

# **Sensors**

Volume 4

Thermal Sensors





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A Comprehensive Survey

Edited by

W. Göpel, J. Hesse, J. N. Zemel

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T. Ricolfi, J. Scholz



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## A Comprehensive Survey

Edited by

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## Preface to the Series

The economic realities of productivity, quality, and reliability for the industrial societies of the 21st century are placing major demands on existing manufacturing technologies. To meet both present and anticipated requirements, new and improved methods are needed. It is now recognized that these methods must be based on the powerful techniques employing computer-assisted information systems and production methods. To be effective, the measurement, electronics and control components, and sub-systems, in particular sensors and sensor systems, have to be developed in parallel as part of computer-controlled manufacturing systems. Full computer compatibility of all components and systems must be aimed for. This strategy will, however, not be easy to implement, as seen from previous experience. One major aspect of meeting future requirements will be to systematize sensor research and development.

Intensive efforts to develop sensors with computer-compatible output signals began in the mid 1970's; relatively late compared to computer and electronic measurement peripherals. The rapidity of the development in recent years has been quite remarkable but its dynamism is affected by the many positive and negative aspects of any rapidly emerging technology. The positive aspect is that the field is advancing as a result of the infusion of inventive and financial capital. The downside is that these investments are distributed over the broad field of measurement technology consisting of many individual topics, a wide range of devices, and a short period of development. As a consequence, it is not surprising that sensor science and technology still lacks systematics. For these reasons, it is not only the user who has difficulties in classifying the flood of emerging technological developments and solutions, but also the research and development scientists and engineers.

The aim of "Sensors" is to give a survey of the latest state of technology and to prepare the ground for a future systematics of sensor research and technology. For these reasons the publishers and the editors have decided that the division of the handbook into several volumes should be based on physical and technical principles.

Volume 1 (editors: T. Grandke/Siemens AG (FRG) and W. H. Ko/Case Western Reserve University (USA)) deals with general aspects and fundamentals: physical principles, basic technologies, and general applications.

Volume 2 (editors: W. Göpel/Tübingen University (FRG), L. Lundström/Linköping University (Sweden), T. A. Jones†/Health and Safety Executive (UK), M. Kleitz/LIENSEEG (France) and T. Seiyama/Kyushu University (Japan)) concentrates on chemical and biochemical sensors.

Volume 3 (editors: N. F. de Rooij/Neuchâtel University (Switzerland), B. Kloeck/Hitachi Ltd. (Japan) and H. H. Bau/University of Pennsylvania (USA)) presents mechanical sensors.

Volume 4 (editors: J. Scholz/Sensycon GmbH (FRG) and T. Ricolfi/Consiglio Nazionale Delle Ricerche (Italy)) refers to thermal sensors.

Volume 5 (editors: R. Boll/Vacuumschmelze GmbH (FRG) and K. J. Overshott/Brighton Polytechnic (UK)) deals with magnetic sensors.

Volume 6 (editors: E. Wagner and K. Spenner/Fraunhofer-Gesellschaft e. V. (FRG) and R. Dändliker/Neuchâtel University (Switzerland)) treats optical sensors.

Each volume is, in general, divided into the following three parts: specific physical and technological fundamentals and relevant measuring parameters; types of sensors and their technologies; most important applications and discussion of emerging trends.

It is planned to close the series with a volume containing a cumulated index.

The series editors wish to thank their colleagues who have contributed to this important enterprise whether in editing or writing articles. Thank is also due to Dipl.-Phys. W. Greulich, Dr. M. Weller, and Mrs. N. Banerjea-Schultz of VCH for their support in bringing this series into existence.

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August 1990



## Preface to Volume 4 of “Sensors”

According to all recent major market surveys, sales of temperature sensors are far higher in numbers than those of other kinds. Due to the wide variety of applications and the wide range of temperatures to be measured and monitored, a multitude of varying physical principles is applied in temperature sensing. The aim of this book is to describe the constructional and applicative aspects of thermal sensors while preserving a rigorous treatment of the underlying physical principles. Emphasis was laid on those principles which are established in the fields of industrial temperature measurement. Other principles which may increase in importance in the future are outlined in the introductory chapter.

General considerations of the physics of temperature measurement are dealt with in Chapter 2. Part of this chapter is devoted to the description of the new International Temperature Scale of 1990 (ITS-90). As reference to the new scale is made wherever applicable in the successive chapters, this book is likely to be the first to have been updated in this respect. (Unfortunately, industrial standards for temperature sensors such as resistance thermometers and thermocouples are not yet adapted to the new temperature scale and therefore all references made to these standards are still on the basis of the former IPTS-68.)

Chapter 2 also includes a systematic survey of the physical principles of all important thermal sensors. Specific categories of sensors are treated in Chapters 3 to 9. The three main categories of temperature sensors, i.e., resistance thermometers, thermocouples, and radiation thermometers are thoroughly discussed in Chapters 3 to 5. In the chapter on radiation thermometers greater emphasis has been placed on applications. This is due to the fact that the modalities of use are often more important than the sensor itself. Chapters 6 and 7 are devoted to noise and acoustical thermometers, respectively. These two sensor types are now the subject of renewed interest due to some recent advances and to their ability to solve special measurement problems in nuclear and very high temperature applications, for example. Heat-flow and mass-flow sensors, i.e., those thermal sensors which differ from thermometers, are described in Chapters 8 and 9. The usefulness of these sensors is mainly found in the wide variety of energy-related applications where they can make important contributions.

Examples of applications are given in Chapters 1 to 9. The applications of thermal sensors in some specific fields, namely, process control, automotive technology and cryogenics are systematically analyzed in Chapters 10 to 12.

When we started our task we were conscious of the difficulties we were going to meet in coordinating the work of a number of colleagues with different backgrounds and perhaps points of view. Now that the task is completed, we realize that it has been a stimulating and gratifying experience and this is due to the enthusiasm and patience of both the authors and the editorial staff to whom we are pleased to express our sincere thanks.

T. Ricolfi and J. Scholz

Torino and Hanau, August 1990



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# 1 General Aspects

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## 1.1 Introductory Remarks

The basic principles of thermal sensors are well established since several years. For this reason, spectacular advances in this area have not been made in recent years nor are to be expected in the near future. Nevertheless, a great deal of work has been and is currently being made in scientific and industrial laboratories to provide adequate solutions to modern measurement needs.

Practical needs and recent solutions are shortly reviewed in this chapter. This also offers the opportunity to outline the present trends in thermal sensors and to give some hints on modern approaches like, for example, fiber-optic techniques that are not treated elsewhere in this volume.

## 1.2 General Needs in Practical Measurements

The growth of process control and automation, the increasing significance of quality control, the recourse to sophisticated technologies in manufacturing processes, the increasing concern to safety problems, are some major aspects of modern manufacturing and technological processes. They entail new requirements for the quality of sensors and measurement approaches.

### 1.2.1 Accuracy

An increased *accuracy* is the main requirement originating from a more rigorous quality control or from the adoption of advanced technologies like, for example, semiconductor processing (silicon, germanium, gallium-indium arsenic mixtures).

The measurement accuracy is partly determined by the intrinsic features of the sensor itself (sensitivity, repeatability, stability) and, in many cases to a larger extent, by the conditions of measurement (thermal gradients, aggressive atmospheres, electromagnetic interferences, etc.).

High sensitivity requirements have produced, for example, a renewed interest for the quartz thermometer in applications up to 300 °C and the development of special fiber-optic thermometers in the high temperature range up to 2000 °C.

Insofar as stability and repeatability are primary concerns, the platinum resistance thermometer (PRT) appears to be the optimum choice in many applications up to about 850 °C. In the high temperature range great improvements in contactless measurements have been derived from the use of stable silicon photodetectors in radiation thermometers.

As to the effect of environmental conditions, again PRTs represent a good choice. In fact, they are less affected by thermal gradients than thermocouples and less expensive than platinum metal thermocouples that are required to withstand most aggressive atmospheres. Some of the advantages of PRTs can also be ascribed to noise thermometers that, although much less diffused, can be of interest for some applications (eg, in presence of neutron irradiation) in a wide temperature range up to 2000 °C. However, electrical thermometers may be of



limited use in the presence of electromagnetic interferences (eg, in microwave heating processes). In these cases advantages are offered by the recently developed thermometers based on optical effects (see Section 1.3).

### 1.2.2 Reliability

In many manufacturing processes, in order to reduce downtime and maintenance requirements, more emphasis is being placed on improving instrument *reliability* than on the measurement accuracy. This is particularly true for automated processes. It is generally recognized that mechanical thermometers (liquid in glass, bimetal, gas, vapor-pressure thermometers) are reliable sensors. Moreover, they are also characterized by intrinsic safety and immunity to electromagnetic interferences. However, they can hardly fulfill the requirements of process automation. So, one of the present points of interest in industrial instrumentation is their replacement with thermometers providing an electrical output.

### 1.2.3 Interchangeability

*Interchangeability* of sensors is another important requirement. Many parameters of a control system in an automated process are determined by the characteristics of the sensor being used. So, in case of failure, it should hopefully be replaced by another sensor of identical characteristics. Otherwise, all the control parameters have to be readjusted. A full interchangeability of sensors even from different sources is ensured by internationally recognized standards for commonly used sensors. From this point of view as well, PRTs appear to be a good choice. On the contrary, other thermometers, like the quartz thermometer, generally need an individual calibration, so their interchangeability is low and no standards are available.

### 1.2.4 Cost

The enhanced performance demands to sensors and their massive use in process control require a *cost reduction* in their fabrication in order to keep the overall cost of a control system within reasonable limits. Mechanical sensors are generally more expensive than electrical and electronic ones, so their replacement also contributes to the objective of cost reduction. As for PRTs, which have been shown to provide the best solution to many requirements, cost reduction is obtained by using thick and thin-film techniques in their fabrication (see Chapter 3). A noticeable cost reduction has also been obtained in infrared thermometers for fixed installation with the use of relatively cheap silicon and pyroelectric detectors and thin-film thermopiles.

### 1.2.5 Safety

*Safety* in industrial plants is another requirement of major concern. Examples of measures dictated by safety requirements are the replacement of mercury thermometers in the food in-

dustry and of electrical thermometers without special safety features where explosion hazards are prevalent. A valuable alternative in the latter case is offered by fiber-optic thermometers.

### 1.2.6 Technical diagnostics

The efficiency and safety in industrial plants are often determined by an accurate *technical diagnostic*. The measurement of thermal contours in tool machines, the monitoring of motor winding temperatures, or the location of defective components in electronic circuits are examples of technical diagnostics concerning thermal measurements. One particular aspect of technical diagnostic refers to the capability of a measuring systems of checking its own integrity, including calibration data. However, these studies are in their early stage insofar as thermal sensors are concerned.

## 1.3 Developments in Sensors and Measurement Techniques

Some recent achievements refer to the development of new sensors that, although based on well known principles of measurement, nevertheless are better suited to overcome some typical limitations of other sensors of the same type. New thermocouples and infrared thermometers may be included in this category.

A second category of achievements has been obtained with the application of modern technologies or devices to the fabrication of sensors or to the setting up of measuring systems. Examples are the use of thick- and thin-film techniques, micromachining, fiber optics and microprocessors.

### 1.3.1 New Thermocouples and Infrared Thermometers

Good results have been obtained with Nicrosil/Nisil, Pt/Au and Pt/Pd thermocouples. The Nicrosil/Nisil thermocouple is characterized by a better stability between 300 °C and 600 °C and above 1000 °C as compared with the popular type *K* thermocouple. The Pt/Au thermocouple is particularly suited for precision measurements due to its high reproducibility that is better than the ones of the various platinum-rhodium/platinum thermocouples. In fact, reproducibilities of the order of  $\pm 0.02$  °C have been found between 0 °C and 1000 °C [1]. Further benefits may stem from the high homogeneity of the wire materials of pure-metal thermocouples. As compared with alloy thermocouples, they should be much less affected by thermal gradients along their legs.

A strong limitation in infrared thermometers is the dependence of their readings on the emissivity of the target materials. To overcome this problem, many solutions have been realized but none of them is universally applicable. So, the predominant philosophy in recent years has been to design thermometers individually for each material or category of materials. Representative examples are described in Chapter 5.

### 1.3.2 Film Techniques

As previously said, cost reduction is one reason for using film techniques in the fabrication of noble-metal thermometers. This is especially true for PRTs that are progressively replacing thermocouples in many applications. Film PRTs are now commercially available and they are characterized by good interchangeability and stability up to 600 °C. The stability is such that after 1000 hours at 600 °C a thin-film PRT can be still within  $\pm 0.05$  °C of its initial reading at 0 °C.

A second reason for adopting film more than wire configurations refers to contact measurements of surface temperatures where it is important to minimize the disturbance of heat transfer on the surface to be measured. A frequent requirement in surface temperature measurements is also a high speed of measurement. This is the case, for example, for laser or electron beam machining where fast temperature transients occur. Thin-film thermocouples can meet both the requirements of low disturbance and high speed. The problems of contamination from the atmosphere or contacting surfaces and that of variable stresses on the conductors, which are typical in thin-film thermocouples for high temperature applications are going to find satisfactory solutions [2], [3]. As to the achievable measuring speed, a response time of 60 ns has been recently found for a Pt/Ir thermocouple up to 790 °C [4].

### 1.3.3 Micromachining

Micromachining techniques utilizing the anisotropic etching of silicon are promising possibilities to manufacture miniaturized sensors in large numbers at low cost.

Although the main emphasis in this technology is put on pressure-, acceleration-, and frequency sensors, some prototypes of thermal mass-flow sensors have been developed. One possible application is the airflow-measurement with ignition control systems of automobiles [23].

### 1.3.4 Fiber-optic Sensors

The use of fiber-optic components is one outstanding feature of the current R & D activity on thermal sensors. Fiber-optic sensors offer immunity to electrical interference and inherent safety. Furthermore, optical fibers are both electrical insulators and poor thermal conductors and these properties can be utilized to insulate the sensor from the monitoring unit or to minimize the heat loss from the object of measurement.

An increasing use of fiber optics is being made in radiation thermometers (see Chapter 5). Current studies are aimed at finding alternative materials to glass and silica (eg, chalcogenide glasses [5]) that can transmit at longer wavelengths up to 10  $\mu\text{m}$ .

A number of physical effects other than thermal radiation have been utilized to make fiber-optic temperature sensors. A comprehensive review on this subject has been recently prepared by *Grattan* [6]. The most promising devices rely upon the following temperature-related physical effects:

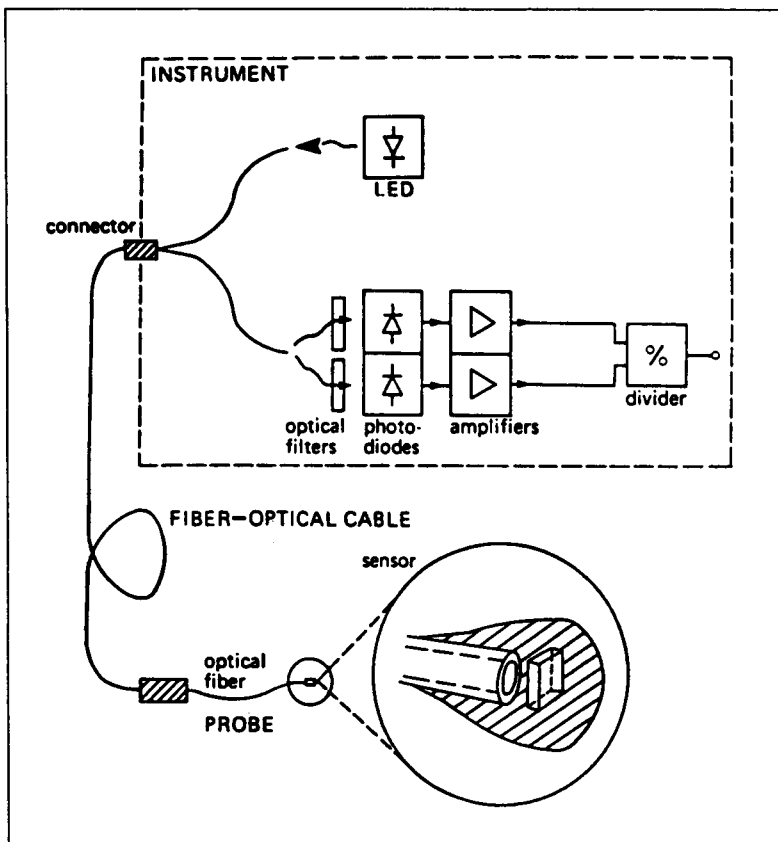
1) *Light scattering by cholesteric liquid crystals*. Sensors utilizing this effect can operate over a 10 °C temperature span within the range 10 °C–50 °C depending on the nature of the liquid crystals used [7].

2) *Color change.* This property is exhibited by the so-called thermochromic materials. A device utilizing a cobalt salt solution in isopropyl alcohol and water, a substance showing a marked color change between 25 °C and 75 °C, has been described by *Scheggi et al.* [8].

3) *Change of refractive index.* Different schemes have been tried utilizing this principle. The sensing substance can be either a liquid of high index range with temperature [9], or the plastic cladding of silica fibers [10].

4) *Change of birefringence.* The temperature variation of birefringence in quartz has been utilized in a prototype sensor [11].

5) *Change of light transmission.* Optical absorption techniques have been described utilizing this effect in filters [12] and in GaAs [13] and ruby glass [14] samples.



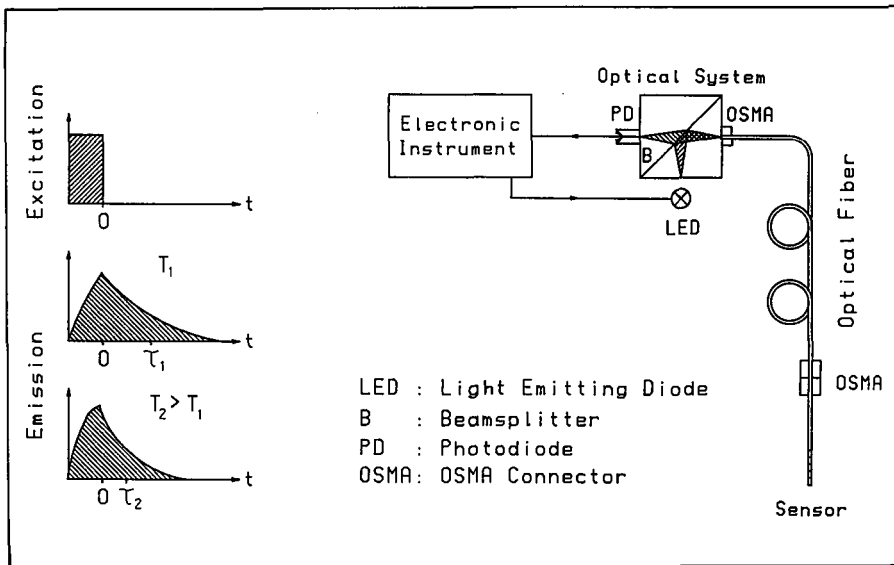
**Figure 1-1.** Schematic of ASEA type 1010 fiber-optic sensor. A GaAs crystal bound at the end of the fiber-optic probe is irradiated by directly modulating light from a LED. The light emitted due to the fluorescent properties of the crystal is conveyed through the fiber and a beam divider to two photodiodes. The ratio of the signals of the photodiodes depends on the wavelength shift of the emitted light and hence on the temperature of the crystal. This sensor can be used from 0 °C to 200 °C. Resolution and accuracy are 0.1 °C and  $\pm 0.5$  °C, respectively.

6) *Change of light intensity.* The intensity of light emitted by rare earth phosphors is temperature dependent. This principle has been utilized in the Luxtron type 1000/2000 system [15].

7) *Wavelength shift of fluorescence.* This effect in GaAs crystals has been utilized in the ASEA type 1010 system [16] (Figure 1-1).

8) *Fluorescence decay time.* Many materials, like neodymium or chromium doped glasses and crystals, magnesium fluorogermanate, alexandrite, and others, show a high rate of change with temperature of the fluorescence decay time. This effect has been utilized in commercial instruments by Luxtron [17] and Degussa (now Sensycon) [18] (Figure 1-2). A major advantage in this technique is that an accurate measurement of the intensity of the excitation light is not needed.

Current problems in the development and use of fiber-optic thermometers refer to inaccuracies due to transmission losses in the fibers, long-term instabilities and cost, with the latter being generally higher than that of conventional measuring systems.



**Figure 1-2.** Schematic of a sensor based on the decay time of fluorescence (after [18]). The excitation radiation is turned off at time  $t = 0$ . The emission of fluorescence radiation is shown for two different temperatures  $T_1$  and  $T_2$  of the sensor element. With  $T_2$  being the higher temperature, the corresponding decay constant  $\tau_2$  is smaller than  $\tau_1$ . LED, light emitting diode; B, beamsplitter; PD, photodiode; OSMA, OSMA connector.

### 1.3.5 Use of Microprocessors

Microprocessors are other important tools for improving and widening the measurement capabilities [19]. The benefits that can be derived from their use in data acquisition and processing are practically unlimited.

Apart from the general convenience in the automatic acquisition of measurement data, in some cases the acquisition would be impossible without microprocessors. This occurs, for ex-

ample, in the measurement of very fast temperature transients with thin-film contact thermometers or high-speed radiation thermometers having a response time of the order of  $1 \mu\text{s}$  [20].

As for data processing, the applications of microprocessors include signal linearization, correction for dynamic response, cold junction compensation, implementation of time functions in radiation thermometers, real-time processing of thermal images, and others.

Also the realization of intelligent instrumentation is an important achievement. For example, "cybernetic" radiation thermometers have been realized that can recognize the conditions of measurement (eg, the degree of oxidation) on the basis of some preliminary information on the emissivity of the target material [5]. Another example is that of intelligent temperature transmitters for thermocouples or resistance thermometers [21]. Their capabilities include that of accepting inputs from sensors of different types and of being customer configurable (Figure 1-3).



**Figure 1-3.** Microprocessor-based temperature transmitter with remote transmitter interface (after [21]).

## 1.4 Needs for Future Developments

Although adequate solutions have been found for most practical measurement problems, there are applications where the available solutions are not fully satisfactory. In some cases, better solutions have already been envisaged, but they are still needing further developments.

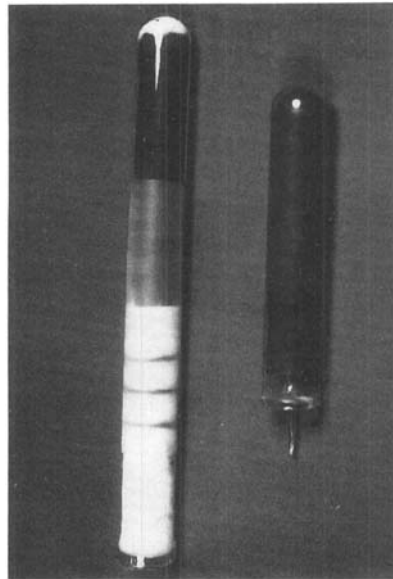
In manufacturing processes, problems still exist in using contact thermometers under chemically aggressive atmospheres (eg, sulphuric atmospheres), in recording temperature profiles inside ducts, in measuring the temperature of molten glass and of metal surfaces during rolling and extrusion processes.

In advanced technological processes, examples of difficulties in temperature measurement are found in laser machining processes, in the adaptive control of tool machines in high-precision machining of large pieces, in cryogenic applications below 10 K under intense magnetic fields ( $>10$  T).

In medicine, the problem of noninvasive internal temperature monitoring has not yet been given a satisfactory solution, although microwave radiometry and ultrasound thermography appears to be the most promising techniques [22].

In instrumentation improvement, there is a need for developing multi-channel systems for fiber-optic sensors and advantages are expected from the replacement of mechanical scanners with sensors arrays in thermal-mapping systems.

In calibration approaches, a growing use of sealed cells for fixed-point temperature calibration is to be expected, since they provide a simple and accurate way for the user to check its own instrumentation for calibration drifts (Figure 1-4). A calibration problem that is still needing a satisfactory solution is the evaluation of the convective heat transfer in radiant flux meters for fire-testing applications.



**Figure 1-4.**  
Sealed cells for metal freezing points (courtesy IMGC).

Finally, some urgent needs stem from the adoption of the new International Temperature Scale of 1990 (ITS-90). They are the need for the standardizing organizations of preparing new industrial standards for temperature sensors and the need for the calibration laboratories at any level of taking appropriate measurements to adequate their standards and procedures to the ITS-90.

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## 2 Physical Principles

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## 2.1 Introduction

Thermal sensors, as the name implies, are those that sense changes in temperature. Their chief use, then, is for the measurement or control of temperature, and when so-used they are called thermometers. Thermometers may be of two general classes: purely thermal sensors that respond to a temperature change caused by absorbed thermal energy, or photo-detectors that depend upon photon-electron interactions instigated by absorbed photons. Thermal sensors are also used to measure heat fluxes as, for example, energy losses through walls, solar radiation (pyrheliometry) and, more broadly, radiometric quantities in general. They can also be used to measure mass flow. Thus, most thermal sensors are thermometers and even when they are not, they are based upon temperature sensing devices. This chapter is concerned chiefly with temperature measurement and here the term thermometer and thermal sensor become almost synonymous. The physical principles underlying thermal sensors require discussion of temperature itself – its concept, measurement methods, and scales – in addition to elucidation of the principles of the various sensors themselves.

Temperature is one of the most important of physical quantities. It appears explicitly in some of the most fundamental laws of physics and pervades almost every part of physical measurements. Its unit, the kelvin,  $K$ , is one of the seven base units of le Système International d'Unités (SI). Measurement of temperature, i.e., the assignment of numerical values to temperature according to some reasonably ordered system that has physical significance, is more complex than for the other base quantities for reasons connected both with temperature being intensive (ie, non-additive) and with the lack of any intuitive quantitative understanding of it. There are few physical properties that are not temperature-dependent. It follows that there is a very large number of different physical properties that can serve, at least in principle, as the basis for thermal sensors with which to measure temperature and temperature changes.

It is the intent in this chapter to describe the thermodynamic basis of temperature, the general principles required for its measurements, and the advantages to be derived from temperature scales that are universal and are related to thermodynamic temperatures in some known way. The International Temperature Scale of 1990 and the reasons for its introduction are outlined. This is followed by a detailed discussion of the physical principles that underlie a large number of thermal sensors (or thermometers) – those that are important for the establishment of thermodynamic temperature and others that are in widespread practical use. There are also included some comments on the measurement of heat flow and heat flux, and some generalities on associated sensors.

## 2.2 Concept of Temperature

### 2.2.1 Historical Resumé

Although the ancients could measure length, time, and mass moderately precisely, they had no notion at all of the fundamental nature of temperature nor is there any record of their attempting to measure it. The invention of the thermometer is relatively recent, being ascribed

to Galileo in 1592. His instrument was based upon the thermal expansion of air. Very soon thereafter liquid-expansion thermometers were introduced in much the same form as they exist today. The development of thermometers was accompanied by the concurrent development of temperature scales with which to compare and record measurements of temperature. Most of these scales were based upon one or other of two principles: (a) calibration of the thermometer at two temperatures to establish two fiduciary marks, division of the intervening interval into equal parts, and linear extrapolation beyond the fiduciary marks; (b) calibration of the thermometer at one temperature with subsequent scale divisions based upon a calculated expansion of the fluid. The first of these is the obvious forerunner of modern practical scales and was the most precise and widest used; the second suggested some fundamental, rather than strictly empirical, basis and hints at present thermodynamic temperatures.

### 2.2.2 Thermodynamic Basis

All of the early temperature scales were simply empirical. However, the basis for a fundamental scale had been laid in experiments on the properties of gases by a succession of workers. Boyle had deduced ( $\sim 1661$ ) that the product of the pressure ( $P$ ) and volume ( $V$ ) of a fixed quantity of air (number of moles,  $N$ ) at constant temperature ( $T$ ) is constant, at least over a moderately wide range of pressure. This may be written

$$PV = \text{constant} \quad (2-1)$$

when  $N$ ,  $T$  are constant. More than a century later, from the results of independent experiments, Charles and Gay-Lussac deduced the relationship

$$V = V_0(1 + \alpha\tau), \quad (2-2)$$

where  $V$  is the volume occupied by  $N$  moles of any gas at temperature  $\tau$  on the arbitrary scale used,  $V_0$  is the volume at the zero of the  $\tau$  scale, and  $\alpha$  is the volume coefficient of thermal expansion. Within the limits of their experiments, Charles and Gay-Lussac found the same value of  $\alpha$  for most gases.

If the temperature  $T$  of Equation (2-1) is related to  $\tau$  by

$$T = \tau + \alpha^{-1} \quad (2-3)$$

then Equation (2-2) has the form

$$V/T = \text{constant} . \quad (2-4)$$

Combining Equations (2-1) and (2-4), we obtain the general gas law

$$PV/T = \text{constant} . \quad (2-5)$$

The value for the constant in Equation (2-5) was deduced to be  $NR$ , where  $R$  is the gas constant (joules per mole kelvin) and  $N$  is the number of moles, so that the gas law is

$$PV = NRT . \quad (2-6)$$

From Equation (2-3), when  $\tau = -\alpha^{-1}$ ,  $T = 0$ , which corresponds in Equation (2-2) to a contraction of the gas to zero volume, and so no lower temperature would be possible. These ideas are, of course, very simplistic, but nevertheless they introduce the notion of a temperature scale ( $T$ ) with an *absolute zero* at which both pressure and volume approach zero. Equation (2-5) also indicates the basis of a gas thermometer for measuring  $T$  by maintaining  $V$  constant and measuring  $P$ , or vice versa. Detailed experiments by Regnault in the early 19th century suggested that Equation (2-5) is only approximately true and that different gases lead to different values of  $\alpha^{-1}$ . We now know that the equation holds for all gases in the limit of very low pressures and high dilution ( $N$  small) and call such gases *ideal* or *perfect*. The corresponding scale for defining  $T$  is called the *absolute temperature scale* or the *ideal gas temperature scale*. Historically, a centigrade scale that assigned  $0^\circ\text{C}$  to the freezing point of water and  $100^\circ\text{C}$  to the boiling point of water had come into use. For conformity in size of the degree, Equation (2-3) leads to  $T = \alpha^{-1} = 273.15^\circ\text{C}$  when  $\tau = 0^\circ\text{C}$  (for the current best value for  $\alpha$  of  $0.003661 (\text{C}^\circ)^{-1}$ ) or, conversely, the zero of the ideal gas scale is at  $-273.15^\circ\text{C}$ .

The need had become evident for a truly fundamental temperature scale independent of the properties of any particular substance. William Thomson (Lord Kelvin), building upon earlier studies by Sadi Carnot on reversible heat engines, provided the solution. A heat engine operates in such a way that during one part of its cycle its working substance absorbs heat from a reservoir at a high temperature and during another part, after using some of this heat to do external work, it rejects a lesser quantity of heat to another reservoir at a lower temperature. Carnot (in 1824) had shown that his idealistic heat engine, in which all of the operations of the cycle are reversible, worked at the maximum possible efficiency and that this efficiency was independent of the nature of the working substance and dependent only upon the temperatures of the two reservoirs. Thomson (in 1848) proposed to define temperature in terms of the efficiency of an ideal Carnot engine. Consider Carnot engines working between successive reservoirs at temperatures  $T_n$  and  $T_{n-1}$ , extracting heat  $Q_n$  from the hotter reservoir, and rejecting heat  $Q_{n-1}$  to the cooler one, as shown schematically in Figure 2-1. By analyzing the efficiencies of successive engines, one can show that

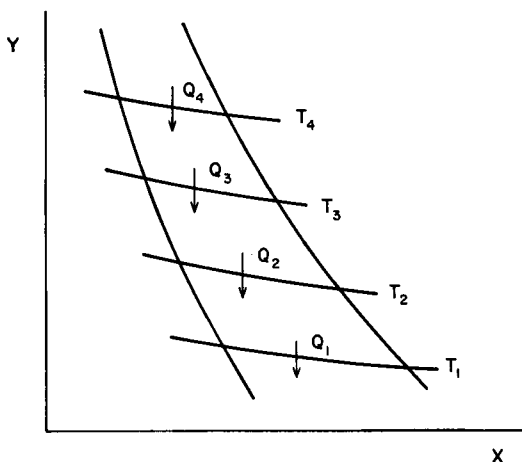
$$\frac{Q_2}{Q_1} = \frac{f(T_2)}{f(T_1)}, \quad (2-7)$$

where  $f$  is some unknown function of  $T$  that depends only upon the temperatures  $T_2$  and  $T_1$ , and not on the nature of the working substance.

Kelvin's proposal for defining *thermodynamic temperatures* was to use for the ratio on the right hand side Equation (2-7) just the ratio of the temperatures themselves, ie,

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}. \quad (2-8)$$

Temperature defined in this way can be shown to be identical to those defined by the ideal gas laws or, indeed, identical to those defined by all the other fundamental equations of physics such as Planck's Law or Nyquist's formula for the mean square electrical noise voltage across an unloaded resistor.



**Figure 2-1.** Carnot cycles represented schematically in the  $(X, Y)$  plane (which could be, for example, the  $(V, P)$  plane). Each cycle is taken clockwise around a closed loop bounded by isotherms  $T_m$  and connecting adiabats.

It remained to assign numerical values to thermodynamic temperatures. Thomson realized that by Equation (2-8) a single reference temperature would suffice; nevertheless, to retain numerical correspondence with the (now equivalent) ideal gas scale, he accepted the two reference point formulation.

In parallel with a thermodynamic basis for temperature obtained from consideration of macroscopic systems, a statistical basis for temperature in terms of microscopic systems was being developed. This had its origin in the studies of Maxwell (1859) and Boltzmann (1869) on the kinetic theory of gases. They derived a relation for the velocity (energy) distribution of the molecules in a fixed volume of gas in thermal equilibrium in which the probability of any particular molecule having a translational kinetic energy in an infinitesimal range about  $E$  is proportional to  $\exp(-E/k_B T)$ , where  $k_B$  is the Boltzmann constant. Here,  $k_B T$  is a characteristic energy and  $T$  (it turns out) is just the thermodynamic temperature of Equation (2-8), so that  $T$  is linked to the kinetic energy of internal molecular motion. More generally, statistical mechanics develops for any system in thermal equilibrium the relationship

$$n_1/n_2 = \exp(-\Delta E/k_B T) \quad (2-9)$$

for the number of particles  $n_1$  and  $n_2$  in two internal states differing in energy by  $\Delta E$ . This concept is useful for interpreting the meaning of temperature in systems for which the ordinary notions of thermodynamics are not applicable. One can deduce from kinetic theory that the average mean square velocity of a particle of mass  $m$  is  $3k_B T/m$  and from classical thermodynamics that it is  $3RT/M$ , where  $M$  is the molar mass. Correspondence gives  $R = k_B M/m = k_B N_a$  where  $N_a$  is Avogadro's number (the number of molecules per mole).

### 2.2.3 Temperature as a Physical Quantity

Temperature is a physical quantity that is more difficult than most others to understand and measure. One reason is connected with its being an intensive quantity with the consequent inability to multiply and subdivide its unit in order to measure over a wide range. However the