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Principles of temperature measurement

Temperature is one of the seven base quantities of the International System of Units (SI) [1], along with mass, length, time, electric current, amount of substance and luminous intensity. Temperature is an intensive quantity, like pressure and density, which means it is not additive like extensive quantities, such as mass or length.

An adequate understanding of temperature was only developed in the 19th century when principles of classical thermodynamics (by Kelvin, Joule, Clausius and others) and statistical mechanics (by Boltzmann, Maxwell and others) were elaborated.

From a classical thermodynamics point of view that understanding is enshrined in the four laws of thermodynamics [9], these are:

The *zeroth* law of thermodynamics describes the existence of thermal equilibrium between two or more macroscopic systems. If, when a system is placed in contact with a second system, there are no changes in the parameters describing the state of the two systems (such as pressure, volume, etc), then these systems are in thermal equilibrium with each other. Thus, temperature is the parameter of state that has the same value for any systems which are in thermal equilibrium.

The *first* law of thermodynamics is concerned with heat and work and is fundamentally a statement of the principle of the conservation of energy applied to thermodynamic systems.

Further ideas about temperature come from the *second* law of thermodynamics, one expression of which is concerned with the efficiencies of heat engines. For an ideal heat engine operating in a cycle, heat Q_1 is taken in from a reservoir at temperature T_1, and heat Q_2 is given out to a cooler reservoir at temperature T_2. The work done is $(Q_1 - Q_2)$, and the ratio of the two heats can be used to define the ratio of the "thermodynamic temperatures" of the reservoirs: $Q_1/Q_2 = T_1/T_2$. The main point here is that the temperatures T_1 and T_2 are independent of the properties of any material substance, which is the working system of the ideal engine.

The *third* law of thermodynamics provides a reference point for the entropy, which is a measure of molecular disorder or molecular randomness. The entropy determined relative to this point is called absolute entropy. As a system becomes more disordered, the positions of the molecules become less predictable and the entropy increases. Thus, it is not surprising that the entropy of a substance is lowest in the solid phase and highest in the gas phase.

When viewed microscopically (from a statistical thermodynamics point of view), an isolated system that appears to be at a state of equilibrium may exhibit a high level of activity because of the continual motion of the molecules. To each state of macroscopic equilibrium there corresponds a large number of possible microscopic states or molecular configurations. The entropy of a system is related to the total number of possible microscopic states of that system, called thermodynamic probability *p*, by the Boltzmann relation [9]**,** expressed as

$$S = k \cdot \ln p \tag{1}$$

where k= 1,3806 x 10^{-23} J/K is the Boltzmann constant**.** Therefore, from a microscopic point of view, the entropy of a system increases whenever the molecular randomness or uncertainty (i.e., molecular probability) of a system increases. The molecules of a substance in solid phase continually oscillate, creating an uncertainty about their position. These oscillations, however, fade as the temperature is decreased, and the molecules supposedly become motionless at absolute zero. This represents a state of ultimate molecular order (and minimum energy). Therefore, the entropy of a pure crystalline substance at absolute zero temperature is zero since there is no uncertainty about the state of the molecules at that instant. This statement is known as the *third law* of thermodynamics. The entropy of a substance that is not pure crystalline, for example, amorphous materials is not zero at absolute zero temperature. This is can be explained by the fact that amorphous materials are not in equilibrium [10].

The other approach to understanding temperature is based on statistical mechanics [3, 11]. This area was developed in parallel with classical thermodynamics by Maxwell in 1859 and by Boltzmann in 1869 and is concerned with the statistical behaviour of large ensembles of particles and shows how, for a given system, the macroscopic properties are related to the kinetics of the microscopic particles of which it is composed. The kinetic approach to the explanation of the behaviour of gases was generalized by Boltzmann in 1872 and later by Gibbs who, in 1902, introduced statistical mechanics [3]. For a system in thermal equilibrium, the Maxwell-Boltzmann distribution function, *f(E),* relates the probability of occupancy for a particular state of energy, *E*, to the temperature:

$$f(E) \sim \exp\left(-\frac{E}{kT}\right) \tag{2}$$

where *k* is the Boltzmann constant. It can be shown that the temperature is a direct measure of the average kinetic energy of the constituent (non-interacting) particles, which is (1/2).*k.T* per degree of freedom.

2.1.Temperature scales

Temperature scales enable us to use, around the world, a common basis for temperature measurements, and several have been introduced throughout history. All temperature scales are based on some easily reproducible states, generally phase changes, such as the freezing and boiling points of water, which are also called the ice point and the steam point, respectively[2]. The temperature scale used in the SI [1] today is the Celsius scale (this was formerly called the Centigrade scale; but in 1948 it was renamed after the Swedish astronomer A. Celsius, 1702–1744, who initially devised it). The Fahrenheit scale (named after the German instrument maker G. Fahrenheit, 1686–1736), widely used in the United States, is generally not used elsewhere, and indeed in the US the Celsius scale is disseminated by their National Measurement Institute, NIST. On the Celsius scale, the ice and steam points were originally assigned the values of 0 °C and 100 °C, respectively. The corresponding values on the Fahrenheit scale are 32 °F and 212 °F. These are often referred to as two-point scales since temperature values are assigned at two different points.

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[2] A mixture of ice and water that is in equilibrium with air saturated with vapour at 1 atm pressure is said to be at the ice point, and a mixture of liquid water and water vapour (with no air) in equilibrium at 1 atm pressure is said to be at the steam point.

However from a more fundamental point of view, for example in thermodynamics, it is very desirable to assign a temperature that is independent of the properties of any substance or substances. Such a temperature scale is called a thermodynamic temperature scale, which was developed in conjunction with the second law of thermodynamics. The thermodynamic temperature scale in the SI is the Kelvin scale, named after Lord Kelvin (1824–1907). The temperature unit on this scale is the kelvin, which is designated by K. As the lowest temperature on the Kelvin scale is absolute zero, or 0 K, it follows that only one nonzero reference point needs to be assigned to establish the slope of this, by definition, linear scale. In practice attaining absolute zero is not possible but, using nonconventional refrigeration techniques, scientists [12] from the Massachusets Institute of Technology (MIT) have approached absolute zero kelvin in 2003, achieving 0,0000000005 K (500 pK). The thermodynamic temperature scale in the English (Imperial) system is the Rankine scale, named after William Rankine (1820 – 1872). The temperature unit on this scale is the rankine, which is designated by R. Rakine temperature is rarely encountered today as nearly all scientists and engineers use kelvin or degrees Celsius.

A temperature determination method that turns out to be nearly identical to thermodynamic temperature (kelvin) is that based on the pressure variation with temperature in a fixed volume of low pressure gas [9]. The temperatures are determined using a constant-volume gas thermometer, which is a rigid vessel filled with a gas, usually hydrogen or helium, at low pressure. This thermometer is based on the principle that at low pressures, the pressure of a gas if linearly proportional to its temperature at constant volume. That is the relationship between the temperature and the pressure of the gas in the vessel can be expressed as

$$T = a + b \cdot P \qquad (3)$$

where the values of the constants a and b for a gas thermometer are determined experimentally. Once a and b are known, the temperature of a medium can be calculated from this relation by immersing the rigid vessel of the gas thermometer into the medium whose temperature needs to be determined and measuring the gas pressure when thermal equilibrium is established between the medium and the gas in the constant volume vessel. This approach can closely approximate to thermodynamic temperature provided the gas is at low pressure and away from its liquefaction point. Using this method, a gas temperature scale can be developed by measuring the pressures of the gas in the fixed volume vessel at two reproducible points (such as the ice and the steam points) and assigning suitable values to temperatures at those two points. Considering that only one straight line passes through two fixed points on a plane, these two measurements are sufficient to determine the constants a and b in Equation (3). Then the unknown temperature T of a medium corresponding to a pressure reading P can be determined from that equation by a simple calculation.

The values of the constants will be different for each thermometer, depending on the type and the amount of the gas in the vessel, and the temperature values assigned at the two reference points. If the ice and steam points are assigned the values are 0 °C and 100 °C, respectively, then the gas temperature scale will be identical to the Celsius scale. In this case, the value of the constant a (which corresponds to an absolute pressure of zero) is determined to be -273,15 °C regardless of the type and the amount of the gas in the vessel of the gas thermometer. That is, on a P-T diagram, all the straight lines passing through the data points in this case will intersect the temperature axis at -273,15 °C when extrapolated backwards. This is the lowest temperature that can be obtained by a gas thermometer, and thus we can obtain an *absolute* (rather than arbitrary) gas temperature scale by assigning a value of zero to the constant a in Equation (3). In that case Equation (3) reduces to $T = b \cdot P$, and thus we need to specify the temperature at only one point to define an *absolute* gas temperature scale.

It should be noted that in practice the absolute gas temperature scale is not thermodynamic temperature because at very low temperatures (due to condensation) and at very high temperatures (due to dissociation and ionization) it cannot be used. However, absolute gas temperature is closely identical to thermodynamic temperature in the temperature range in which the gas thermometer can be used. Thus thermodynamic temperature can be obtained from an absolute gas temperature scale that utilizes an “ideal” or “imaginary” gas that always acts as a low-pressure gas regardless of the temperature. If such a gas thermometer existed, it would read zero kelvin at zero pressure, which corresponds to – 273,15 °C on the Celsius scale.

The reference temperature chosen in the original kelvin scale was 273,15 K (or 0 °C), which is the temperature at which water freezes (or ice melts) and water exists as a solid–liquid mixture in equilibrium under standard atmospheric pressure (the ice point). At the Tenth General Conference on Weights and Measures in 1954, the reference point was changed to a much more precisely reproducible point, the triple point of water (the state at which all three phases of water coexist in equilibrium), which is assigned the value 273,16 K. The Celsius scale was also redefined at this conference in terms of the ideal-gas temperature scale and a single fixed point, which is again the triple point of water with an assigned value of 0,01 °C. The boiling temperature of water (the steam point) was experimentally determined, at that time, to be again 100,00 °C, and thus the new and old Celsius scales were in good agreement [9].

2.2. The International Temperature Scale of 1990 (ITS-90)

In principle one could establish a quasi-thermodynamic temperature measurement system to determine temperature. However, this is totally impractical. So, in order to make temperature measurements in a uniform manner throughout the world, the International Temperature Scale of 1990 (ITS-90) was established. The ITS-90 was adopted by the International Committee of Weights and Measures at its meeting in 1989 at the request of the Eighteenth General Conference on Weights and Measures. This scale supersedes the International Practical Temperature Scale of 1968 (amended edition of 1975) and the 1976 Provisional 0,5 K to 30 K Temperature Scale [2].

The unit of the fundamental physical quantity known as thermodynamic temperature, symbol T, is the kelvin, symbol K, defined as the fraction 1/273,16 of the thermodynamic temperature of the triple point of water. It remains common practice to express a temperature in terms of its difference from the ice point (273,15 K). A thermodynamic temperature expressed in this way is known as a Celsius temperature, symbol t, defined by:

$$T(K) = T(°C) + 273{,}15 \qquad (4)$$

The ITS-90 defines both International Kelvin Temperatures, symbol T_{90}, and International Celsius Temperatures, symbol t_{90}. The relation between T_{90} and t_{90} is the same as that between T and t.

The ITS-90 extends upwards from 0,65 K to the highest temperature practicably measurable in terms of the Planck radiation. The ITS-90 comprises a number of ranges and sub-ranges throughout each of which temperatures T_{90} are defined. The ITS-90 has been constructed in such a way that, throughout its range, for any given temperature the numerical value of T_{90} is a close approximation to the numerical value of T according to best estimates at the time the scale was adopted.

The ITS-90 has three components:

a) Fixed points based on thermodynamic invariant points. These are highly reproducible phase transitions (like triple points, melting points and freezing points) of specific systems. The temperatures of the fixed points are established as accurately as possible on the thermodynamic temperature scale by international comparison and agreement. Where appropriate and necessary, pressure corrections are applied to the melting and freezing points.

b) The instruments to be used in interpolating temperatures between the defining fixed points.

c) The interpolation equations to be used to calculate the intermediate temperatures.

Between 0,65 K and 5,0 K T_{90} is defined in terms of the vapour-pressure temperature relations of ^{3}He and ^{4}He.

Between 3,0 K and the triple point of neon (24,5561 K) T_{90} is defined by means of a helium gas thermometer calibrated at three experimentally realizable temperatures having assigned numerical values (defining fixed points) and using specified interpolation procedures.

Between the triple point of equilibrium hydrogen (13,8033 K) and the freezing point of silver (1234,93 K) T_{90} is defined by means of platinum resistance thermometers calibrated at specified sets of defining fixed points and using specified interpolation procedures.

Above the freezing point of silver (1234,93 K) T_{90} is defined in terms of a defining fixed point and the Planck radiation law:

$$\frac{L_\lambda(T_{90})}{L_\lambda[T_{90}(X)]} = \frac{\exp(c_2[\lambda T_{90}(X)]^{-1}) - 1}{\exp(c_2[\lambda T_{90}]^{-1}) - 1} \tag{5}$$

where T_{90}(X) refers to any one of the silver, gold and copper freezing points (1234,93 K, 1337,33 K and 1357,77 K respectively), L is the spectral radiance at the wavelength λ (in vacuum) and c_2=0,014388 mK. All the defining fixed points of the ITS-90 are listed in Table 3.

Table 3: Defining fixed-points of the ITS-90

Fixed-point	State[d]	T_{90} / K	t_{90} / °C	ΔT_1/mK	ΔT_2/mK
^{4}He	VP	3 to 5	-270,15 to -268,15	0,3	0,1
e-H_2	TP	13,8033	-259,3467	0,5	0,1
e-H_2 (or He)	VP	17	-256,15	0,5	0,2
e-H_2 (or He)	VP	20,3	-252,85	0,5	0,2
Ne	TP	24,5561	-248,5939	0,5	0,2
O_2	TP	54,3584	-218,7916	1	0,1
Ar	TP	83,8058	-189,3442	1,5	0,1
Hg	TP	234,3156	-38,8344	1,5	0,05
H_2O	TP	273,16	0,01	0	0,02
Ga	MP	302,9146	29,7646	1	0,05
In	FP	429,7485	156,5985	3	0,1
Sn	FP	505,078	231,928	5	0,1
Zn	FP	692,677	419,527	15	0,1
Al	FP	933,473	660,323	25	0,3
Ag	FP	1234,93	961,78	40	1[b], 10[c]
Au	FP	1337,33	1064,18	50	10[c]
Cu	FP	1357,77	1084,62	60	15[c]

(a) All substances except He (both ^{3}He and ^{4}He are used) are of natural isotopic composition, e-H_2 is hydrogen at the equilibrium concentration of the ortho- and para-molecular forms. Additionally, estimates of the (k=1) uncertainty in the values ΔT_1 of thermodynamic temperature and in the best practical realisations ΔT_2 of some of the defining fixed-points of ITS-90 are stated.

(b) for platinum resistance

(c) for radiation thermometry

(d) VP: vapor pressure, TP: triple point, MP: melting point and FP: freezing point

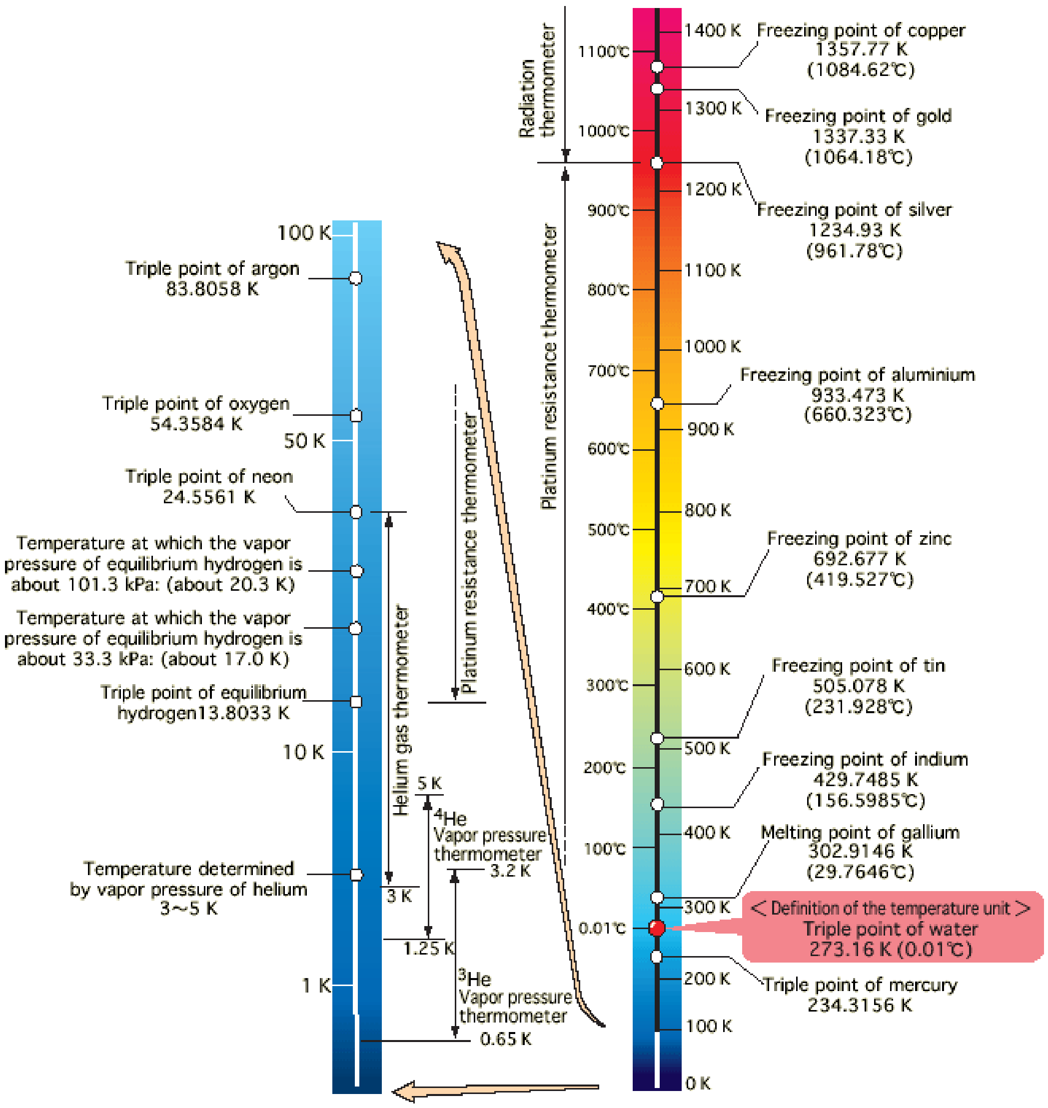

Figure 1: Defining fixed points of the ITS-90 and interpolating thermometers

In Figure 1, it can be observed a schematically design of the ITS-90, showing the interpolating thermometers for the various temperature ranges.

One of the guiding principles in establishing the ITS-90 was that it should allow the user as much choice in its realisation as was compatible with an accurate and reproducible scale. For this reason, the scale includes many sub-ranges; within all except one of these T_{90} is defined independently of calibration points outside the range. Thus, if a platinum resistance thermometer is to be calibrated over the whole of the low temperature range from ≈ 13,8 K to 273,16 K, all of the eight calibration points in that range must be used. If, however, a calibration is required only in the range from the argon point (≈ 84 K) to the triple point of water, then only the three calibration points in this range are needed, ≈ 84 K (Ar), ≈ 234 K (Hg) and 273,16 K (H_2O). Similarly, in the range above the water triple point, a thermometer may be calibrated from the water triple point to 30 °C using just the triple point of water and the melting point of gallium. It should be noted that this last range offers the simplest possible way of achieving the highest accuracy thermometry in room temperature range. In general this approach allows the user to avoid the trouble and expense of setting up calibration points at temperatures outside the range of interest. In addition it allows the thermometer itself to be maintained under the best possible conditions by not requiring it to be calibrated at temperatures well outside of its required temperature of normal use.

2.3.Temperature sensors

The most common instruments used to measure temperature in everyday life are described in this section. Temperature sensors can be divided into two large groups: contact sensors and non-contact sensors.

2.3.1.Contact sensors

2.3.1.1.Liquid in glass thermometers

Liquid-in-glass thermometers were one of the earliest forms of thermometer and their use dominated temperature measurement for at least 200 years [13]. They have had a profound effect on the development of thermometry. Liquid-in-glass thermometers were developed to fill nearly every niche in temperature measurement from -190 °C to 600 °C, including measurement of very small temperature differences to of order of a milikelvin.

The operation of liquid-in-glass thermometers is based on the expansion of the liquid with temperature, that is, the liquid acts a transducer to convert thermal energy into a mechanical form. As the liquid in the bulb becomes hotter it expands and is forced up the capillary stem. The temperature is indicated by the position of the top of the liquid column with respect to the marked scale.

The popularity of these types of thermometers continues in some jurisdictions in spite of the fragile nature of the glass and the toxicity of the commonly used thermometric liquid. However, in some regions, notably Europe the use in liquid-in-glass thermometers has significantly declined due to the banning of the use of mercury in most situations.

However, despite that liquid-in-glass thermometers are still specified in many test procedures worldwide and they represent a cost-effective solution in situations where only a few temperature measurements are required. The trend is, however, to move away from liquid-in-glass thermometers, not only due to the mercury toxicity but also because the thermometer itself is fragile and does not lend itself to automation. Where they remain popular, mercury is being abandoned as the thermometric fluid in favour of organic fluids or even synthetic fluids.

2.3.1.2.Resistance thermometers and thermistors

Resistance thermometers essentially use the physical property of the variation of resistance with temperature as a method of producing a reliable temperature sensor [13]. There are several types both metallic and semiconductor – these are described in general terms below.

Platinum, other in fine wire form, is the most widely used metal for resistance thermometry, although it is not the only one. Other metals include copper, nickel and nickel-iron, as well as rhodium-iron whose use is generally restricted to cryogenic thermometry.

Platinum resistance thermometers (PRTs) are instruments that, over various forms, can measure temperature over the range 14 K to 960 °C, to, for the best devices, ie those defined as interpolating devices of the ITS-90, an accuracy approaching 1 mK. They can be cycled over several hundred degrees and still provide a very severe test of the best resistance bridge. Few material artefacts can be treated in this manner and remain as stable.

A wide range of PRTs is available, from the standard PRT (SPRT) used as the interpolating instrument in the ITS-90 to more robust, though still wire based, industrial PRTs which may be accurate to only a few hundredths of a degree. Film based PRTs are also widely used and these are generally reliable to a few tenths of a degree. The lower overall cost and higher accuracy of platinum thermometry make it the preferred means to measure temperature for many applications.

Thermistors are semiconducting ceramic resistors made from various metal oxides. They have one outstanding advantage over all other resistance thermometers, namely very high sensitivity. It is not difficult to build thermistor thermometers with sensitivities of more than 100 times that of most platinum thermometers and more than 1000 times that of most thermocouples. They are also very small and fast to respond – again with care, over restricted ranges, uncertainties can be of order hundredths of a degree.

Resistance thermometers are unlike other temperature sensors in that they require external stimulation in the form of a measuring current or voltage. This gives rise to errors associated with resistance-measuring instruments that must be considered in addition to those due to the sensor itself. In addition, the method of measurement needs to be carefully implemented or the uncertainty due to the resistance of the sensing leads can introduce difficult to quantify uncertainties.

2.3.1.3.Thermocouples

Thermocouples are the most widely used of all temperature sensors. Their basic simplicity and reliability have an obvious appeal for many industrial applications. Most of the basic principles for thermocouple thermometry were known around 1900 but partly obscured by the development of the laws of thermoelectricity [13]. The thermocouple gives a measure of the temperature difference between the hot (measurement) and cold (reference) junctions through a measurement of the potential difference between the two junctions. The potential difference is established in the temperature gradient between the measurement and reference junctions. This is an important point to stress as it is sometimes erroneously stated that the thermovoltage is established at the measurement junction which it isn’t. For an ideal homogeneous thermocouple, the thermovoltage is a function only of the temperature difference between the two junctions [3]. However for a real thermocouple, inhomogeneities of one sort or another, which occur in the wires must be taken into account and indeed constitute the limiting factor in the accuracy with which thermocouples can be used.

Depending on the application and temperature range, many combinations of thermoelements exist, normally designated by letters like type S, R and B for noble metal based thermocouples and type K, J, N, T and many others, for simple metal alloy thermocouples. More recently, pure metal thermocouples like Pt-Au and Pt-Pd have been developed, which offer better stability and performance when compared to the noble metal types.

2.3.2. Non-contact temperature sensors

This kind of temperature sensors presents many advantages when compared to contact thermometers [14]. These are:

1) They are fast (in the milliseconds range). Time is saved, allowing for more measurements and accumulation of data.
2) It facilitates measurement of moving targets.
3) Measurements can be taken of hazardous or physically inaccessible objects (high-voltage parts, great measurement distance).
4) Measurements of high temperatures (greater than 1300 °C) present no problems. In similar cases, contact thermometers cannot be used, or have a limited life.
5) There is no interference. No energy is lost from the target than otherwise would be lost by thermal radiation. For example, in the case of a poor heat conductor such as plastic or wood, measurements can be extremely accurate with no distortion of measured values, as compared to measurements with contact thermometers.
6) There is no risk of contamination and no mechanical effect on the surface of the object; thus wear-free. Lacquered surfaces, for example, are not scratched and soft surfaces can also be measured.

It is possible to find sensors employing this technique using many different names, like radiation thermometers, optical pyrometers, total radiation thermometers, band-pass pyrometers, infrared pyrometers, thermal imagers, among others.

All these instruments employ measurement methods of thermometry based upon the measurement of thermal radiation. In this field, the words “pyrometry” and “thermometry” tend to be used as synonyms, although the use of “pyrometry”, with its connotation of fire, seems inadequate when referring to infrared measurements of temperature below 100 °C [3].

In radiation thermometry, in contrast to resistance thermometry or thermocouple thermometry explicit equations relating thermodynamic temperature to the measured quantity can be used: in this case spectral radiance. This is possible because the thermal radiation existing inside a closed cavity (blackbody radiation), depends only upon the temperature of the walls and not at all upon their shape or material provided that the cavity dimensions are much larger than the wavelengths involved. The radiation escaping from a small hole in the cavity wall departs from blackbody radiation by only an amount determined by how much the state of equilibrium within the cavity is perturbed by the presence of the hole. By careful design, this perturbation can be made negligibly small, so that equilibrium blackbody radiation is accessible for measurement. Thus, thermodynamic temperature may be measured very precisely by means of radiation thermometry [3]. The central problems in applying the technique of radiation thermometry are the determination of the target emissivity (which depends on temperature, material, surface finish and angle of view) and the reduction of the influence of surrounding radiation and environmental effects (i.e. absorption along the viewing path) so that the true surface temperature can be obtained.

Another important difference between radiation thermometry and other methods of thermometry, and one that has deeply influenced its development is that for the former, there exists a natural sensor: the human eye. The most widely used instrument for radiation thermometry was, until quite recently, the disappearing filament optical pyrometer. In this instrument, the human eye is used to judge equality of brightness between a glowing filament and an image of the source whose temperature is being measured. Under good conditions of illumination, the eye can detect differences in brightness of as little as 1% between adjacent fields, which are equivalent to a temperature difference of only 1 °C between blackbodies near 1000 °C [3].