual comparison of the location of the surface with an adjacent length scale. This comparison may be aided by a sighting ring that can be slid up or down a glass manometer tube until the bottom of the ring is coincident with the top of the meniscus. A manometer using this technique to measure the height of one of the columns is illustrated in Figure 2.3. An attached vernier transfers the location to an etched length scale. Theodolites are also used to transfer the location of the meniscus horizontally to an adjacent scale. Cathetometers are similarly used but with the scale built into the cathetometer. Some automated mercury manometers use the meniscus to interrupt the light between a bulb and a photocell. The bulb–photocell combination, a servosystem, and length measuring mechanism are used to track and measure the height of the meniscus. Some short-range instruments and limited-range barometers locate the surface by observing the slight indentation when a pointed tip,

[†] Interpolated values of g and estimated errors for a specified location (latitude, longitude, and elevation) can be obtained in the United States for a fee from the National Geodetic Information Center (N/CG174), National Oceanic and Atmospheric Administration, Rockville, MD 20852, telephone: (301) 443-8623.

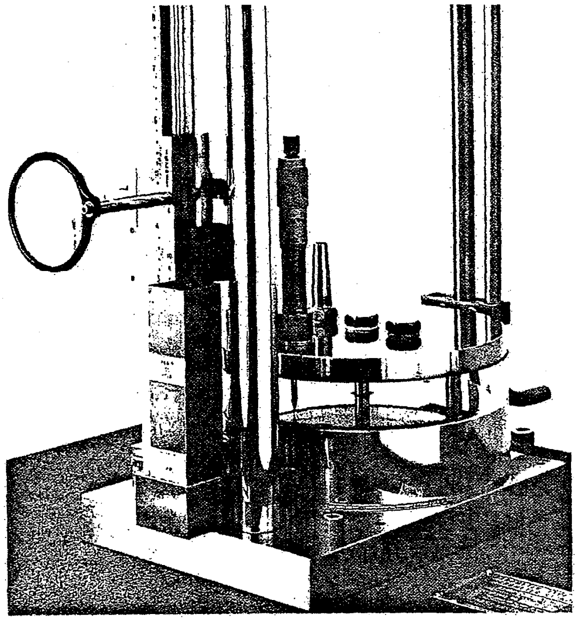

Figure 2.3 Commercial *single-cistern* mercury manometer using a sighting ring and micrometer screw to measure the column heights. Pressure is applied to the large diameter cistern; the height of the mercury in the cistern is measured using the micrometer screw mounted on top of the cistern. The reference pressure is maintained in the smaller diameter glass tube; the height of the mercury in the tube is measured using the sighting ring around the tube, the attached vernier, and the length scale to the left of the tube. The sighting ring rests on a stack of gauge blocks used to calibrate the length scale.

attached to a length scale, just touches the surface [11]. Two such instruments are illustrated in Figure 2.2. The precision of the visual techniques usually depends on the visual acuity of the operator. Attempts are generally made to enhance the operator's vision by special lighting techniques. At the best, imprecisions of about 10^{-3} mm can be achieved with careful design and practiced skill. The accuracy of both the visual and the automated techniques can be compromised by irregularities in the glass tubes.

Some high-performance, and high-cost, commercial mercury manometers effectively eliminate the problems due to capillary depression (see below) and operator skill by locating the mercury menisci in large-diameter (7–10-cm) cisterns with a capacitor plate above the mercury surface, as shown in Figure 2.4. The mercury in the cisterns is connected by a small flexible tube, and a

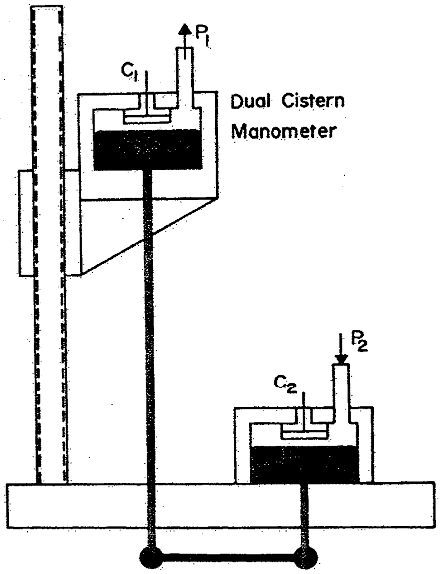

Figure 2.4 *Dual-cistern* type manometer: P_1 is the reference pressure and P_2 is the applied pressure. The height of the mercury in the cisterns is measured using capacitor plates C_1 and C_2. The upper cistern is supported by a movable carriage that is adjusted as the pressure changes so that the height of the mercury in each cistern remains constant.

servomechanism adjusts the height of the reference–pressure cistern so that, as the pressure is varied, the mercury surfaces remain a fixed distance below the capacitor plates. The variable height of the moveable cistern is measured by a calibrated lead screw or a laser interferometer. The original of this design used gauge blocks to measure the cistern height, as described in detail in [17].

Since mercury has a highly reflective surface, it has occurred to many investigators to use the mercury surfaces as mirrors in a laser-illuminated Michelson interferometer, providing a high-accuracy and high-resolution measurement of the displaced height of the mercury column. Unfortunately, mercury is mercurial, and even with good vibration isolation a free mercury surface has standing and random surface waves with amplitudes of micrometers, which greatly complicates the interferometry. Similarly, placing cube-corner reflectors on floats in the mercury is complicated by capillary forces that perturb the height of the floats, and it is difficult to keep the floats centered in the manometer tubes. Several successful high-accuracy manometers have been built that employ a variety of techniques to overcome these problems [15, 18–22]. However, each has required a major effort, and the use of a laser interferometer for manometry is not the undergraduate laboratory exercise it may appear to be at first glance.

Users should be aware that, for computational convenience, the length scales of some commercial manometers are not calibrated in true length units, although they are marked as millimeters or inches. In these instruments the length scales have been adjusted from true length by the ratio of local to standard gravity, and, for some temperature-controlled manometers, for the ratio of the operating temperature to 0°C. If these instruments are used without correction at another location or at a different temperature, significant errors can result.

The accuracy of the length-measuring apparatus is not the only factor limiting the accuracy of the height measurement. The surface of any confined liquid will be displaced by capillary forces. These forces vary with surface conditions at the liquid–tube interface, so that the capillary depression or elevation can vary significantly with time and conditions of use. Since [5] assumes that h is the displaced height of a free surface, these capillary variations can cause additional errors. This is a particularly difficult problem with mercury. Even with carefully cleaned glass tubes and very pure mercury it is possible to observe a wide range of contact angles at the mercury–glass interface, including inverted menisci where the contact between the mercury and the glass is higher than the center of the meniscus. Capillary depression correction tables for mercury in glass have been developed [23], with the correction given as a function of the tube diameter and the height of the meniscus. However, determination of the meniscus height is difficult and the capillary corrections are of questionable reliability. The best practice is to use tubes large enough that the maximum capillary deviations are negligible. A conservative upper bound for possible capillary variations can be calculated from expressions for the meniscus shape of a sessile drop [24]. The depression of the center of a drop of specified diameter, relative to the surface of an infinitely large drop, corresponds to the capillary depression in a tube of the same diameter if the mercury–tube contact angle is 180°. This is an upper bound for possible capillary distortions. As can be seen from Table 2.2, for tube diameters above 10 mm the maximum capillary depression decreases by an order of magnitude for each 10-mm increase in tube diameter. Using small tube diameters in mercury manometers is a false economy.

Since (5) requires the measured height, the length measurement must be made along the vertical axis. Verticality errors depend on the square of the misalignment from the vertical. Therefore, alignment to within 1 mrad, which is not a difficult task, will keep this uncertainty below 1 ppm. Tilt of the manometer during a measurement will cause apparent length changes that introduce errors to the height measurement. Special multiple-column manometer designs [14] can compensate for this effect, but a stable mechanical foundation is highly desirable.

The limited precision with which the surfaces of the liquid can be located will cause random errors in the height measurements. The magnitude can be

Table 2.2 Maximum Mercury Capillary Depressions[a]

Tube Diameter (mm)	*Maximum Depression* (μm)
10	555
15	161
20	46
25	13
30	3.7
35	1.0
40	2.8×10^{-1}
50	2.0×10^{-2}
60	1.5×10^{-3}
70	1.0×10^{-4}
80	7.3×10^{-6}
90	5.1×10^{-7}
100	3.6×10^{-8}

[a] Values are for mercury with a surface tension of 450 dyn·cm.

evaluated from repeated measurements with zero applied differential pressure. These measurements will be most meaningful if they are repeated several times after the surfaces have been displaced from their rest positions and allowed to return to equilibrium with zero applied differential pressure.

4.1.3 Density

As previously mentioned, many fluids are used for manometry, but mercury possesses unique properties that have made it the most widely used manometric liquid. However, measuring the absolute density of a sample of mercury at the parts per million level is a major experiment, and the results of only a few such experiments have been published. Recently, comparative measurements have been made with imprecisions of less than 0.01 ppm [25]. This technique, and a reference sample with a known density, are used to determine absolute densities of submitted samples on a for-fee basis.† More common is the use of published reference values for the density of mercury. Several factors must be considered, however, in evaluating the uncertainty of such a reference value when it is used for a specific sample.

To use a reference density value with any confidence the mercury must be pure. Mercury can be purified at the parts per billion level, but particular attention must be paid to the removal of base metals impurities, such as copper or lead. The most commonly used purification technique, vacuum distillation,

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readily removes noble metal impurities, such as gold or platinum; however, the more volatile base metals can distill over with the mercury. Unfortunately, many commercial mercury processors only vacuum distill. The base metals can be removed by distillation in air or by washing the mercury with nitric acid. Some impurities are more effectively removed by washing with a potassium or sodium hydroxide solution. Various cleaning techniques are discussed and referenced by Wilkinson [9]. Exposed to air, very pure mercury will develop a visible film on the surface with time. Sensitive measurements can detect this film within a period of days, over longer periods it will become visible to the eye; but, even after periods of years it will still be thin and 'patchy." However, the development of a thicker "scum" indicates the presence of base metal impurities. With high levels of contamination a readily apparent scum will develop in a matter of days. In general, mercury that has been acid-washed and vacuum distilled, or distilled in air, and that retains a bright surface, will have impurities well below the parts per million level.

Even with very pure mercury the possibility still exists of significant density differences from one sample to another due to isotopic abundance differences. Six different isotopes contribute between 7 and 30% to the natural abundance of mercury. Samples from different mines can have different isotopic abundances, and distillation can cause significant isotopic fractionation. Mass spectrometric measurements have yet to be published with an accuracy that will allow density differences to be determined at the parts per million level. However, an analysis of the densities of 13 different samples determined by three different experiments [25–27] found a standard deviation, due to sample differences, of 0.7 ppm. This indicates that with a high degree of confidence, near 99%, the densities of different samples can be expected to be within ±2 ppm of the mean density of mercury.

Of the limited number of absolute density measurements, the best known are those of Cook [26]. Cook measured seven different samples and averaged data from five of the samples to obtain a reference value widely used as *the* density of mercury. Unfortunately, Cook's analysis of his systematic uncertainties is very brief and somewhat cryptic. Comparison with a more recent set of absolute measurements [27], with a more thorough uncertainty analysis, indicates that a reasonable systematic uncertainty for Cook's measurements is 0.3 ppm (1σ). Thus, we would predict that, within three standard deviations the density of a sample of pure mercury is within ±3.1 ppm of Cook's reference value.

Since mercury expands with temperature and is compressible, its density depends on both temperature and pressure. Therefore, reference values are specified for a particular temperature and pressure, most commonly 20°C and 1 atm (101 kPa). Densities at other temperatures and pressures can be calculated using the thermal expansivity values of Beattie and co-workers [28] and the compressibility values of Grindley and Lind [29]. For most manometry applications the pressure correction is relatively small; the fractional correction is 4.0×10^{-11} Pa^{-1}. Generally, the temperature correction is much larger, and the situation is somewhat confused by changes in the internationally accepted temperature scale, the most recent of which occurred in 1990.

Realization of thermodynamic temperatures at the millikelvin level is very difficult. Therefore, these experiments are carried out at only a few laboratories, and the results are combined in an agreed-upon temperature scale that is considered to be the best available approximation to true thermodynamic temperatures. Periodically, improvements in the determination of thermodynamic temperatures prompt a revision of the accepted temperature scale. This, of course, does not imply any change in thermodynamic properties, but it does mean a change in the values that are assigned to them. For example, Cook determined the density of mercury using thermometers calibrated on the International Temperature Scale of 1948 (ITS-48), and specified his mean value at 20°C on ITS-48. In 1968 ITS-48 was replaced by the International Practical Temperature Scale of 1968 (IPTS-68). Since most thermometers are now calibrated on IPTS-68, and very few ITS-48 calibrations are still in use, Cook's value is generally corrected to the value corresponding to 20°C on IPTS-68. At the time of this writing most thermometers have been calibrated on IPTS-68, but this scale has recently been replaced by the ITS-90, and as time passes an increasing fraction of thermometers will be calibrated on ITS-90.

Between -200 and 630°C the differences between temperatures measured on ITS-90 and IPTS-68, T_{90} and T_{68}, are given in degree Celsius by

$$\begin{aligned} T_{90} - T_{68} = {} & -0.148759 \times (T_{90}/630) - 0.267408 \times (T_{90}/630)^2 \\ & + 1.080760 \times (T_{90}/630)^3 + 1.269056 \times (T_{90}/630)^4 - 4.089591 \\ & \times (T_{90}/630)^5 - 1.871251 \times (T_{90}/630)^6 + 7.438081 \times (T_{90}/630)^7 \\ & - 3.536296 \times (T_{90}/630)^8 \end{aligned} \tag{7}$$

Using Cook's density reference value and the thermal expansivity of Beattie and co-workers, the density of mercury at 101-kPa pressure is given between 0 and 40°C by

$$\begin{aligned} \rho_{68}(\mathrm{kg/m^3}) = {} & 13{,}545.866 \times [1 - 1.8115 \times 10^{-4} (T_{68} - 20) \\ & + 2.5 \times 10^{-8} (T_{68} - 20)^2] \end{aligned} \tag{8a}$$

for thermometers calibrated on IPTS-68 and

$$\begin{aligned} \rho_{90}(\mathrm{kg/m^3}) = {} & 13{,}545.854 \times [1 - 1.812 \times 10^{-4} (T_{90} - 20) \\ & + 2.5 \times 10^{-8} (T_{90} - 20)^2] \end{aligned} \tag{8b}$$

for thermometers calibrated on ITS-90.

Because of the uncertainty in the thermal expansivity values, the uncertainty

***Table* 2.3** Temperature Scale Differences, Mercury Density at 101 kPa, Mercury Volume Thermal Expansivity, and Vapor Pressure of Mercury

T (°C)	$T_{90} - T_{68}$ (mK)	ρ_{68} (kg/m^3)	ρ_{90} (kg/m^3)	β (ppm/K)	P (mPa)
0	0	13,595.08	13,595.08	181.5	26.8
5	−1.2	13,582.75	13,582.75	181.4	43.6
10	−2.4	13,570.44	13,570.43	181.3	69.7
15	−3.7	13,558.14	13,558.13	181.2	110
20	−5.0	13,545.87	13,545.85	181.2	170
25	−6.3	13,533.61	13,533.59	181.1	259
30	−7.6	13,521.36	13,521.34	181.0	390
35	−8.9	13,509.13	13,509.11	180.9	579
40	−10.2	13,496.92	13,496.90	180.8	849

in the density will linearly increase from ±3.1 ppm at 20°C, to ±4.1 ppm at the extreme temperatures.

These same data can be used to derive the values in Table 2.3. Also included are differences between ITS-90 and IPTS-68, the volume thermal expansivity of mercury [28], and the mercury vapor pressure [30]. To use the density values in Table 2.3 it is necessary to determine whether the thermometer has been calibrated on IPTS-68 or ITS-90, and then use the corresponding density values, ρ_{68} or ρ_{90}. The expansivity can be used to interpolate between entries. There is no significant difference between the thermal expansivity and vapor pressure values on the two temperature scales.

As noted, the density values in (8a), (8b), and Table 2.3 are for a pressure of 101 kPa. For manometry one should correct the density to the mean of the applied and reference pressures $(P + P_{\text{ref}})/2$ by using

$$(1/\rho)(\partial\rho/\partial P)_T = 4 \times 10^{-11}\ \text{Pa}^{-1} \tag{9}$$

Thus, for a manometer measuring an absolute pressure of 100 kPa the densities given by (8a), (8b), or Table 2.3 should be reduced by 2 ppm to obtain the value at the mean pressure, 50 kPa.

Despite the impressive accuracies attained in the determination of the properties of mercury, the uncertainty in the density is often the limiting factor in high-accuracy manometry. This is because the average density of the liquid in all vertical portions of the manometer is required. Since the temperature of the liquid varies with location and time, and the thermometer(s) used to determine the temperature can have different response times and may not be suitably located or adequate in number to obtain a good spatial average, a significant error may exist in the indicated average temperature of the mercury. This error can be minimized by controlling the temperature, minimizing spatial gradients, and recognizing that even changing the pressure of the gas will change the temperature (adiabatic heating and cooling, discussed in Section 6.1).

4.1.4 Reference Pressure

Manometers inherently measure differential pressures. To determine an absolute pressure the pressure on the reference or low-pressure side of the manometer must either be known, or be so small that it can be neglected. Thus, the reference pressure is an additional, and in some cases, significant source of error for absolute pressure measurements. The vapor pressure of mercury is low enough to be a negligible correction for most measurements in the atmospheric pressure range, although for the most accurate measurements corrections must be made. Reference [30] presents an equation for the saturated mercury vapor pressure derived from a fit to three different sets of experimental data; tabulated values are presented in Table 2.3. Unfortunately, the reference pressure may differ significantly from the mercury vapor pressure. As mentioned, some barometers used for the routine measurement of atmospheric pressure have a sealed reference pressure at the top of the mercury column. If the glass tube is carefully cleaned and properly filled this can give low and stable reference pressures over periods of many years, but significant errors can result if these conditions are not met. Higher accuracy instruments use a pumped reference vacuum, generally employing a mechanical vacuum pump. For best results a two-stage pump should be used. It should be connected to the manometer by clean tubing, preferably metal or glass, with a minimum of rubber or plastic tubing, and the pump should preferably be operated continuously, or, at a minimum, for 24 h before use of the manometer. Adequacy of the vacuum should be checked by a thermocouple or similar vacuum gauge. These precautions are particularly advised when uncertainties of 10–20 Pa or less are required. If uncertainties of 1–2 Pa or less are required, the mechanical pump should be supplemented by a diffusion pump, preferably a mercury diffusion pump. If the pumping system includes a chilled baffle, the pressure can actually be reduced below the saturated vapor pressure of mercury, and for high-accuracy or low-pressure measurements the reference pressure should be monitored by a capacitance diaphragm gauge (discussed in Section 5.1) or a similar device. For measurements in the low-vacuum range, low-vapor pressure oils have been used as manometer fluids. Diffusion pump fluids are available with specified room temperature vapor pressures in the micropascal range; however, unless properly outgassed, the reference pressures can be several orders of magnitude higher than this.

The total uncertainty of a manometer is the sum of both random and systematic errors. The magnitude of the random errors, due to factors such as the imprecision in locating the liquid surfaces and measuring the height differences, variations in capillary effects, and variations in temperature gradients, can be evaluated experimentally by making repeated readings of the indicated pressure with zero applied differential pressure. If these zero readings are made over a period of time and after the liquid has repeatedly been displaced and allowed to return to "zero," the repeatability of the readings (characterized by a standard deviation) should be characteristic of the random errors of the measurement. The evaluation of systematic errors requires a theoretical model of possible error sources and estimates of their magnitudes, and it is much more a matter of judgment. Confidence in the uncertainty analysis can be increased greatly if the manometer is compared with another pressure instrument of comparable or better accuracy.

Manometers are most generally used as primary standards. While they could be calibrated against another standard of superior accuracy and used as a transfer standard, this in general has dubious advantages for mercury manometers. The performance of a manometer depends on environmental conditions and operator skill, as well as on the length and temperature measurements, and these factors can vary considerably. Therefore, at the time of use the performance of the manometer can differ significantly from that at the time of calibration. In short, the reproducibility of a manometer is generally not significantly better than its total uncertainty. It is much better to calibrate the thermometers and the length scale, maintain a stable and uniform temperature environment, and evaluate the manometer as a primary standard. One exception is the calibration of barometers with a sealed reference vacuum. In this case the calibration primarily serves to verify that the vacuum, which is not accessible for independent measurement, has not deteriorated. However, as with any standard, it is a good practice to compare a manometer periodically with another pressure standard to determine if the agreement between the two standards is in reasonable accord with the combined uncertainties of the standards.

4.2 Piston Gauges

The piston gauge, also known as a deadweight tester or pressure balance, is shown schematically in Figure 2.5. The force generated by a pressure P, applied to the bottom of a carefully fabricated piston–cylinder combination with effective area A_{eff}, is balanced by the weight F of the free-floating piston and associated weights, and the reference pressure P_{ref} acting on the effective area

$$P = F/A_{\mathrm{eff}} + P_{\mathrm{ref}} \tag{10}$$

Piston gauges can be operated with either oil or gas as the pressure fluid. Oil-operated gauges are widely used in the high- and very-high-pressure ranges; gas gauges are used primarily in the atmospheric pressure range and the lower part of the high-pressure range. Commercial oil gauges are available with ranges up to 1.3 GPa (200,000 psi), and special purpose gauges have been built for operation as high as 2.6 GPa [31–33]. Since piston gauges measure, or more properly, generate differential pressures, and their operation generally requires frequent access to the weights, they are typically used for the measurement of

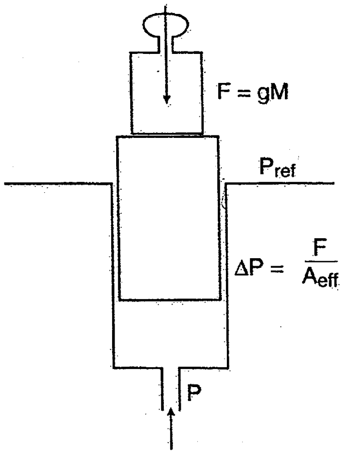

Figure 2.5 Schematic illustration of a piston gauge. The effective area A_{eff} is very nearly the mean of the piston and the cylinder cross-sectional areas. The pressure applied to the effective area is balanced by a stack of weights attached to the piston. The piston is rotated with respect to the cylinder to relieve friction. Typical clearances between the piston and cylinder are 1 or 2 μm for a good quality gas-operated gauge, twice this for an oil-operated gauge.

gauge pressures—differential pressures with an atmospheric reference. This is true of virtually all oil-operated gauges, but gas-operated gauges are used for both gauge and absolute pressures. In the latter case the outside of the piston–cylinder assembly and the weights are surrounded by an evacuated bell jar, as can be seen in Figure 2.6. In all high-quality gauges the force balancing the pressure is generated by the mass of a set of weights (including the piston mass) supported by the free-floating piston. High accuracy requires that contact and friction between the piston and cylinder be minimized. For most piston gauges this is achieved by rotating the piston and weight stack with respect to the cylinder so that viscous forces will center the piston within the cylinder and maintain a lubricating film between the two surfaces. In most gauges the lubricating film is provided by a slow flow of the pressure fluid escaping from the high pressure at the bottom of the piston to the lower pressure at the top. Proper operation requires high-quality pistons and cylinders; both pieces must be straight and round with good surface finish, and the clearance between the piston and cylinder must be small, typically a few micrometers or less. These qualities are particularly important for gas-operated, gas-lubricated gauges, where proper operation further requires careful cleaning of the piston and cylinder and the use of gases free of oil or particulate contamination. A few gas-operated gauges maintain a lubricating film of oil between the piston and cylinder. For all piston gauges the piston and weights will be freely floating, or

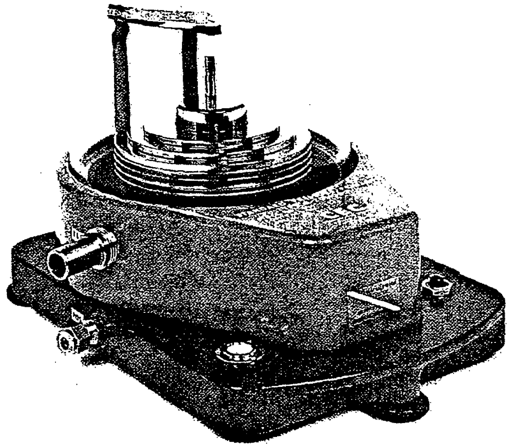

Figure 2.6 Gas-operated piston gauge equipped for operation in the absolute mode. The piston and cylinder assembly is located under the stack of weights and is not visible. For absolute measurements the piston and weights are enclosed under a bell jar that can be evacuated through the large port on the left side of the housing. The pressure to be measured is applied to the lower pressure fitting, which connects to the bottom of the piston–cylinder assembly. The base includes a drive mechanism to allow rotation of the piston and weights when the bell jar is evacuated. Three different piston and cylinder combinations provide full-scale ranges of 5, 50, and 500 psi (33, 330, and 3300 kPa).

balanced, only for the discrete pressure that balances the force on the piston; and if the pressure changes, the weights must be adjusted accordingly. This greatly restricts the ability of the piston gauge to follow changing pressures, particularly for gas gauges operating in the absolute mode, where the weights are located inside an evacuated bell jar. References [34] and [35] discuss both the theory and operation of piston gauges; [35] is particularly suitable both for the first-time user and the specialist.

The uncertainty of the pressures generated by a piston gauge are determined by the uncertainties of the acceleration of gravity, the mass of the weights, the effective area, and, for absolute mode operation, the reference pressure. As discussed in Section 4.1.1, the local acceleration of gravity can be determined with uncertainties as small as a fraction of 1 ppm. A competent mass laboratory typically can determine the masses with an uncertainty of less than a few parts per million. In most cases the critical factor limiting the accuracy of a piston gauge is the uncertainty of the effective area. To a good approximation the effective area is the mean of the geometric cross sections of the piston and the cylinder. The accurate determination of the effective area of a primary standard piston gauge is a difficult process. It is generally limited by imperfections in the geometries of the piston and cylinder and by uncertainties in the dimensional measurements. Stated uncertainties typically vary from 20 to 100 ppm, where the lower values are for large diameter (up to 35 mm), low-pressure, gas-operated gauges. As discussed below, further reductions in the low-pressure uncertainties are limited by our lack of detailed understanding of the momentum transfer between the gas and the cylindrical surface of the piston. At high pressures, above about 1 MPa, distortion of the piston and cylinder introduce additional uncertainties, the magnitude of the problem increasing with pressure. Not only will the effective area change with pressure, but the operation of most gauges will also deteriorate since there will be an increased loss of pressurizing fluid through the enlarged annular space between the piston and cylinder, to the point that pressure equilibrium and free floating of the piston cannot be maintained.

Several approaches have been taken to minimize or compensate for the high-pressure distortion. These are illustrated in Figure 2.7. One is to use heavy-walled cylinders in the common *simple* piston gauge. Simple gauges are generally used for pressures lower than 100 MPa, but a commercial simple gauge is available with a range of 700 MPa. The cylinder can also be constructed so that the pressure is applied to the outside of the cylinder as well as to the inside. Depending on the dimensions, the annular space of such a *reentrant* piston gauge can actually decrease with increasing pressure. The reentrant

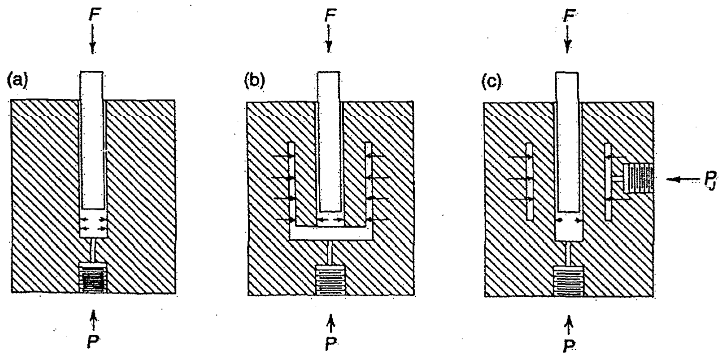

Figure 2.7 Cylinder configurations used in simple, reentrant, and controlled-clearance piston gauges. The operating range of the simple gauge (*a*) will be limited by expansion of the cylinder with increasing pressure. The reentrant design (*b*) decreases the distortion of the cylinder. Depending on the details of the design, a reentrant cylinder will either expand or contract with increasing pressure. The distortion of the cylinder in a controlled-clearance gauge (*c*) can be controlled independently by varying the jacket pressure P_J.

technique is used in commercial gauges operating at up to 300 MPa. However, while the reentrant design maintains satisfactory operation of the gauge at higher pressures, the calculation of the changes with pressure of the effective area is even more difficult than for a simple cylinder. The *controlled-clearance* gauge employs an independent jacket pressure on the outside of the cylinder to control the clearance between the piston and cylinder. This not only permits useful operation of the gauge to pressures above 1 GPa, it also permits, through a self-calibration procedure discussed in [34], a more accurate determination of the effective area than is possible with either simple or reentrant gauges. For this reason controlled clearance gauges have also been used as low-pressure, gas-operated primary standards. Both oil- and gas-operated controlled clearance gauges are available commercially, but their complexity of operation generally restricts their use to standards laboratories. Figure 2.8 shows a high-pressure controlled-clearance piston gauge.

Piston gauges are most widely used as transfer standards, in which case they are calibrated against either a mercury manometer, or another piston gauge

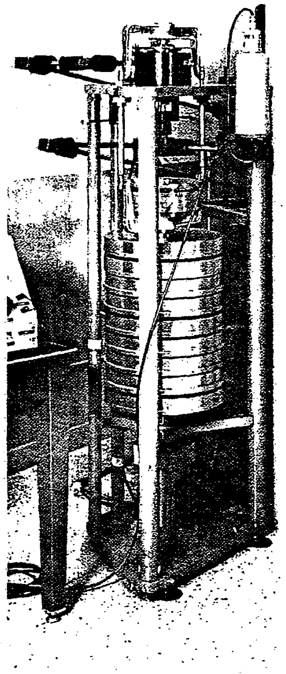

Figure 2.8 Controlled-clearance piston gauge with a range of 200,000 psi (1.3 GPa). The piston and cylinder assembly are located in the housing at the top of the apparatus. The jacket pressure is applied through the pressure line connected to the side of the housing. The presure to be measured is applied through the line connected to the bottom of the housing. The weights are suspended beneath the piston–cylinder housing by a yoke that is attached to the piston at the top of the housing. A bearing and drive motor allow rotation of the piston while the weights remain stationary. The pressure vessel at the upper right of the apparatus encloses a high-pressure transducer.

standard. The piston gauge is very sensitive and stable and much less susceptible to environmental and operator variables than are liquid–column manometers. Good quality gas-operated gauges will achieve imprecisions in the pressure of a few parts per million or less and can be expected to have irreproducibilities of 10 ppm or better. Piston gauge temperature coefficients are an order of magnitude smaller than those of a mercury manometer, and the small size of the gauge further simplifies the temperature-measurement problem. The primary operator skills required are the ability to clean the piston and cylinder, handle the weights with proper care, and control the pressure. Absolute mode measurements require the maintenance of a reference pressure that is low enough that the error in its measurement does not contribute a significant error to the measured pressure. This reference pressure is limited primarily by the gas flowing between the piston and cylinder. For a typical gas-operated gauge a two-stage mechanical vacuum pump with a nominal capacity of 160 L/min will suffice to maintain a pressure below 5 Pa (5×10^{-2} torr) after 15-min pumping time, and the addition of a 2-in. diffusion pump will maintain the pressure at a few tenths of a pascal. It should be noted that at least one piston gauge manufacturer recommends that the reference pressure be maintained at about 1 Pa. This significantly increases the possibility of errors in the absolute pressure due to the measurement of the reference pressure. Our experience has been that we can successfully operate gauges produced by that manufacturer, and others, with reference pressures below 0.1 Pa. With but a few exceptions, most gauges operate better in the absolute mode, with low-reference pressures, than they do in the gauge mode.

As noted, the necessity to balance changing pressures by changing weights restricts the applicability of piston gauges. However, their exceptional stability makes them ideal as calibration reference and check standards. An example of the latter application is the periodic comparison of a gas-operated piston gauge with a mercury manometer. Changes with time of the measured effective area probably indicate a problem with the mercury manometer. Piston gauges can be used to measure changing pressures over a restricted range by combining them with a low-range differential pressure transducer. In this case the piston gauge maintains a stable reference pressure on one side of the differential pressure transducer, and the transducer measures small changes in pressure about that reference pressure. The low-pressure limit of a piston gauge is determined by the weight of the piston. As an example, the lowest pressure attainable with a widely used 50-psi range piston gauge is 10 kPa (1.5 psi, 76 torr). However, operation of piston gauges becomes more difficult at low-mass loadings, and they generally are not used much below 10% of the full range.

Relatively large errors can occur during operation in the gauge mode because of the rotation of the weights. As noted earlier, the piston and weights are generally rotated with respect to the cylinder to center the piston within the cylinder and to minimize friction. Generally, the piston and weights are spun up to some initial rotation rate and then allowed to coast freely until mechanical contact between the piston and cylinder occurs and rotation stops. The minimum rotation rate varies between different gauges from less than 0.1 to about 2 Hz. Most commercial piston gauge bases include a mechanism for rotating the piston and weights. In some cases the initial rotation rate may be as high as 16 Hz. When operating in the gauge mode, the rotation of the weights will generate an aerodynamic force that depends on the diameter of the weights and the square of the rotation rate [36 and 37, p. 105]. The error in the generated pressure can exceed 100 ppm. This error can be minimized by operating at low-rotation rates and using weights with an outer diameter near 80 mm.

Evaluation of the systematic uncertainties of a primary standard is as much an art as a science. Anticipating and assigning magnitudes to all possible sources of error is very difficult. Therefore, it is always desirable to compare standards to see if the measurements agree to within the estimated uncertainties, particularly if the standards employ different measurement techniques and are therefore susceptible to different types of errors. Since primary standard piston gauges and mercury manometers are of quite different design, it is useful to compare them and determine whether the results lie within the combined uncertainties. A few such studies have been made, using gas-operated piston gauges whose areas have been determined by dimensional measurements. At the National Research Council, Ottawa [38], the measurements were made for one piston gauge at about 100 kPa in both the absolute and gauge modes. Measurements at the National Physical Laboratory, Teddington, UK [39], were made at a nominal absolute pressure of 100 kPa with two gases (helium and nitrogen) for four different gauges. In both cases the results were within the combined uncertainties; however, there was some evidence of systematic differences dependent on operating gas or mode of operation.

Recent work at NIST (National Institute of Standards and Technology) has found definite evidence that the effective area of gas-operated piston gauges depends on the gas; mode of operation; and, at low pressures where distortion is insignificant, pressure. Figure 2.9 shows the results of the calibration of a gas-operated piston gauge, with a nominal 2-cm-diameter piston cylinder, against an ultrasonic interferometer manometer [37, 37a]. Data were taken in both the absolute and differential (gauge) modes, and with different gases: helium, nitrogen, and argon. As can be seen in Figure 2.9, at higher pressures there is a systematic difference of about 6 ppm between the absolute and gauge mode effective areas. The increase in the absolute-mode effective area with decreasing pressure has also been observed for other, although not all, gauges. For other gauges the change is as large as 25 ppm. The results in Figure 2.9 for the three different gases are industinguishable; but for other gauges the effective area has differed for different gases by as much as 30 ppm [40]. The geometric cross sections of the piston and cylinder clearly do not depend on the operating gas, and mechanical distortions of these parts over this pressure range are less than 1 ppm. Therefore, the observed changes in the pressure, mode of operation, and operating gas are not explained by current piston gauge theory and indicate that approximating the effective area as the mean of the geometric cross sections of the piston and cylinder is probably not valid if uncertainties of less than 20 or

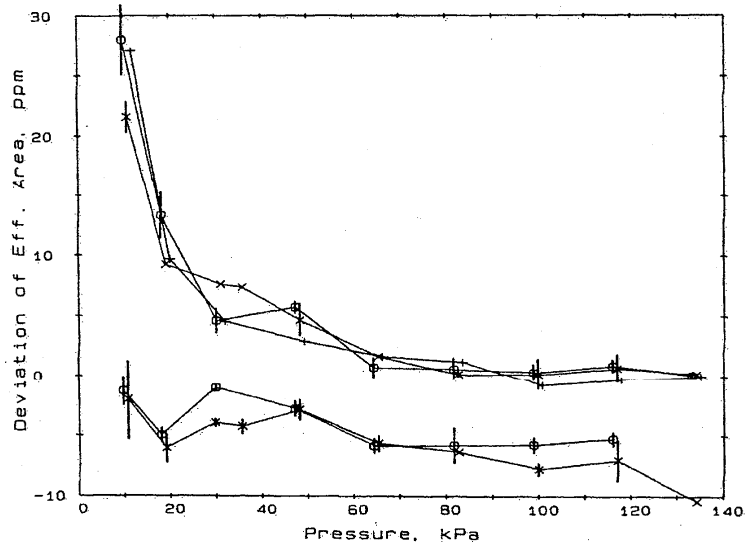

Figure 2.9 The effective area of a 2-cm-diameter, gas-operated piston gauge determined in the absolute and gauge modes for nitrogen (×), argon (+), and helium (O) using an ultrasonic interferometer manometer. The absolute-mode data are plotted at the top and the gauge-mode data, at the bottom. The differences between the gauge and absolute mode effective areas and the pressure dependence of the absolute mode data are not predicted by present piston gauge theory.

30 ppm are desired. The reasons for these changes in the effective area, and in particular why the magnitude of the changes vary so much from gauge to gauge, are not understood at this time, but they clearly are caused by changes in the interaction between gas molecules in the annular space and the piston. Although these systematic effects limit the uncertainty of the piston gauge as a primary standard, it is apparent from the data in Figure 2.9, which includes the random errors of both the manometer and the piston gauge, that piston gauges make excellent transfer standards. Changes in the measured effective area over the 2 months of this experiment were less than a few parts per million. Similar data taken with other gauges over periods of several years indicate changes of less than 2–3 ppm.

4.3 McLeod Gauges

McLeod gauges measure absolute pressures in the low- and high-vacuum ranges and have a distinguished history in vacuum science, having been an essential part of many notable experiments. They also have been used to make a great many very bad measurements.

The construction and accurate use of a McLeod gauge requires a high degree of skill and attention to detail. The principle of the McLeod gauge is very straightforward and applicable throughout the transition range. A known volume of gas is trapped: it is compressed to a much smaller volume using a mercury piston, and the pressure in the smaller volume is measured with a mercury manometer. The original pressure is derived from the pressure in the small volume using the ideal gas law and the known ratio of the volumes. The simplicity of this concept conceals several practical difficulties. The ideal gas law is not applicable if condensable gases are present. Reasonable values of pressure multiplication and the constraints of apparatus size requires very small final volumes, which are difficult to measure. Furthermore, the small-diameter capillaries (a few mm to fractions of a mm) used for the final volume include one arm of the mercury manometer, and capillary effects are very large. The measurement is static and the apparatus has a high surface-to-volume ratio so that outgassing or adsorption can generate significant errors. Mercury vapor "streaming" from the McLeod gauge to cold traps elsewhere in the vacuum system can generate significant pressure gradients between the gauge and the region where the pressure must be known.

McLeod gauges have been used successfully with uncertainties of a few percent down to 10^{-4} Pa (10^{-6} torr), but the novice considering their use is advised to consult the literature for an appreciation of what must be done to use them properly. McLeod gauges are reviewed in [7] and [41]. More recent work is described in [42], and examples of the care that must be taken to obtain reliable results with McLeod gauges can be found in [43–46].

4.4 Volume Expansion Systems

Volume expansion systems, also known as *static*, *Knudsen*, or *series expansion systems*, are the complement of McLeod gauges. A small volume of gas at a known "high" pressure is expanded into a larger volume, generating a lower pressure that can be calculated from the measured volume ratio and the equation of state of the gas. To attain still lower pressures this process can be repeated by additional expansions into still larger volumes, or by reevacuating the large volume and then again expanding the gas remaining in the high-pressure volume into the now empty low-pressure volume. This gives rise to the term *series expansion*. As with McLeod gauges, these devices are simple in concept and the physics of the measurement process is independent of the pressure, so that they can be used in the transition range, as well as at higher and lower pressures. Volume expansion systems have been built and are in regular use in national standards laboratories for the generation of absolute pressures down to the very high vacuum range (10^{-6} Pa). They can achieve uncertainties of the order of 1% in the high-vacuum range for inert gases (e.g., nitrogen and rare gases). This type of standard is reviewed and discussed in detail in Poulter's review [41], with particular reference to the system first described in [45].

Descriptions of systems at two other national standards laboratories are in [47–49]. This type of standard is also discussed in [7] and [50].

The theory of volume expanders is so simple that it appears rather straightforward to generate arbitrarily small pressures by use of the series expansion technique. The number of such systems that have been designed on paper and described at conferences rivals or exceeds the number of proposals for high-accuracy mercury manometers employing laser interferometers. However, since these systems utilize a fixed amount of gas, increasing care must be taken as the pressure is lowered to avoid leaks and outgassing that will add gas, and corrections must be made for the pumping or removal of gas by ion gauges and surface adsorption. The very high vacuum systems have been constructed of specially treated stainless steel or glass to minimize or eliminate the bulk permeation of hydrogen from stainless steel, and their operation is limited to inert gases. To achieve low pressures, starting with measurably high pressures (typically, 100–10^5 Pa), very large volume ratios must be used. These are difficult to measure and the attendant errors are multiplied in each step of the series expansion process, so that the final generated pressure may have a very large uncertainty from this source alone. Practical limitations require that large-volume-ratio systems employ a very small volume (typically a few cubic centimeters or less), and this may change with time or operation due to deformation of mechanical components, such as bellows or valve sealing materials (including those in all-metal valves). Volume expansion systems can be a reasonable and accurate way of generating pressures in the low-vacuum and upper end of the high-vacuum ranges. Anyone contemplating using this technique for lower pressures is advised to review the experiences of those that have built, operated, and carefully evaluated such systems, such as are presented in [41, 47, 48].

4.5 Orifice-Flow Systems

Orifice-flow systems, also known as *dynamic expanders* or *conductance-limited expanders*, are illustrated in Figure 2.10. These generate a known pressure difference by passing a measured flow of gas through a known conductance, quite analogous to generating a known voltage by passing a measured current through a known resistance. If the pressure on the downstream side of the conductance can be maintained at a low enough value either to be neglected or to be measured with a small error, then the absolute pressure on the upstream side can be determined. Since these devices operate with a continual flow of gas, the problems due to leaks, outgassing, and gauge interactions are significantly reduced compared to static expansion devices. Thus, dynamic systems are more suitable for operation at lower pressures or with reactive gases. In addition, the pressure can be changed to a new stable value much faster with these devices than with a static system, and they can maintain a stable pressure for prolonged periods of time. However, the value of the conductance can be reliably

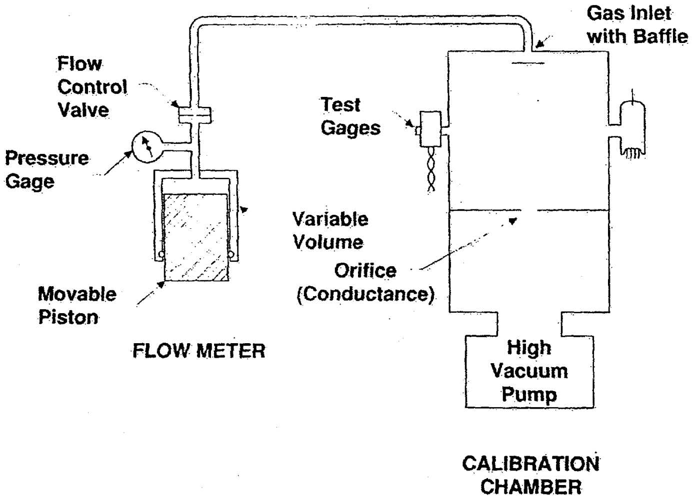

Figure 2.10 Schematic of an orifice-flow primary vacuum standard. Gas flows from the flowmeter into the upper part of the calibration chamber, where the test gauges are attached, and is pumped out through the orifice. Knowing the conductance of the orifice, the flow, and the pressure in the lower part of the calibration chamber, the absolute pressure in the upper part can be calculated. The flow can be measured by monitoring the pressure in the flowmeter and decreasing the flowmeter gas volume at a rate that will maintain a constant pressure. This is accomplished by driving a servo-controlled movable piston into the flowmeter gas volume.

calculated only in the molecular flow regime, generally restricting the upper end of the range of these devices to 10^{-1} Pa (10^{-3} torr) or below, although a few extended range devices have been built that operate in the transition range [51]. Orifice-flow standards are used for vacuum calibrations at both national standards laboratories [49, 52, 53] and industrial standards laboratories. In some cases the operating ranges have been extended down into the UHV range by the use of cryocondensation pumps [54, 55]. Further references to these standards can be found in [41] and [56], and the performance of an orifice-flow system is compared with a volume expansion system in [57].

The fabrication of an orifice such that the conductance can be calculated accurately requires considerable care, the maintenance of a low pressure below the conductance requires a large stable pumping capacity, and the measurement of the small flows required is not trivial. It seems that each designer of an orifice-flow standard seeks a different orifice design; but typically the orifices are a fraction to a few centimeters in diameter, and are fabricated either as "thin" orifices out of shim stock or with a geometry that allows an accurate calculation of edge corrections [52]. The conductance of these orifices requires a pumping speed below the orifice of a few tenths to 1 m^3/s in order to maintain the pressure below the orifice to a few percent of the generated pressure. The flows that must be measured are well below the range of conventional flow standards, and considerable effort has gone into addressing this problem. The constant-pressure flowmeter, illustrated in Figure 2.10, can achieve uncertainties of a few percent for flows as small as 10^{-11} mol/s (10^{-7} std cm^3/s) [58]. In this type of flowmeter the gas flows into the calibration chamber, at a rate determined by a control valve, from a small volume. The pressure in this volume is monitored continually, and the size of the volume is decreased at a rate that will keep the pressure constant. One way to achieve the volume decrease is to advance a piston into the volume through a sliding seal. The flow can be calculated from the pressure, temperature, and rate of volume decrease. Other techniques to measure the flow have been reviewed by Peggs [59]. These include constant-volume flowmeters, in which the flow is calculated from the rate of pressure decrease as the flows out of a small known volume. This has the disadvantage that the flow and the pressure in the vacuum chamber also decrease with the pressure in the flowmeter, but constant-volume flowmeters are in general simpler to build than the constant-pressure type. Variable-pressure flow elements, typically sintered plugs, have also been used. They require calibration as a function of the upstream pressure against a constant-pressure or constant-volume flowmeter. If the conductance of the flow element is stable and they are operated in the molecular flow regime, the flow can be calculated from the measured upstream pressure. Some orifice-flow standards also use flow-division schemes to extend the effective lower range of the flowmeter and, therefore, the range of pressures that can be generated.

5 PRESSURE GAUGES AND TRANSDUCERS

Pressure standards, even those that measure rather than generate a pressure, are designed to optimize accuracy, generally at the expense of low cost, speed, and ease of use. Therefore, most measurements are made with pressure gauges or transducers that must be calibrated against a pressure standard and then rely on their reproducibility and stability to maintain the accuracy of their calibration. Typically, although the relationship between the output of such devices and the applied pressure may be quite stable, it cannot be derived with adequate accuracy from a fundamental theory. As an example, the deformation of a coiled metal tube as a function of pressure applied to the inside of the tube may be reproducible to 0.1% or better, but a calculation of the deformation, based on properties of the material and mechanical deformation theory, will have a much larger uncertainty. Therefore, measurements with such a gauge will have reasonable accuracy only if the gauge is calibrated against a pressure standard. It is possible for the stability and precision of a gauge or transducer to exceed hat of the standard against which it is calibrated, but it can never be more ccurate.

Pressure gauges can be divided into two broad types: those that are sensitive o the force generated by the pressure (mechanical deflection gauges), and those hat are sensitive to gas density. The latter are found almost exclusively in the acuum ranges where (3) can be used to convert from pressure to density. The liversity of techniques used in different pressure gauges and the range of erformance observed is so great, particularly in the atmospheric range, that it is mpossible to describe them in any detail. Several general comments can be nade, however, about the different types of gauges, their generic strengths and veaknesses, and techniques for evaluating their performance.

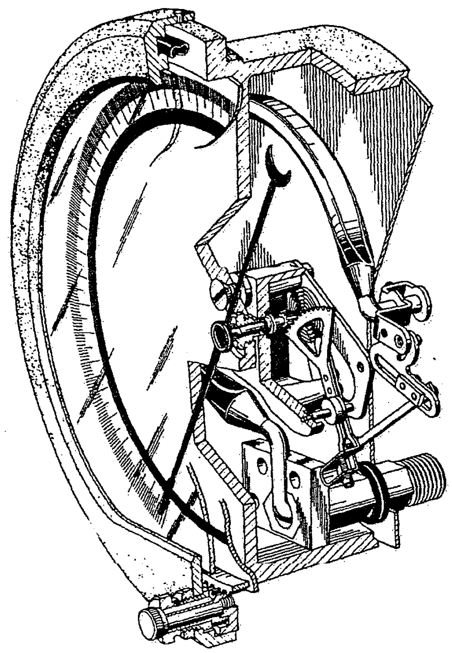

Figure 2.11 Bourdon tube pressure gauge with mechanical readout mechanism. Adjustments in the linkage between the Bourdon tube and the pointer allow compensation for zero, span, and linearity differences.

5.1 Mechanical Deflection Gauges

Figure 2.11 illustrates the familiar Bourdon tube pressure gauge and can serve as the basis for a general discussion of the basic principles and limitations of pressure gauges. Pressure applied to the inside of the tube causes the tube to "uncoil." The motion of the tip of the tube is amplified mechanically and transmitted to a pointer and scale. Gauges of this type are produced with a wide variety of full-scale pressures, level of performance, and cost. The best of them exhibit both ingenious design and quality craftsmanship, and this type of gauge is a cost-effective solution for many pressure measurement needs. For a number of reasons, however, the performance of even the best gauges is limited to an uncertainty of about 0.1%. The precision of the measurement is limited by visual detection of the pointer location and the repeatability of the mechanical linkage. The repeatability of the gauge will also be limited by inelastic behavior of the Bourdon tube, which will depend on the material properties and the level of strain induced by the pressure. Using a more compliant tube may improve the sensitivity, but result in less reproducible behavior. Temperature changes will alter the gauge reading because of thermal expansion of the components and temperature dependence of the elastic coefficients (thermoelastic coefficients). Temperature changes are caused not only by changes in the ambient temperature, but also by the adiabatic heating and cooling induced by pressure changes, as discussed in Section 6.1.

A number of techniques, most employing electronics, can and have been used to reduce these problems. These techniques are incorporated in a wide variety of commercial electromechanical pressure transducers. The mechanical linkage, pointer, and dial in Figure 2.11 can be replaced with an optical lever. The deflection of the tube end can be detected electronically and the output displayed digitally. Or, the electronic signal from the tube deflection detector can be used with a feedback circuit to maintain the tube end in a null position, limiting the strain of the tube and consequent inelastic behavior. In this case the magnitude of the feedback signal, rather than the deflection of the tube, constitutes the gauge output. Since electronic position detection techniques are available that are far more sensitive than mechanical techniques, a stiffer tube, operating with lower strains and closer to pure elastic behavior, can be used. Materials with improved elastic behavior, such as fused quartz, can be used for the sensing element. These changes may cause other problems, however. For example, although the thermal expansion of fused quartz is relatively small, its thermoelastic coefficients are rather large, and fused quartz gauges are correspondingly more temperature sensitive. Temperature sensitivity can be reduced by temperature controlling the sensor or temperature compensating the output.

These same techniques have also been used with sensor configurations other than Bourdon tubes, for example, diaphragms. Diaphragm gauges, where one side of the diaphragm is evacuated or a differential pressure is applied across the diaphragm, are available with capacitive, inductive, or strain gauge sensing of the diaphragm position. The capacitance type is illustrated in Figure 2.12. When

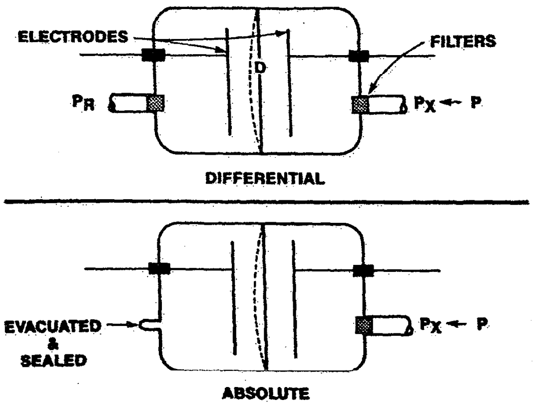

Figure 2.12 Schematic of absolute and differential capacitance diaphragm pressure sensors. Applied pressure P_X causes the diaphragm D to deflect, as shown by the dashed line. This in turn causes a change in the capacitance between each of the electrodes and the diaphragm. This change is measured by external circuitry and converted to equivalent pressure units.

strain gauges are used, the sensor may be either bonded to the diaphragm or implanted in the diaphragm material. Gauges are available with diaphragms made of a variety of materials, including: Ni-Span C, Inconel, titanium alloys, 400-series stainless steels, beryllium copper, fused quartz, and silicon, to name but part of what is undoubtedly a longer list. Other sensor types may be advantageous for different applications. Increased sensitivity can be achieved by using a sensor in the form of a capsule or bellows, which are more compliant than a Bourdon tube or diaphragm. At higher pressures the limitations of material strength can be minimized by using a sensor that is placed in compressive rather than tensile stress. One such transducer used in the very high pressure range employs a coaxial capacitor, with one capacitor plate deposited on a fused quartz rod and the other deposited on the inside of a surrounding fused quartz cylinder. The cylinder and rod are fused together at the ends and pressure is applied to the outside of the cylinder, minimizing tensile stress and taking advantage of the superior compressive strength of the quartz.

The techniques discussed so far rely on measuring the deflection or strain of a sensing element. An alternate approach is to measure the change in frequency of a resonant structure as the applied pressure changes the stress in the structure. Examples include cylindrical cans employing a feedback circuit to sustain a resonant radial oscillation. Pressure applied to the inside of the can changes the resonant frequency in a reproducible manner. However, because of viscous damping, the frequency also depends on the pressurizing gas. The force generated by the pressure applied to a diaphragm can be used to tension an oscillating wire, with corresponding changes in the oscillation frequency of the wire as the pressure changes. A high-pressure sensor applies the pressure to the outside of a structure fabricated from a single crystal of quartz. Electrodes plated on an internal part of the structure are used to excite and measure the frequency of the resonant quartz structure as a function of the pressure. A different quartz resonant-frequency sensor design is used in the atmospheric and high-pressure ranges; the pressure applied to a bellows generates a force that is transmitted to a single-crystal quartz oscillator using a lever and fulcrum mechanism machined out of the same block of quartz as the oscillator. In these single-crystal quartz sensors the crystal is cut to minimize the temperature coefficient. Unfortunately, the crystal orientation for zero temperature coefficient varies with stress, or pressure, so that the sensor will still have a pressure-dependent temperature coefficient.

The performance of a pressure gauge or transducer will depend on the design, materials, manufacturing techniques, and operating environment. Subtle changes in these factors can sometimes cause the performance to vary significantly from one gauge to another of the same design and mnaufacturer. The influence of environmental parameters will depend in part on the effectiveness of the design, for example, the adequacy of temperature control or compensation, if used. This makes it difficult to make a priori predictions of performance based on the design type; different implementations of the same technology can have quite different results. Keeping this in mind, the following discussion should be regarded as only a general guideline.

As noted, the best Bourdon-type gauge with mechanical readout can be expected to have an imprecision and long-term instability of about 0.1%; the performance of less-expensive instruments of this type can be one or two orders of magnitude poorer. High-quality capsule gauges with mechanical readouts, used in the atmospheric range, may exhibit instabilities significantly smaller than 0.1%. The use of force-balance techniques with metal Bourdon tubes will significantly improve their performance below the 0.1% level, as will the use of fused quartz for the tube material. Force-balance fused quartz Bourdon tube gauges can achieve instabilities of about 0.01% over periods of a year or more. This level of performance can also be observed for several atmospheric range transducers employing resonant structures. However, even of the types that can be found with this superior level of performance, not all units will demonstrate a consistent level of performance.

Other factors can limit the performance of high-quality electromechanical sensors. Some of the strain or stress measurement techniques used are highly nonlinear and/or temperature dependent, and careful attention must be paid to the statistical treatment of calibration data to derive the optimum relationship between the applied pressure and the output. For at least one commercial instrument 16 calibration constants must be determined. The failure of some manufacturers or users to consider this problem has resulted in cases where the transducer performance is significantly worse than what the intrinsic capabilities of the instrument will allow. Even where the manufacturer has addressed this problem with an extensive calibration as a function of pressure and temperature, and a careful statistical treatment of the data, the problem remains for the user to verify, at some future time, that the calibration is still valid in the temperature and pressure ranges over which it will be used. The larger the number of parameters required for proper gauge performance, the larger the amount of data required for initial calibration and subsequent verification. The performance of the gauge for some applications may also be limited by secondary design features. Many of the atmospheric range, high-performance gauge types have been designed for aircraft altimetry applications. While demanding of pressure measurement accuracy, this application does not require the chemical resistance or low leak rates required by many chemical-process or vacuum applications. Some, but not all, high-accuracy sensors are designed to be compatible with leak-free systems and/or aggressive chemicals. Some gauge

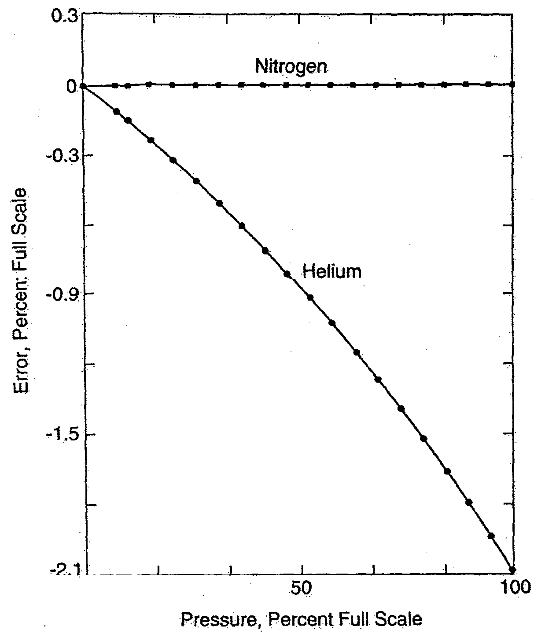

Figure 2.13 Gas density dependence of a vibrating-can pressure transducer. The transducer was calibrated with nitrogen, and can repeat its calibration at the 0.01% level over periods of years. However, if it is operated with helium, the indicated pressure will be in error by about 2% of the reading; when the transducer is operated with air, the error will be about a factor of 4 smaller. Some commercial gauges of this type include an automatic compensation for the air–nitrogen difference.

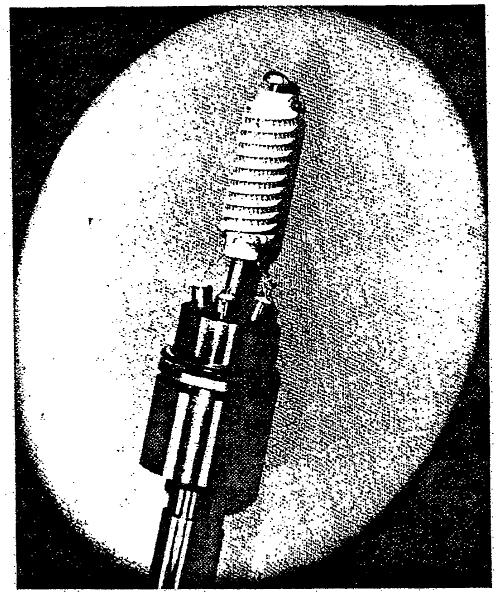

Figure 2.14 Manganin pressure sensor used in the very high pressure range. The resistance of the coil of wire at the bottom of the figure depends on pressure. The assembly attached to the coil includes electrical feedthroughs required for the resistance measurement, and seals to a high-pressure vessel of the type seen in the upper right side of Figure 2.8.

types are sensitive to the density of the pressurizing gas. Data for a vibrating-can-type transducer are shown in Figure 2.13. Although this type of gauge can achieve long-term instabilities of the order of 0.01%, significant errors will occur if the gauge is used with a gas different from the one with which it was calibrated. Some types of gauges may be sensitive to changes in power supply voltage. Proper power supply design can readily avoid this problem, but it does exist with some instruments. Some transducers can exhibit hysteresis after thermal cycling (such as occurs during shipment in an unheated aircraft cargo hold). This is particularly bad if it occurs during shipment between a calibration laboratory and the user.

The mechanical aspects of some pressure gauges may not be entirely obvious. In the high-pressure and very high pressure ranges a number of gauges rely on electrical property changes of a bulk material. The sensor of one such gauge, illustrated in Figure 2.14, is a coil of Manganin wire, a nickel–manganese–copper alloy. Pressure is determined from changes in the reistance of the wire. While these do not involve a macroscopic mechanical deflection, and the gauges may appear to be strictly electrical instruments, the electrical changes are caused by pressure-induced changes in the interatomic spacing. The performance of this type of gauge is limited, just as is a Bourdon-tube gauge, by temperature dependencies and inelastic behavior.

The adverse effects of temperature dependencies and an interesting solution to this problem are illustrated by the dielectric or capacitance high-pressure gauge constructed by Andeen and co-workers [60]. This gauge employs the change of capacitance with pressure of a parallel plate capacitor with a CaF_2 solid dielectric. Use of three-terminal capacitance measurement techniques allows very good sensitivity; and repeatability of the pressure measurement, 0.01% or better for pressures above 100 MPa, is a significant improvement over the performance of Manganin gauges, discussed later in this section. However, the capacitance gauge has a large temperature coefficient, and to achieve the best pressure reproducibility the temperature must be controlled to within a few tenths of a millikelvin, a difficult task in any case, considerably complicated by the adiabatic heating and cooling encountered in a high-pressure apparatus. Colwell [61] made two significant improvements in the design of this gauge. Instead of using a single dielectric material, he measured the ratio of two capacitors employing different dielectric materials with similar temperature coefficients but different pressure coefficients. Both capacitors are contained in the pressure vessel so their temperatures track one another closely. Colwell found the best material combinations to be single crystals of calcite ($CaCO_3$) cut parallel to and perpendicular to the *c* axis, and arsenic trisulfide (As_2S_3, a glass) and BGO ($Bi_{12}GeO_{20}$). He also was able to reduce the adiabatic heating and cooling problem significantly (see Section 6.1) by minimizing the amount of pressure fluid in the pressure vessel and balancing the adiabatic heating and cooling of different parts of the system to achieve close to zero net change. Instabilities of the gauge could be reduced to a few kilopascals and seemed to be determined primarily by material inhomogeneities.

In selecting a commercial gauge the user should first consult the manufacturer's specifications, keeping in mind that some manufacturers are more optimistic than others in projecting their product's performance and that the meaning of even commonly used terms may vary from one specification to another. Additional considerations are the thoroughness of the specifications and the extent to which they are substantiated by supporting material, and whatever is known of the manufacturer's reputation or the observed performance of a given type of instrument. However, even if experience with several units of a type is available, allowance should be made for unit-to-unit variations, and users are advised to monitor the performance of each gauge used.

One factor to be examined is the stability of the instrument zero. Our experience shows that for several types of high-performance gauges, instabilities are dominated by zero shifts, with changes of the calibration constants (linear and higher order terms in the functional relationship between pressure and gauge output) being much less of a problem. As an example, apart from zero drifts, the response of some force-balance quartz Bourdon-tube gauges will be stable to within 0.01% of the reading, over the upper 50–90% of the full range, for periods of years. For some of these gauges, however, the zero drift can amount to 0.01% of the full-scale pressure over a few days time. Therefore, the magnitude of the zero instabilities for a particular gauge should be evaluated so that zero corrections can be made at appropriate intervals. The zero stability can be evaluated by applying "zero" pressure to the gauge and recording its output as a function of time, temperature, and any other parameter of concern, such as power line voltage. For a differential gauge this requires the application of the same pressure to both sides of the gauge, for an absolute gauge a vacuum must be applied so that the gauge effectively sees "zero" absolute pressure. For an electromechanical transducer this type of test requires little more than a strip chart recorder and possibly a vacuum pump. The same technique can be used to make necessary zero corrections. With zero applied pressure the instrument zero control (if so equipped) is adjusted so that zero pressure is indicated, or the indicated pressure is recorded for later correction of the data.

Determining the accuracy of the calibration constants requires a pressure standard with an adequate uncertainty. If an appropriate pressure standard is not available, the calibration stability can be evaluated by periodic comparisons with another stable pressure gauge or some stable natural phenomena, for example, the vapor pressure of a pure material at a known temperature. The use of multiple sensors, even if of the same type, will help detect random shifts in the gauges and determine what degree of conficence should be placed in the reading of any one gauge.

As more zero and calibration stability data are gathered for a gauge, it will be possible to better predict how often the zero should be checked and how often the gauge should be recalibrated to maintain a desired level of accuracy. Historical data of this type are invaluable in evaluating the expected performance of gauge types as well as that of the individual instruments being monitored.

Unfortunately, performance data of this type are seldom published in readily accessible sources, and much of what is available is published by manufacturers for their own products. In many cases the manufacturer has conducted and reported the tests in a scrupulous manner; in other cases, there may be reason to suspect that "good" news is given more weight than "bad" news. Most of the published independent data for mechanical pressure gauges is for types used at the extreme ranges: very high pressures and low vacuums. The expense and complexity of primary standards in these extreme ranges results in the availability of relatively few primary standards and an increased reliance on the use of gauges as transfer standards. This has prompted different national standards laboratories to undertake studies of the performance of gauges that might be used as transfer standards.

Peggs [62] reviewed the performance of different high-pressure gauges, including several types employing electrical property changes. The most widely used such gauge is the Manganin gauge, illustrated in Figure 2.14. Typically, a Manganin gauge includes a 100-Ω coil of Manganin wire immersed in the pressure fluid, and a temperature-compensating resistor mounted outside the pressure vessel. The resistivity of the Manganin changes as a function of pressure. The better gauges use four-terminal resistors, and care is taken to minimize strains in the resistor winding. An initial "seasoning," consisting of thermal and pressure cycling, will generally improve the performance. Several laboratories have investigated the performance of these gauges, and Molinar and co-workers [63, 64] published results indicating that if precautions are taken, it is possible to achieve long-term instabilities in the measured pressure of 0.04–0.05% between 200 and 1200 MPa.

At the other extreme, low pressures or vacuums, capacitance diaphragm gauges or capacitance manometers are widely used as transfer standards. This type of gauge, illustrated in Figure 2.12, employs a thin stretched metal diaphragm, typically several centimeters in diameter. Deflection of the diaphragm by the applied pressure is detected by measuring the capacitance between the diaphragm and the nearby capacitor plates attached to the gauge housing. The use of thin diaphragms and the high sensitivity to length changes of the capacitance technique allow a pressure sensitivity that is superior to most, if not all, other mechanical deflection pressure gauges. These gauges may have pressure access to both sides of the diaphragm for differential measurements or a reference vacuum on one side for absolute measurements. Most of the gauges are temperature controlled for improved stability, although some use temperature compensation. Several variations of this design are marketed. Performance tests of these gauges show not only characteristic features of the type, but also significant variations from one unit to another.

The experience at NIST [65] indicates that zero instabilities for low-range gauges (1 and 10 torr full scale) are typically 10^{-2} Pa (10^{-4} torr) over a day's time, but there is a difference of three orders of magnitude between the performance of individual gauges, some performing much better, some much worse than this. Figure 2.15 is an example of zero stability data. As can be seen, changes in the gauge output tend to be highly correlated with ambient temperature changes, although these particular gauges are temperature controlled. Also evident in the figure are abrupt changes in the zero, apparently due to instabilities in the electronics or mechanical stresses caused by abrupt changes in temperature. The zero stability of this type of gauge is superior to most others, and is achieved by the design, choice of materials, and manufacturing techniques. The large range of zero instabilities observed for different gauges is probably indicative of subtle differences in material properties or strains induced during manufacturing. If these gauges are used in the high-vacuum range, optimum performance will require; ambient temperature control; frequent zero checks; and, if possible, selection of better than average units.

Evaluation of calibration stability is, as noted, a more difficult task. Figure 2.16 illustrates changes in the calibration of 4 capacitance diaphragm gauges over 11 years. As can be seen, the level of instability differs from one gauge to another, and, for two of the gauges, appears to improve with time. Evaluation of less extensive calibration data for 23 gauges of this same type [65] found the

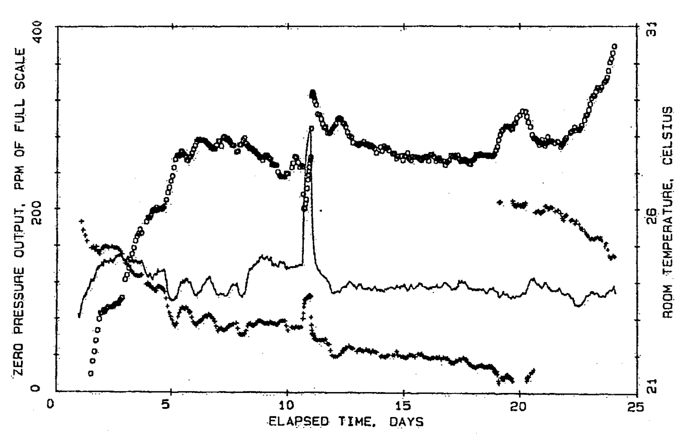

Figure 2.15 Stability as a function of time and ambient temperature with "zero" applied pressure for two different low-range capacitance diaphragm gauges. Indicated pressure outputs for the two gauges are plotted with an ○ and an +; the solid line is room temperature. The time scale starts when the gauges are turned on; the initial trend in the gauge outputs is a warm-up effect. The obvious correlation between temperature and gauge output indicates incomplete temperature control or compensation of the gauges. The discontinuous changes for one gauge at around day 20 are probably due to problems with its electronics.

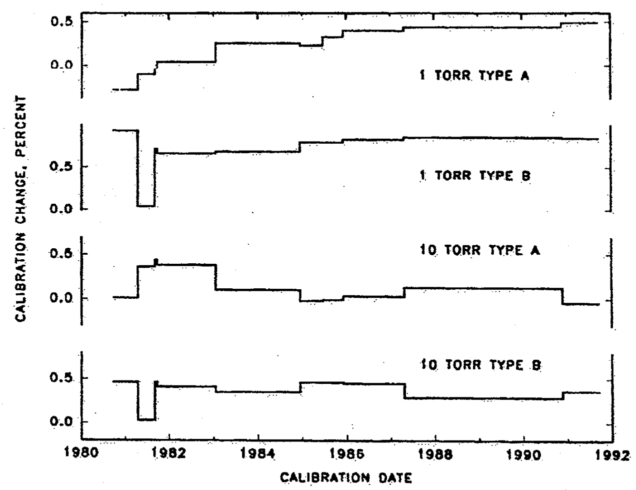

Figure 2.16 Change in calibration with time for four different 1- and 10-torr-range capacitance diaphragm gauges from two different manufacturers, *A* and *B*. The gauges were recalibrated at the times indicated by the vertical discontinuities in the data. The behavior of the instruments between calibrations is unknown; the horizontal data lines merely connect successive calibrations.

instability of the calibration factor over 1 yr to be typically about 0.4%. However, changes for some gauges were only 0.01 or 0.02%, while for others they were as large as 3%. For this type of gauge the changes appear to occur as abrupt shifts rather than a steady drift. Most of the gauges were monitored and used under laboratory conditions, although the question remains in some cases as to whether or not the change may be due to abnormal use of the gauge. These results are very similar to those obtained by other national standards laboratories [66–68]. While some gauges were found to be more stable, and others less so, typical long-term instabilities in laboratory use are about 0.4%.

These data indicate the selection of capacitance diaphragm gauges for applications in the low- and high-vacuum ranges requiring uncertainties better than a few percent. Above 1–10 kPa, other transducer types exhibit better calibration stability and might be preferred for measurement applications requiring uncertainties better than a few tenths of a percent; or the same level of performance can be achieved by transducers that are much less expensive than the capacitance diaphragm gauges. Other selection factors may also be important, however. The materials and construction techniques used in capacitance diaphragm gauges are not only compatible with UHV systems, they can also be used with chemicals that might be dangerous to use with other transducer types. Capacitance diaphragm gauge readings are effectively independent of the gas species, a virtue not shared by the density-sensitive gauges used in the low- and high-vacuum ranges. Note that when elevated-temperature gauges, such as the capacitance diaphragm gauges, are used in the low- and high-vacuum ranges, significant errors can result if thermal transpiration, discussed in Section 6.3, is not taken into account.

5.2 Density Gauges

Gauges that respond to gas density and to some species-dependent molecular property, rather than to a mechanical force, are widely used for vacuum measurements. The measurement result is generally given in terms of pressure units, and the gauges are sometimes calibrated against pressure standards. As can be seen from (3), the relationship between density and pressure is temperature dependent and a correction is required if the gauge is used at a temperature different from the calibration temperature. For most measurements this correction is small—a 3 K temperature change will cause a 1% error—and is generally ignored except for the most accurate measurements or cases where temperatures may differ significantly from normal room temperature. Published literature on the performance of several different types of density gauges is reviewed in [69].

As discussed in Section 1, in the ranges where most density gauges are used a number of factors, in addition to instrument performance, can contribute to measurement errors. It is important to examine the entire system to determine whether the pressure gauge is measuring the pressure or density of interest and to be aware of the possible interactions between the gas(es) and the gauge.

5.2.1 Thermal Conductivity Gauges

A relatively inexpensive alternative to capacitance diaphragm gauges for gauging in the low-vacuum range is the thermal conductivity gauge, common types being *thermocouple*, *thermistor*, or *Pirani* gauges. These gauges determine the pressure as a function of the gaseous conductance between a heated element and a temperature sensor within the gauge. Although they have been used at the 1% level [70], for most applications these gauges have much larger uncertainties. They are nonlinear, and the indicated pressure is a function of the gas species and cleanliness of the gauge. Because of their low cost, small size, and sensitivity they are widely used in the low-vacuum range for routine measurements where accuracy is not critical. Capacitance diaphragm gauges should be used for more critical applications. Extended range thermal conductivity gauges are available for use up to atmospheric pressure, although care should be exercised in their use at higher pressures. If the gauge is used with a gas, for example, argon, with a lower thermal conductivity than the air or nitrogen for which the gauge is usually calibrated, the gauge will always indicate a pressure below atmospheric, even though the actual pressure may be much higher. The consequences, particularly in a glass vacuum system, can be disruptive.

5.2.2 Ionization Gauges

The lack of adequate sensitivity limits the useful range of even the best mechanical deflection gauges to the upper part of the high-vacuum range. For measurements at lower pressures a different technique must be used; the solution usually employed is the ionization or ion gauge. Ion gauges employ electron-impact ionization to ionize gas-phase molecules. To a first approximation, the rate of ionization is proportional to the gas pressure, or more properly, gas density. Arguably, the ion gauge is the most widely used vacuum instrumentation, so it will be discussed in some detail. Ion gauges can be categorized into two types, cold and hot cathode, depending on how the ionizing electrons are generated; both types are discussed by Peacock [71].

In cold-cathode gauges the ionizing electrons are generated by a high-voltage (typically, 1000–3000 V) discharge between the cathode and anode. The electron discharge is confined by crossed magnetic and electric fields and amplified by secondary electrons emitted when an energetic electron ionizes a molecule. The discharge current increases with increasing pressure until the electron mean free path decreases to a length so short that the electrons cannot be accelerated between collisions to energies above the ionization threshold. The measured discharge current can be used as a measure of the pressure from the UHV up to the low-vacuum range. Two different gauge types, the *Penning* and *inverted magnetron*, are commonly used.

The simple geometry, rugged construction, and absence of a hot filament that are characteristic of cold-cathode gauges allow them to operate under conditions that would quickly destroy a hot-cathode gauge, such as exposure to atmospheric pressures. In addition, their low-power consumption and the absence of the heat and light generated by a hot filament make them uniquely suited for certain applications. Unfortunately, they also have a number of undesirable features. The discharge current is a distinctly nonlinear function of the pressure, with characteristics depending on the magnetic field and pressure range [71]. The discharge characteristics are not always stable, which can lead to abrupt changes in pressure readings. The discharge can also generate a significant ion pumping speed. For these reasons, with the exception of specialized gauge types developed for the UHV range, most cold-cathode gauges are used for relatively inaccurate measurement of pressures in the high- and low-vacuum ranges, and they are often used in applications where the gauge may be exposed to "dirty" gases or to pressures above their normal operating range. Relatively little effort has been made to evaluate their accuracy, but errors of a factor of 2 or more are believed to be typical for most cold-cathode gauges.

Most cold-cathode gauges are the Penning type, but recently two new cold-cathode inverted magnetron gauges have been commercially introduced. Both employ microprocessors to linearize the output, are available in bakeable versions, and have operating ranges extending from the UHV to the upper end of the high-vacuum range. Both gauges employ design features intended to stabilize the discharge characteristics and improve the accuracy of the indicated pressure. Limited testing of several units of each type at NIST has found that over a period of several months the errors in measured nitrogen pressures, due to residual nonlinearities and hysteresis with pressure, and changes with time, are typically within ±20% for pressures below 10^{-2} Pa. At low pressures relative sensitivities for other gases were found to be about the same as those for hot-cathode gauges, which are discussed below. Near the top of their operating range, however, about 0.1 Pa, the readings for other gases could be in error by as much as an order of magnitude. After longer periods of use, for pressures below about 10^{-6} Pa, these gases may read low by as much as an order of magnitude.

The hot-filament or hot-cathode ion gauge, which is the more widely used type of ion gauge, is illustrated in Figure 2.17. The earliest version of this gauge was the *conventional triode*, basically an outgrowth of the triode vacuum amplifier tube. The filament is heated to maintain an electron emission current, typically 1 mA, that is accelerated by a bias voltage, typically 150 V, between the filament (cathode) and the grid (anode). The ions produced by electron–molecule collisions are attracted to the collector, which is maintained at a negative bias with respect to the grid and filament. The pressure is determined from the ratio of the measured ion current I_C, corrected for a residual current I_R (discussed below), to the measured electron emission current I_e

$$P = (I_C - I_R)/I_e S \tag{11}$$

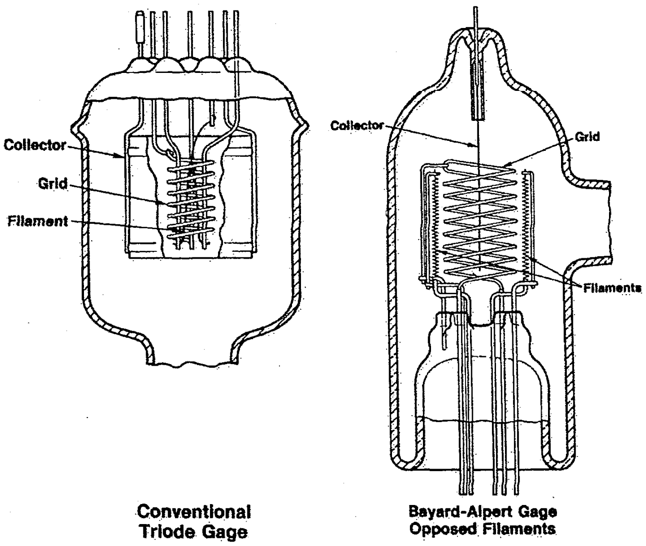

Figure 2.17 Schematics of conventional triode and Bayard–Alpert hot-cathode or hot-filament tubulated ionization gauges.

To a first approximation the sensitivity S is a constant. In fact, it depends on a number of parameters; it can vary with gas species, bias voltages, electron emission current, and the geometry and surface condition of the electrodes. Above 10^{-3}–10^{-1} Pa a number of effects combine to make the ionization process nonlinear, causing the sensitivity to vary with pressure culminating in a rapid decrease in the sensitivity with increasing pressure. This establishes an upper pressure limit for the gauge that varies with gauge design; some gauges have been designed to raise the upper limit of their operation, but for most gauges this upper limit is near the lower end of the transition range from viscous to molecular flow (10^{-1} Pa).

A lower limit to hot-cathode ion gauge usefulness is established by a pressure-independent residual current, I_R in (11). A major contribution to this current is caused by the generation of soft X rays when electrons strike the grid. If these X rays in turn strike the collector, photoelectrons are ejected. Since the emission of an electron cannot be distinguished from the arrival of a positive ion, this *X-ray current* appears as a pressure-independent collector current. Ion currents at lower pressure are masked by this residual current. The large cylindrical collector used in conventional triode gauges will intercept a large fraction of the X rays, and the residual current in these gauges typically corresponds to pressures of about 10^{-6} Pa (10^{-8} torr). This limit presented a barrier to the extension of vacuum science and technology to lower pressures until Bayard and Alpert's development of the inverted triode geometry, commonly known as the *Bayard–Alpert* or *BA gauge*. As seen in Figure 2.17, the BA gauge has the filament outside the grid and a thin wire collector in the center. The thin wire intercepts only a small fraction of the X rays generated at the grid, but electrostatic forces maintain a high ion collection efficiency. This effectively extends the lower limit of the ion gauge down in pressure by two orders of magnitude (to around 10^{-8} Pa). Other designs to further reduce the effect of the residual current have included the *extractor gauge*, in which the collector is moved outside the grid volume and shielded from the X rays. The positive ions are extracted from the grid volume to the collector by electrostatic fields, and in some variants, a magnetic field as well. This can reduce the residual current by about another two orders of magnitude below that found in BA gauges. An alternate approach is to use an additional electrode near the collector in a BA gauge to modulate the collection efficiency for ions. In theory, the residual currents in such a *modulation gauge* are not influenced by the modulating field and the residual current can be determined from the difference of the collector currents when the modulator is alternately maintained at collector and grid potentials.

Significant contributions to the residual current can also be generated by ions desorbed from parts of the gauge structure, particularly the grid, by electron collisions. These electron-stimulated desorption currents will depend very much on the history of the gauge and can be a major problem when the gauge is used with gases that absorb at room temperature.

Operation of the gauge requires power supplies to maintain constant bias voltages and regulate the filament power to maintain a constant emission current. An ammeter or electrometer is needed to measure the collector current, ranging from 10 μA at the highest pressures, to 1 pA at about 10^{-8} Pa. The combination of power supplies and ammeter is generally called a controller. Controller designs are relatively straightforward and their operation should introduce negligible errors, although the measurement of currents below 1 pA is not trivial. Unfortunately, in our experience, this is not the case with some commercial gauge controllers. Apparently, the excitement of digital displays and computer interfaces causes some designers to forget or ignore the fundamentals, so that in some instruments bias voltages and emission currents are not sufficiently regulated and collector currents are poorly measured. Therefore, the user is advised to make independent checks of the electrical operation of the controller.

The major determinant of ion gauge performance is the gauge structure or "tube." The relation of the ion current to the emission current depends not only on the pressure or gas density, but also on the ionization probability of the different molecules in the gas, bias voltages, emission current, electrode geometry, and electrode surface conditions. These will change with gas species, pressure, and time. In other words, the gauge sensitivity depends on a great many factors, the effects of many of which cannot be predicted adequately from theory, so that the behavior of ion gauges is best determined by experiment. The results of some such experiments are summarized below.

Although the emphasis is on UHV measurements, Weston's review [72] includes a great deal of information on general ion gauge theory and different designs. Nash [73] discusses many of the practical aspects of ion gauge use and performance. Much experimental ion gauge work was carried out in the 1950s and 1960s; most of that work is summarized in [56]. The rapid growth over the last two decades of industrial and scientific applications of vacuum technology has prompted a renewed interest in vacuum gauging focused largely on commercial instrumentation. Summarizing this work is complicated by the variety of instrumentation in use and sometimes conflicting results.

Of the types commonly used in the United States, we found [74] the best overall performance in the high- and very-high-vacuum ranges, in terms of linearity, stability, and constancy of sensitivity from one unit to another, to be obtained from a common glass-tubulated BA design with tungsten filaments, in particular, a design with two filaments (only one is used at a time) 180° apart about the central collector, as illustrated in Figure 2.17. Variations of sensitivity with time in a benign environment for a sample of this type of gauge were found to be relatively small [75], about 6% over 10,000 h of operation, while variations of sensitivity from gauge to gauge for this type were generally less than $\pm 10\%$. Conventional triode gauges with tungsten filaments, of the type illustrated in Figure 2.17, showed similar unit-to-unit variations, but varied about twice as much with time. Another study has found similar levels of instabilities for a slightly different triode gauge [76]. However, the stability of BA gauges with different filaments, thoria-coated iridium, were found to be inferior to conventional triode gauges [77]. Thorium oxide is a low work function material that can achieve a given emission current at a significantly lower temperature than a tungsten surface, and thoria-coated iridium filaments can withstand limited exposure to atmospheric air (they are sometimes marketed as "burnout proof"). However, the stability of gauges with thoria-coated filaments is generally inferior to that of gauges with tungsten filaments. Other studies [67, 73], of gauges of the same types, but with somewhat different construction than those illustrated in Figure 2.17, have observed larger instabilities; in one case, BA gauges have been found to change by as much as 25% over short periods of time [78]. In general, instabilities may be due to geometry changes [76], and/or electrode surface changes [79].

In our experience the performance of some types of commercial gauges is less predictable than that observed for the conventional triode and conventional tubulated BA gauges illustrated in Figure 2.17. Nude BA gauges, illustrated in Figure 2.18, have the same basic electrode structure as tubulated BA gauges, but are constructed on a flange and designed to be mounted directly in the vacuum system without a surrounding enclosure or tube. They were originally designed for use in the UHV range, but are often used in the high-vacuum range. They have been found to have sensitivities varying from 40 to 130% of the specified

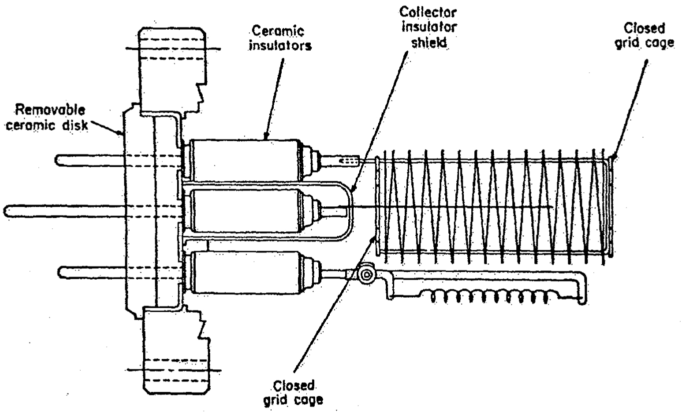

Figure 2.18 Schematic of a nude Bayard–Alpert gauge. The gauge is constructed on a stainless steel and ceramic flange, which is mounted directly to the vacuum chamber. This provides a much higher degree of mechanical integrity than a glass tube.

value [74], and significant changes in the sensitivity with pressure can occur for pressures as low as 10^{-3} Pa. As illustrated in Figure 2.19, the nude gauges will typically have a maximum in the sensitivity at some pressure near 10^{-3} Pa and then, a rapid drop in sensitivity with increasing pressures. This may be due to the closed grid generally used to enhance the sensitivity of these gauges [80]. The sensitivities shown in the figure for tubulated BA gauges are relatively constant over a wider pressure range, which is typical for this type of gauge. It is not known to what extent the data in the figure are typical of extractor and modulated gauges. Another variant of the BA gauge, designed for use at pressures as high as the low-vacuum range, was observed to exhibit sensitivities as low as one-half that specified [81]. They also appeared prone to unstable operation.

Since the development of the BA gauge in 1958 a considerable amount of work has been done on UHV gauging. Particle accelerator and storage ring design and operation and the recent development of semiconductor production processes operating in the UHV stimulated renewed interest in this field. Several reviews addressing the particular problems of UHV gauging have been published [72, 82–84], and additional work is described in the proceedings of a workshop on UHV gauging [85]. Results of particular interest include the observation that the residual currents of different BA gauges of the same design can vary by an order of magnitude [86, 87], and that significant modulation of the residual current can occur in at least one type of modulator gauge [86],

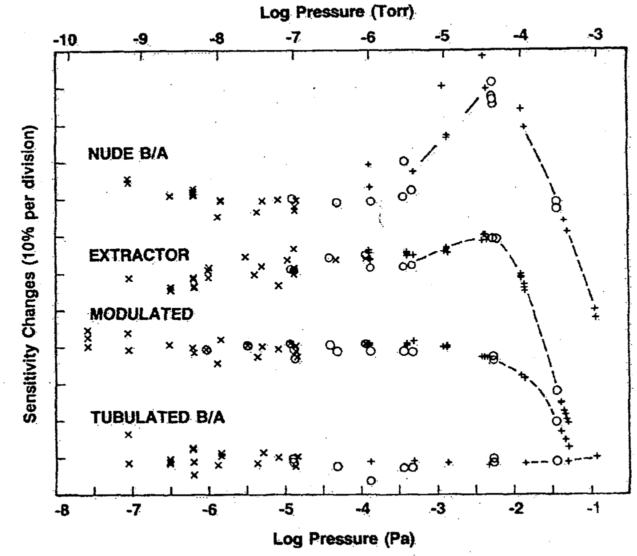

Figure 2.19 Sensitivities of tubulated, nude, and modulated Bayard–Alpert, and extractor ionization gauges. The data were obtained over several months using an orifice-flow primary standard [52] operating in two different modes (O, X) and a calibrated spinning rotor gauge, discussed in Section 5.2.3 (+). The lines connecting points have been added for visual clarity.

rendering worthless, for this particular gauge design, the modulation technique of determining residual currents.

When the gas is not specified, ion gauge sensitivities are generally quoted for nitrogen, although in some cases the argon sensitivity may be quoted. The sensitivities for other gases, if given, are often given in terms of the *relative sensitivity*, the ratio of the sensitivity for the specified gas to that for nitrogen or argon. This is done with the hope or expectation that relative sensitivities for a specific gas will be a constant for different gauges and/or that relative sensitivities can be correlated with a known property of the gas, such as the number of valence electrons, first ionization energies, or the electron-ionization cross section. Holanda's review [88] of older published relative sensitivities found variations greater than a factor of 2 in the published values for some gases, and the closest correlation was found to be between relative sensitivity and electron-ionization cross section. Significant variations can also be found between relative sensitivities in later published work [56, 77, 89–91]. Some of this variation is undoubtedly due to experimental errors in determining gauge

Table 2.4 Ion Gauge Sensitivities Relative to Nitrogen, S_r[a]

Gas	S_r	*Gas*	S_r
He	0.17	CH_4	1.6
Ne	0.28	C_2H_2	0.6
Ar	1.3	C_2H_6	2.6
Kr	1.9	C_3H_4	1.3
Xe	2.7	C_3H_6	1.8
H_2	0.4	C_3H_8	3.4
O_2	0.9	C_4H_8	2.1
CO	1.0	C_4H_{10}	4.0
CO_2	1.4	C_6H_6	3.8
NH_3	0.6	$C_6H_5CH_3$	6.8

[a] Relative sensitivities for different ion gauges can differ by as much as 30% from these values. Relative sensitivities for partial pressure analyzers can differ by as much as an order of magnitude.

sensitivities, but some is also due to real differences in the relative sensitivities for different gauge designs and variations in the relative sensitivities with gauge potentials and pressure. Table 2.4 presents "typical" relative sensitivities for a number of gases for BA gauges, obtained in our laboratory [56] or selected from other published work [77, 89–91]. For some gauges these values can be in error by 10–30%, with even larger errors possible at the high-pressure end of the high-vacuum range. These values can also be used for conventional triode gauges, and our limited experience indicates that they are also applicable to cold-cathode gauges. However, they should not be presumed to apply to partial pressure or residual gas analyzers, discussed in Section 5.2.4. If more accurate values are needed the gauge to be used should be calibrated with the gas to be used, using a vacuum standard with a predictable performance for that gas.

As noted in Section 1, a number of problems complicate vacuum measurements. One such problem with hot-filament ion gauges is dissociation of gases at the hot filament or reactions of the gases with the filament material and included impurities. In an effort to minimize these effects, filaments have been coated with low-work-function materials, thorium oxide being the most common, so that adequate electron emissions can be obtained with lower temperatures. Unfortunately, as previously noted, gauges equipped with coated filaments tend to be less stable than the same gauge type equipped with tungsten filaments. We believe that part of the problem with coated filaments may be the tendency for the adherence of the coating to the heated substrate to change with time, causing varying electron emission patterns, with consequent sensitivity changes. This defect may be reduced by different filament designs. In addition, we have found that when operated with water, thoria-coated filaments produce significant quantities of several reaction products, principally, hydrogen, carbon monoxide, carbon dioxide, and oxygen. Cold-cathode gauges produce quantities of these products comparable to a thoria-coated filament operating at 1 mA emission, while tungsten filaments, operated at the same emission current produce somewhat smaller quantities.

Another major vacuum measurement problem is nonisotropic and nonuniform pressure and flux distributions. Major problems of this type can be encountered in vacuum systems with cryopanels and/or solar simulators, such as space simulation chambers. The difficulties and some solutions encountered in measuring pressures in space simulation chambers are discussed in detail in [92] and [93]. To measure flux asymmetries gauges have been designed with highly directional characteristics [94].

The available data indicate that, under optimum conditions and after calibration, it is possible to make ion gauge measurements with uncertainties approaching a few percent. However, not all gauge types perform equally well, and for critical applications it is wise to calibrate frequently, if possible, and/or to use multiple gauges that can be cross-checked for stability. A more important concern is that the laboratory results cited here have been obtained under carefully controlled conditions and much poorer results can be expected if any of a number of factors are overlooked. Chief among these are cleanliness of the gauge and vacuum system, pressure equilibrium between the gauge and the system, and orientation of the gauge when temperature or flow asymmetries exist. As examples, order-of-magnitude pressure differences can exist within a laboratory-scale vacuum system when it is pumped down after exposure to atmospheric air. During pumpdown in the high-vacuum range there are probably more water molecules on the vessel wall than there are molecules of any kind in the gas phase. Outgassing of this material can maintain large pressure gradients between the gauge and critical parts of the system. Contamination of gauges with hydrocarbons or overheating of the electrodes can change the sensitivity by large factors. Young [89] found changes of a factor of 4 or more in ion-gauge sensitivities with time when ion gauges were operated with hydrocarbon gases. He convincingly argues that this is due to the buildup of carbonaceous deposits on the collector. These high-resistivity deposits can significantly alter electrical potentials within the gauge. Hydrocarbons are a major source of contamination in some vacuum systems. Depending on its history and the gas in the system, an ion gauge can be either a source or a sink for gas, and the pressure in a tubulated gauge can differ significantly from that in the rest of the vacuum system, particularly if the gauge is attached to the system by a restricted conductance. Tubulated gauges should be purchased with tubulation at least 2 cm or 1 in. in diameter and attached as directly as possible to the vacuum system. Even in a clean and properly conditioned system, large errors can result if the gas composition is not known or controlled. It is apparent from the values presented in Table 2.4 that a small amount of a high molecular weight hydrocarbon can give erroneously high-pressure readings, particularly if one is attempting to measure the pressure of helium or hydrogen. Partial pressure analyzers, briefly discussed in Section 5.2.4, can be quite useful in detecting and analyzing such problems.

5.2.3 Molecular Drag Gauges

Several high-vacuum gauges have been proposed and a few built that rely on the exchange of momentum between gas molecules and some mechanical structure. One such gauge [95, 96] is now available commercially. Variously referred to as a spinning rotor gauge, molecular drag gauge, or viscosity gauge, it is shown in Figure 2.20. The sensor is a 4.5-mm or $\frac{3}{16}$-in.-diameter magnetic steel ball, which is contained in a 1-cm-diameter, thin-walled extension of the vacuum system (thimble). The ball is levitated magnetically by a combination of permanent and electromagnets contained in a suspension head mounted on the exterior of the thimble. A differential transformer position sensor and feedback circuit maintain the vertical position of the ball. A set of drive coils and an inductive drive circuit are used to rotate the ball up to about 400 Hz. Once up to speed, the ball is allowed to coast, and its rate of rotation is determined by timing the signal induced in a set of pickup coils by the rotating component of the ball's magnetic moment. Collisions with gas molecules generate a *molecular drag*, which causes the ball to slow down, the rate of slowing depending on the ball's moment of inertia, the molecular weight of the gas, and the gas density or pressure. If the

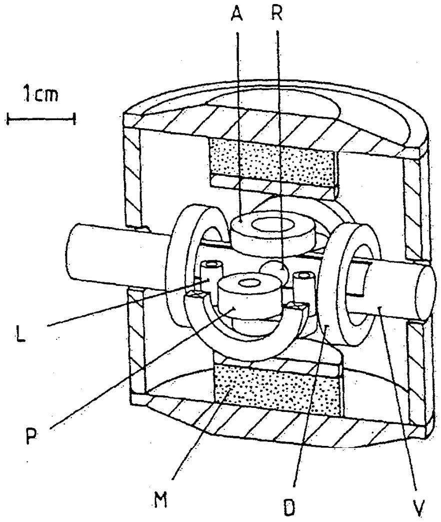

Figure 2.20 Sensor and suspension head of a commercial molecular drag high-vacuum gauge. The bearing ball (sensor) *R* is located in an extension of the vacuum system *V*. Permanent magnets *M* and electromagnets *A* levitate the ball. Horizontal stability is provided by coils *L*. Coils *D* are used to spin the ball up to about 400 Hz. Pickup coils *P* sense the rotation of the ball.

other factors are known, the density or pressure can be determined from the rate of slowing. The imprecision of this gauge is determined largely by difficulties in measuring the rate of change of the rotational speed and mechanical and thermal noise. With a reasonable signal strength, a quiet mechanical environment, several minutes measuring time, and a statistical procedure that uses multiple zero crossing of the timing signal [96], the rotation period can be determined with about a 1-μs imprecision, with a corresponding imprecision in the equivalent pressure of between 10^{-6} and 10^{-5} Pa. The molecular drag will vary linearly with pressure to better than 1% for pressures below 10^{-1} Pa. Above this pressure, corrections must be made for viscous drag effects.

To obtain optimum performance from the spinning rotor gauge, several departures from this simple model must be taken into account. Asymmetries in the magnetic suspension field will induce eddy currents in the rotating ball. Similarly, the rotating component of the ball's magnetic moment will induce eddy currents in surrounding metallic components. These combine to generate a pressure-independent slowing of the ball, or *residual drag* (RD). The rate of slowing due to molecular drag will depend on the average momentum transfer during a molecule–ball collision. This will depend on the gas molecular weight, the tangential momentum accommodation coefficient, and the ball's surface roughness. The last two factors are generally combined as the *effective accommodation coefficient* σ_{eff}, which is effectively the calibration constant for the gauge. Taking these factors into account, the pressure is given by

$$P = \sqrt{8kT/\pi m}\,(a\rho\pi/10\sigma_{\text{eff}})\cdot(-\dot{\omega}/\omega - RD) \tag{12}$$

where k is Boltzmann's constant, T is the absolute temperature of the gas, m is the gas molecular mass, a is the radius of the ball, ρ is the density of the ball, and $\dot{\omega}$ is the measured rate of change of the ball's rotation rate ω. These factors are readily determined, assuming that the gas composition is known or controlled, except for the effective accommodation coefficient and the residual drag.

The residual drag, which is typically equivalent to a nitrogen pressure between 10^{-4} and 10^{-3} Pa, is experimentally determined by measuring the rate of slowing of the ball at "zero" pressure, that is, any pressure below the desired imprecision of the pressure measurement. The commercial gauge units then automatically compensate for this residual drag or *offset* in subsequent measurements. The residual drag depends on a number of factors; changes in these factors must be minimized to stabilize the residual drag, and several precautions must be taken to determine accurate values. Temperature changes will cause changes in the ball's moment of inertia and rotation rate. These changes will cause errors in the determination of the residual drag, as well as errors in later pressure measurements. Fortunately, since the ball is magnetically suspended in a high vacuum, it has a long thermal time constant, and typical short-term laboratory temperature variations are highly attenuated and have a small effect [97]. However, the inductive drive circuit will cause significant heating of the ball and the surrounding thimble, and the ball's temperature will not stabilize for 4–7 h after it is spun to its operating frequency [98]. Attempts are being made to reduce this effect by redesign of the suspension head and drive circuit and the use of ball materials with a small thermal expansion coefficient [99]. If the apparatus is tilted, the ball will move slightly with respect to the suspension field, changing the residual drag [100]. Orientation of the gauge must be maintained within 1°, which is not a difficult task in a laboratory environment. Competition between inertial and magnetic forces may cause the axis of rotation of the ball to change slightly as it slows down, causing a change in residual drag [101]. For some balls this effect is large enough that corrections must be made to the residual drag as a function of the frequency. Even if these effects are minimized, it is necessary to monitor the stability of the residual drag by periodic redeterminations. In particular, if possible the residual drag or offset should be determined just before measurements are made at the lower end of the range.

A ball that is smooth on the atomic scale and with total momentum accommodation will have an effective accommodation coefficient of 1. For real "smooth" balls, that is, bearing balls as fabricated with a shiny surface, the effective accommodation coefficient for nitrogen can vary from ball to ball as shown in Figure 2.21. Effective accommodation coefficients less than 1 are caused by elastic collisions with no momentum exchange; values over 1 are due to the increased tangential momentum transfer incurred in normal or near-normal collisions with the perturbations of a rough surface. To obtain a more

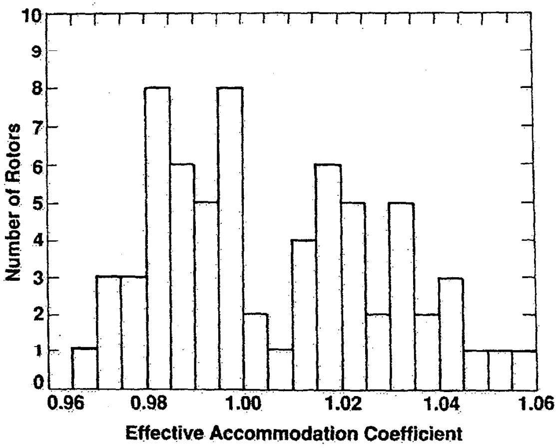

Figure 2.21 Nitrogen effective accommodation coefficients for a sample of 67 "smooth" (as fabricated) bearing balls. All balls were cleaned with solvents and baked under vacuum at 200°C before calibration.

accurate value of σ_{eff} than can be estimated from Figure 2.21, it is necessary to calibrate the gauge against a vacuum standard. For a given ball there can be an additional variation in σ_{eff} of up to about 2% from one gas to another [102].

Published changes that have been observed in effective accommodation coefficients over longer terms are typically 0.5% over a few months, and generally no more than 1 or 2% over 1- or 2-years time [102–104]. Analysis of the data obtained for a group of spinning rotor gauges used in an international comparison of primary vacuum standards [105] shows, after excluding one set of data because of obvious changes in the surface of the balls, that the average change in the calibrations during the 1–4 months between recalibrations against a reference standard was 0.4% for argon and 0.5% for hydrogen. These data are all consistent in predicting that for nonreactive gases, if the ball's surface is not mechanically or chemically altered, the spinning rotor gauge can be expected to be stable to within about 0.3–0.5% over a period of a few months, and to within 1–2% over a 1- or 2-yr period.

These gauges are relatively expensive, slow to operate, cannot be used for pressures much below 10^{-4} Pa, and become nonlinear in the transition region starting around 10^{-1} Pa. Their superior stability, however, is a major advantage where measurements accurate to within a few percent are required, and they serve very well as transfer or calibration standards in the high-vacuum range. With viscosity corrections they can be used for pressures as high as 10 Pa. Their lack of a hot filament or electrical discharge is a significant advantage, and they should be relatively compatible with many reactive gases, although gases that will alter the ball's surface will clearly cause changes in the gauge's sensitivity. Furthermore, they are, to at least first order, immune to thermal transpiration effects (Section 6.3). Efforts in several laboratories are under way to better understand and improve the performance of this gauge.

5.2.4 Partial Pressure Analyzers

In many vacuum systems the total pressure is of less interest than the partial pressures of one or more molecular species. Partial pressure or residual gas analyzers (*PPAs* or *RGAs*) are widely used for this purpose. These are mass spectrometers of relatively small size that are designed to be attached to a vacuum system as an appendage instrument. Most of them can be baked and are constructed to be compatible with UHV systems. They are generally designed for high sensitivity so that they can detect and analyze the residual gases in a vacuum system. They consist of an electron-impact ionizer, in some cases similar to the filament and grid structure of a BA gauge; extraction electrodes to remove ions from the ionizer and accelerate them into a mass filter; and a detector at the far end of the mass filter. Most PPAs have used mass filters of the magnetic sector or quadrupole type. Over the last decade quadrupole PPAs have come to dominate the commercial market. A schematic of a typical quadrupole PPA is shown in Figure 2.22. A combination of DC and radio frequency (rf) voltages in the megahertz range are impressed on the quadrupole rods. The applied rf

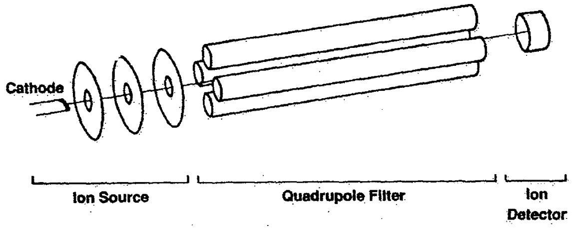

Figure 2.22 Basic schematic of a quadrupole partial pressure analyzer. Ion source designs vary considerably from one instrument to another, and Faraday cups and/or secondary electron multipliers are used for ion detection.

allows ions with the selected charge-to-mass ratio to travel down the axis of the quadrupole structure to the detector; other ions are deflected to the rods or the surrounding structure. The detector may be a Faraday cup, as shown in the figure, or, for increased sensitivity, a secondary electron multiplier (SEM), either of the discrete or continuous dynode types. The SEM may be used as an analog current amplifier, or at very low pressures it can be combined with a fast-rise amplifier and used to detect the arrival of individual ions. The mass ranges of different instruments vary considerably, but ranges of 50–200 charge-to-mass ratio are typical. The pressure range of these instruments is limited at high pressures by nonlinearities in the ion source to total pressures of the order of 10^{-3}–10^{-1} Pa. The low-pressure limit, or minimum detectable partial pressure, is determined by a number of factors, most notably, instrument sensitivity and detector characteristics. Using Faraday cup detection and a typical picoammeter, partial pressures of the order of 10^{-7} Pa can be detected, although this limit can vary from one instrument to another by an order of magnitude or more. State-of-the-art ammeters, with noise currents of the order of 10^{-16} A, can reduce this limit by 2 or 3 decades. A similar reduction, and faster response times, can be achieved using SEMs. Ion counting, using a fast-rise SEM, can further improve the minimum detectable partial pressure by about a decade.

Lichtman [106] recently reviewed the development of these instruments, many of which were originally intended to provide only a qualitative assessment of the relative quantities of different gases remaining in a vacuum system at its base vacuum. This capability can be invaluable in diagnosing and troubleshooting a vacuum system or process and has made PPAs or RGAs a common vacuum system accessory. Modern electronics has made possible decreased cost and improved ease of operation, further increasing PPA use. Many users now desire to use PPAs for quantitative gas analysis, such as might be required for on-line process control. This trend has probably been encouraged by the use, in some instruments, of microprocessors to analyze the measured ion currents and display them as equivalent pressures for different gas species. The high cost of

PPAs, relative to ordinary vacuum gauges, and the impressive graphic or multidigit displays now available lead some users to expect correspondingly accurate results. This expectation is generally misleading. While quantitative results accurate at the few percent level are possible with some PPAs, this level of accuracy requires frequent calibration, which in many cases may be complicated and time-consuming. For other instruments, instabilities, nonlinearities, and interactions between gases may cause order of magnitude errors even after the instrument has been calibrated.

Leaving aside the problems of interpreting mass spectrometer cracking patterns (the pattern of signals at lower mass-to-charge ratios generated by multiply charged ions and fragments of the parent molecule generated by electron impact), the difficulties in obtaining quantitative partial pressure measurements from PPAs arise from their complicated nature; they are susceptible to a number of design, manufacturing, and operating variables. Some of these can be manipulated by the designer, or, with some instruments, the user, to enhance one or more characteristics at the expense of others. For example, the sensitivities of different instruments, operating with the same electron emission current and detector configuration, may differ by as much as two orders of magnitude. The high sensitivity of the more sensitive instruments may be achieved, in part, by using space charges to create a high-efficiency ion source. However, space charge effects are very pressure dependent, and they may cause the sensitivity to be correspondingly dependent on pressure. The sensitivity of less sensitive instruments, with less efficient ion sources, may be relatively constant with pressure. The more sensitive instrument may be useful for detecting residual gases in a baked UHV system, but variations in their sensitivities with pressure may make them useless for quantitative analysis of partial pressures. For all instruments, drifts with time of electrical potentials or deposition during operation of conducting or insulating layers on insulators or electrodes can cause significant changes in sensitivity. Since the gain of secondary electron multipliers is very sensitive to the condition of the electrode surfaces, their gain, and the instrument sensitivity, may change significantly with time and use. At very low pressures, however, this instability can be greatly reduced by using ion-counting techniques since the SEM pulses counted are independent of amplitude, except for the small fraction near the detector threshold.

In recent years a number of PPA performance studies have been conducted [91, 107–113]). Depending on the instrument and selection of operating parameters, the sensitivity can vary, in some cases by as much as one or two orders of magnitude, with the ion source parameters, the molecular species, and the pressure. The relative sensitivities, that is, the ratios of the sensitivities of an instrument for different gases to the sensitivity of the same instrument for a reference gas (typically nitrogen or argon), can vary from one instrument to another by an order of magnitude (for this reason the relative sensitivities given in Table 2.4 for ion gauges should not be assumed applicable to PPAs). The choice of filament material can significantly alter the relative sensitivities for different molecular species. For some PPAs the sensitivity will vary significantly with total pressure for pressures as low as 10^{-7} Pa.

The nonlinearity with pressure of some instruments will be strongly affected by ion source parameters: electron emission current, electron accelerating voltage, and, especially, the ion extraction voltage. Note that the ion extraction voltage control is labeled *ion energy* on many PPAs; however, because of space charge effects the actual ion energy may differ significantly from this extraction voltage. Similarly, the electron accelerating voltage control is often labeled *electron energy*. A study of five different commercial instruments [113] found that the nonlinearities could be broadly categorized as "low" pressure, typically occurring during operation with high ion extraction voltage settings, and "high" pressure, typically occurring with low ion extraction voltage settings. The range of possible performances can be appreciated from the data of Figures 2.23 and 2.24 for two different PPAs. The instruments were calibrated with argon from 10^{-6} to 10^{-1} Pa for 27 different combinations of emission current, electron accelerating voltage, and ion extraction voltage. The data in Figures 2.23 and 2.24 were selected from the 27 different calibrations to illustrate the conditions that produced the maximum low-pressure nonlinearity (solid circles), the maximum high-pressure nonlinearity (solid squares), and the best linearity (solid line, no symbol). In both figures the sensitivities for a given set of parameters were normalized to 1 at 10^{-4} Pa. The data in Figure 2.23 were obtained from the most linear instrument, and the nonlinearities evident at high pressures were

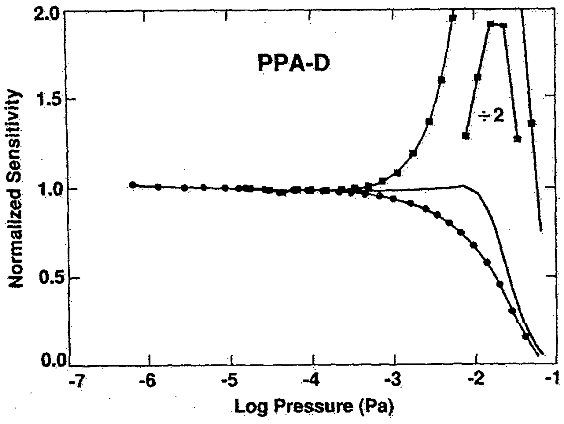

Figure 2.23 Normalized argon sensitivities for a PPA operated with three different combinations of ion source parameters. The electron emission current–electron accelerating voltage–ion extraction voltage combinations (in mA, V, V) were ●, 0.5, 60, 10; —, 1, 100, 10; ■, 2, 100, 3.

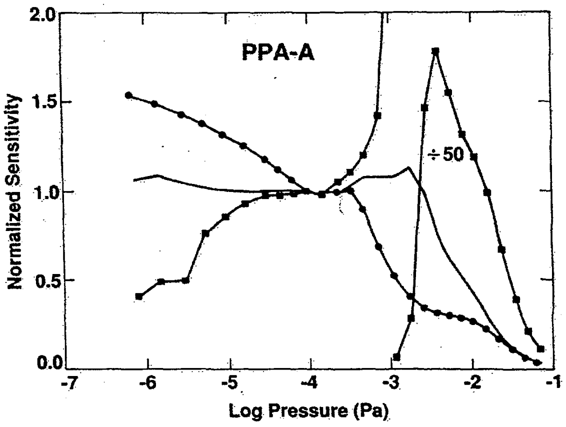

Figure 2.24 Normalized argon sensitivities for a second PPA operated with three different combinations of ion source parameters. The electron emission current–electron accelerating voltage–ion extraction voltage combinations (in mA, V, V) were ●, 0.5, 93, 10; —, 1, 93, 10; ■, 2, 93, 3.

observed only under extreme settings of the operating parameters. No significant nonlinearities could be observed at low pressures. The "best" performance was typical of that observed over a range of ion source parameters. In contrast, the instrument used for Figure 2.24 evidenced significant nonlinearities for all combinations of operating parameters. The solid line was truly the best performance, and large low- and high-pressure nonlinearities were observed for a wide range of operating parameters. Note in particular, that when operated at low ion extraction voltages the sensitivity of this instrument will change by more than two orders of magnitude as a function of pressure.

Clearly, a significant dependence on pressure of the sensitivity complicates the calibration and use of a PPA. A further problem was observed for instruments that showed significant nonlinearities. For these instruments the sensitivity for a specific gas tended to change not just as the partial pressure of that gas is changed, but also varied as the pressures of other gases were changed. Thus, the sensitivity for a trace gas can depend on the background gas pressure, in some cases the changes can be as large as two orders of magnitude, a highly undesirable feature. For all instruments, exposure to active gases, such as, CO_2, O_2, H_2O, caused changes of 10–20% in the sensitivity for all gases. With removal of the active gases the sensitivity returned to original values over periods of days. Over periods of weeks, changes in the sensitivity as large as an order of magnitude have been observed for some PPAs operated with secondary electron multipliers [111]. On the other hand, it has been found [113] that with the use of Faraday cup detectors some PPAs change by less than 10% over 2 months, although others changed by an order of magnitude under the same conditions.

Various combinations of the factors previously noted can combine to cause errors, in some cases as large as several orders of magnitude, in the partial pressures indicated by PPAs. This difficulty should not discourage their use since the qualitative diagnostic information that can be obtained with an RGA generally more than justifies their cost, particularly with UHV systems. However, it does indicate the need to exercise some judgment in the selection of PPAs and is a clear warning that some effort will be required to obtain quantitative measures of partial pressure. If a minimum detectable partial pressure is the primary consideration, the instrument can be selected on the basis of maximum sensitivity alone. But, if the objective is to monitor a trace gas in the presence of a varying background gas, a different selection may be appropriate. In particular, for this application it would be highly desirable to have a constant sensitivity over the operating pressure range. It is possible to calibrate some PPAs and obtain accuracies as good as a few percent in the measured partial pressures. For other instruments this is a fool's errand: some instruments are unpredictable, dependent on too many variables, and are unstable with time and use. Unfortunately, repeated calibrations will be required to distinguish the two categories of instruments. Lacking a primary vacuum standard, PPAs can probably best be calibrated by comparing them, as a function of pressure, with BA ion gauges, operated with reliable controllers. These calibrations should be done for different pure gases of interest, taking into account the different sensitivities of the ion gauge for different gases. For better accuracy, the ion gauge and the PPA can be compared with a molecular drag gauge in the high-vacuum range. Determination of the sensitivity to one gas species as a function of the pressure of other species will require more elaborate calibration apparatus and procedures [113]. If the PPA has both a Faraday cup and a secondary electron multiplier, confidence in the electron multiplier measurements can be improved if it is periodically compared with the Faraday cup in a pressure range where both detectors can be used.

6 GENERAL CONSIDERATIONS

6.1 Adiabatic Heating and Cooling

When pressure is changed, mechanical work is done on, or extracted from, the pressure medium. This work will cause a change in the temperature of the medium and the surroundings, including pressure sensors. This temperature change can cause significant perturbations in the performance of pressure sensors. In the extreme in which the pressure fluid is thermally isolated from its surroundings, so that the process occurs under adiabatic conditions, that is, constant entropy S, the temperature change with pressure can be derived using Maxwell's thermodynamic relations

$$(\partial T/\partial P)_S = T\beta/\rho C_P \tag{13}$$

where β is the volume thermal expansion coefficient, ρ is the fluid density, and C_P is its constant-pressure heat capacity. Similarly, the heat Q generated per volume of fluid V is

$$Q/V = T\beta\Delta P \tag{14}$$

where ΔP is the total pressure change and β is the average thermal expansion coefficient.

In a real apparatus, conditions are, of course, not adiabatic, and the temperature changes will attenuate with a time constant dependent on the thermal behavior of the entire apparatus. However, (13) demonstrates that the upper bound of the temperature change depends on the thermal expansion of the fluid, which is large for liquids and larger still for gases. The initial temperature perturbation of the sensor will depend on its heat capacity relative to that of the pressure medium. In a sealed system, this effect will also cause a relaxation of the initial pressure change as the fluid temperature returns to equilibrium. This relaxation complicates the determination of the magnitude of the sensor perturbation.

An example of this effect can be seen in the operation of temperature-controlled, force-balance quartz spiral gauges, which are available for gas pressures up to 33 MPa (5000 psi). Because of the limited tensile strength of fused quartz, in high-range gauges the pressure is applied to the outside of the quartz spiral and is contained in a surrounding pressure housing. This results in a relatively large volume of pressure fluid; and after a full-scale pressure change, times on the order of $\frac{1}{2}$ h are required before temperature equilibrium is adequate for the perturbation of the pressure reading to be reduced below 0.01%. For mercury manometers, temperature changes of tens of millikelvins can occur for 100 kPa pressure changes. This will cause a significant perturbation for high-accuracy instruments. With liquid (oil) pressure systems, the thermal expansion coefficient is smaller, but the pressure changes can be much larger, so that adiabatic temperature changes may be a significant perturbation for many measurements. With high-pressure systems the thermal situation can also be very complicated as the apparatus often involves thick-walled steel vessels. A pressure increase will heat the oil and the inside of the vessel, but the outside of the vessel will cool because it is under increased tension. In this situation the return to thermal equilibrium may be both long and complicated.

Adiabatic effects can be reduced by minimizing the volume of the pressure fluid and maintaining good thermal contact with a large thermal mass. A thermometer mounted as close as possible to the sensor may help to indicate if the sensor has been significantly affected. Ultimately, accurate measurements may require additional time to allow for a return to thermal equilibrium.

6.2 Hydrostatic Head Corrections

Any pressure fluid in a gravitational field will develop a vertical pressure gradient equal to the density of the fluid times the gravitational acceleration. Thus, a pressure sensor connected to a process at a different elevation will not sense the true process pressure. Similarly, if a pressure gauge is calibrated against a pressure standard that is at a different elevation, the hydrostatic head will contribute an error to the calibration unless an appropriate correction is made. In many cases the consequent error will be trivial; but, in many others it will not be, and it is important, for a given situation, to calculate at least the magnitude of the correction to determine whether it can be ignored.

Since liquids are relatively incompressible, with an approximately constant density, the hydrostatic head correction will be independent of pressure. Thus, for a fluid with a density of 1 g/cm^3 in a gravitational acceleration of 980 cm/s^2, the correction will be -98 Pa for each centimeter increase in height. As an example, for a pressure of 100 MPa (15,000 psi), a 1-m difference in height will require a 98 ppm correction, which will be of consequence for even some routine measurements. At a pressure one decade lower, 10 MPa (1500 psi), for the same conditions the correction will be correspondingly larger, 0.1%.

Since gases are compressible, with a density approximately proportional to pressure, the correction will be a constant fraction of the pressure, per unit height. Thus, for air at 297 K, with a nominal molecular weight MW_{air} of 29, the correction will be -1.15 ppm of the pressure per 1 cm increase in height. The correction for other gases and temperatures will be proportional to the molecular weight and the inverse of the absolute temperature.

For reasons unknown, hydrostatic head corrections seem to be a major cause of confusion and consequent errors. Two rules seem to help: (1) the pressure always decreases as the height increases, and (2) always make corrections based on absolute pressures. Even for differential or gauge pressures the corrections should be independently made to the low and high absolute pressures, and the differential pressure obtained from the difference of the corrected absolute pressures.

An example is shown in Figure 2.25. In this case a pressure transducer is being calibrated in a room temperature environment, 297 K, against a piston gauge with argon, molecular weight MW_{Ar} of 40, at a nominal gauge pressure of 1 MPa. Both the transducer and the piston gauge have an atmospheric reference at a nominal pressure of 100 kPa, so that the nominal absolute high pressure is 1.1 MPa. The pressure port of the transducer is located 50 cm above the reference level of the piston gauge, which is at the bottom of the piston.

The correction to the atmospheric reference pressure will be

$$(-1.15\ \text{ppm/cm}) \times (50\ \text{cm}) \times (10^5\ \text{Pa}) = -5.8\ \text{Pa}.$$

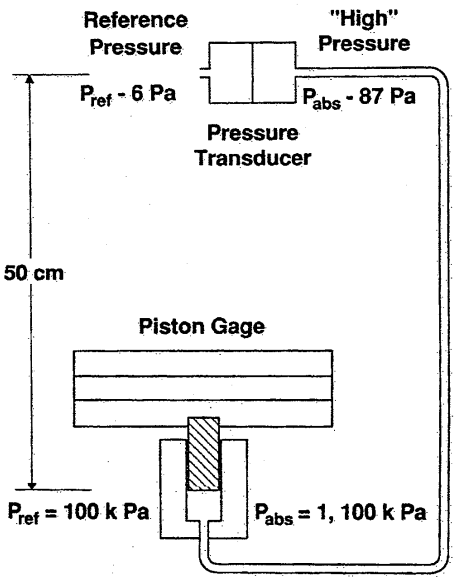

Figure 2.25 Example of hydrostatic head pressure corrections. When making corrections to gauge pressures, independent corrections should be made to both the absolute reference and absolute "high" pressures, and the correction to the gauge pressure is calculated from the difference.

The correction for the nominal high pressure of 1.1 MPa will be

$$(-1.15\ \text{ppm/cm}) \times (\text{MW}_{\text{Ar}}/\text{MW}_{\text{air}}) \times (50\ \text{cm}) \times (1.1 \times 10^6\ \text{Pa}) = -87.2\ \text{Pa}.$$

Thus, the corrected gauge pressure at the transducer will be

$$(1{,}100{,}000 - 87.2) - (100{,}000 - 5.8) = 999{,}919\ \text{Pa}.$$

This amounts to a −81 ppm correction to the gauge pressure.

6.3 Thermal Transpiration

In higher pressure gases, where the mean free path between collisions is small compared to dimensions of the apparatus and molecule–molecule collisions dominate, the frequent collisions between gas molecules maintain temperature and molecular speed equilibrium on a local scale. This condition is known as the viscous flow regime and prevails for typical laboratory apparatus at pressure above about 10 Pa. At lower pressures, where molecule–molecule collisions are rare, the speed and temperature of a molecule will be determined primarily by the temperature of the last surface it struck, and may be quite different from other molecules in the immediate vicinity. This condition is known as the molecular flow regime and, for typical laboratory apparatus, prevails for pressures below about 0.1 Pa. If two connected chambers are maintained at different temperatures in the molecular flow regime, the gas molecules can intermix with two different velocity distributions. Thus, as in Figure 2.26, gas molecules in the warmer chamber will pass through the connection between the chambers at a faster rate than those from the cooler chamber, until an equilibrium is established, where the same number of molecules pass each way per second. Using the kinetic theory of gases it can be shown that, if the chambers are connected by an orifice, at equilibrium

$$\rho_1/\rho_2 = (T_2/T_1)^{1/2} \tag{15}$$

where ρ and T are the corresponding densities and absolute temperatures. The pressures can similarly be related by

$$P_1/P_2 = (T_1/T_2)^{1/2} \tag{16}$$

As the pressure is raised from the molecular flow regime through the transition regime into the viscous flow regime the pressures in the two chambers will approach equality. The departure from pressure equality, which is quite real, is generally known as the *thermal transpiration* or thermomolecular effect.

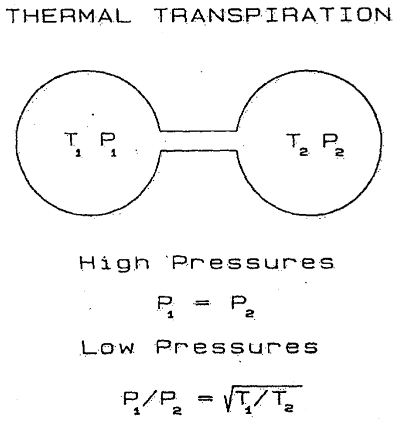

Figure 2.26 Thermal transpiration. As the pressure is lowered to the point that collisions between molecules become infrequent, a pressure difference will develop between the two chambers. At very low pressures gas kinetic theory predicts a limiting difference, $P_1/P_2 = (T_1/T_2)^{1/2}$.

In most practical cases two volumes of gas at different temperatures will communicate by something more complicated than an orifice, and some or all of the molecules will collide with a wall at an intermediate temperature during the passage from one chamber to another. In the simplest approximation, (15) and (16) will still apply. However, there is experimental evidence [114, 115] that for such an apparatus the actual pressure difference in the molecular flow regime will be less than that predicted by (16). This deviation appears to depend on the condition of the surfaces between the two vessels, which presumably affects the efficiency of energy exchange at these surfaces. The situation for pressures above the molecular flow regime is even more difficult. Although it is clear that the pressures gradually approach equilibrium with increasing pressures, theoretical predictions [116, 117] of the pressure differences as a function of pressure through the transition range have met with only limited success.

Theoretical difficulties aside, the thermal transpiration effect must be taken into account when measuring pressures in the transition or molecular flow regimes. If the pressure gauge is at a different temperature than the region where one wants to know the pressure, the gauge will sense a different pressure. This is of particular concern for capacitance diaphragm gauges and instruments employing a hot-cathode.

Capacitance diaphragm gauges, discussed in Section 5.1, are widely used throughout the transition range. Generally, these gauges are controlled at an elevated temperature, typically 35–50°C, to improve thermal and mechanical stability. Generally, the manufacturer's calibration of these gauges does not take thermal transpiration into account, so that as the pressure is reduced through the low-vacuum range into the high-vacuum range, there is an increasing difference between the pressure reading of the gauge and the pressure it is supposed to measure. Since this effect is controlled primarily by mean free paths, it will depend not only on the pressure, but also on the gas molecular weight, temperature of the vacuum chamber, control temperature of the particular gauge, and the dimensions and surface condition of the plumbing between the gauge and the vacuum system. Experimental investigations of this effect [118, 119] show the offset at low pressures to be between 2 and 4%, depending on the gauge. Data obtained over the transition range at the National Physical Laboratory, Teddington, UK [118] were fit as a function of pressure to the equations proposed by Liang [116] and Takaishi and Sensui [117]. The best fit was found for the Takaishi and Sensui equation. Similar data [119] were successfully fit to the Takaishi and Sensui equation for two gauges. Data for two other gauges, however, did not conform to this functional form.

Tubulated hot-cathode ionization gauges operate well above ambient temperature due to the power, typically about 10–20 W, dissipated by the hot filament. The temperature of the gauge structure and envelope is very nonuniform, and it is almost impossible to determine an effective temperature. Whatever the temperature, the thermal transpiration effect will be taken into account if the gauge is calibrated against a vacuum standard. However, if the gauge is subsequently used in a different environment or if its filament power should change so that its effective temperature is different from when it was calibrated, additional errors will be incurred. With reasonable care these can be kept small: a 70°C change will cause an error of only about 10%. If the operating gauge is insulated, however, the temperature can increase by as much as 100–150°C, with consequent errors as large as 20%. Similar effects can occur with PPAs or RGAs.

If the thermal transpiration follows the ideal behavior predicted by (16), it compensates for the temperature dependence predicted by (12) for a molecular drag gauge. Therefore, to first approximation, a molecular drag gauge is not affected by thermal transpiration.

7 FURTHER READINGS

Both the high- and low-pressure extremes are covered by general reviews of the measurement science and technology. The review by Decker and co-workers [120] is older and directed primarily to pressures above the range of this discussion, but it is very comprehensive with an extensive set of references. The review by Liu and co-workers [121], although also oriented toward higher pressures, covers the high- and very high pressure ranges in more detail. The book edited by Peggs on high-pressure measurement [122] includes chapters on both static and dynamic pressures, fixed points, and high-pressure transducers. Pavese and Molinar [123] cover gas-pressure measurements from the low-vacuum to high-pressure ranges. Berman's book [124], as the title suggests, discusses "total," as opposed to partial, pressure measurements from atmospheric pressures to UHV. Leck's book [125] is an update of his earlier standard reference and addresses partial pressure measurements as well as total pressure or vacuum measurements. General readers should be aware that vacuum measurement technology has evolved so recently and has been such an active field that general reviews often include discussions and references to instruments that are no longer available commercially, or may exist only in a few specialized laboratories, if at all. Blake [126] discusses differential pressure measurements, with emphasis on probes and sensors used for flow measurements.

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