# TEMPERATURE MEASUREMENT

## 1. Introduction

Historically, temperature measurements were made on empirical scales that simply assigned numbers to temperatures (1,2). These scales were constructed with arbitrarily defined temperatures for calibration points, such as the freezing and boiling points of water. Some convenient temperature-dependent effect, such as the expansion of mercury, was then used to interpolate between the calibration points. The names of Fahrenheit and Celsius are associated with the two best known examples of such scales.

William Thompson, later Lord Kelvin, sought a scale based on physical principles that would give the numbers assigned to temperatures a physical meaning. Following Carnot's observations, Thompson defined temperature in terms of the efficiency of ideal heat engines (3,4) (see also Thermodynamics). He related temperature directly to the heats entering and leaving an ideal heat engine:

$$\frac{Q_\mathrm{C}}{T_\mathrm{C}} = \frac{Q_\mathrm{H}}{T_\mathrm{H}} \tag{1}$$

where $Q_\mathrm{H}$ is the heat flowing into the engine from a hot reservoir at temperature $T_\mathrm{H}$, and $Q_\mathrm{C}$ is the heat flowing out of the engine to a cold reservoir at temperature $T_\mathrm{C}$.

The understanding of heat engines had been complicated by the fact that changes in heat associated with thermal processes were dependent on the path of a process rather than the known state variables representing the endpoints of the process. Clausius observed that one of the consequences of Thompson's definition was that the sum of all of the heats flowing out of a heat engine multiplied by $1/T$ was identically 0 for reversible processes and $>0$ for irreversible processes, ie,

$$\sum_i \frac{Q_i}{T_i} \geq 0 \tag{2}$$

Clausius called the new quantity, $S = Q/T$, entropy, being a sort of transformed energy (from the Greek *trope* meaning transformation). Boltzmann subsequently showed, using statistical arguments, that the entropy of a system is related to the number of ways the constituent atoms and molecules can be arranged into the observed macroscopic state.

The temperature defined by Thompson was still somewhat arbitrarily based on the conceptual device of the ideal heat engine. The mathematician Carathéodory showed that such devices were not necessary (5,6). He showed that in any system where there are irreversible thermal processes, there exists a unique state variable that characterizes the reversibility of a process, and that this variable is proportional to the integral of the heats associated with the process multiplied by a unique "integrating factor". Comparison of Carathéodory's result with equation 2 shows that the state variable is the entropy defined by Clausius and the integrating factor is the reciprocal of the temperature defined by Thompson.

Carathéodory's result leads to a definition of temperature:

$$\frac{1}{T} = \frac{dS}{dU} = k\frac{d\sigma}{dU} \tag{3}$$

where $U$ is the internal energy of the system, $S$ is the conventional entropy, $k$ is Boltzmann's constant, and $\sigma$ is the entropy according to Boltzmann's statistical definition.

Temperature and entropy are conjugate state variables so that the product, $TS$, characterizes a contribution to the energy of a system in the same way as pressure and volume, or force and distance. For unbound atoms and molecules, temperature is proportional to the mean translational kinetic energy. Thus, unlike the empirical temperature scales, the thermodynamic scale is linear and rational: equal intervals or ratios of temperature correspond to equal differences or ratios of mean kinetic energy, respectively.

The numerical value of Boltzmann's constant is implicitly fixed by the definition of the kelvin (7) promulgated by the Comité International des Poids et Mesures (CIPM) under the Convention du Mètre, the treaty underlying the International System of Units (SI):

> The kelvin, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water. This definition refers to water having the isotopic composition defined exactly by the following amount-of-substance ratios: 0.000 155 76 mole of $^2$H per mole of $^1$H, 0.000 379 9 mole of $^{17}$O per mole of $^{16}$O and 0.002 0052 mole of $^{18}$O per mole of $^{16}$O.

The CIPM also defines the degree Celsius. The zero on the Celsius scale is 273.15 K, and a 1°C interval is identical to a 1 K interval. It is usual to use $T$ (upper case) to represent temperatures on the thermodynamic scale and $t$ (lower case) to represent temperatures on the Celsius scale, so that

$$t = T - 273.15 \tag{4}$$

On the Celsius scale, the temperature of the triple point of water is 0.01°C.

Equation 3 applied to a variety of idealized systems yields thermodynamic relations that can be used to measure temperature. Some of the most commonly used thermodynamic thermometers and the associated thermodynamic relations are listed in Table 1.

## 2. The International Temperature Scales

Thermodynamic temperature measurements are not sufficiently accurate or reproducible to satisfy all trade and scientific needs. Most thermodynamic measurements are also technically difficult and time consuming. For these reasons, the CIPM has, at $\sim$ 20-year intervals, promulgated a series of international temperature scales (ITS). The ITS are empirical approximations to the thermodynamic scale, but are more precise, more reproducible, and more convenient. Through the Convention du Mètre, the ITS have scientific and legal status in almost all nations.

The most recent of the ITS is the International Temperature Scale of 1990 (9), or ITS-90. The scale covers temperatures in the range 0.65 K to the highest temperatures measurable in terms of Planck's blackbody radiation law. In 2000, the scale was extended down to 1 mK by the provisional low temperature scale of 2000 (PLTS-2000) (10). In the core range from $-200$ to 960°C, the ITS-90 is reproducible to $\sim 1$ mK, $\sim 10$ times better than most of the thermodynamic measurements.

Within nations, the ITS-90 is maintained by national measurement institutes; eg, in the United States the National Institute for Standards and Technology (NIST), in the United Kingdom the National Physical Laboratory (NPL), and in Germany the Physikalisch-Technische Bundesanstalt (PTB). The ITS-90, or any of its subranges, can also be realized in any appropriately equipped laboratory, and many companies and research institutes do so. Important practical advice on the realization of the ITS-90 can be found in the booklet *Supplementary Information for the International Temperature Scale of 1990* (11), which is published by the Bureau International des Poids et Mesures (BIPM) and is available on the BIPM website.

The differences between successive ITS, although small, can be important for some applications. For example, the boiling point of water was defined on IPTS-68 to be 100°C exactly; on the ITS-90 it is not defined, but has a measured value of $\sim 99.974$°C. Because of the differences between the various ITS and the thermodynamic scale, and because they have the same name for their units, it is occasionally necessary to distinguish between the various scales. The symbols $T_{90}$ and $t_{90}$ are used for temperatures on the ITS-90, and temperatures on the 1968, 1948, and 1927 scales are similarly denoted. The differences between the successive scales are tabulated in Ref. 11.

The CIPMs Consultative Committee on Thermometry regularly reviews thermodynamic temperature determinations and measurements of $T-T_{90}$. A summary is shown in Figure 1 (12). Although the uncertainties in the thermodynamic measurements are comparable to the measured differences, three trends are emerging. First, in the temperature range $\sim 150$ K, the ITS-90 appears to be high by $\sim 12$ mK. Second, in the temperature range between 200 and 360 K, there appears to be a linear difference between $T$ and $T_{90}$, with a maximum error of perhaps 10 mK at 360 K. Between 600 and 1200 K there is a consistent, probably quadratic, divergence between the two scales.

## 3. The International Temperature Scale of 1990

The ITS-90 is based on three components:

1. Fixed points: These are apparatus for realizing the melting, freezing or triple points of various specified pure substances. Each point is highly reproducible and is assigned a temperature that is believed to be close to the thermodynamic temperature of the point.
2. Thermometers: These are highly reproducible thermometers of four types: helium vapor pressure thermometer, helium gas thermometer, platinum

resistance thermometer, and radiation thermometer. Each thermometer has a defined temperature range.

3. Equations: Defined equations are used to convert the thermometer readings to temperature. Where there are free parameters in the equations, the thermometer readings at specified fixed points are used to determine the parameter values. The equations have been chosen to ensure a close match to thermodynamic temperature and continuity of the first derivative of $T_{90}$ with respect to $T$. (13)

PLTS-2000 defines the temperature in terms of the melting pressure of helium. Within the PLTS-2000 temperature range, helium exhibits four natural features that may be used as fixed points for the calibration of the pressure transducer.

Figure 2 summarizes the fixed-point temperatures, the thermometers, and the ranges of the equations for both the ITS-90 and the PLTS-2000.

## 4. The Triple Point of Water

The triple point of water is the one point that the thermodynamic scale and the ITS-90 have in common, and can easily be realized with an accuracy of better than 0.5 mK. Typical water triple-point cells are made of borosilicate glass with constructions as shown in Figure 3. The cells include a reentrant well that enables the thermometer to be immersed sufficiently to eliminate heat leakage effects. The cell is almost filled with very pure water of known isotopic composition. Ideally, the space above the water contains pure water vapor, which at the triple-point temperature has a pressure of $\sim 612$ Pa.

Because of its simplicity and accuracy, the water triple point enables simple confidence-building checks on the condition of a laboratory's thermometers. For most types of thermometer, any undesirable change in condition is normally manifest at all temperatures, and therefore unexpected changes or instabilities can be detected at the water triple point. Conversely, if the thermometer reading is unchanged at the water triple point, it is likely to be unchanged at other temperatures. For this reason alone, any laboratory requiring highly confident or accurate temperature measurement should be equipped to realize the triple point of water. The cost of purchasing a triple-point cell is comparable to the cost of recalibrating a standard platinum resistance thermometer, and a triple-point check may eliminate the need for recalibration. If accuracies of no better than 2 mK are required, the lower cost ice point (14,15) may prove to be a satisfactory alternative.

To prepare the triple-point-of-water cell for use, a mantle of ice is frozen onto the outer surface of the thermometer well. A common method is to fill the well with crushed dry ice until a good thickness of ice has formed. The mantle should then be allowed to anneal for a few days. Once prepared, the thermometer well is filled with water to just below the water level within the cell. This will later serve to enhance the heat transfer between the cell and the thermometer. The cell is then stored in crushed ice or a temperature controlled water bath near 0.01°C, and can be maintained in a usable condition for several months.

When used to calibrate a thermometer, a thin layer of ice is melted around the thermometer well by placing a warm (room temperature) metal rod in the water within the well. The water film should allow the mantle to float freely as the cell is gently rotated. The thermometer is then in close thermal contact with, and completely surrounded by, a water–ice interface. Strictly, the triple-point temperature is realized only at the surface of the water where all three phases of water are present. The temperature at the water–ice interface below the surface of the water is determined by the melting point, which is sensitive to pressure. The temperature measured within the thermometer well must therefore be corrected according to

$$T_{\mathrm{meas}} = 273.16\mathrm{K} - h \times 0.73\mathrm{mK/m} \tag{5}$$

where $h$ is the depth of the thermometer sensing element below the surface of the water of the cell. The hydrostatic-head correction in most cells is ~200–250 μK. With modest care and the hydrostatic correction applied, the triple point can be realized easily within ~500 μK. If the cell contains water of the highest purity and little air, the ice is fully annealed, isotopic corrections are applied, and care taken to avoid some minor effects, the triple point can be realized with an accuracy of ~50μK. A full description of the technique for using triple-point-of-water cells may be found in Ref. 11. Less detailed information is readily available in Refs. 16, 17 and usually also in the cell manufacturer's literature.

## 5. Other Useful Fixed Points

In addition to the triple point of water, there are many other fixed points that may be used to calibrate or check thermometers. Table 2 lists those employed by the ITS-90. These are points for which the temperature, $T_{90}$, is defined and their properties are such that the points can be readily realized at accuracies approaching or exceeding 1 mK. The substances used in the ITS-90 fixed-points should be better than 99.9999% pure by weight.

There are also a large number of fixed points for which the temperature has been measured to high accuracy. Table 3 summarizes those in the range 100–2000 K along with the required purity of the material and an estimate of the uncertainty of the temperature, $T_{90}$, of the point. A full list of these secondary points with bibliographic references to descriptions of the realizations is in Ref. 19 and is available on the BIPM website.

An important class of fixed points is the freezing points of high purity metals. There are several within the temperature range from 0 to 1100°C, they are generally very reproducible, use a similar apparatus for realization, and many are commercially available. As solid–liquid equilibria, they are pressure dependent, but this dependence is small (see Table 2 for examples) and pressure effects can be corrected with negligible uncertainty.

As shown in Figure 4, the metal is contained in a crucible of high purity graphite. The assembled fixed-point cells may be sealed or open. Open cells have the filled crucible contained within a long fused-silica (quartz) tube that also contains various layers of thermal insulation, thermal shunts, and radiation shields. An additional fused-silica thermometer well extends from the cell cap into the graphite thermometer well. When open cells are used, the air is evacuated and replaced with an inert gas, such as argon. Sealed cells are simply the filled crucible enclosed in a fused-silica envelope filled with inert gas at 101.325 kPa (1 atm) at the freezing temperature of the metal. In use, the sealed cell is placed in a second tube, often Inconel®, which contains all of the insulation, shunts, radiation shields, and thermometer guide. Sealed cells are generally treated as secondary points requiring calibration because, once sealed, the gas pressure is not measurable. Open cells, on the other hand, carry an increased risk of contamination of the metal.

To perform calibrations with fixed-point cells, the cells are heated in vertical tube furnaces with the central zone of the furnace (containing the crucible) uniform to ~ 0.1 K or better. The metal is first melted by setting the furnace temperature a few kelvin above the melting temperature. As the temperature of the metal increases, the onset of melting is indicated when the monitoring thermometer in the fixed-point cell indicates a constant temperature as the heat of transition is taken up by the melting metal (see Fig. 5). When the melt is complete, the temperature continues to increase to the furnace setpoint. After some time, the furnace is set to ~ 1 K below the freezing temperature. The monitoring thermometer usually indicates a small supercool as the temperature falls below the freezing point. Once the temperature falls sufficiently to ensure nucleation, crystallization occurs, heat of transition is released, and the temperature rises to the freezing point. At this point, there is a layer of crystalline metal on the inside of the outer wall of the crucible. In most fixed-point procedures, a second crystalline layer is formed on the inner-wall (thermometer well) by inserting cold metal or fused-silica rods into the thermometer well. This two-layer nucleation procedure ensures a more uniform temperature around the thermometer and almost equilibrium conditions for the inner solid–liquid interface.

For most metals, both the melting and freezing points can be used to calibrate thermometers. However, the beginning of the freeze plateau is generally more reproducible, more amenable to modeling of impurity effects, and less dependent on past thermal treatment of the cell. For this reason, most of the ITS-90 metal fixed points are defined as freezing points.

The detailed procedures for achieving a satisfactory fixed-point realization are dependent to some degree on the thermophysical properties of the metal. Tin, for example, supercools at ~ 20 K, which requires removal of the cell from the furnace for a short period. When properly realized, most of the ITS-90 points should settle very quickly to a stable temperature that can be maintained within 1 mK for 10 h or more. For the best results consult Ref. 11, the references accompanying Ref. 19, or the manufacturer's guidelines. Some experimentation may be required to fine tune the procedure.

## 6. The ITS-90 Platinum Resistance Thermometer Range: 13.8033–1234.93 K

The standard platinum resistance thermometer (SPRT) subranges of the ITS-90 are the most important of the ITS-90 subranges and the easiest to realize. Three basic SPRT designs are used to cover the range from 13 to 1234.93 K (961.78°C):

- Capsule SPRTs are small, typically mounted within a platinum sheath 50–60 mm long by 5-mm diameter. The lead wires are usually 30–50 mm long and mounted in a glass seal at one end of the capsule. The SPRTs have a triple-point resistance, $R$(273.16 K), of ~25.5 Ω and are used from 13 K to a maximum of 430 K (156°C).
- Long-stem SPRTs are typically 450 mm long with a tubular sheath of ~8-mm diameter. The sheath is normally glass or fused-silica, although more robust stainless-steel sheathed thermometers are readily available. The platinum sensing element is ~30–50 mm long and mounted on a former in one end of the tube. The lead wires to the sensor are connected via a glass seal at the other end of the tube, usually through a handle to flexible leads (see Fig. 6). They have $R$(273.16 K) of ~25.5 Ω and may be used from ~84 K (−190°C) to 933 (660°C).
- High temperature long-stem SPRTs usually have a fused silica sheath, are 600 mm long, and have an $R$(273.16 K) value $< 2.5\,\Omega$ to minimize electrical leakage problems at high temperatures. They are typically used from 0 to 962°C.

The sensing elements of SPRTs are made from very pure, and therefore very soft, platinum wire mounted delicately on an insulating former (see Fig. 6). This construction prevents thermal expansion and contraction from straining the wire, but makes the thermometers very fragile and susceptible to mechanical shock and vibration. Long-stem SPRTs require occasional annealing at 450°C or higher to maintain the SPRT in a strain-free condition. Capsule SPRTs cannot be annealed.

The resistance–temperature relationship for SPRTs is remarkably linear over the temperature range from −200 to 960°C. The average temperature coefficient over the range 0–100°C is $\sim 0.003\,925\,^\circ\mathrm{C}^{-1}$ giving the 25.5-Ω thermometers a sensitivity of ~0.1 Ω/°C. There is also a weak quadratic temperature dependence so that the sensitivity falls slightly with increasing temperature.

The mathematical definition of $T_{90}$ in terms of the SPRT resistance involves extensive calculations best carried out using a computer. A short summary is presented here and the full details are in the ITS-90 definition (9) available on the BIPM website. First, the resistance ratio is calculated as

$$W(T_{90}) = \frac{R(T_{90})}{R(273.16K)} \tag{6}$$

where $R(T)$ is the resistance of the SPRT at temperature $T$, and $R$(273.16 K) is the resistance of the SPRT at the triple point of water. The selection criteria imposed by the ITS-90 ensure that SPRTs all have a very similar $W(T_{90})$ relationship.

To compensate for the slight differences in the $W(T_{90})$ behavior of different SPRTs, each SPRT is used to interpolate between reference resistance ratios, $W_\mathrm{r}$, defined for each fixed point (see Table 2 for the defined $W_\mathrm{r}$ values). The SPRT interpolations all have the form

$$W_\mathrm{r}(W) = W - \Delta W(W) \tag{7}$$

where the deviation functions, $\Delta W(W)$, are typically polynomials in $W-1$ and/or $\ln(W)$. There are 8 different equations used to cover the 11 different SPRT subranges (see Fig. 2). The multiple subranges enable flexibility and reduction of the cost of SPRT calibrations for different applications.

Finally, once the $W_r$ value has been calculated, the temperature is calculated using a defined $W_r(T_{90})$ function. The function is defined in two segments, one for temperatures $< 0.01°\mathrm{C}$ and one for temperatures $> 0°\mathrm{C}$.

The absolute accuracy of SPRT measurements is generally limited by the performance of the SPRTs (11). Over most of the 13 K–960°C range, accuracies of a few millikelvin are relatively easy to achieve. Accuracies of $> 2\,\mathrm{mK}$ require great care.

The variations between temperatures measured by different SPRTs give rise to an ambiguity in the ITS-90 known as nonuniqueness. Similar uncertainties arise from the propagated uncertainty in the realizations of the fixed points. The uncertainty due to nonuniqueness ranges from a few tenths of a millikelvin near 0°C to as much as 1 mK at temperatures between 660 and 960°C.

In the range from 0 to 600°C, pure platinum exhibits oxidation effects giving rise to hysteresis of up to 2 mK or so. The resulting uncertainties can be reduced significantly with appropriate measurement procedures and careful thermal treatment of the SPRT.

Accurate resistance thermometry requires accurate resistance measurements. For example, measurements at the level of 1 mK for a 25.5 Ω SPRT require resistance measurements accurate to $\sim 100\,\mu\Omega$ ($\sim 4$ parts in $10^6$ of the resistance at 0°C). There are many commercial resistance thermometry bridges available for this purpose with accuracies well in excess of this requirement. They all measure using an alternating sensing current [either sinusoidal or switched direct current (dc)] to eliminate thermoelectric effects, and use a four-wire measurement technique to eliminate the effects of lead resistances. Some resistance bridges have a resolution of $< 10\,\mu\mathrm{K}$, which is useful for measuring small temperature differences and comparing fixed points.

In the process of measuring the resistance of the SPRT, a sensing current must be passed through the sensing element. This leads to a small temperature rise of between 0.3 and 5 mK depending on the temperature, the sensing current, the resistance of the SPRT, the construction of the SPRT, and the thermal conductivity of the environment around the SPRT. This “self-heating” effect is usually corrected by making measurements at two currents and extrapolating the resistance measurement to zero current. Otherwise SPRTs must be used and calibrated with the same sensing current and under the same thermal conditions. Detailed guidance on the use of SPRTs can be found in Ref. 11.

## 7. Industrial Platinum Resistance Thermometry

The delicate construction and high cost of SPRTs makes them unsuitable for most industrial and some laboratory applications. The alternative is so-called industrial platinum resistance thermometers (IPRT), also known as RTDs (resistance temperature detectors) or Pt100s (100-Ω platinum thermometers).

Industrial resistance thermometers are usually made of platinum wire of lower purity than SPRTs to reduce oxidation effects and sensitivity to impurity effects. The alloyed wire is also less sensitive to mechanical shock and vibration. Copper, nickel, and some nickel alloys are also used instead of platinum for some specific applications. The sensitive element is usually a wound coil mounted onto or within a ceramic substrate, and often the individual turns of wire are partially or fully fixed in place by some means. Glass is occasionally used both as a coating and as a substrate, but differences in the temperature coefficients of expansion and the imperfect insulating properties of glasses at high temperatures limit its use. These forms of mechanical protection stabilize the sensing element against resistance changes caused by vibration and shock. However, this robustness is achieved at the expense of hysteresis arising from the wire movement and strain generated by the differential coefficient of expansion of the wire and substrate. Thus, for most IPRT designs there is a compromise between robustness and accuracy. The best partially supported IPRTs have hysteresis $< 1\,\text{mK}$ and some of the more robust fully supported types may exhibit hysteresis of $> 0.2\,\text{K}$ when cycled over wide temperature ranges.

Some IPRTs are also manufactured using thick-film techniques. These have the advantage of small size, fast response, and low hysteresis, but can depart significantly from expected resistance–temperature characteristics because of the strain arising from the differential thermal expansion of the platinum film and the substrate to which the film is bonded. They may also have a reduced temperature range and be less stable in long-term applications.

IPRTs are generally smaller than SPRT elements and may be as small as 2-mm square and as large as $20 \times 100\,\text{mm}$. Most are $\sim 2\,\text{mm}$ in diameter and 25 mm long. They are available with various nominal $R(0^\circ\text{C})$ values ranging from 25 to 2000 Ω with the 100-Ω models being the most common. They are available as unsheathed elements or in a wide variety of sheaths and enclosures, both standard and custom. They are relatively inexpensive with a cost comparable to that of metal-sheathed base-metal thermocouples, although the very low hysteresis versions suitable for high accuracy laboratory applications can be more expensive. The normal operating range for stainless steel sheathed IPRTs is about−50–250°C. With appropriate construction of the sheath and choice of sensing element, this can be extended to −200–850°C.

The resistance–temperature characteristics of IPRTs are usually defined by national or international documentary standards. In recent years many, but not all, of the standards have been harmonized and the most common standards (eg, 20,21) define the resistance–temperature characteristic as

$$R(t) = R(0^\circ\text{C})(1 + At + Bt^2) \tag{8a}$$

for the temperature range 0–850°C, and

$$R(t) = R(0^\circ\text{C})(1 + At + Bt^2 + Ct^3(t - 100)) \tag{8b}$$

for temperatures in the range −200–0°C. The nominal values of the coefficients in the equations are

$$A = 3.9083 \times 10^{-3}\,^\circ\text{C}^{-1}$$

$$B = -5.775 \times 10^{-7}\,{}^{\mathrm{o}}\mathrm{C}^{-2}$$
$$C = -4.183 \times 10^{-12}\,{}^{\mathrm{o}}\mathrm{C}^{-4}$$

Commonly, IPRTs are classified according to their temperature coefficient, often called the alpha value:

$$\alpha = \frac{R(100^{\mathrm{o}}\mathrm{C}) - \mathrm{R}(0^{\mathrm{o}}\mathrm{C})}{100 \times R(0^{\mathrm{o}}\mathrm{C})} \tag{9}$$

which is both a measure of the purity of the wire and the average temperature coefficient between 0 and 100°C. The most common IPRTs have a nominal alpha value of $0.003\,85^{\circ}\mathrm{C}^{-1}$. Higher grade IPRTs have nominal alpha values of 0.003 916, 0.003 920, or $0.003\,925^{\circ}\mathrm{C}^{-1}$, the latter value being for wire suitable for use in SPRTs.

In general, manufacturers do not report the calibrations of individual sensors, but instead publish tables of resistance versus temperature with a variety of tolerance classes. A typical tolerance statement for the lowest grade IPRTs is

$$\text{Deviation from nominal } \leq \pm\,(0.3 + 0.005|t|)^{\mathrm{o}}\mathrm{C} \tag{10}$$

Tighter tolerances are readily available.

When IPRTs are calibrated, it is usual for the calibrating laboratory to measure $R(t)$ for the thermometer over the temperature range requested by the customer, and then determine the exact values of the $A$, $B$, and $C$ coefficients (equation 8) for the thermometer. The highest quality IPRTs calibrated in this way and restricted to a total temperature range of $< 200^{\circ}\mathrm{C}$ can achieve uncertainties $< 5\,\mathrm{mK}$. For higher accuracy or wider temperature ranges, better equations are required. Often equation 8a is extended from the quadratic form to cubic or quartic form, and for the best accuracy the ITS-90 SPRT equations are often used.

Sheathed IPRTs are usually supplied with two, three, or four lead wires depending on the resistance measurement method employed. Figure 7 shows the different electrical connections to the sensing element for the different methods. With two-wire IPRTs, which are very common, the resistance of the two lead wires is indistinguishable from that of the sensor. Two-wire measurements are therefore susceptible to errors of $\sim 2.5^{\circ}\mathrm{C}$ for every ohm of lead resistance (for 100-Ω sensors). Usually indicating instruments can be adjusted to compensate for the error, but the overall accuracy is limited to a few tenths of a degree (for a 100-Ω sensor). For IPRTs with a high $R(0^{\circ}\mathrm{C})$ value, the effect is reduced proportionally.

The ideal resistance measurement method uses four lead wires. The sensing current is passed through two of the leads and the voltage across the sensor is measured using the other two leads (Fig. 7b). This method eliminates the lead-resistance errors and is used universally for high accuracy laboratory measurements and occasionally for industrial measurements.

Three-wire resistance measurements are a common industrial compromise between the two- and four-wire methods. In this method, the voltage drop across one of the lead resistances is measured and used to compensate for the other. This requires matching of the two lead resistances to be effective, but the method is useful where there are long cable runs between the instrumentation and the sensor.

Nearly all industrial IPRT instruments and most laboratory instruments use a dc sensing current. The accuracy of the measurements is generally limited to $\sim 0.02^{\circ}$C due to stray thermoelectric effects, and offsets in the instrumentation. These effects may be eliminated by using an alternating current (ac) sensing current: either a switched dc current, or a true sinusoidal ac current. Alternating current measuring instruments are generally more expensive than dc instruments.

The main contributions to uncertainties in temperatures measured using IPRTs are hysteresis, self-heating due to the sensing current, drift due to mechanical shock and migration of impurities, and propagated uncertainties from the calibration. For detailed guidelines on the calibration and use of IPRTs refer to the booklet *Techniques for Approximating the International Temperature Scale of 1990* (14) published by the BIPM and available on the BIPM website. Additional information on IPRTs can also be found in Ref. 17 and in the manufacturers' literature.

## 8. Thermistor Thermometry

NTC-thermistors are ceramic semiconducting devices that exhibit a negative temperature coefficient of resistance. They have the advantages of smaller size, faster response, and higher sensitivity than platinum resistance thermometers. The disadvantages are high nonlinearity, relatively high self-heating effects due to the sensing current, and a limited temperature range. At one time, thermistors also had the reputation of being unstable. Nowadays, glass-bead thermistors are available for use $< 100^{\circ}$C with long-term drifts $< 1$ mK/year.

The resistance–temperature characteristic of thermistors is usually written in the form

$$R(T) = R(T_0)\exp\left[\beta\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{11}$$

where $T_0$ is some convenient reference temperature, often 298.15 K (25°C). The parameter $\beta$ is a characteristic of the thermistor material with typical values in the range 2000–6000 K. The nominal resistance values are determined by the $R(25^{\circ}\mathrm{C})$ value, which typically ranges from $\sim 100\,\Omega$ to $1\,\mathrm{M}\Omega$, with the most commonly used values in the 1–50 k Ω range.

The sensitivity, $S$, of the thermistor is given by

$$S = \frac{1}{R}\frac{dR}{dT} = \frac{d\ln R}{dT} = -\frac{\beta}{T^2} \tag{12}$$

with typical values about $-4\%/^{\circ}$C. That is, thermistors are $\sim 10$ times more sensitive to temperature than platinum resistance thermometers (the $S$ for

IPRTs is ~0.4%/°C). The high sensitivity makes thermistors useful for applications such as precision temperature controllers and differential thermometers.

A variety of calibration equations have been used for thermistors, including equation 11. For higher accuracy, an extended series expansion of equation 11 in terms of the logarithm of resistance has proven to be the most useful:

$$\frac{1}{T} = A_0 + A_1 \ln(R/R_0) + \cdots + A_{N-1}[\ln(\mathrm{R}/\mathrm{R}_0)]^{N-1} \tag{13}$$

where $N$ is the number of terms in the series, and $R_0$ is a convenient reference resistance for the measurement, eg, $1\,\Omega$ or $1\,\mathrm{k}\Omega$. The equation is most commonly used with up to four terms ($N = 4$). Equation 13 has the advantage over other calibration equations of giving temperature directly from the measured resistance as well as being linear in the coefficients, and hence amenable to least-squares fits and uncertainty analysis. Figure 8 summarizes the performance of the various versions of equation 13.

Thermistor manufacturers often recommend a three-term variation on equation 13 with $A_3 \neq 0$ and $A_2 = 0$, called the Steinhart-Hart equation. However, the performance of this equation is less predictable than equation 13, sensitive to the choice of $R_0$ and the value of $R(25°\mathrm{C})$, and not always as accurate as the normal three-term version of equation 13.

The high sensitivity of thermistors comes at the price of high nonlinearity and a wide range of resistance values for modest changes in temperature. A wide variety of measurement circuits have been developed to linearize thermistor responses, including simple one-resistor circuits (22), which are good over ranges of 10°C or so; multiple thermistor and resistor circuits (23) for ranges up to 100°C; solutions based on antilog amplifiers or threshold oscillator circuits; and digital approaches using equation 13 or look-up tables. In general, the most accurate and wide-range measurements involve direct measurement of the thermistor resistance, eg, using digital multimeters and calibration using equation 13 with $N = 4$.

The main factors contributing to uncertainties in temperature measurements using thermistors are propagated uncertainties from the calibration, hysteresis, lead resistances, insulation resistance effects, and self-heating due to the sensing current. For additional information on the use and calibration of thermistors, refer to Ref. 14.

## 9. The ITS-90 Radiation Thermometer Range: 1234.93 K Upward

All objects emit electromagnetic radiation with a spectral distribution and intensity largely determined by the temperature of the object. The amount of radiation emitted is characterized by the spectral radiance of the surface, which is the energy emitted per unit area, per unit wavelength, per unit solid angle. For a blackbody, a perfect emitter and absorber of radiation, the spectral radiance is given by Planck's blackbody radiation law:

$$L_{\mathrm{b}}(\lambda, T) = \frac{c_1}{\lambda^5}\left[\exp\left(\frac{c_2}{\lambda T}\right) - 1\right]^{-1} \tag{14}$$

where $\lambda$ is the wavelength of the radiation in a vacuum, $T$ is the temperature of the object, and $c_1$ and $c_2$ are known as the first and second radiation constants. Planck's law is plotted in Figure 9 for a few temperatures in the range 300–5800 K.

Real surfaces emit less radiation than predicted by Planck's law by a factor called the spectral emissivity, which is the ratio of the spectral radiance of the object to the spectral radiance of a blackbody at the same temperature:

$$\varepsilon(\lambda) = \frac{L(\lambda, T)}{L_b(\lambda, T)} \tag{15}$$

By definition, the emissivity of materials ranges between 0 for perfect reflectors and 1.0 for blackbodies.

Radiation thermometers infer an object's temperature from measurements of spectral radiance made using a radiometer, as shown in Figure 10. The key elements of the radiometer are the two stops that define the geometric parameters of the radiometer, and the optical filter and detector that define the optical bandwidth and electrical properties. The objective lens ensures the image projected onto the field stop is in focus so that the field is well defined, and the relay lenses ensure that all of the radiation passes through the filter at the same angle. Not shown in the diagram is the temperature control system used to stabilize the response of the filter and detector. Good quality radiometers are available commercially. For an opaque object free of reflections, the signal from the radiometer, $S(T)$, is

$$S(T) = \int_0^\infty \varepsilon(\lambda) R(\lambda) L_b(\lambda,\, T)\, d\lambda \tag{16}$$

where $R(\lambda)$ is the spectral responsivity of the radiometer, which characterizes the electrical and optical response of the radiometer to radiation of different wavelengths.

Above the freezing point of silver, 1234.93 K (961.78°C), $T_{90}$ is defined by a relationship based on Planck's blackbody radiation law:

$$\frac{L_{\mathrm{b}}(\lambda,\, T_{90})}{L_{\mathrm{b}}(\lambda,\, T(90)(X))} = \frac{\exp[c_2/(\lambda T_{90}(X))] - 1}{\exp(c_2/\lambda T_{90}) - 1} \tag{17}$$

where $L_{\mathrm{b}}(\lambda,\, T_{90})$ and $L_{\mathrm{b}}[\lambda,\, T_{90}(\mathrm{X})]$ are the spectral radiance of a blackbody at wavelength $\lambda$ (in vacuum) at $T_{90}$ and at $T_{90}(X)$, respectively. The temperature $T_{90}(X)$ refers to the silver freezing point $T_{90}(\mathrm{Ag}) = 1234.93\,\mathrm{K}$, the gold freezing point $T_{90}(\mathrm{Au}) = 1337.33\,\mathrm{K}$ (1084.18°C), or the copper freezing point $T_{90}(\mathrm{Cu}) =$ 1357.77 K (1084.62), and $c_2 = 0.014388\,\mathrm{mK}$ is the second radiation constant.

Equation 17 defines temperature assuming an idealized monochromatic radiometer. However, practical radiometers operate over finite bandwidths, typically of the order of 10–100 nm. Determination of temperature using equation 17 therefore requires the solution of the integral equation obtained by replacing the left-hand side of equation 17 with the ratio of the integrals given by equation 16 with $\varepsilon(\lambda) = 1.0$. The exact solution requires numerical integration and iteration. An alternative and simpler approach is based on the use of the Sakuma-Hattori interpolating equation:

$$S_{\mathrm{b}}\left(T\right) = C\left[\exp\left(\frac{c_2}{AT + B}\right) - 1\right]^{-1} \tag{18}$$

which approximates the thermometer response to a blackbody using a function similar to Planck's law. For radiometers with a sufficiently narrow spectral bandwidth (24, 25), the parameter $C$ is determined from the measured radiance at the fixed point, and the parameters $A$ and $B$ are calculated directly from the measured spectral responsivity.

Equation 18 is also commonly used to calibrate radiation thermometers for use $< 960^{\circ}$C. In this case, three fixed points are used to determine all three parameters, and no measurements of spectral responsivity are required. There are many commercial fixed-point blackbody sources available for this purpose. The recent development of metal–carbon eutectic fixed points in the range 1100–3400°C (26) promises a similarly simple calibration procedure for radiometers used at high temperatures.

The calibration of radiation thermometers is dependent on the availability of blackbodies. Since all radiation falling on a surface must be absorbed, reflected, or transmitted, it follows that the spectral emissivity (equal to absorptance), reflectance, and transmittance sum to 1.0:

$$\varepsilon(\lambda) + \rho(\lambda) + \tau(\lambda) = 1.0 \tag{19}$$

It follows also that objects with an emissivity of 1.0 must be opaque and have zero reflectance. Practical blackbodies are therefore not surfaces, but cavities that trap and absorb radiation. Figure 11 shows a simple schematic example. If it is assumed that the reflections within the cavity are diffuse and the cavity walls are uniform in temperature, then the effective emissivity of the cavity is approximately

$$\varepsilon_{\mathrm{eff}} = 1 - \left(1 - \varepsilon_s\right)\frac{r^2}{R^2} \tag{20}$$

where $\varepsilon_s$ is the intrinsic emissivity of the cavity material, $r$ is the radius of the aperture, and $R$ is the depth of the cavity.

Fixed-point blackbodies are typically made from graphite, which has an emissivity of $\sim 0.9$, and may be up to 100-mm deep with apertures ranging from 1–6 mm diameter. This yields effective emissivities better than 0.999. The cavity is manufactured as an integral part of a graphite crucible containing the fixed-point metal, and the melt or freeze plateaus last for 10–20 min.

All radiation thermometers are designed to detect radiation from a well-defined field of view. Invariably, however, minor distortions and scattering in the optical system lead to the boundaries of the field becoming blurred. This results in so-called size-of-source effects; ie, the temperature reading depends on the size of the object being viewed. This effect is one of the major sources of uncertainty in all radiation thermometry.

The measurements used to characterize and calibrate the ITS-90 radiometers are demanding. If the operating band is in the 550–1600 nm range, which is typical of modern radiometers, the relative spectral responsivity of the radiometer must be measured with a wavelength accuracy of $\sim 0.02\,\mathrm{nm}$. Signal ratios of the order of $10^4$ must be measured, and linearity corrections to the radiometer response are essential. At best, radiation thermometry has an uncertainty of 50 mK at the silver point (~960°C). Uncertainties in measurements at other temperatures tend to scale as $T^2$.

Detailed descriptions of the procedures for calibrating radiation thermometers, including information on all sources of uncertainty in the realization of the ITS-90 radiation thermometer subrange can be found in Refs. 11, 27. References 3, 4, 28 provide good theoretical background and advice.

## 10. Industrial Radiation Thermometry

The practical use of radiation thermometers exposes the measurements to a variety of additional sources of error. Because the object of interest is external to the radiometer, radiance measurements may be affected by reflected radiation from other objects, radiation loss, or gain due to scattering and size-of-source effects, and absorption or emission in the atmosphere between the target and radiometer. The temperature error, $\Delta T_{\mathrm{m}}$, in any measurement due to error $\Delta S(T)$ in the measured radiance is approximately

$$\Delta T_{\mathrm{m}} = \frac{\lambda T^2}{c_2}\frac{\Delta S(T)}{S(T)} \tag{21}$$

This shows that the errors tend to scale as $T^2$. Additionally, the accuracy of thermometers increases with decreasing operating wavelength and, for most applications, the shortest practical operating wavelength should be chosen. For applications near room temperature, thermometers with a responsivity centered on 10 μm are common. For temperatures $> 600°\mathrm{C}$ wavelengths of 1 μm or less are more practical. In most applications, a 1% error in the radiance measurement gives rise to a 0.5–2°C error in the temperature measurement: 1°C for each 1% error is a good rule-of-thumb.

In almost all practical applications, the first problem is to determine the emissivity, $\varepsilon$, of the surface. The temperature can then be inferred from

$$S(T) = \varepsilon S_{\mathrm{b}}(T) \tag{22}$$

where $S(T)$ is the measured signal, and $S_{\mathrm{b}}(T)$ is the calibration equation giving the signal expected from a blackbody at the same temperature. Most commercial radiation thermometers have a facility for making the emissivity compensation implied by equation 22. The values of emissivity for real materials vary between 0.05 and 0.95 depending on the material and surface condition. It is usually necessary to estimate the emissivity from published data, the thermometer manufacturer's tables, or experiment, all of which may be subject to uncertainties of 0.05 or more. This uncertainty in emissivity results in uncertainties in temperature of between 2–20°C depending on operating wavelength, temperature, and emissivity. Care must be taken because the emissivity of some materials is strongly wavelength dependent and visual appearance is misleading. Ice and glass, eg, are opaque and have an emissivity of $\sim 0.96$ at long wavelengths. In some applications natural blackbody cavities, eg, bolt holes, cracks, or empty containers, can be exploited to reduce the uncertainty in emissivity.

Reflections due to radiation from other hot objects lead to an increase in the measured radiance:

$$S(T) = \varepsilon S_{\mathrm{b}}(T) + (1-\varepsilon)S_{\mathrm{b}}(T_{\mathrm{W}}) \tag{23}$$

where $T_{\mathrm{W}}$ is the effective radiance temperature of the "walls" surrounding the object. Note that for $T_{\mathrm{W}} = T$, the object is enclosed in an isothermal cavity so it behaves as a blackbody ($\varepsilon = 1$). It is common for the measurements to be subject to errors of several degrees and, where the object is heated indirectly in a furnace, the error may be as large as many tens of degrees. Most low temperature (10 μm) thermometers include a reflection correction algorithm, although the manufacturers rarely state this in the specifications or explain the conditions under which it is valid (17). Reflection correction algorithms are also special features of a few commercial high temperature thermometers.

The measurement equation for gas absorption is very similar to that for reflection. When viewing a blackbody through an absorbing gas (or other absorbing medium, eg, a window) the measured signal is

$$S(T) = (1-\alpha)S_{\mathrm{b}}(T) + \alpha S_{\mathrm{b}}(T_G) \tag{24}$$

where $\alpha$ is the absorptance of the intervening gas at the operating wavelength of the thermometer, which increases with path length, and $T_{\mathrm{G}}$ is the temperature of the gas. At some wavelengths air is completely opaque ($\alpha = 1$), so measurement of the object is impossible (see Fig. 12). Most frequently, the absorption is due to water and carbon dioxide vapor, and commercially available spectral-band radiation thermometers are generally designed to avoid these bands. Radiation thermometers operating at 0.9, 1.6, 2.2, 3.9, and 10 μm are the most common. In applications involving other gases or high concentrations of water and carbon dioxide, the effects can be as much as several degrees per meter of path length. If the gas is at the same temperature as the object, the errors are much reduced.

Among the hundreds of commercially available radiation thermometers there are a few designed for specific applications. These include some with narrow spectral bands centered on 3.43 or 7.9 μm. These are used in plastics industries because most plastics have very strong absorption lines (hence high emissivity) at these wavelengths.

Ratio or "two-color" thermometers measure at two wavelengths and use the ratio of the measured radiances to infer temperature. These are useful where the emissivity is unknown or changes during a process, where objects, eg, wires underfill the field of view, or where there is an intervening window. Ratio thermometers have a higher sensitivity to errors than given by equation 21 so should not be the first choice where spectral-band thermometers work well. Multiwavelength thermometers, using more than two wavelengths, should be avoided because the uncertainties increase exponentially with the number of wavelengths used (29). References 4, 17, 28, 30 give more detail on these and other less common radiation thermometers.

Size-of-source effects, due to scattering in the optical systems of thermometers, tend to be larger in industrial radiation thermometers than in the ITS-90 radiometers. The optical components in low temperature thermometers (ie, long wavelength) are particularly susceptible to these problems. The errors typically range between a few tenths of a degree for high quality short-wavelength instruments to many degrees for lower quality long-wavelength instruments. Thermal imaging systems also suffer more from these effects and the errors can be as large as 40°C.

Most commercial radiation thermometers read directly in temperature. The calibration process, therefore, must determine the corrections to readings at different operating temperatures. The calibration source is usually a variable-temperature blackbody cavity, typically a heated, heavily-oxidized-metal sphere or cylinder, with the temperature monitored by a thermocouple, platinum resistance thermometer, or ITS-90 radiometer. The emissivity of these cavities is $\sim 0.99$ and the accuracy of the indicators, which must be independently calibrated, is $\sim 0.1–5$°C.

Radiation thermometers have a reputation of being somewhat erratic in their utility, but this is rarely due to the inherent limitations in the instruments. The problem is generally the operator's lack of familiarity with subtle and counterintuitive effects, such as associated with reflections or absorption. This is often compounded by the very wide range of instruments available, few of which may be suitable for some applications. Most radiation thermometer manufacturers are able to provide advice on specific applications, often supported by application notes, and some conduct regular training courses on practical thermometry. General advice can also be found in Refs. 17, 28.

Further information on the procedures and uncertainties associated with the calibration of spectral-band radiation thermometers can be found in Ref. 14, which is available on the BIPM website.

## 11. Thermocouple Thermometry

Simplicity, wide temperature range, and low cost make thermocouples the most widely used thermometer. Unfortunately, they are also the most misunderstood. Numerous textbooks, scientific papers, and manufacturers' application notes cite the thermocouple junction as the source of the thermocouple voltage, when in fact in a well-designed thermocouple installation the junction contributes nothing to the voltage generated.

The Seebeck effect, which is the basis for the thermocouple, arises from the redistribution of charge that occurs when electrons diffuse and carry heat in response to a temperature gradient. The charge redistribution depends on both the temperature gradient and chemical potential of the electrons in the conductor. It is manifest as a voltage generated wherever heat flows in the conductor, ie, at temperature gradients only. The effect does not require an electrical current to flow.

Figure 13 shows a hydraulic analogue model of a thermocouple wire. Within the fluid in the tube, the pressure is generated where there are gradients in the elevation of the tube. If the fluid within the tube is the same density throughout, then the pressure generated depends only on the elevations of the two ends. Similarly, in any conductor, a thermoelectric voltage is generated only at temperature gradients, and if the conductor is homogeneous (to be explained shortly) the total voltage depends only on the end temperatures.

The equation describing the thermocouple operation is

$$dE = S(T)dt \tag{25}$$

where $dE$ is the differential voltage generated by a section of wire with Seebeck coefficient $S(T)$ at temperature $T$, and exposed to temperature differential of $dT$. In order for the thermocouple voltage to be dependent on the end temperatures only, the Seebeck coefficient, $S(T)$, must be the same for all sections of wire. Such wire is said to be homogeneous. Unfortunately, almost all of the problems with thermocouples arise from localized changes in the Seebeck coefficient due to mechanical, thermal, chemical, metallurgical, and radiological effects. For example:

- A single bend in a Type K thermocouple, located at a temperature gradient, has been observed to cause a 3°C shift in the temperature reading.
- Type K thermocouples operated at high temperatures and deprived of oxygen develop "green rot" due to preferential oxidation of chromium. Prolonged exposure may cause a 30% decrease in the Seebeck coefficient.
- Type K wire cycled between temperatures $< 250°\mathrm{C}$ and $> 550°\mathrm{C}$ will exhibit hysteresis of between 2.5 and 8°C, depending on wire composition and rate of change of temperature.
- The Seebeck coefficient for some Type K wires in normal use increases $\sim 1\%$ for every 1000 h at 1000°C.
- Thermocouple Types R, S, B drift when exposed to a thermal neutron flux due to the transmutation of the rhodium into palladium.

To overcome these difficulties, there are two guiding principles for all thermocouple circuits:

1. Where the wire is exposed to temperature gradients, eg, where the thermocouple passes through a furnace wall, ensure it is protected and maintained in a homogenous condition.
2. Where wire is inhomogeneous, eg, the damaged wire near the junction, ensure it is maintained in an isothermal environment. If there is no temperature gradient there can be no voltage generated.

The first of these principles can be impossible to satisfy in some circumstances. In long-term and high temperature installations particularly, most thermocouples suffer changes in the Seebeck coefficient due to the migration of impurities, chemical changes with oxidation, or metallurgical phase changes. Further, these changes can be localized so that changes in immersion conditions or removal for calibration can change the temperature reading considerably. Where high confidence and/or high accuracy are required, thermocouples should be (*1*) fixed in place, (*2*) calibrated *in situ*, and (*3*) used only for a single installation. The use of separate thermocouples for control and indicator instruments combined with an alternating replacement schedule can provide information on the rate of drift and, hence, the frequency of replacement required to meet tolerances.

The function of the junction in a thermocouple is simply to ensure electrical conductivity between the conductors, and so long as the junction and the damaged wire associated with the junction is isothermal, it does not matter how the junction is made; eg, by welding, brazing, crimping, etc, as long as it has the mechanical strength to ensure electrical conductivity.

Figure 14 shows a simplified circuit for a thermocouple. Following the two guidelines above, the measurement junction, the reference junction and the voltmeter (a complex inhomogeneous device) are maintained in isothermal environments. In this state, there are four sections of wire that generate a voltage. The two homogeneous copper leads, because they generate equal and opposite voltages, have no net effect on the measurement. The remaining voltages are due to the homogeneous wires A and B, which generate net voltage according to the end temperatures:

$$E_{\mathrm{meas}} = E_{\mathrm{A}}(T_{\mathrm{m}}) - E_{\mathrm{A}}(T_{\mathrm{r}}) + E_{\mathrm{B}}(T_{\mathrm{r}}) - E_{\mathrm{B}}(T_{\mathrm{m}}) \tag{26}$$

This equation is simplified by associating the materials A and B as a thermocouple pair and by defining $E\ (0^{\circ}\mathrm{C}) = 0$ for all thermocouple wire. Equation 26 then simplifies to

$$E_{\mathrm{meas}} = E_{\mathrm{AB}}(t_{\mathrm{m}}) \tag{27}$$

and this is the deceptively simple relationship defined by thermocouple standards (31–34). Where the reference junction is at a temperature $t_{\mathrm{r}}$ instead of 0°C, the net voltage from the thermocouple is

$$E_{\mathrm{meas}} = E_{\mathrm{AB}}(t_{\mathrm{m}}) - E_{\mathrm{AB}}(t_{\mathrm{r}}) \tag{28}$$

Correction of the measured voltage from equation 28 to equation 27 is usually referred to as “cold junction compensation”, and requires an independent measure of the reference junction temperature. The compensation may be carried out electronically or in software.

Historically, thermocouples were defined by the chemical composition of the wire. Nowadays, the definitions are mathematical equations of the form of equation 27. This gives thermocouple manufacturers the freedom to modify the wire composition to suit different environments and accommodate compositional variations in wire production. For this reason, most thermocouple types (types E, K, J, especially) should be purchased as a pair, and wire from different sources should not be mixed.

Prior to 1990, not all national documentary standards had the same definition for some thermocouple types. Since 1990 standards have become increasingly harmonized so most wire now complies with international documentary standards. However, some indicators on older equipment may be based on the older standards. Note too that descriptive terms, eg, constantan, may cover a wide range of different alloys used for a variety of purposes.

Table 4 summarizes the temperature range and properties of the standard letter-designated thermocouples. There are two main groups. Rare metal thermocouples, Types B, R, and S, are made with platinum and platinum–rhodium alloys, and have Seebeck coefficients of the order of 10 μV/°C. With care, they are capable of uncertainties as low as 0.3°C for ranges up to 1000°C, but they are relatively expensive. The remainder, types E, J, K, N, and T, have a Seebeck coefficient of the order of 20 μV/°C to 80 μV/°C, and are known as base-metal thermocouples. Base-metal thermocouples are low cost, but the alloy composition makes them prone to developing inhomogeneities with thermal treatment, and they may exhibit errors of a few degrees or more. With care and operating conditions restricted to low temperatures, some types can achieve uncertainties as low as 0.2°C. The tables and reference functions for the letter-designated thermocouples, as well as detailed advice on applications and limitations, are given in Ref. 31. The reference functions can be downloaded from the NIST thermocouple database on the NIST website.

Table 5 summarizes the performance of four other thermocouples that are used occasionally and satisfy needs not met by the standard letter-designated types. In particular, the tungsten–rhenium thermocouple is used for high temperature and reducing environments. The gold–platinum and platinum–palladium thermocouples both have pure single-element wires and are capable of uncertainties of 20 and 150 mK, respectively, $< 1000°C$. The thermocouples of Table 5 are specified in ASTM E 1751-00 (32).

High temperature applications often require large-diameter thermocouple wire that is not appropriate for making connections to thermocouple instrumentation. For this reason, flexible, multistrand, “extension cables” are available. These are usually made from materials similar to the thermocouple wires, but are generally suited only for temperatures between 0 and 50°C. For rare-metal thermocouples, the cost of long leads is an additional concern so compensating extension leads or “compensating cables” are available. These are made from low cost alloys that mimic the behavior of the rare-metal thermocouples for temperatures in the range 0–50°C.

Because the leads transmitting the signal to the instrumentation are an integral part of the sensor and contribute to the thermoelectric voltage, care must be taken to ensure the leads to the reference junction are all thermocouple material in a homogeneous state. Connectors manufactured from the thermocouple materials are an important aid and are readily available. Increasingly, long runs of thermocouple cable are being avoided with the use of local instruments and distributed digital communications networks, eg, Fieldbus (35).

The low signal levels associated with thermocouples can be a problem in industries where large electrical machinery operates. Electromagnetic interference (EMI) can result in noisy and erratic temperature readings. Since the interference is usually due to magnetic fields, shielded cable is ineffective in preventing EMI. Instead, twisted pair thermocouple leads or local instruments with digital communication links should be used.

Thermocouples come in a variety of wire diameters and insulating materials. The insulating materials range from plastics, eg, poly(vinyl chloride) (PVC) and polytetrafluoroethylene (PTFE), through glass fiber to various ceramics. One particularly useful form is the mineral-insulated-metal-sheathed (MIMS) thermocouple. This construction provides protection for the wire using a chemically compatible sheath material, is flexible, and easily adapted to suit a wide variety of installations. They are readily available in diameters ranging from 0.5 to 25 mm and with a variety of stainless steel or other alloy sheaths depending on operating range and thermocouple type.

General advice on thermocouples can be found in Refs. 17, 31, 36, 37. Kinsey (38) summarizes the performance of a very large number of different thermocouples and their operation in a wide variety of environments. Detailed advice on the calibration of thermocouples can be found in Refs. 14, 37.

## 12. Liquid-in-Glass Thermometry

Liquid-in-glass thermometers were the first reliable thermometers and are still in common use today. Progressively, however, they are being replaced by electronic thermometers based on industrial platinum resistance thermometers, which are more reliable, more accurate, nontoxic, and usually have a lower cost of ownership. Nevertheless, there remain applications where liquid-in-glass thermometers are either most suitable or required by documentary standards.

The typical liquid-in-glass thermometer has a thin-walled glass bulb attached to a capillary stem partially filled with a visible liquid and sealed against the environment. The first thermometers were based on distilled wine spirit. Subsequently, other pigmented organic fluids (often still called spirit or alcohol) and mercury have proven to yield more reproducible thermometers. Mercury thermometers are usually more linear and more accurate than those based on organic fluids. Spirit thermometers also have a longer settling time due to the slow drainage of the fluid wetting the capillary, are prone to column breakage and to polymerization of the fluid under ultraviolet (uv) light. However, they will function below the mercury freezing point (near $-38^\circ$C).

The portion of the capillary above the liquid is usually filled with a dry gas to prevent column separation, and a scale is etched or fused onto the stem. If the nominal temperature range of the thermometer does not include $0^\circ$C, an auxiliary scale showing a few scale divisions $\sim 0^\circ$C is usually provided to allow a calibration check at the ice point. A contraction chamber may be provided between the two scale segments to avoid the need for a long stem.

The main complication with liquid-in-glass thermometers is that both the liquid and the glass are sensitive to temperature. In a mercury thermometer, $\sim 10\%$ of the mercury expansion is offset by expansion in the volume of the bulb. The mercury responds very quickly to temperature changes, but the glass, being an amorphous solid, responds relatively slowly and does not have a well-defined thermodynamically stable state. Thus, liquid-in-glass thermometers exhibit hysteresis reflecting the past thermal exposure of the thermometer. In the worst case, the thermometers exhibit hysteresis of $\sim 0.1\%$ ($0.1^\circ$C for each $100^\circ$C of temperature change). At best, if the thermometer is conditioned into a well-defined state, accuracies of 0.01% are possible. The hysteresis can be reduced by allowing a few days for recovery from high temperature exposure and by cooling the thermometer slowly. Most of the observed nonlinearity in mercury thermometers is due to the nonlinear expansion of glass with temperature.

Ideally, all of the liquid in the thermometer should be exposed to the temperature of interest; ie, the thermometer should be immersed to the level of the liquid meniscus in the capillary. While “total immersion” thermometers are manufactured for such immersion conditions, “partial immersion” thermometers are made for immersion to a specified depth, typically 75 or 100 mm. Partial immersion thermometers are, therefore, sensitive to the ambient temperature and “stem corrections” must be made if the calibration conditions differ from the conditions in use. For partial immersion thermometers, the true temperature reading, $t$, is given by

$$t = t_i + N(t_2 - t_1)\kappa \tag{29}$$

where $t_i =$ the indicated temperature; $N =$ the length of the emergent column expressed in degrees, as determined by the thermometer’s scale; $t_2 =$ the mean temperature of the emergent column when calibrated (ie, the stem temperature on a certificate for partial immersion or the thermometer reading for a total-immersion certificate); $t_1 =$ the mean temperature of the emergent column in use; and $\kappa =$ the coefficient of expansion of the thermometric liquid used, in the glass of which the thermometer stem is made. The typical value for mercury is $0.000\,16^\circ\mathrm{C}^{-1}$.

The stem error is $\sim 1.5^\circ$C for a total immersion thermometer used in partial immersion at 100°C. The emergent column length, $N$, tends to be of the order of $t_2 - t_1$ so the effect tends to scale as $(t_2 - t_1)^2$.

There are many minor problems to be considered and avoided when using liquid-in-glass thermometers. Because the bulb is thin, mercury thermometers exhibit a pressure sensitivity of $\sim 0.1^\circ$C per atmosphere. This gives rise to different readings in the vertical and horizontal positions because of the weight of the mercury column on the bulb, and sensitivity to pressure fluctuations in stirred fluids.

The interpolating quality of the scale marked on the thermometer depends both on the quality of the scale markings and on the uniformity of the capillary. Good quality thermometers can be interpolated to ~ one-fifth of a scale division, poor thermometers to ~ one-half of a scale division.

Parallax errors arise because the scale and the capillary are usually in a different plane. For accurate measurements, the operator must take care to observe the scale at right angles to the axis of the thermometer. Telescopes help to force the operator to read from the correct angle and magnify the scale. Included-scale thermometers, which have a separate capillary and glass scale within the thermometer stem, also reduce the parallax effect.

Stiction, caused by the failure of the mercury to wet the capillary, causes the mercury column to rise and fall erratically rather than continuously. The effect can be avoided by gently tapping the thermometer with a pencil, or similar object, immediately before reading the thermometer.

Mercury thermometers are subject to separation of the mercury column or to inclusion of bubbles of the fill gas. These commonly occur during shipping, are usually easily seen, and can always be detected with an ice-point check. With care, the column can usually be rejoined by cooling the thermometer to just above the freezing point of mercury at −38°C.

Change in the bulb volume is the major cause of changes in calibration of thermometers. Therefore, changes in calibration can be compensated by a single offset measured as the change in the ice-point reading. Further information on liquid-in-glass thermometers can be found in Refs. 17, 37. Advice on calibration of liquid-in-glass thermometers can be found in Refs. 14, 17, 39.

## 13. Other Thermometers

Because almost every physical property is dependent on temperature, almost every property has at some time been used as the basis for a temperature sensor. The sensors described above are those in common usage and best understood, and therefore generally accepted as a means for making traceable temperature measurements. However, there are a wide variety of other thermometers that may be useful for specific applications. These include vapor pressure thermometers, a wide variety of other types of resistance thermometer, solid-state semiconductor devices, magnetic, fluorescence, noise, thermochromic, ultrasonic, microwave, and acoustic thermometers. Information on other temperature sensors can be found in Refs. 4, 30, 40. Advice on calibrating some of these sensors can be found in Ref. 14.

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Table 1. **Some Types of Thermodynamic Thermometer and the Associated Thermodynamic Relations**[a]

| Thermometer | Thermodynamic relation |
|---|---|
| gas thermometer: pressure, $P$, and volume, $V$, of an ideal gas versus number of molecules, $n$, or number of moles, $N$, and temperature. | $PV = nkT = NRT$ |
| dielectric constant gas thermometer: pressure, $P$, versus dielectric constant, $\varepsilon$, static dipole polarizability $\alpha_0$, and temperature. | $P = kT(\varepsilon - \varepsilon_0)/\alpha_0$ |
| acoustic thermometer: speed of sound, $c_s$, versus specific heat ratio, $\gamma$, molecular mass, $m$, or molar mass, $M$, and temperature. | $c_s^2 = \dfrac{\gamma k T}{m} = \dfrac{\gamma RT}{M}$ |
| total radiation thermometer: total radiance, $L$, versus temperature. | $L = \dfrac{2\pi^5 k^4}{15 c^2 h^3} T^4$ |
| spectral-band radiation thermometer: spectral radiance, $L_\lambda$, versus wavelength, $\lambda$, and temperature. | $L_\lambda = \dfrac{2hc^2}{\lambda^5}\left[\exp\left(\dfrac{hc}{\lambda kT}\right) - 1\right]^{-1}$ |
| noise thermometer: mean square noise voltage $\overline{V_T^2}$ versus real part of impedance, $Z$, bandwidth, $\Delta f$, and temperature. | $\overline{V_T^2} = 4kT\mathrm{Re}(Z)\Delta f$ |
| molar gas constant, $R = 8.314472\ \mathrm{J/(mol{\cdot}K)}$ | speed of light, $c = 299\ 792\ 458\ \mathrm{m/s}$ |
| Planck's constant, $h = 6.62606893 \times 10^{-34}\ \mathrm{J\ s}$ | Boltzmann constant, $k = 1.3806505 \times 10^{-23}\ \mathrm{J/K}$ |
| permittivity of free space, $\varepsilon_0 = c/4\pi \times 10^{-7} = 8.854187817\cdots \times 10^{-12}\mathrm{F/m}$ | |

[a] The values of the fundamental constants are from Ref. 8.

Table 2. **Fixed Points of the ITS-90**[a]

| Substance[b,c] | Temperature | | $dT/dP$[d] | $dT/dh$[e] | $W_r(T_{90})$[f] |
|---|---|---|---|---|---|
| | $T_{90}$, K | $t_{90}$, °C | | | |
| $^3$He (V) or $^4$He (V) | 3 to 5 | −270.15 to −268.15 | | | |
| e-$H_2$ (T) | 13.8033 | −259.3467 | 34 | 0.25 | 0.001 190 07 |
| e-$H_2$(V) or $^3$He (G) or $^4$He(G) | ca. 17 | ca. −256.15 | | | |
| e-$H_2$(V) or $^3$He (G) or $^4$He(G) | ca. 20.3 | ca. −252.85 | | | |
| Ne (T) | 24.5561 | −248.5939 | 16 | 1.9 | 0.008 449 74 |
| $O_2$ (T) | 54.3584 | −218.7916 | 12 | 1.5 | 0.091 718 04 |
| Ar (T) | 83.8058 | −189.3442 | 25 | 3.3 | 0.215 859 75 |
| Hg (T) | 234.3156 | −38.8344 | 5.4 | 7.1 | 0.844 142 11 |
| $H_2O$ (T) | 273.16 | 0.01 | −7.5 | −0.73 | 1.000 000 00 |
| Ga (M) | 302.9146 | 29.7646 | −2.0 | −1.2 | 1.118 138 89 |
| ln (F) | 429.7485 | 156.5985 | 4.9 | 3.3 | 1.609 801 85 |
| Sn (F) | 505.078 | 231.928 | 3.3 | 2.2 | 1.892 797 68 |
| Zn (F) | 692.677 | 419.527 | 4.3 | 2.7 | 2.568 917 30 |
| Al (F) | 933.473 | 660.323 | 7.0 | 1.6 | 3.376 008 60 |
| Ag (F) | 1234.93 | 961.78 | 6.0 | 5.4 | 4.286 420 53 |
| Au (F) | 1337.33 | 1064.18 | 6.1 | 10 | |
| Cu (F) | 1357.77 | 1084.62 | 3.3 | 2.6 | |

[a] See Ref. 9.

[b] The substance $^3$He is a pure isotope, $H_2O$ and $H_2$ are of defined isotopic composition (7,18), the composition of Ne is expected to be defined in the near future, and all other substances are of natural isotopic composition. e-$H_2$ is hydrogen at the equilibrium concentration of the ortho- and para-molecular forms.

[c] The symbols have the following meanings: V = vapor pressure point; T = triple point; G = gas-thermometer point; M, F = melting point, freezing point (temperature, at a pressure of 101, 325 Pa, at which the solid and liquid phases are in equilibrium).

[d] $dT/\mathrm{dP}$ is the rate of change of the temperature with pressure. The units are $10^{-8}$ K/Pa, which is equivalent to millikelvin per atmosphere.

[e] $dT/\mathrm{dh}$ is the rate of change of the temperature with depth. The units are $10^{-3}$ K/m, which is equivalent to millikelvin per metre.

[f] $W_r$ values are the reference resistance ratios used in the interpolation equations for standard platinum resistance thermometers.

Table 3. **Values of $T_{90}$ for Selected Secondary Fixed Points**[a]

| Phase transition | $T_{90}$, K | $t_{90}$, °C | $u_T$, K[b] | Quality[c] | Purity[d] |
|---|---|---|---|---|---|
| boiling point of methane | 111.64 | −161.51 | 0.05 | 2(vp) | 99.99 |
| triple point of krypton | 115.775 | −157.375 | 0.001 | 2 | 99.995 |
| triple point of xenon | 161.405 | −111.745 | 0.001 | 1 | 99.995 |
| sublimation point of carbon dioxide | 194.686 | −78.464 | 0.003 | 2(vp) | 99.99 |
| triple point of carbon dioxide | 216.592 | −56.558 | 0.001 | 1 | 99.99 |
| triple point of sulfurhexafluoride | 223.554 | −49.596 | 0.005 | 2 | 99.998 |
| freezing point of mercury | 234.3210 | −38.8284 | 0.0005 | 1 | 99.9999 |
| ice point | 273.15 | 0 | 0.0005 | 1 | 99.99999 |
| melting point of gallium/20.5 mass percent indium eutectic | 288.800 | 15.650 | 0.001 | 2 | 99.999 |
| melting point of gallium/8 mass percent tin eutectic | 293.626 | 20.476 | 0.002 | 2 | 99.999 |
| triple point of phenoxybenzene (diphenyl ether) | 300.014 | 26.864 | 0.001 | 2 | 99.9998 |
| triple point of gallium | 302.9166 | 29.7666 | 0.0001 | 1 | 99.99999 |
| triple point of ethylene carbonate ($C_3H_4O_3$) | 309.465 | 36.315 | 0.001 | 2 | 99.9999 |
| triple point of succinonitrile | 331.215 | 58.065 | 0.002 | 2 | 99.9995 |
| freezing point of sodium | 370.944 | 97.794 | 0.005 | 2 | 99.99 |
| boiling point of water | 373.124 | 99.974 | 0.001 | 1(vp) | 99.999 |
| triple point of benzoic acid | 395.486 | 122.336 | 0.002 | 2 | 99.999 |
| freezing point of benzoic acid | 395.502 | 122.352 | 0.007 | 2 | 99.999 |
| triple point of indium | 429.7436 | 156.5936 | 0.0002 | 1 | 99.9999 |
| freezing point of bismuth | 544.552 | 271.402 | 0.001 | 1 | 99.9999 |
| freezing point of cadmium | 594.219 | 321.069 | 0.001 | 1 | 99.9999 |
| freezing point of lead | 600.612 | 327.462 | 0.001 | 1 | 99.9999 |
| boiling point of mercury | 629.769 | 356.619 | 0.010 | 2(vp) | 99.9999 |
| boiling point of sulfur | 717.764 | 444.614 | 0.005 | 2(vp) | 99.995 |
| melting point of copper/66.9 mass percent aluminum eutectic | 821.308 | 548.158 | 0.010 | 2 | 99.9999 |
| melting point of silver/30 mass percent aluminum eutectic | 840.957 | 567.807 | 0.002 | 2 | 99.9999 |
| freezing point of antimony | 903.778 | 630.628 | 0.001 | 1 | 99.9999 |
| melting point of copper/71.9 mass percent silver eutectic | 1052.78 | 779.63 | 0.05 | 1 | 99.999 |
| freezing point of sodium chloride | 1075.168 | 802.018 | 0.011 | 2 | 99.99 |
| boiling point of sodium | 1156.090 | 882.940 | 0.006 | 2(vp) | 99.93 |
| freezing point of nickel | 1728 | 1455 | 1 | 2 | 99.99+ |
| freezing point of cobalt | 1768 | 1495 | 3 | 2 | 99.9 |
| freezing point of iron | 1811 | 1537 | 3 | 2 | 99.99 |
| freezing point of palladium | 1828.0 | 1554.8 | 0.1 | 1 | 99.999 |

[a] See Ref. 19.

[b] A “1” signifies a high quality fixed point that is relatively easily achieved and of high accuracy, whereas a “2” is a not-so-easily achieved fixed point, usually of lower accuracy. Where the vapor pressure relationship is known around the fixed point it is denoted by “vp”.

[c] The pressure for triple points is determined by physical conditions. For the other fixed points, it is usually 101, 325 Pa.

[d] The quoted uncertainty is given as a single standard deviation, ie, a 68% confidence interval. The uncertainty for quality levels 1 and 2 includes conversion from IPTS-68 to ITS-90 as well as the consistency between different realizations of the fixed point.

[e] The purities are expressed as volume percent for materials that are usually liquids and gases, and mass percent for those that are usually solids.

Table 4. **Summary of the Standard Letter Designated Thermocouples**[a]

| Type | Common description[b] | Temperature range[c] | Properties and utility |
|---|---|---|---|
| B | platinum 30% rhodium versus platinum 6% rhodium | 0–1810°C | most stable thermocouple > 1100°C<br>avoid reducing atmospheres<br>susceptible to contamination<br>negligible output between 0 and 50°C |
| R | platinum 13% rhodium versus platinum | −50–1768°C | types R and S most accurate < 1100°C<br>avoid reducing atmospheres<br>susceptible to contamination |
| S | platinum 10% rhodium versus platinum | −50–1768°C | types R and S most accurate < 1100°C<br>avoid reducing atmospheres<br>susceptible to contamination |
| E | chromel versus constantan | −270–1000°C | highest Seebeck coefficient<br>best thermocouple for low temperatures<br>avoid low oxygen, reducing atmospheres and vacuum<br>low susceptibility to thermally induced inhomogeneities |
| J | iron versus constantan | −210–1200°C | highly variable composition and output<br>suitable for vacuum, oxidizing, and reducing atmospheres<br>iron leg is prone to rapid corrosion<br>standards for different countries vary |
| K | chromel versus alumel | −270–1372°C | resistance to oxidation at high temperatures<br>avoid low oxygen, reducing atmospheres and vacuum<br>High susceptibility to thermally induced inhomogeneities<br>most common industrial thermocouple |
| N | nicrosil versus nisil | −270–1300°C | improved replacement for type K<br>resistance to oxidation at high temperatures<br>avoid low oxygen, reducing atmospheres and vacuum |
| T | copper verus constantan | −270–400°C | good for general purpose, low temperature<br>low susceptibility to thermal inhomogeneities<br>high thermal conductivity of copper can affect reference junction and measurements<br>standards for different countries vary |

[a] See Ref. 31.

[b] The description is not a specification. The actual wire composition can vary significantly. Chromel and Alumel are trademarks of the Hoskins Manufacturing Company.

[c] The temperature range given is the range of the tables (31–34). The upper limit may be achievable only intermittently or with large wire gages.

Table 5. **Other Useful Thermocouples**[a]

| Description | Range, °C | Comments |
|---|---|---|
| tungsten 5% rhenium versus tungsten 26% rhenium | 0–2315 | suited to very high temperatures<br>avoid oxidizing atmospheres, tolerates inert and hydrogen atmospheres<br>defined as type C by ASTM (33) |
| Chromel versus gold-0.07% iron | −273–7 | high Seebeck coefficient at low temperatures |
| gold versus platinum | 0–1000 | very high accuracy: uncertainty of 20 mK possible<br>practical alternative to SPRTs > 660°C |
| platinum versus palladium | 0–1500 | very high accuracy: uncertainty of 0.15°C up to 1500°C |

[a] See Refs. 32, 33.

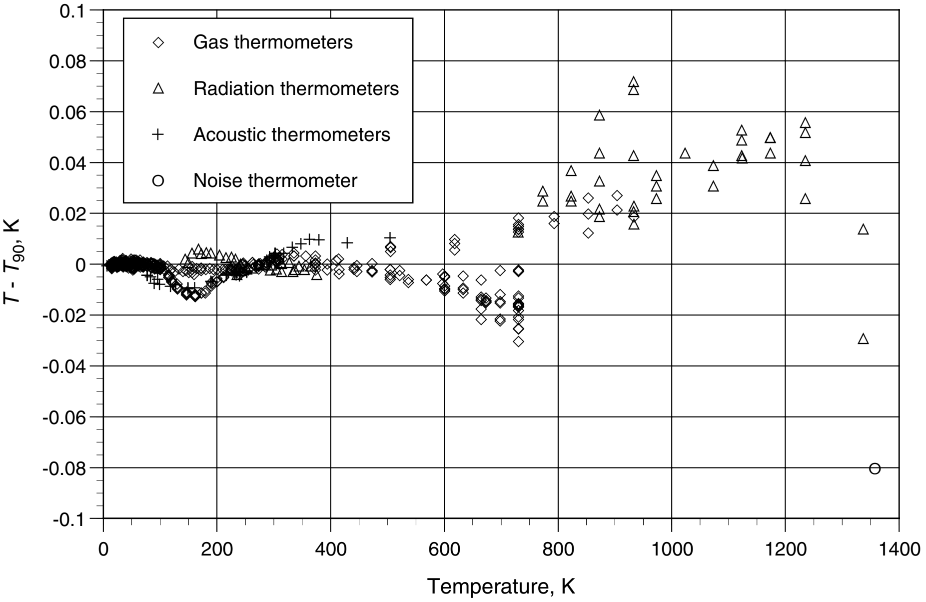

**Fig. 1.** A summary of determinations of the differences between thermodynamic temperature and the ITS-90. For most of the measurements, the uncertainties are similar to the magnitude of the differences. For acoustic thermometers the uncertainties are of the order of 1 mK.

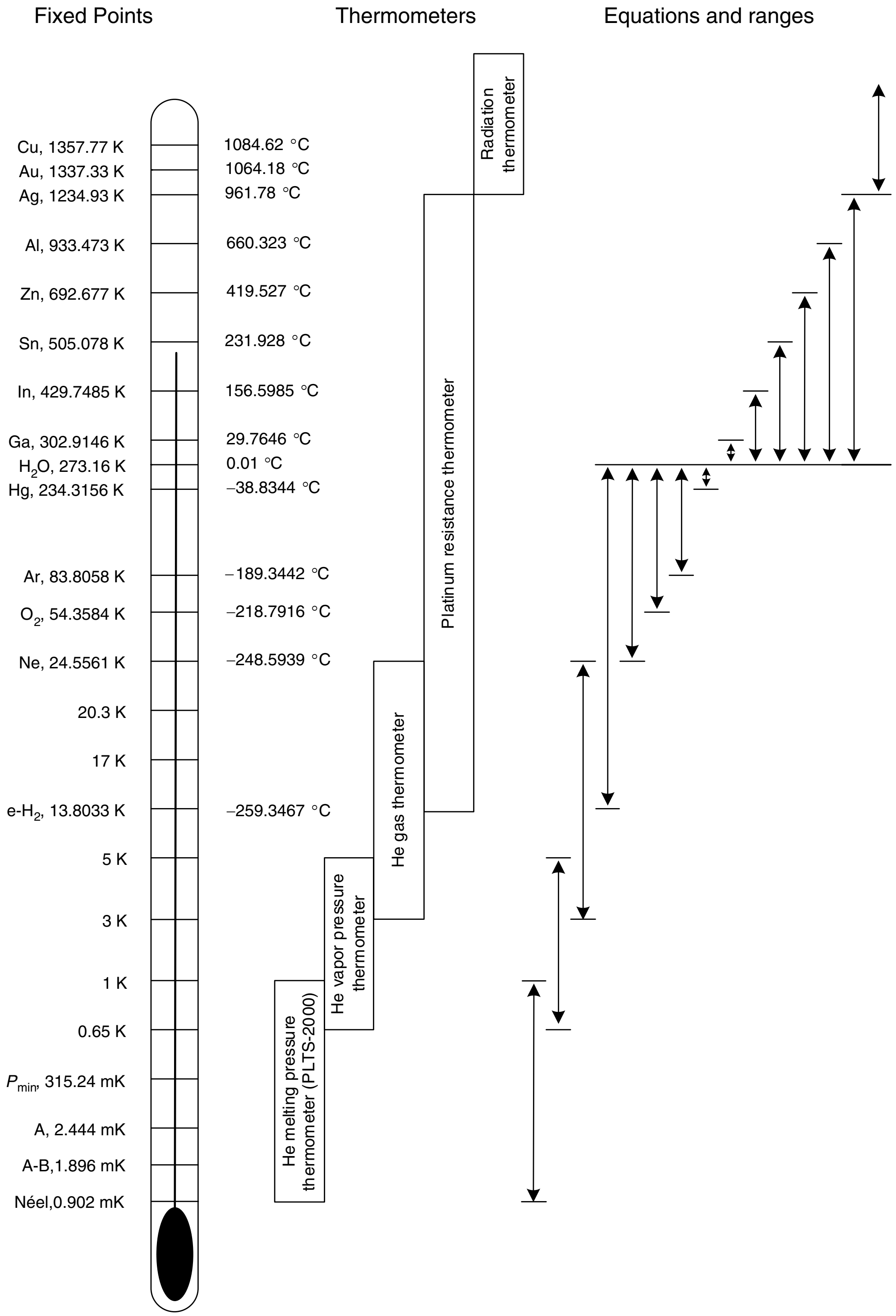

**Fig. 2.** A simplified guide to the main features of the ITS-90 and the PLTS-2000.

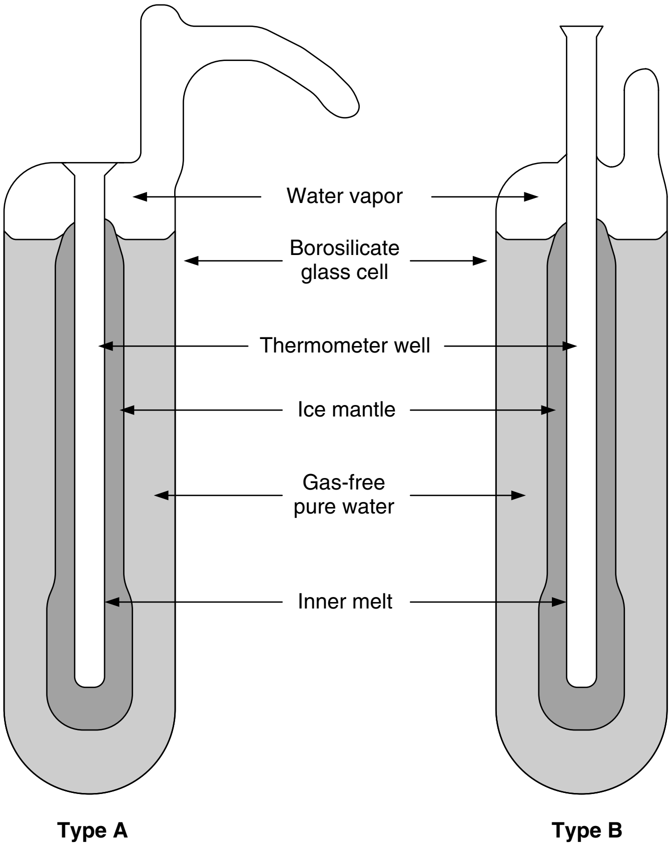

**Fig. 3.** Triple-point-of-water cells are typically 300–400 mm in total length and 50–60 mm in diameter. The type A cell includes a McLeod gauge extension for testing for residual air. In the type B cell the remnant seal-off tube can be used for the same purpose.

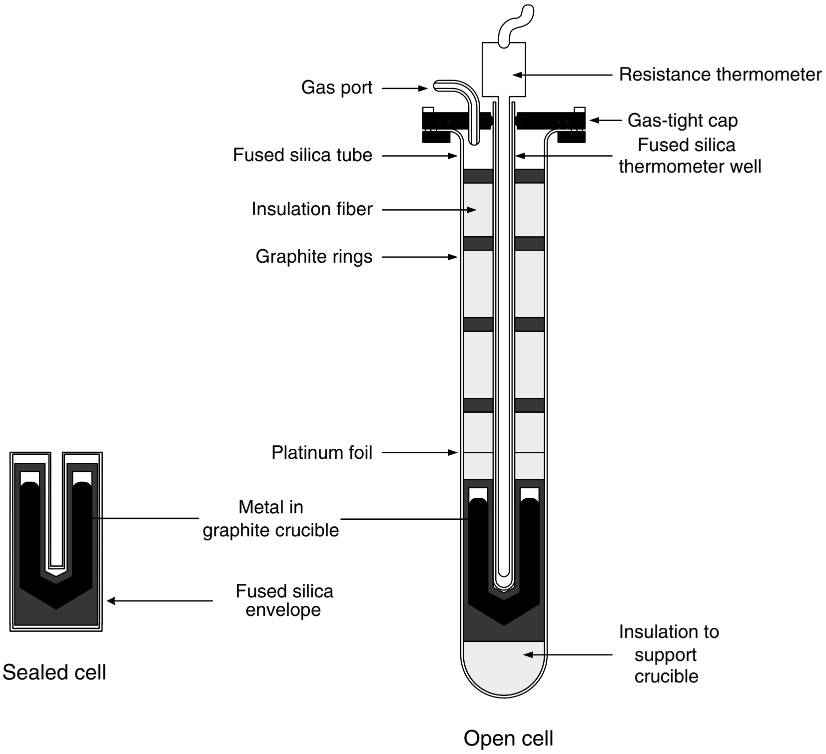

**Fig. 4.** Simplified diagram showing the construction of metal fixed-point cells (not to scale). The details of the internal construction of the open cells vary according to the fixed point and the furnace with which they are used. Reproduced from Ref. 17.

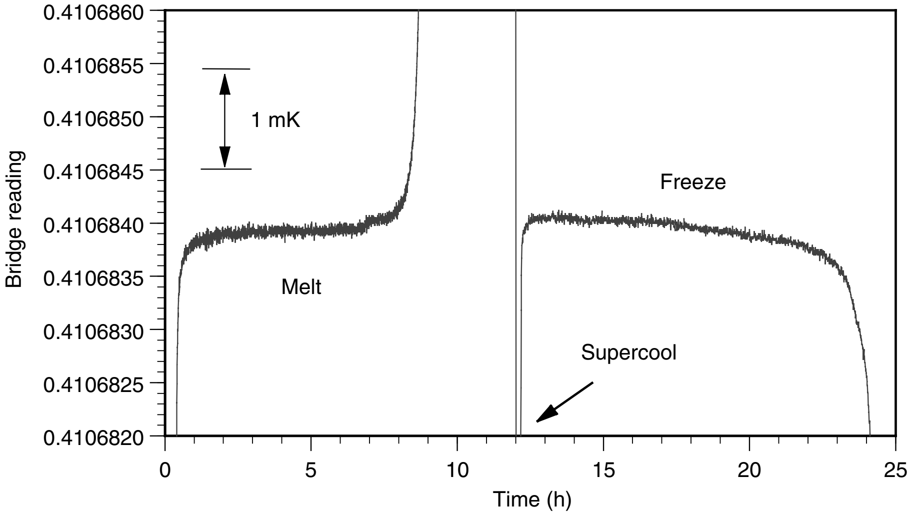

**Fig. 5.** Example of an indium-point realization (156.5985°C). The vertical axis indicates the reading of a resistance bridge used to monitor a standard platinum resistance thermometer in the cell.

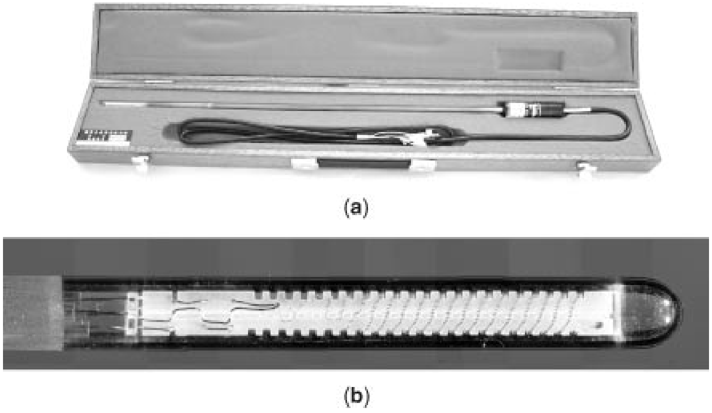

**Fig. 6.** A long-stem standard platinum resistance thermometer. (**a**) The complete assembly in carrying case. (**b**) An enlargement showing the construction of the sensing element.

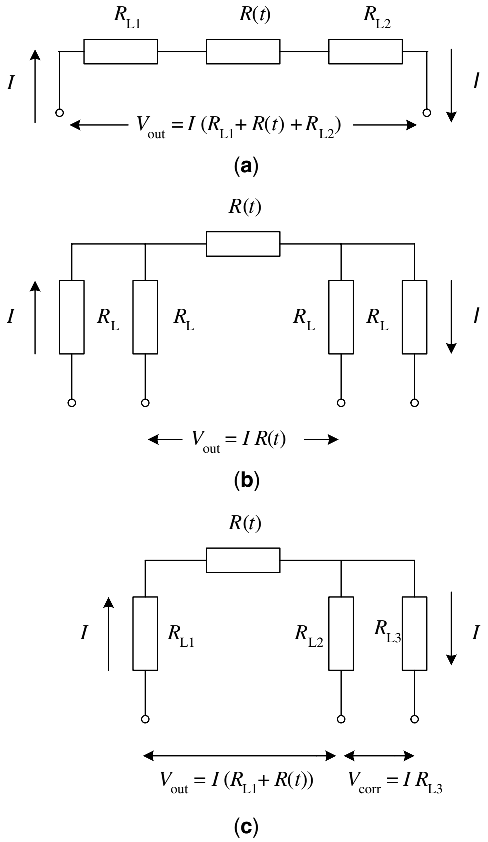

**Fig. 7.** The different lead-wire configurations for industrial resistance thermometers. (**a**) 2-wire; (**b**) 4-wire; (**c**) 3-wire.

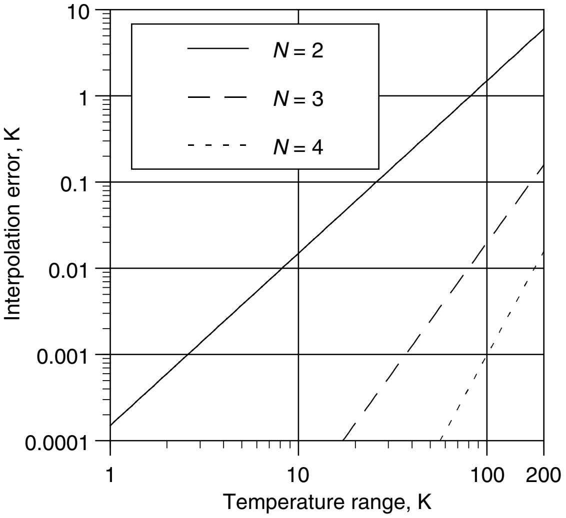

**Fig. 8.** The standard deviation of interpolation errors for equation 9 versus temperature range with different numbers of terms (*N*) included. The lines are indicative only. Actual interpolation errors may be larger or smaller than indicated depending on the $\beta$ value and operating temperature of the thermistor.

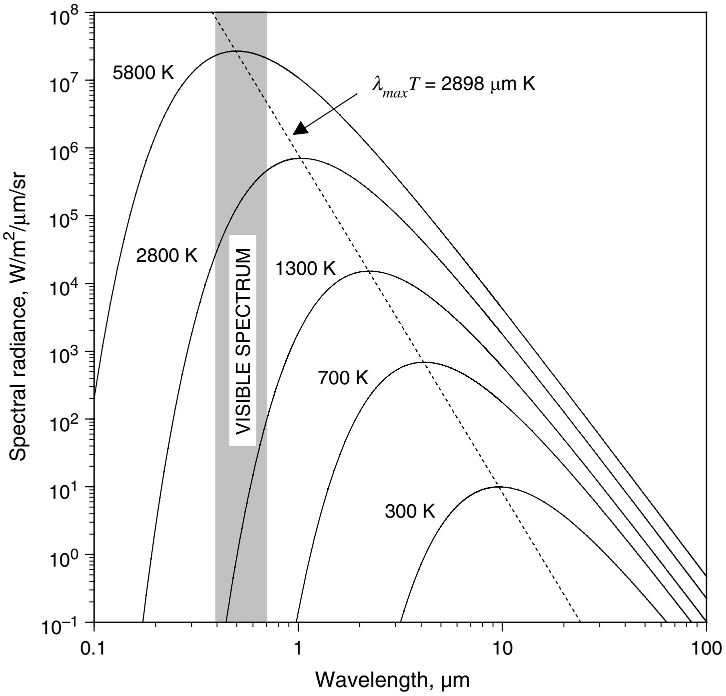

**Fig. 9.** Planck's blackbody radiation law. Reproduced from Ref. 17.

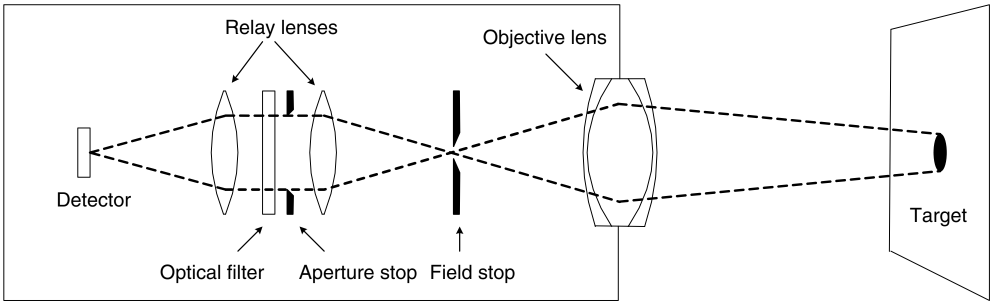

**Fig. 10.** Simplified diagram of a spectral-band radiometer.

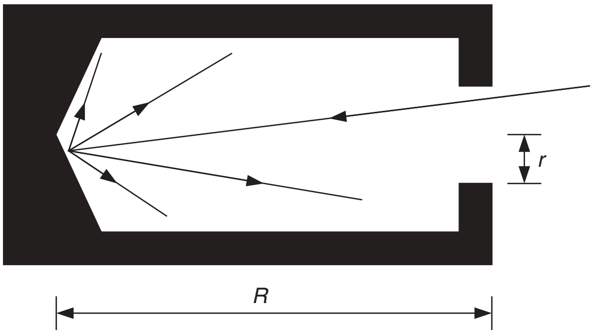

**Fig. 11.** A simple blackbody cavity. Reproduced from Ref. 17.

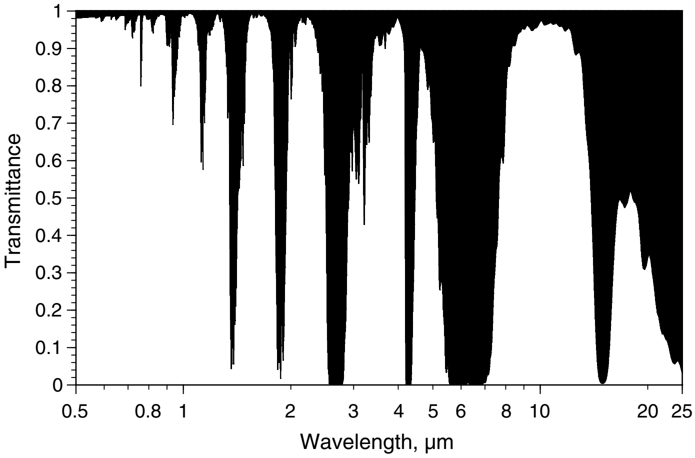

**Fig. 12.** The transmittance of 300 m of air at sea level. The filled areas indicate spectral bands where air is opaque. Reproduced from Ref. 17.

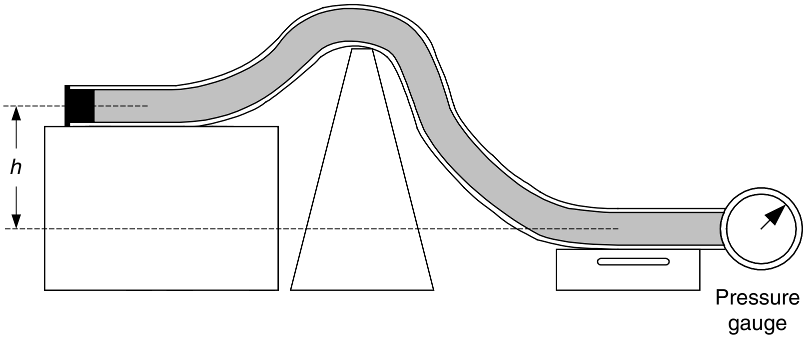

**Fig. 13.** A hydraulic analogue model of the Seebeck effect. The pressure in the tube is generated at gradients, but the total pressure depends only on the elevation of the ends. Reproduced from Ref. 17.

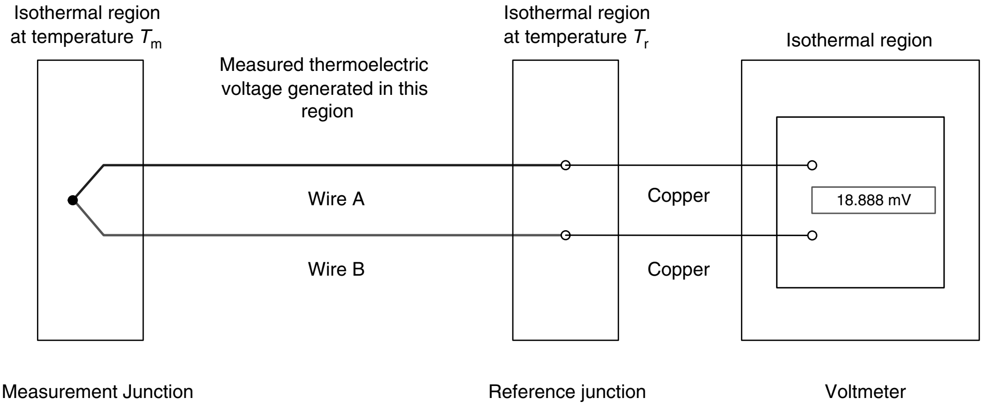

**Fig. 14.** A simple thermocouple circuit.