7.1 THE MEASUREMENT OF TEMPERATURE

A thermometer can be any system with a measurable property which depends strongly on temperature. We will discuss here the *working* thermometers useful in most laboratories, as opposed to *standard* thermometers, used in calibration laboratories.[7–9]

7.1.1 Expansion Thermometers

Expansion thermometers use the volume of the thermometric system as the thermometric property. For example, the common mercury thermometer uses the change in volume (as reflected in the change in length) of a column of mercury confined to a cylindrical capillary tube. There exist other kinds of expansion thermometers—depending, for example, on the thermal expansion of a metal—that have industrial applications.[8] We will limit ourselves to the *liquid-in-glass thermometers* used in scientific research.[9]

Such thermometers are limited in range by the freezing and boiling points of the liquids used and by the softening point of the glass in which the liquid is contained. Liquids other than mercury can be used—for example, pentane can be used to 143 K. Design considerations also include the choice of glass and the relative dimensions of the parts of the thermometer.[9] Thermometers can be designed for high sensitivity in a particular range by including a section of larger diameter—a contraction chamber—in the liquid column so that the liquid expands in that volume before it reaches the range of interest (see Figure 7.1). The Beckmann differential thermometer is a mercury thermometer with a mercury reservoir that allows the amount of mercury in the stem—and thus the range of the thermometer—to be adjusted.[7]

There are a number of difficulties encountered when trying to obtain high accuracy and precision with liquid-in-glass thermometers.[7–9] Good thermal contact between the thermometer and the system of interest is difficult to achieve for systems other than fluids. The thermometer can be sensitive to pressure changes. If the thermometer is heated to its highest temperatures, it will require days to return to its original calibration because of hysteresis in the glass.

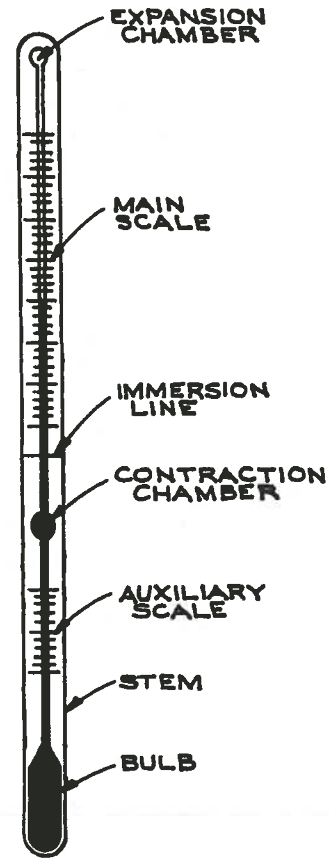

Figure 7.1 Mercury-in-glass thermometer. The auxiliary scale is designed to allow calibration at the ice point. The contraction chamber permits high sensitivity (a small capillary diameter) without having a very long stem. The immersion line indicates the depth to which the thermometer was immersed in the calibration bath. The expansion chamber prevents the buildup of pressure and avoids breakage on overheating.

In truth, a liquid-in-glass thermometer is seldom the best choice for thermometry in the modern laboratory. In addition to the problems of obtaining good accuracy and precision, liquid-in-glass thermometers do not lend themselves readily to computer automation of the measurement process. The best uses of liquid-in-glass

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thermometers are for approximate measurements (±0.1 K) that need not be automated, or as laboratory standards for the calibration to 0.01 K of other thermometers.

Mercury thermometers designed to be accurate and stable to about 0.01 K over temperature ranges of 3 to 5 K are commercially available (see "Manufacturers and Suppliers" at the end of this chapter). Care must be taken in using them as standards. Mount the mercury thermometers in a stirred bath with a controlled temperature (see Section 7.2). Be careful when reading the meniscus position to avoid parallax error—a telescope makes this easier. Use the thermometer at the same immersion depth at which it was originally calibrated—a difference in immersion depth will necessitate stem corrections.[7,9] Tap the thermometer before each measurement to avoid sticking of the mercury column to the stem wall. Monitor the stability of the thermometer by regularly measuring the ice point (see Section 7.1.6). A final hint: If the mercury in a thermometer becomes separated, it can be rejoined by cooling the thermometer bulb with dry ice shavings until all the mercury is back in the bulb.[9]

7.1.2 Thermocouples

Thermocouples use the voltage that develops between two junctions of two different metals when the junctions are at different temperatures as the thermometric property.[9–11] When a difference in electron density exists between two points in a metallic conductor, a voltage develops between those two points. Such a difference in electron density can arise even in a conductor made of a homogeneous metal because the electron density varies when the temperature varies. Thus a temperature gradient across a metallic material causes a voltage to develop across that material. If we try to measure this voltage by attaching leads made of the same metal, then the voltage difference will also develop in the leads and the lead voltages will cancel.[12] If the leads are of a different metal, as shown in Figure 7.2a, then the difference in the thermally induced voltages between the two metals will cause a net voltage between the junctions—the Seebeck effect. This thermoelectric voltage, or *thermal emf*, depends upon the particular choice of metals and upon the difference in temperature between the junctions, and depends only slightly on the pressure. It is important to realize that the Seebeck effect is a bulk property of metals in a temperature gradient. It is not a property of the junctions themselves. It is not a *contact potential*, and treating it as such can lead to mistakes in the use of thermocouples.[13]

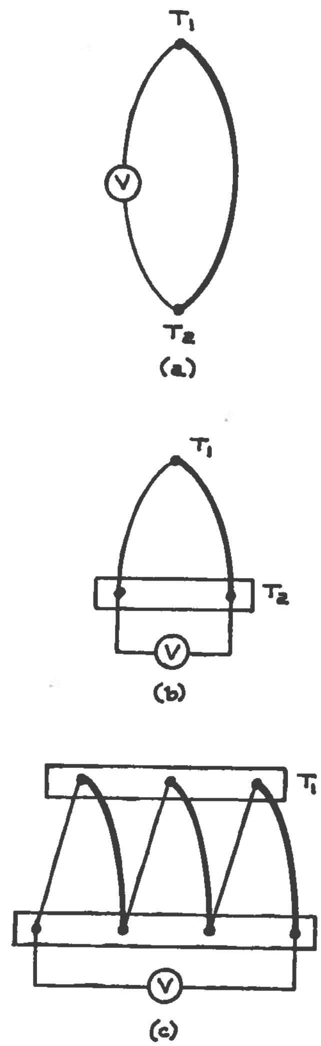

Figure 7.2 Thermocouple configurations. Lines of different thicknesses represent wires of different metals or alloys. T_1 and T_2 are two different temperatures. V is a voltmeter.

The connection of two wires of two different metals at junctions with two different temperatures, as in Figure 7.2a, is called a *thermocouple*. The voltage developed across the thermocouple is a measure of the difference in temperature ($T_1 - T_2$). The relationship between the thermoelectric voltage and the temperature difference, while nearly a direct proportionality, cannot be predicted, but must be measured for a given pair of metals. The nature of the Seebeck effect leads to several principles useful in the design of such thermocouple thermometers:[8,14,15]

1. *The law of homogeneous metals:* A thermocouple requires two different metals. If the two wires are of the same material, then no net thermal voltage will develop, even in the presence of a temperature gradient. Voltmeter lead wires, as shown in Figure 7.2b, will therefore not contribute to the measured voltage if they are made of the same metal, and if their ends (at T_2 and at the voltmeter) are at the same temperatures so that they are under the same temperature gradient. On the other hand, inhomogeneities due to strains or impurities in the metal conductor will be, in effect, regions of a different metal. They will act as mini-thermocouples in the presence of a temperature gradient, generating spurious thermal voltages and leading to inaccuracies in the thermometry.

2. *The law of intermediate metals:* A thermocouple requires two different temperatures. If there is no difference in temperature between the ends of a pair of wires, then no net thermal voltage will develop between them, even if the wires are of different metals. In Figure 7.2a, for example, if $T_1 = T_2$, no voltage develops. A consequence of this law is that another wire may be inserted into the thermocouple circuit, as long as both ends of that wire are at a common temperature, which need not be either of the temperatures involved in the actual thermocouple (T_1 or T_2). This means that the thermocouple junctions may be made with any kind of solder or any other method of attachment, since the junction itself is all at the same temperature.

3. *The law of successive metals:* If thermocouples are made of pairs of metal *A* with metal *B*, metal *B* with metal *C*, and metal *A* with metal *C*, then the voltages developed between a given pair of junction temperatures will be related as $V_{AC} = V_{AB} + V_{BC}$. This equation allows the calculation of tables of thermocouple voltages for any pair of metals *A* and *C* if the tables are already available for *A* and *C* with respect to a reference metal *B*.

4. *The law of successive temperatures:* If a given thermocouple develops a voltage V_a between T_1 and T_2 and a voltage V_b between T_2 and T_3, then it will develop a voltage $V_c = V_a + V_b$ between T_1 and T_3. It follows that only the junction temperatures matter and that intermediate temperatures along homogeneous wires do not matter. It also follows that if thermocouple tables are available in which voltages are given for each temperature T_1 with respect to a reference temperature T_2, then voltages may be calculated with respect to a different reference temperature T_3 if the voltage V_b is known.

Thermocouple junctions may be placed in series in order to amplify the voltage signal. Such a *thermopile* is shown in Figure 7.2c, in which there are three identical thermocouples in series, producing (since voltages in series add) a voltage three times that of a single thermocouple.

Since any two metals or alloys can form a thermocouple, there are a great many possible thermocouple pairs. The choice of a particular pair will depend upon its sensitivity in the temperature range of interest and upon such considerations as corrosion resistance. Several thermocouple pairs have come into common use—their properties are well known, and good-quality wire is readily available. Table 7.1 gives the most common thermocouple types and their properties. Types C, D, and G are all various combinations of tungsten and rhenium alloys and are valuable at high temperatures because these metals do not readily vaporize. Type E is common in low-temperature applications because the thermal conductivities of the materials are low. Type J has the advantage of high sensitivity and the disadvantage that iron is readily oxidized. Type K has a wide range of usefulness, low thermal conductivity, and good resistance to oxidation, but cannot be used in a reducing atmosphere above 1100 K and shows instability in the calibration due to a phase transition in Chromel at 570 K. Type N is a relatively new thermocouple, intended as a much more stable substitute for Type K. Type S has low sensitivity, but has high stability and thus is useful as a standard. Type T, probably used most often, has the advantage that one material is copper, from which the voltmeter leads are also likely to be made. The chance of extraneous thermal voltages is therefore reduced. On the other hand, copper oxidizes above 620 K and has a very high thermal conductivity (see Table 7.4 in Section 7.2.2 below). The last two Chromel thermocouples in Table 7.1, one with gold-iron and one with copper-iron alloys, are used at cryogenic temperatures, along with types E, K, and T.

The construction of reliable thermocouple thermometers requires some care. Use good-quality, annealed thermocouple wire. Each wire can be individually tested for homogeneity by connecting its ends to a voltmeter and passing the wire slowly through liquid nitrogen. Wires that do not show any measurable thermoelectric voltage are suitable for use.[16] Use the largest-diameter wire that you can tolerate—large wire is more likely to be homogeneous and is less susceptible to strains. Make the junctions mechanically sound and electrically and thermally continuous. In principle, thermocouple wires can be twisted or clamped to make a junction.[9] In practice, better results are obtained if they are soldered or welded (see Section 1.3). For work below 443 K, Type T can be joined with ordinary tin-lead solder, using a rosin flux. All can be soldered with low melting tin-silver solder. For work at higher temperatures and for better mechanical strength, all can be brazed with a high-melting silver alloy (see Section 1.3.2). All but Type T can be spot welded.[17] All can be welded with a torch. In this welding process, a reducing flame of oxygen with either natural gas or acetylene is used to melt the two wires together into a firm bead. Ready-made thermocouples, thermopiles, and thermopile arrays can be purchased from SensArray, InstruLab, Omega, et al.

Make good thermal contact between the junctions and the points at which the temperatures are to be measured. Junctions may be mechanically attached to solids using a thermally conducting grease, or bonded with a thermally conducting adhesive (Cotronics, Omega, Wakefield). Thermocouples are often placed in protective Pyrex or ceramic tubes (usually in a thermally conducting oil), but such arrangements increase the response time. Protect the wires from stresses. The wires may be electrically

Table 7.1 PROPERTIES OF COMMON THERMOCOUPLES

Type[a]	Materials	Useful Range (K)	Sensitivity (μV/K) 20 K	Sensitivity (μV/K) 300 K
C, D, G	Tungsten/Rhenium	32–2600	—	20
E	Chromel[b]/Constantan[c]	10–700	8.5	61
J	Iron/Constantan[c]	60–1000	—	52
K	Chromel[b]/Alumel[d]	10–1500	4.1	41
N	Nicrosil/Nisil[e]	10–1500	3	26
S	Platinum/PtRh	220–1800	—	6
T	Copper/Constantan[c]	20–700	4.6	41
	Chromel[b]/AuFe	10–1000	15	20
	Chromel[b]/CuFe	10–300	>11	—

[a] The type designation is that of the Instrument Society of America.
[b] Chromel is an alloy of nickel with 10% chromium.
[c] Constantan is an alloy of copper with 43% nickel.
[d] Alumel is an alloy of nickel with 2% aluminum, 2% manganese, and 1% silicon.
[e] Nicrosil is a alloy of nickel, chromium, and silicon; Nisil is an alloy of nickel, magnesium, and silicon.

insulated with Teflon (to 553 K) or Kapton (to 700 K)—fiberglass or ceramic is required for higher temperatures. Thermocouples produce low-level dc voltages, which require particular care in measurement.[18,19] Appropriate procedures should be followed for shielding and grounding in the measurement circuitry (see Section 6.9). Commercial thermocouple IC amplifiers are available (Analog Devices, Linear Technology) for $15 to $50.[11] Sometimes (e. g., for control purposes) it is desirable to linearize the output signal, and such circuits have been designed.[11] A digital voltmeter of appropriate sensitivity suffices for the measurement of the thermocouple voltage.

Thermocouples measure the temperature differences between junctions. This property is advantageous when a difference is just what is required, as in some temperature-control circuits. If, instead, an absolute temperature measurement is required, then one junction (the *reference junction*) must be kept at a constant, known temperature. For example, let T_2 in Figure 7.2 be the reference junction. The absolute temperature at T_1 is then obtained by combining the known T_2 and the difference ($T_1 - T_2$) as obtained from the thermocouple voltage (see later in this section). One way to do this is to keep the reference junction at 273.15 K by immersing it in a slurry of ice and water (all made from distilled water). The reference temperature can also be established with commercially available (but expensive) fixed point cells (Hart, Omega).[9]

Two less expensive methods are making an isothermal block, or using an electronic compensation circuit. An isothermal block consists of a material of high thermal conductivity (see Table 7.4) onto which the reference junctions and an independent thermometer are mounted with good thermal contact and surrounded by thermal insulation (see Table 7.4). The independent thermometer is then used to establish the reference temperature. This is useful even though it requires an independent thermometer because that thermometer only needs to function near room temperature, but then permits thermocouple measurements far from room temperature.

An electronic compensation circuit or *electronic ice point* is an electronic circuit which measures the temperature at the reference junction and then adds a voltage to the thermocouple circuit that compensates for the fact that the reference junction is not actually at 273.15 K.[11,20] Complete devices are available (Omega) for about $100. Analog Devices and Linear Technology make integrated circuits (AD594, AD595, LT1025) that include compensator and amplifier for $15 to $40. Circuits can also be made from components.[19] Reference junctions made from ice baths or other fixed point baths allow temperatures to be measured with higher accuracy (±0.01 K) than do isothermal blocks or electronic ice points (±0.4 to ±1 K).

In order to convert the thermocouple voltage to a temperature, it is necessary to use conversion tables or to calibrate directly. The National Institute of Standards and Technology has published extensive tables of thermocouple voltages.[21] A calibration using the tables is likely to be accurate only to a few degrees, due to variations among wires. For more accurate measurements (0.1 K), the thermocouple must be compared with a standard thermometer—usually a platinum resistance thermometer (see Section 7.1.3)—over the temperature range of interest. Voltage-temperature points from either the tables or from a direct calibration can be fitted by a polynomial:

$$T = a_0 + a_1 V + a_2 V^2 + \dots \qquad (7.1)$$

where T is the temperature, V is the voltage, and enough terms are included to describe the data. The calibration determines the accuracy of the temperature measurement on the ITS (see Section 7.1.6). The precision of temperature measurements with thermocouples is considerably better than the accuracy because temperature differences can be resolved to 0.001 K using thermopiles and sensitive amplifiers/voltmeters.

The advantages of thermocouples as thermometers are: they are simple and inexpensive, thermopiles can have a resolution of 0.001 K, they can be used over a very broad range of temperature (see Table 7.1), they are small, and they respond quickly. The disadvantages are: the signals are small and hard to measure, accuracy is hard to attain and maintain, and a reference junction is necessary for absolute temperature measurements.

7.1.3 Resistance Thermometers

Resistance thermometers use the dependence of electrical resistance on temperature as the thermometric property.

There are two main kinds of resistance temperature detectors (*RTDs*)—metal RTDs and thermistors.

Metal resistance thermometers consist of wire coils or thin films of metals such as nickel or platinum, together with the instrumentation needed to measure the electrical resistance. Platinum is common because it is resistant to corrosion and its electrical resistance is nearly linearly dependent on temperature.[9,22] Indeed, the platinum resistance thermometer (PRT) is the standard device for the ITS of 1990 between 13.8033 K and 961.78 K (see Section 7.1.4).[23] As the temperature increases, the increase in kinetic energy of the platinum atoms leads to an increase in the electrical resistivity of about 0.4 percent/K. Some typical platinum resistance thermometers are shown in Figure 7.3. Usually, at room temperature, PRTs have resistances of 25 or 100 Ω, but thin-film PRTs can have resistances of 1000 to 2000 Ω. The resistance as a function of temperature behaves as (see Figure 7.4)

$$R = R_0 + R_1T + R_2T^2 + \ldots \quad (7.2)$$

where the T^2 term is important for measurement with a resolution of millikelvins. With care in the resistor construction and in the measurement circuitry, a resolution of 0.1 mK can be achieved with platinum resistance thermometers over a very broad range of temperatures (see Figure 7.4 and Table 7.2).

Thin *surface mount* foil resistance thermometers made from platinum, nickel-iron, and copper are available (Minco). For cryogenic temperatures, copper, constantan, manganin, ruthenium oxide, and rhodium-iron make useful resistance thermometers.[3,24]

Thermistors are small beads of semiconducting material (metal oxides).[25] While electrons flow freely in a metal, in a semiconductor the electrons must first be excited into a conducting state. This makes a thermistor different from a resistance thermometer in that the electrical resistance is much more sensitive to temperature change, the resistance decreases as temperature increases, and the resistance is not linear in its temperature dependence. The resistance of a thermistor decreases at a rate of about 4 percent/K, which is ten times more sensitivity than that of a PRT. The best empirical function for a thermistor is (see Figure 7.4)

$$1/T = A + B(\ln R) + C(\ln R)^3 + \ldots \quad (7.3)$$

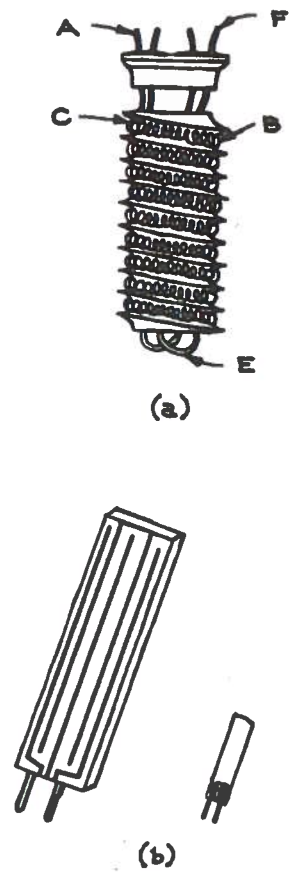

Figure 7.3 Platinum resistance thermometers. (a) Standard, high-resolution model made by Minco Products, Inc., in which the platinum is wound as a wire coil on a ceramic base. Two leads (A) pass through the lid and attach to one end of the coil (B) at C. At the other end, two leads are again attached (E) and pass through the center of the base to the lid at F. The assembly is then enclosed in an inert atmosphere. This PRT is 3/8 in. long. (b) Film RTDs such as those made by Omega Engineering, Inc. These are called *thick* and *thin* film RTDs, repectively. They can be very small—1/8 in. or less in length.

where A, B, and C are empirical constants and in which higher-order terms of odd power may be required for a broad temperature range or for high resolution.[8,26] If a linearized resistance is required, then linearizing circuits can be made or bought.[19] For example, the YSI model 4800 ($75) linearizes to ±0.1 K from 273 K to 373 K.

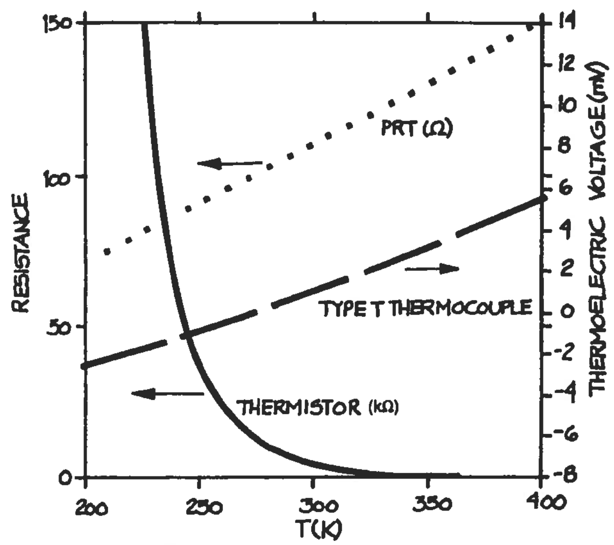

Figure 7.4 The left ordinate gives the resistance as a function of temperature *T* for a thermistor (solid line) that has a room temperature resistance of about 4 kΩ and for a platinum resistance thermometer, PRT, (dotted line) that has a room temperature resistance of about 100 Ω. Note that the scales differ by a factor of 1000. The right ordinate gives the thermoelectric voltage referenced to 273 K of a Type T copper/constantan thermocouple (dashed line) as a function of temperature.

Typical thermistor resistances are 1 to 10 kΩ. Thermistors readily resolve a millikelvin and can be made to resolve a microkelvin.[27] The disadvantage is that their resistance rapidly decreases with increasing temperature and thus their usefulness decreases above about 373 K. Thermistors designed for use up to 523 K, however, are available (YSI). Interchangeable thermistors (matched as well as ±0.05 K over 50 K) and ultra-stable thermistors are also available (YSI, Thermometrics, Betatherm).

Thin surface-mount thermistors are available from YSI and Thermometrics. Special thermistors for radio frequency field environments are available (BSD Medical Corp.) and are known as *Vitek probes*; they require special circuits to measure their high (5 MΩ) resistances,[28] and are fragile and fail if their probes are kinked or bent.

For cryogenic temperatures, there are a number of special semiconductor resistance thermometers available, including doped germanium, carbon (graphite), and carbon-in-glass.[3,24] The carbon resistors have long been used for cryogenic thermometry, but suffer from considerable instability on temperature cycling; the carbon-in-glass resistors are somewhat more stable. Table 7.2 gives typical ranges and sensitivities for these thermometers.

Complete resistance thermometry systems are commercially available for low-resolution (0.1–1 K) measurements (Barnant, Hart, Omega, Techne, Yokagawa) and for high-resolution measurements to 1 mK (Guildline, Hart, Instrulab, YSI, Lake Shore), 0.1 mK (Julius Peters) or even 0.01 mK (Hart). Nevertheless, it is useful to understand the considerations in constructing the resistance-measuring equipment so that one may take advantage of equipment one already has, or make a thermometer for a special need, such as for very high resolution in a particular temperature range.

The first consideration for a resistance thermometer is its stability. The stability requirements depend on the resolution required and determine the price of the resistor. Thermistors and RTDs have been developed which drift less than 5 mK per year (YSI, Thermometrics). Mechanical stresses caused by mounting (e. g., use of hard adhesives) can cause drifts in resistance thermometers.

The second consideration for a resistance thermometer is its *self-heating*—the current in the resistor must be sufficiently low that the resistor itself is not heated above the temperature of its surroundings. The *dissipation factor* of the resistor specifies the self-heating. For example, a typical dissipation factor for a thermistor is 4 μW/mK. This means that a current resulting in 4 μW of power will heat the thermistor by 1 mK. To obtain a resolution of 1 mK with a 4 kΩ thermistor, the current is thus limited to 3×10^{-5} A. For a 25 Ω PRT, the current limit is about 3 mA for a resolution of 1 mK.

The third consideration is the possibility of thermal emfs in the thermometer circuit. These are the very effects that make thermocouple thermometers possible (see Section 7.1.2), but as extraneous voltages they can interfere with resistance thermometry when the resistance is determined by measuring a voltage. Thermal emfs may be evaluated by reversing the current in the resistance circuit. The effect will add for one current direction and

TABLE 7.2 PROPERTIES OF COMMON RESISTANCE THERMOMETERS

Type[a]	Materials	Useful Range (K)	Sensitivity (μV/K) 20 K	300 K
Conductor	Platinum	20–1,000	10	0.1
	Rhodium-iron[b]	0.5–300	0.05	5
	Ruthenium oxide	0.04–40	5[c]	—
Semiconductor	Thermistor	77–600	—	0.01
	Germanium[b]	1–30	0.5	—
	Carbon	0.04–300	1	10^3
	Carbon-in-glass	1–100	0.75	—
Diode	Silicon[b]	0.01–300	20	15
	Gallium arsenide[b]	0.01–300	15	100

[a] Approximate resolution under typical conditions.
[b] Not recommended for use in magnetic field.[24]
[c] Stability at 4.2 K.

subtract for the other. If such effects are present, they may be corrected by averaging the two readings or by using an ac resistance-measuring method.

The fourth consideration is the effect of the resistor leads. If the resistance of the lead wires enters into the resistance measurement, then that resistance and its temperature dependence can cause an error in the thermometry. Using short wires of large diameter can minimize lead effects. They can be eliminated by using *four-wire measurement* techniques—techniques in which two wires carry the current through the resistor and two other wires are used to measure the voltage across it. If the voltage is measured with a high-impedance device, then no significant current is carried in the voltage leads, no significant voltage drop occurs across those leads, and there is no lead error.

The design of precision resistance-measuring circuits is an art that changes as technology advances.[4,7,9,15,29] We will not discuss the details of such designs here, but refer the reader to the literature[4,30] and to the manufacturers of resistance instruments (Guildline, Hart, Linear Research, and various manufacturers of digital multimeters). In Figure 7.5, we present a simple circuit that requires only a digital voltmeter, a mercury battery, and a standard resistor for the assembly of a resistance thermometer with a resolution of 1 mK. For a 4 kΩ thermistor, a standard resistor of 50 kΩ is required to keep the current below the level of self-heating. The standard resistor must be stable with time and temperature. Vishay Resistor Products makes such stable resistors. A mercury battery is a cheap and stable voltage source. The resistance R_T will indicate the temperature. R_T equals V_T/I, where V_T is the voltage drop across R_T and I is the current through R_T. The current I is the same in R_S, thus I equals V_S/R_S, where V_S is the voltage drop across the standard resistor and R_S is its resistance. Thus

$$R_T = R_S\,(V_T/V_S) \tag{7.4}$$

If R_S is known, then only V_T and V_S need to be measured to obtain R_T. R_S need not be known exactly, since it is a constant. The ratio $R = V_T/V_S$ can be used as the thermometric variable when the thermometer is calibrated, and Equation 7.3 can be written with this ratio replacing R. In order to measure temperature to 1 mK, the voltage drops of 0.1 to 1 V need to be measured to six significant figures; some voltmeters will directly measure the ratio R.

7.1.4 Integrated Circuit Thermometers

A number of integrated circuit thermometers have been developed in recent years. They produce voltages or currents that are linear (within about 1 K) in temperature,[19] or even digital outputs.[31] Typical sensitivities are 1 μA/K and 10 mV/K, leading to typical

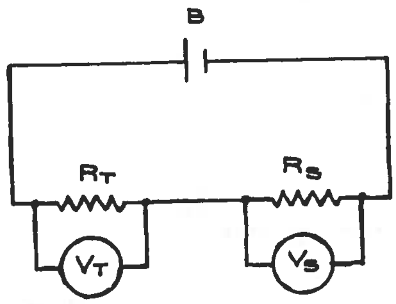

Figure 7.5 A simple resistance thermometry circuit: a series arrangement of a thermistor or a platinum resistance thermometer (R_T), a standard resistor (R_S), and a 1.35 V mercury battery (B).

of 223 to 423 K. IC thermometers therefore may be useful for some purposes. They are used as the independent thermometers in the thermocouple reference junction circuits discussed earlier, and they have many uses in general manufacturing. They are not yet capable of refined temperature measurements.

Most versions have the temperature variation of a silicon junction potential or some other silicon circuit topology as the working principle.[32] Examples are the LM335 (+10 mV/K, $1), the LM35 (+10 mV/K, $1),[33] the AD590 (+1 μA/K, $2), and the AD7416 (10-bit temperature-to-digit converter, $1). Silicon and gallium arsenide diodes use the voltage drop across the diode at constant current as the thermometric property—they are sensitive and stable (see Table 7.2). There are also temperature sensors (e. g., AD22100, +22.5 mV/K, $1) that have the temperature dependence of a thin metal film as the working principle, so that they are *IC resistance thermometers*. Analog Devices and National Semiconductor describe their wide selection of devices on their web pages (see Manufacturers and Suppliers).

7.1.5 Comparison of Thermometers

Mercury thermometers are cheap and easy to use, but are limited in precision (0.01 K) and in means of automation. Thermocouples are cheap, are useful over a wide range, have good precision (mK), and can be automated. They must, however, be designed with attention to the minimization of spurious voltages. Platinum resistance thermometers offer broad range and very good precision (0.1 mK), at higher cost. Thermistors allow extremely high precision (1 μK), but for a limited range in temperature. Resistance thermometers are readily automated. Integrated circuit thermometers offer simple, easily automated temperature measurement when low resolution of 0.1 to 1 K is all that is required.

Thermometry is a very broad subject and there is much that we have not been able to include here. We have not discussed techniques peculiar to very high temperatures, such as optical pyrometry.[1] We have also not discussed techniques peculiar to very low temperatures (<1 K), such as vapor-pressure thermometry or magnetic thermometry.[30,34–36] Several kinds of thermocouples and resistance thermometers, however, are useful at both high and low temperatures. Gas thermometry is rarely of value in other than standards laboratories.[5,6] Fiber optic thermometry,[5] especially fiber optic fluorescence thermometry,[37,38] is emerging as important for the remote sensing of temperature.

7.1.6 Thermometer Calibration

Ideally, the working scientist would like to have temperature measurements which are on the fundamental, thermodynamic temperature scale. Such measurements can be achieved only in standards laboratories, with very expensive and very complex thermometers such as ideal-gas thermometers.[39] The thermodynamic temperature is conveyed to the working laboratory by means of the International Temperature Scale, which was last redefined in 1990 (ITS-90).[23] The ITS approximates the thermodynamic temperature scale as closely as is technically and practically possible by defining the temperatures for a set of fixed points and by specifying the means for interpolation between those fixed points. *Fixed points* are temperatures that can always be reproduced, usually the temperatures at which phase transitions occur. The ITS is maintained in the United States at the National Institute of Standards and Technology (NIST). Differences between the thermodynamic temperature scale and ITS-90 are 0.020 K at 373 K and 0.150 K at 903 K.[23]

Other laboratories may send a thermometer (usually a platinum resistance thermometer) to NIST for calibration on the ITS-90, and then use that *working standard* to calibrate still other thermometers. Such a calibration can cost $1000 or more. Most companies which make and sell thermometers maintain such secondary standards, with which they can perform calibrations traceable to NIST.

For most scientific laboratories, the best procedure is to acquire a thermometer calibrated to the accuracy needed for that laboratory, either by purchasing a calibrated thermometer or by sending a thermometer to NIST for calibration. Once calibrated, the thermometer should be regularly checked for shifts or drifts in its calibration by measuring a fixed point. The most reliable of such fixed points is the triple point of water, which can be reproduced to better than 0.001 K. Triple point cells are commercially available (Hart). However, triple point measurements are not made without difficulty.[9] It is much easier to use the ice point as the fixed point. The temperature at which ice and water coexist at one atmosphere of pressure is 273.15 K and can be reproduced in most laboratories to 0.002 K. Distilled water is first degassed by several cycles of freezing it, evacuating the gas above it, and then remelting it. The ice point can then be achieved by mixing distilled, degassed water with small pieces of ice made from distilled, degassed water, and then continuously stirring the resultant slurry while the temperature measurement is made. NIST[40] sells fourteeen other phase transition fixed point cells ranging from –235 to +1235 K, including the tin freezing point (505.078 K) and the mercury triple point (234.316 K), and also sells six superconductive fixed-point devices for temperatures between 0.5 and 9.2 K. The prices range from $100 to $1000 per cell. In addition, many fixed-point cells are now commercially available (Hart).

Other thermometers can be compared with the working standard by placing both in a temperature-controlled environment (see Section 7.2; also see calibration systems from Cole-Parmer), close together, and under the same conditions at which the working standard was calibrated. The temperature is then varied over the range of interest, and measurements are made on the working standard and on the thermometer under calibration. The temperature is taken from the working standard, and an appropriate equation (see previous sections) is fitted to the thermometric property of the second thermometer as a function of temperature. Keep in mind E. B. Wilson's admonition that "An experimenter of experience would as soon use calibrations carried out by others as he [or she] would use a stranger's toothbrush."[41]

7.2 THE CONTROL OF TEMPERATURE

We will first consider cases for which the temperature is to be controlled at a single fixed value. Usually such cases require only rough control, to a degree or two. For example, we may want a trap that will condense one vapor, but not others, in a vacuum system. Precise control at fixed temperatures would be required for thermometer calibrations with fixed points (see Section 7.1.6). We will also consider the control of temperature over a range, within which any value may be selected. We will discuss how to achieve such control at various levels of precision.

7.2.1 Temperature Control at Fixed Temperatures

Control at fixed temperatures is most easily achieved at points of phase equilibrium.[7,8] For example, the point at which the solid, liquid, and gas phases of a pure substance coexist (the triple point) has a completely determined pressure and a completely determined temperature. Triple points thus make excellent temperature reference points, with accuracies of about 0.001 K. As discussed in Section 7.1.5, several triple points are used to define the ITS. However, since triple points can be difficult to achieve and to maintain, they are not appropriate for temperature control in most laboratories.

The temperatures of vaporization, sublimation, and melting of pure substances are fully determined when the pressure is fixed. These phase transitions are readily achieved and maintained, and are therefore very useful for temperature control. The *eutectic temperature,* the temperature in a two-component mixture at which a liquid solution and both pure solids coexist at a fixed pressure, can also serve as a temperature control point. For all these phase equilibria, the accuracy and stability of the