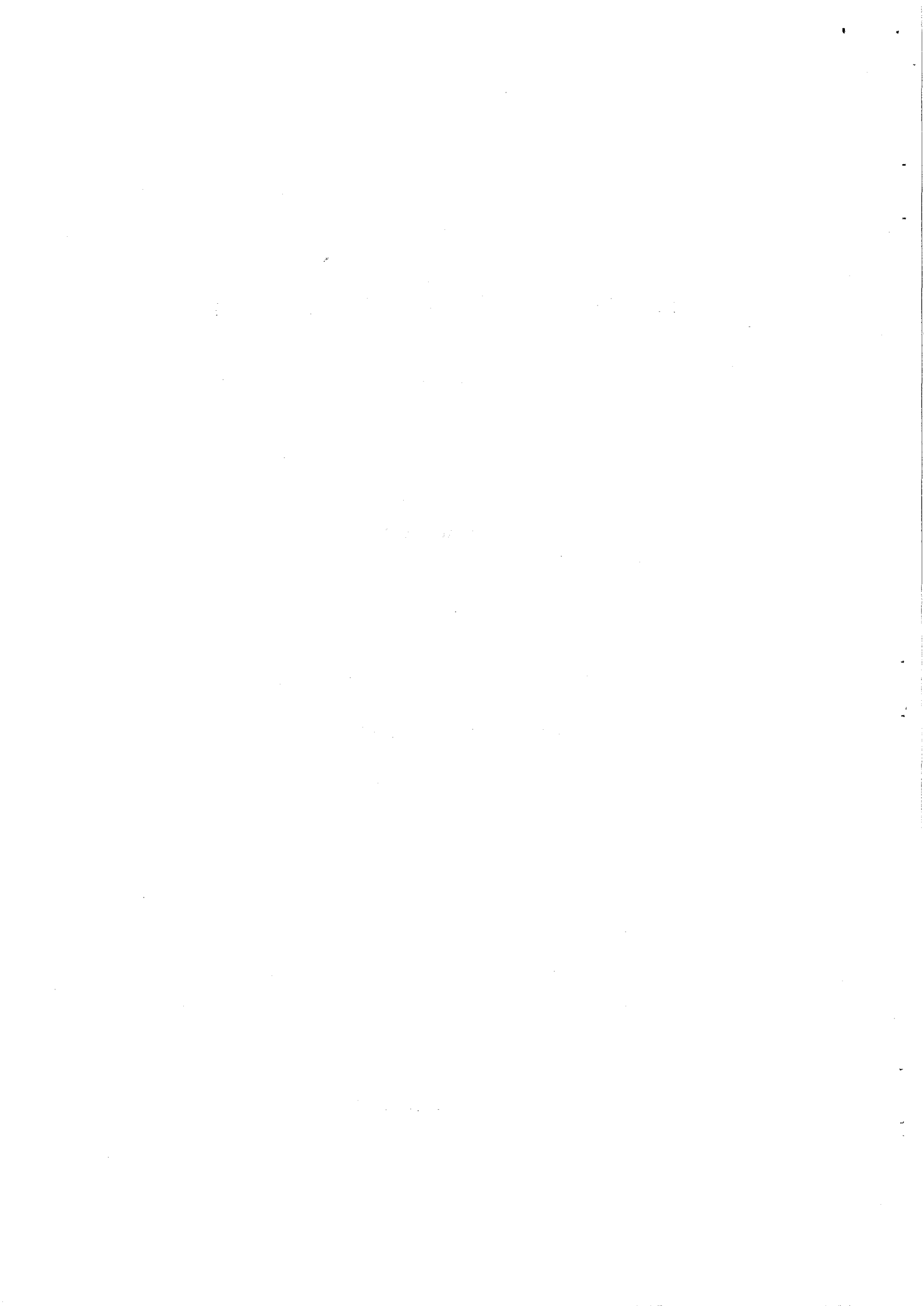


# RESISTANCE THERMOMETER SENSORS

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### Introduction

Any property which varies with temperature in a regular way can be used as a thermometer. Electrical resistance is such a property and many materials could be used to provide a resistance thermometer, but the choice is limited by requirements such as stability. Platinum proves to be the best material for most purposes, so the platinum resistance thermometer is the most common form of the instrument.

The primary standards of temperature from  $-260$  to  $+630^{\circ}\text{C}$  at present, and to  $+962^{\circ}\text{C}$  after the planned revision of the International Practical Temperature Scale in 1990, are provided by platinum resistance thermometers. With meticulous attention to technique very good accuracy can be attained so that primary laboratories can agree to better than  $0.0005^{\circ}\text{C}$  from  $-260$  to  $+250^{\circ}\text{C}$ . With much simpler equipment it is fairly straightforward to measure to  $0.01^{\circ}\text{C}$ ; indeed many industrial quality control facilities are now asking for uncertainties of this level.

Such industrial secondary standards are replacing mercury-in-glass thermometers in many applications between  $-30$  and  $+250^{\circ}\text{C}$ ; a single resistance thermometer can cover this range, whereas a mercury thermometer of high sensitivity spans only  $10^{\circ}\text{C}$  so that many such instruments must be used. Resistance can be measured with a variety of instruments some of which provide digital output for data logging or computer control, or analog output for continuous monitoring. In contrast, a well-trained observer must read mercury-in-glass thermometers continuously to obtain a similar record.

Resistance thermometer systems can give industrial accuracy in some situations where thermocouples are unstable and they can be used with greater precision than thermocouples. Therefore they can monitor the deterioration of important thermocouples in an installation and thus signal when maintenance or replacement is warranted. For example, in some steam turbine generators spare probe wells are provided near critical thermocouples for spot checks with resistance thermometers.

The emphasis below is on properties and characteristics which can give misleading results and which often lead to conflicting requirements when selecting a suitable instrument. Under laboratory conditions an effect may be small and would be trivial in an industrial situation, but industrial conditions are often much more severe and may magnify the effect 100 times. Vibration in a stirred bath might change a calibration by  $0.005^{\circ}\text{C}$ , disastrous for a primary standard and serious for the best industrial standards, but the interior components of a well-built thermometer can crumble to powder if it has a mechanical resonance near a vibration frequency of the device it is measuring.

Very few people are likely to construct their own resistance thermometers but it is desirable to know the principles involved and the design compromises which must be made. There is a wide variety of commercial thermometers and without adequate background one cannot make an informed selection or decide which of the parameters in the standard code specifications are important for an application. Nor can one recognise sources of systematic error and ensure that they have been kept under control. The discussion which follows deals primarily with

the measurement of temperatures above 0°C; the measurement of low temperatures is dealt with in the paper on cryogenic thermometry.

### Basic Properties

Usually the temperature-sensitive resistor is made from a pure metal (platinum, nickel or copper) but some alloys are used, particularly for low temperature measurements, and semiconductor devices are employed in some applications (germanium, silicon and carbon for low temperatures, thermistors near room temperature). Desirable properties are :-

- (1) large change of resistance with temperature
- (2) linear change of resistance with temperature
- (3) stable resistance-temperature characteristic
- (4) high resistivity of metal
- (5) material suitable for wide temperature range
- (6) simple manufacture
- (7) robust construction - no effect of vibration
- (8) low cost.

The properties of some materials are listed in Table 1. Of these platinum is by far the most often used by manufacturers despite its cost because the metal is usually an insignificant part of the cost of the total thermometer and platinum's properties are superior in most other respects to the other materials. Nickel is used for some applications where its larger temperature coefficient is helpful but usually the sensitivity of modern measuring instruments is sufficient to allow platinum to be used. The alloy of rhodium with 0.5% of iron provides a thermometer which has extra sensitivity down to -272°C and can be used up to +400°C and for this reason is sometimes used in applications which span such a wide temperature range. Metals do not depart far from a linear relation between resistance and temperature except at very low temperatures. Copper is almost perfectly linear, particularly in the refrigeration and room temperature regions, and this simplifies its use; however, in all but the cheapest instruments the less linear response of platinum can be allowed for without undue complication.

TABLE 1

	Temp coeff %R/°C	Law	Resistivity	Range °C	Stability
Pt	0.4	$R=a+b.T+c.T^2$	Medium	-260 to + 960	High
Ni	0.6	$R=a+b.T+c.T^2$	Medium	-200 to + 350	Medium
Cu	0.4	$R=a+b.T$	Low	-200 to + 200	Medium
Rh-0.5% Fe	0.4	$R=a+b.T+c.T^2$	Medium	-272 to + 400	High
Thermistor	-4	$R=a.e^{b/T}$	High	-200 to + 200	Medium

### Resistance-Temperature Characteristics of Platinum

Above 0°C the International Practical Temperature Scale (1968) specifies that platinum follows a quadratic law

$$R_t / R_0 = 1 + A.t' + B.(t')^2$$

where the quantity  $t'$  comes from the correction term

$$t = t' + 0.045.(t'/100).(t'/100 - 1).(t'/419.58 - 1).(t'/630.74 - 1)$$

which is the same for all thermometers. The difference between  $t$  and  $t'$  is small, always  $< 0.05^\circ\text{C}$ , and changes slowly with temperature, so the main interest is in the behaviour of the quadratic equation. The ratio  $R_t/R_0$  (called  $W_t$ ) is used so that the formula holds for all platinum and is independent of the quality of the platinum.

The quadratic equation can be solved simply to obtain  $t'$  in terms of  $A, B$  and  $W_t$ , but if high accuracy is needed it is necessary to ensure that rounding errors do not become significant in the solution. An alternative form is sometimes used:

$$t' = (W_t - 1)/a + \delta.(t'/100).(t'/100 - 1)$$

where  $A = a.(1 + \delta/100)$  and  $\cong 0.00398$        $a = A + 100.B$  and  $\cong 0.00392$   
and  $B = -a.\delta.10^{-4}$  and  $\cong 5.8.10^{-7}$        $\delta = -10^4.B/(A + 100.B)$  and  $\cong 1.5$ .

The  $a, \delta$  form is suitable for use in a loop routine to solve for  $t'$  to a preset precision and is therefore useful with calculators of limited capacity. Also, the  $\delta$  term is small and changes slowly, especially in the range 0 to  $100^\circ\text{C}$ , where resistance thermometry is most used. Using this form therefore, a quick estimate of temperature, and especially of temperature change, can be made without a calculator.

The linear term  $A.t'$  is much larger than the quadratic term  $B.(t')^2$ . As  $A = 0.004$  and  $B = -6.10^{-7}$ , the ratio  $B.(t')^2/(A.t') = -1.5.10^{-4}.t'$ . Table 2 shows this proportion at various temperatures together with the error generated in the calculated temperature if the  $B$  term is ignored (so that  $W_t = 1 + A.t'$ ). The sizes of the  $a$  and  $0.045$  terms are given for comparison.

The  $0.045$  term should be included if measurements are to be made to better than  $\pm 0.03^\circ\text{C}$  between 0 and  $120^\circ\text{C}$ , or to better than  $\pm 0.1^\circ\text{C}$  above  $120^\circ\text{C}$ . It is very small near the fixed point temperatures 0, 100, 419.58 and  $630.74^\circ\text{C}$ .

TABLE 2

Temp °C	B. (t') % of A. t'	term °C	a term °C	0.045 term °C
50	0.73	0.36	-0.38	-0.009
100	1.46	1.46	0.00	0.000
150	2.19	3.28	1.13	0.017
200	2.92	5.83	3.00	0.032
250	3.64	9.11	5.63	0.041
300	4.37	13.11	9.00	0.040
350	5.10	17.85	13.13	0.029
400	5.83	23.32	18.00	0.009
450	6.56	29.51	23.63	-0.015
500	7.29	36.44	30.00	-0.036
550	8.02	44.09	37.13	-0.044
600	8.74	52.47	45.00	-0.028

### Standard Codes and Tolerances

Most industrial codes are being brought into conformity with the International Electrotechnical Commission standard, IEC 751 (1983). The UK equivalent is the BS 1904 (1984) and the West German DIN 14360. All these standards specify  $a = 0.003850$  for the platinum used. The Australian standard is AS 2091 (1981), and varies from the IEC code by allowing  $a$  to be specified, by giving tables for  $a = 0.00391$  and  $0.00385$ , and by also covering nickel and copper resistance thermometers.

When reading these standards confusion can arise over the words used to describe (a) the sensing resistor whose characteristic changes with temperature and (b) the assembly of the resistor plus leads and sheath. In some usages "sensor" refers to (a), in others to (b). The IEC and BS codes use "sensing resistor" for (a) and refer to (b) as "platinum resistance thermometer" or as "resistance thermometer" or just "thermometer". However, in some cases, especially for a direct-reading digital instrument, "thermometer" includes the measuring device. In this text, the AS usage is followed in that (a) is referred to as the "element" and (b) as the "thermometer".

Impurities and strain decrease the change of resistivity (i.e.  $a$ ) with temperature of an element. The IPTS specifies that pure platinum should be used and demands an  $a > 0.003925$ . Earlier versions of this standard, promulgated when very pure platinum was not commercially available, specified  $a > 0.00391$ , and thermometers are still produced to provide replacements conforming to such codes. New instruments follow the codes noted above. The values of constants in industrial standard IEC 751 are

$$A = 0.00390802$$

$$a = 0.00385$$

$$B = -5.802.10^{-7}$$

$$\delta = -1.50701.$$

To match industrial-grade thermometers to this lower  $a$  requirement,

manufacturers deliberately dope the wire before assembly. Because of differences in doping and residual strain, the quadratic terms vary slightly between different designs but are very consistent among samples of the one design. Consequently members of a batch are likely to show similar deviations from the mean of a standard code while remaining within its tolerances. This can be a useful feature when selecting thermometers for interchangeability or when measuring temperature gradients between thermometers.

The industrial codes give two tolerance grades, Class A having limits approximately half the width of those for Class B. In IEC 751 the tolerances are

Class A	$0.15 + 0.002 \cdot  t $ °C
Class B	$0.30 + 0.005 \cdot  t $ °C.

Most industrial thermometers have an ice-point resistance  $R_0 = 100 \Omega$ , but for high temperatures when insulation leakage can be large  $R_0 = 10 \Omega$  is sometimes used. Primary standard thermometers often have  $R_0 = 25.5 \Omega$  to give a thermometer sensitivity close to  $0.1 \Omega/^\circ\text{C}$ , and other values are found in special purpose thermometers, but  $100 \Omega$  is by far the most common. At  $500^\circ\text{C}$  the resistance of such a device is about  $285 \Omega$  and thus a general purpose measuring instrument for resistance thermometry should be able to measure up to  $300 \Omega$  with adequate resolution.

Tolerances are important when deciding on limits for interchangeability without having to check the thermometers. Many of the designs of the industrial Class A thermometers depart from the nominal  $R_0$  by an appreciable part of the tolerance limit, but are close to nominal  $\alpha$  and are quite stable. Some give performance not much inferior to that of primary standard thermometers at a fraction of the cost. Simplified methods of calibration of such thermometers are described below.

The industrial codes do not account for the  $0.045$  term in their type calibration. As Table 2 shows, the greatest error from this is about  $0.04^\circ\text{C}$  at  $250^\circ\text{C}$  where the Class A tolerance is  $0.65^\circ\text{C}$ . If such a thermometer is calibrated, the term should be included for the best results, but it is unimportant when considering tolerances.

The standard codes describe type tests which are carried out on each particular design and range of thermometer, and routine production tests which should be made on every thermometer which complies with that standard. The latter are checks on insulation resistance and on resistance tolerance. Type tests are much more extensive and include tests on insulation at the rated maximum temperature, response time in air and water, self-heating by a measuring current, immersion errors, thermoelectric effects, drift at limiting temperatures, stability to thermal cycling, and vibration and pressure tests. The importance of a particular test will depend upon the application of the thermometer.

#### Platinum Wire Resistance Thermometers

Thermometers with wire elements are usually several millimetres in diameter and perhaps 30 mm long, though some smaller ones are made. The

wire is mounted on an insulating support in as strain-free a manner as possible, and in such a way that no strain is produced by differential thermal expansion (platinum makes a very good strain gauge if mounted rigidly). However, vibration can cause mechanical working of the wire and permanently change the resistance, so that some mechanical support of the annealed wire is essential. Many designs have been tried with varying suitability for different applications. In most types the wire is wound in a coil with a double start to minimise induction and electrical interference. Some of the designs for very precise measurement provide very reproducible temperatures only if there is no vibration present. Fully-annealed platinum is very soft and coils can sag to destruction under quite mild vibration, e.g. in stirred baths. The measurement leads must be attached to the element and its support, and enter the lead insulation, in such a way that thermal expansion or vibration cannot cause them to touch.

A wire element is usually in a sheath (glass or stainless steel) which protects it from damage but provides as good a thermal contact as practicable with the surroundings. A metal sheath should be thin-walled if possible to reduce heat conduction along it. The sheath is often sealed after filling with dry gas (dry air serves for thermometers to be used at all but the lowest temperatures) to prevent condensation on insulators below room temperature, or transfer of moisture from hot regions to room temperature components. If condensation is present in the terminal head, the size of its effect can be estimated by heating the head with a hot air stream and noting any change in the indicated temperature. If possible some helium is included in the sheath to improve thermal transfer between element and sheath, as limited thermal transfer in the gas is usually the cause of a slow thermometer response. However, this measure is of no use if the thermometer is used for extended periods above 400°C because at these temperatures helium diffuses through the sheath.

At NML industrial elements are often mounted with glass insulators and sheath to make simple measurements. Leads are dried and annealed by heating in a clean silica tube under a stream of dry oxygen produced by boiloff from the liquid. This assembly is immediately placed in the dried glass sheath and the leads are soldered to a small socket mounted in plastic. This is fixed on the sheath by 'heat shrink' plastic tubing allowing easy removal for repair. The flexible leads are connected via a mating plug and are removed to simplify storage. Through the plastic socket a 0.5 mm hole is drilled lengthwise to ensure that there is no overpressure on thermal cycling. This exchanges air with the surroundings on each thermal cycle. Experience has shown that there is negligible introduction of moisture unless water condenses on to the socket, as can happen if it is too close to the ice when  $R_0$  is measured.

Two types of primary standard platinum resistance thermometers are made; one for use below 0°C, and one above. The low temperature, or 'capsule', version is discussed in the companion paper on cryogenic thermometry. A typical primary standard resistance thermometer suitable for use to 500°C consists of a carefully constructed and supported element in one end of a 500 mm long silica sheath of diameter 8 mm. It is capable of withstanding a reasonable degree of laboratory vibration, but is too fragile for industrial use. Its internal leads are insulated with high-purity ceramic, silica, or mica. They must have high thermal resistance to limit heat flow along them and yet must not have too high



an electrical resistance or the measurement sensitivity is impaired. The insulators should provide radiation shielding between the element and the room temperature end. Neither insulator or sheath should permit radiation piping, which is detectable with silica sheaths above 200°C unless the silica surface has been roughened to reduce total internal reflections. The lead arrangement in a standard thermometer risks allowing two leads to touch if they buckle through thermal expansion, but it has the advantage that the insulators are very light, reducing the thermal lag of the instrument.

Industrial sub-standards use a metal sheath and the leads must be well insulated from this as well as from each other. A 100 Ω thermometer at 0°C changes by the equivalent of 0.025°C if the insulation resistance falls to 1 MΩ. At 250°C a similar error is caused by insulation of 2 MΩ and the insulation usually deteriorates as the temperature rises. The IEC 751 code requires all thermometers to have a resistance to sheath at room temperature of more than 100 MΩ, and the type tests specify >10 MΩ from 100 to 300°C, and >2 MΩ from 300 to 500°C.

Flexible leads attached to the thermometer must have high quality insulation. PVC is suitable for d.c. measurements, but is lossy with a.c. At room temperature it reduces the measured temperature by a few mK which is unimportant for all but the most precise work, but the effect becomes much larger as the PVC becomes hot, e.g. in testing a furnace whose exterior is at 50°C. In such a situation even d.c. measurements are affected so care is needed in the use of PVC leads.

Shielding is needed if long runs of lead are used or if the environment is electrically noisy. Sometimes special precautions are needed to suppress unwanted signals, for example from TV or radar transmitters, which can enter the measuring system through the leads.

A metal cover is usually placed over the thermometer 'head'. This keeps dirt and moisture from the insulation surface and provides a uniform temperature volume to reduce thermal emfs which can be troublesome in d.c. measurements. Erratic thermometer behaviour can often be due to leads fraying where they connect to the measuring instrument or inside the head cover. If the leads have an earthed shield the cover too is usually earthed.

### Encapsulated Elements

Standards-type instruments are hand-made and therefore expensive, and very fragile. Many manufacturers of industrial thermometers have designed elements where the wire is supported on (or in) glass or ceramic with a glaze to hold the wire in place, to provide electrical insulation from the sheath, and to protect the wire from moisture.

Most designs of this type have two leads sealed in, but a few have four lead junctions inside the ceramic. This simplifies the connection of longer leads for potential lead thermometers, reduces the risk of short circuits and makes the assembly less fragile. Leads which seal through the ceramic are often made from an alloy and not pure platinum to better match the expansion of the glass and to provide greater strength.

The ceramic is usually alumina (Al<sub>2</sub>O<sub>3</sub>) which is cheap, is a good

insulator, and whose thermal expansion reduces strain on the wire. The glazes used are much more diverse. They are in close contact with the wire and must match its expansion as well as possible. Variation in the insulation resistance of the completed thermometers of different manufacturers, particularly at temperatures above 300°C, is probably due mainly to differences in the glazes used. Some designs show great variation in insulation resistance between batches, even at room temperature, and this is probably due to either the varying porosity of the glaze, permitting different amounts of moisture to reach the wire, or to differing degrees of removal of volatile components during the firing of the glaze.

Because many types of thermometers have slightly porous exterior surfaces, care must be taken when mounting them with epoxy or some other potting compound. If this material gives off volatile products during curing (e.g. acetic acid from some silicone rubbers), they can be trapped inside the thermometer and cause very bad dielectric leakage.

Many ceramic-mounted elements have the unfortunate property that their  $R_0$  has two fairly stable values, a low value after the thermometer has been subjected to temperatures below, say, -40°C, and a high value when it has been above 100°C. The discrepancy is equivalent to several hundredths of a degree at 0°C.  $R_0$  should be checked after a low temperature measurement, and the thermometer taken to about 200°C and  $R_0$  rechecked before using it again for accurate work above 0°C. This change does not seem to have a marked effect on the other thermometer constants. It has been attributed to differential strain effects in the region between 0 to -100°C.

Most of the encapsulated industrial elements conform to the IEC 751 code with  $\alpha = 0.00385$ , but some are made to the older 0.00391 code, and some extremely good types are made with  $\alpha > 0.003925$ . Almost all have  $\delta \approx 1.51$ . Variation of the thermometric constants within a batch is usually very small and is particularly so for  $\alpha$  and  $\delta$ .

### Thick-film Platinum Resistance Thermometers

Industrial platinum wire thermometers can be obtained with standard dimensions and  $R_0$  of 20, 50 or 100  $\Omega$  at a cost of \$50 to \$100. A standards quality thermometer can cost as much as \$4000. Because of these costs manufacturers are now producing elements by a different technique more suited to mass production, in which a thick film of platinum is laid down on a ceramic or glass substrate, leads are attached and the sensor encapsulated in ceramic or glass. These are commonly known as thick-film platinum thermometers and their cost is about half that of the industrial wire thermometers, say \$20 to \$50. The material selected as the substrate has a similar thermal expansion coefficient to the platinum, reducing strain effects, and is suitable for use up to a temperature of 500°C in most cases. The resistance-temperature characteristic has the same  $\alpha$  as BS 1904 and DIN 14360, 0.00385, but the non-linear term is somewhat higher, so that the thermometers often go outside the Class A specification near the top of the temperature range.

These elements have been developed for large markets (pollution control in cars, thermostats in household appliances, etc.) where Class B

tolerances on reliability are needed but even this level of accuracy is unnecessary in the specification of  $\alpha$ . In the range  $-40$  to  $100^\circ\text{C}$ , many of these thermometers are well within Class B tolerances and some are within Class A, and can replace wire-wound resistors. They are robust, unaffected by vibration, and because of the film structure, they are completely non-inductive, making them insensitive to stray electrical fields. Like the wire elements mounted on ceramic, they display an instability when used below  $-40^\circ\text{C}$ , which can be corrected for if the required accuracy demands.

These elements at present are available only with  $R_0 = 100 \Omega$ . It is likely that future instrumentation will involve a standard of  $R_0 = 100 \Omega$  and  $\alpha = 0.00385$ , with  $\delta = 1.53$  to  $1.56$  depending on the manufacturer.

A few of the designs of ceramic-encapsulated elements perform nearly as well as the best primary thermometers between  $0$  and  $450^\circ\text{C}$ . Because they are less sensitive to vibration and much less expensive, they can be used for precise measurement where the risk of breakage is high. They can be calibrated in a conventional sheath and later mounted in small or curved sheaths, or directly in equipment such as a calorimeter, without great loss in precision.

Rhodium-iron thermometers too are now available in a thin-film version. Such devices have total substrate areas of about  $25 \text{ mm}^2$ , an active element area of  $5 \text{ mm}^2$ , and resistance in the range of  $300$  to  $500 \Omega$ . They display similar properties to the wire resistors.

### Lead Configurations

There are a number of possibilities for the lead arrangement for the connection of the thermometer element to a measuring circuit. In general, the simpler the configuration the greater are the errors generated by it. Some of the most commonly used are as follows:-

**(a) Two lead configuration:** Because there is no compensation for lead resistance, it must be kept low compared to the resistance of the element and if possible the leads should be made of a material with a low temperature coefficient of resistance. This design is widely used for industrial measurement, giving accuracies of about  $\pm 1\%$ . If much better accuracy is required, some form of lead compensation is needed. Two-lead thermometers are restricted to Class B tolerance.

**(b) Three-lead (Siemens) configuration:** This configuration uses a third lead to branch the current at the element. This puts the other leads in opposing arms of the bridge circuit to which they are attached. As long as the leads are closely equal in resistance they are compensated. Accuracies of a few hundredths of a degree are readily achievable with such a system and temperature variation in the leads produces effects which are an order of magnitude smaller than in a two-lead configuration. Thus, for control purposes the instrument can be used to a precision of a few mK.

**(c) Callendar (or 4-lead compensating) configuration:** The element is given a 2-lead connection but there are two additional leads of the same material which form a loop alongside the element leads. This loop is connected in the opposing arm of the bridge circuit and balances in the same way as a 3-lead system. However, the extra lead to conducting heat

is a disadvantage and the sensitivity is reduced by the increased electrical resistance in series with the element. The configuration was once a common feature of British instrumentation but is not used in modern systems.

**(d) Potential (4-lead) configuration:** This arrangement is used for all precise work either with bridges or potentiometers. Two leads are attached to each end of the element. Several types of measuring instruments can eliminate the lead resistance from the measurement and the temperature-active area of the thermometer is then limited to the actual platinum coil.

### Industrial and Secondary Standard Resistance Thermometers

Ceramic-mounted elements are available commercially from several suppliers made up into thermometers with stainless steel or nickel sheaths for high temperature use or in copper capsules for use as refrigeration sensors. Normally such thermometers have short or very robust stems, causing thermal conduction problems in accurate work, and often they are to be used over only a restricted range, commonly 0 to 200°C. Such thermometers are being sold in increasing numbers for use with modern a.c. bridges.

NML now calibrates such thermometers by comparison with standards in stirred baths of water or oil. The best of them can be calibrated to  $\pm 0.005^\circ\text{C}$ , but usually they show slight instabilities during calibration and an accuracy of 0.01 or 0.02°C is more usual. They provide an accuracy comparable to the best mercury-in-glass thermometers over a greater range, and when a bridge coupled to a recording device is used they can provide continuous temperature monitoring with minimum supervision. They have proved very useful for such tasks as checking the temperature uniformity of precise temperature enclosures.

These thermometers show a very small cubic or higher order effect in their resistance-temperature relationship, which may be caused by differential thermal expansion between wire and support. These effects are very reproducible for any one thermometer and are usually only 2 to 3 mK in magnitude, although they can approach 0.01°C. In such cases extra terms must be included in the calibration formulae or the calibration uncertainty must be increased appropriately.

### Calibration

For thermometry to an accuracy of 0.3°C it is usually adequate to check that the resistance is within tolerance at a reference temperature (usually the ice point), and then to use the manufacturer's data. Usually the thermometers follow a standard code specification. However, it is worth noting the improvement over the code tolerance limits that a 1 or 2 point check can give. A measurement at 0°C to an accuracy of  $\pm 0.05^\circ\text{C}$  reduces the uncertainty at this point from 0.015°C for Class A and from 0.03°C for Class B. The same procedure gives an improvement at 100°C from 0.35°C to 0.25°C for Class A, so that the improvement is only appreciable from 0 to about 25°C.

However, a check at both 0 and 100°C to an accuracy of  $\pm 0.05^\circ\text{C}$  still

gives an accuracy of  $\pm 0.08^\circ\text{C}$  at  $50^\circ\text{C}$  and  $\pm 0.1^\circ\text{C}$  at  $200^\circ\text{C}$ . In principle a third check at  $50^\circ\text{C}$ , or preferably  $200^\circ\text{C}$ , would determine  $\delta$  also, but in practice the variation in  $\delta$  is so small that this is not worth doing unless the highest accuracy is used. For example, a third measurement at  $200^\circ\text{C}$  to  $\pm 0.05^\circ\text{C}$  would give  $\delta$  to only  $\pm 0.05$  whereas all thermometers of the one type have the same value of  $\delta$  to  $\pm 0.01$  in any case.

To summarise, a single check at  $0^\circ\text{C}$  confirms that tolerances are met and improves accuracy slightly, while a check at a second point reduces uncertainties substantially. Checks at additional points are seldom warranted.

For accuracy to  $0.1^\circ\text{C}$  or better a calibration on the IPTS is desirable, directly via the fixed points if possible, but if necessary by comparison with a calibrated thermometer in a stirred bath or a very uniform furnace. If the thermometer does not meet the specifications of the IPTS, calibration at more than the minimum number of points (three) is desirable to ensure that a curve like that of the IPTS is followed.

When large numbers of calibrations at a particular fixed point are required, measurements are expedited by replacing one thermometer with another in the same fixed point cell. However, above room temperature each new thermometer chills a freezing point cell and so only a few thermometers can be measured before the freeze is finished. If melts are used, the chilling by a new thermometer merely returns the point to an earlier stage so that many thermometers can be measured in a single melt. Melts are not as precise as freezes for metallurgical reasons, but they can be used for all but the most precise calibrations.

Users should consult the calibration laboratory before buying or constructing thermometric equipment which to ensure calibration must be compatible with the laboratory standards and calibration equipment. Calibration by comparison with standard thermometers is inevitably less accurate and the situation worsens if the thermometer has a short immersion depth. A metal point crucible with too large a diameter cannot be calibrated.

An IPTS calibration above  $0^\circ\text{C}$  at NML involves annealing combined with  $R_0$  measurements until the thermometer is stable. Usually 30 min at  $470^\circ\text{C}$  is adequate annealing, preferably followed by slow cooling to  $300^\circ\text{C}$  to avoid thermal shock. Two freezing point determinations in different freezes are made at each of the zinc, cadmium and tin points, and a spot check is made in a melt to ensure that heat leakage from the outside has negligible effect, as during a freeze the furnace is colder than the element and heat leaks outwards. Water triple point measurements are made before and after each metal fixed point to detect and correct for the effects of drifts in both measuring equipment and thermometers and to make sure that there has been no sudden change (perhaps due to vibration) in the thermometer. The water triple point, zinc and tin values are sufficient for calibration and the cadmium point is used to ensure that there has not been some unusual feature, such as insulation breakdown at the zinc temperature, which might give the thermometer a non-standard resistance-temperature characteristic.

Extensive calibrations carried out at NML have provided a pool of experience regarding the reliability of such procedures. Forty three thermometers deriving from several manufacturers and of several designs

when calibrated by the above method gave values at the cadmium point with a standard deviation of 0.7 mK and a greatest departure from the mean of 1.7 mK. Ceramic-insulated thermometers were no different from other sensors in this respect. This is in contrast to their behaviour when calibration between 0 and 250°C is made by comparison methods when small higher order terms are necessary for their resistance-temperature formulation.

### Response Time

The time taken by a thermometer to respond to a step change is often determined by several effects, radiation transfer (rapid), heating of sheath and insulators (slow), and heating of element (variable). A simple exponential is frequently not an adequate description of the thermal time behaviour, and the usual 'time constant' ( $1-1/e$ , or about 63% to equilibrium) can be misleading. The response of a thermometer may continue for a long time if a sizeable part of the change is controlled by a long time time constant. For example, a device withdrawn from a furnace cools rapidly to about 400°C by radiation, then far more slowly to room temperature by air convection. The same device on being returned to the furnace heats rapidly by radiation. The 50% response times for heating and cooling are similar, but the 90% times differ by a ratio of 1:5.

If the device is to be used for control, a measure of the largest component is required, the small part being masked by other changes, so the user should employ the time taken for a small fraction of the total change, perhaps 50%, though sometimes even 25 or 33% is appropriate. If the thermometer is to be used for measurement, the total change is what is required and the time taken for 90, 95 or even 99% of the total change may be what is required.

Naturally, the response time should be measured with a detector which is much faster than the thermometer or the detector response will mask that of the thermometer.

When one process controls most of the response characteristic of a thermometer, a simple exponential describes the system satisfactorily and the classical time constant  $T$  is a useful parameter. If the temperature of the environment is changing at a steady rate, the thermometer lags behind and indicates the temperature of the environment at a time  $T$  earlier.  $T$  is thus a measure of the systematic error due to the thermal lag in the system.

In the calibration of a fast-response instrument against a slow one (e.g. a thermocouple or thermistor against a mercury-in-glass or resistance thermometer) lags can cause a systematic error, equal to the change in conditions between the different thermal response times. In a bath with a control cycle, for example, it is possible to have one instrument showing a temperature rise, while another registers a fall.

### Use and Maintenance

Laboratory quality instruments should not be subjected to vibration or excessive handling. All thermometers should be checked periodically or

after unusual usage to ascertain whether drifts have occurred. The easiest check is at the ice-point, either with a standard triple point cell or a simple crushed-ice point. Such an ice bath will sometimes have warm water at the bottom because water between 0 and 4°C is denser than water at 0°C, so the thermometer should not be placed within 40 mm of the bottom of the cell. The element of the thermometer should be well immersed with preferably 300 mm of the sheath in the cell to avoid thermal conduction problems, and the temperature indication should not change when the thermometer is raised several centimetres to increase the heat leak.

Other fixed points above 100°C require a well-designed, uniform furnace, and graphite crucibles in glass protecting tubes containing good commercial quality (approximate purity 99.99%) zinc, cadmium, lead or tin. Such a system will give freezes good to  $\pm 0.01$  K or better, and the fixed points can be calibrated by a standardising laboratory. However, unless a large number of calibrations are required, it is cheaper to do  $R_0$  checks only and to leave all other fixed point calibrations to a standards laboratory. To ensure that conduction errors are not significant it should be possible to move a thermometer 1 or 2 cm out of a temperature enclosure without causing a change in reading. A change implies bad thermometer conduction or a non-uniform enclosure.

Because the thermometer formulae involve  $R_t/R_0$ , temperature is measured by ratio only. Absolute temperature measurement is only needed to check long-term drift and  $R_0$  should always be measured on the same instrument as  $R_t$  so that only non-linearity instrument errors are of significance.

When ceramic-encapsulated elements are cycled from below -40°C to above about 80°C their bistable  $R_0$  variation must be checked carefully as described above, if accuracy of  $\pm 0.05^\circ\text{C}$  or better is wanted.

### Measurement Currents

The current flowing through the element during measurement produces electrical heating ( $I^2.R$ ) and this must raise the element temperature slightly above that of the surroundings. Because it is more expensive to use a sensitive detector with small measuring current than a less sensitive detector with a large current, an economical design will have a measuring current that produces almost significant heating effects, e.g. 1/3 the desired accuracy.

It is desirable to check that these effects are not important by using two currents, making sure that there is no significant difference in the temperature indication, and then using the smaller current for normal measurement. For a laboratory thermometer in a liquid bath, using a 1 mA current produces an effect of about  $0.001^\circ\text{C}$ , though its magnitude is several times larger in air. Small (matchstick size) elements encapsulated in glass or ceramic usually show an effect 3 or more times as large. Moreover, an element heated  $0.001^\circ\text{C}$  by 1 mA is heated  $0.1^\circ\text{C}$  by 10 mA, a more usual industrial measuring current.

Many measuring instruments operate with a fixed current. The heating should be checked with a variable current instrument, as outlined below, but when this is not possible the best that can be done is to observe the drift in indication just after the current is switched on. There is

a rapid rise in a few seconds, usually over 50% of the total rise, as the wire heats. Then there is a further slow rise as the supports and sheath heat. Where the measuring system responds too slowly, the first effect will not be detected and all that will be seen is the latter, slower effect.

In a well-designed system the effect will just be detected with the sensitivity available and will be about 20% of the uncertainty of the instrument calibration. Such heating does not change much with temperature but will vary with the thermometer's environment, e.g. placed in direct contact with a water bath as opposed to being in a protective well with an associated air gap. In any specific situation the heating effect need only be checked once unless very precise measurements are being made.

When two measuring currents are available, the effect can be corrected for. Because the changes are small, the resistance change is proportional to the temperature change as squared and higher order terms can be neglected.

If  $R$  is the value of resistance at current  $I = 0$ , and  $R_i$  is that measured at current  $I_i$ , with consequent heating  $I_i^2 \cdot R_i$ , then the resistance rise  $\delta R_i (= R_i - R)$  is proportional to the heating and is  $\delta R_i = k \cdot I_i^2$ .

A different  $I_j = n \cdot I_i$  would cause a rise

$$\delta R_j = R_j - R = k \cdot I_j^2 = k \cdot n^2 \cdot I_i^2.$$

The difference between the rises is

$$\delta R_j - \delta R_i = R_j - R_i = (n^2 - 1) \cdot k \cdot I_i^2.$$

So the first rise is

$$\delta R_i = k \cdot I_i^2 = (R_j - R_i) / (n^2 - 1)$$

and therefore the true (zero current) resistance is

$$R = R_i - (R_j - R_i) / (n^2 - 1).$$

For example, if the current is doubled from  $I_i$  to  $I_j$ , i.e.  $I_j = 2 \cdot I_i$ , then

$$\begin{aligned} R &= R_i - (R_j - R_i) / (2^2 - 1) \\ &= R_i - (R_j - R_i) / 3. \end{aligned}$$

Thus the zero resistance value can be found by measurements at two currents. Convenient values for 'n' are  $\sqrt{2}$ , 2, 3, and 10.

### Thermistors

Thermistors are mixtures of complex metallic oxide compounds which are semiconductors. The desired resistivity and temperature coefficients are obtained by control of the composition and heat treatment. They have a high negative temperature coefficient of resistance (-3 to



-5 %/°C compared with a value of about +0.4 %/°C for most metals). The resistivity too is normally much higher than that of metals which enables the thermistor sensor to be of quite small dimensions. They can be obtained commercially in a standardised range of room-temperature resistances from 500 to 500 000  $\Omega$ , and will maintain their calibration for long periods if not maltreated. They are useful for temperature measurement from about -200 to +300°C, particularly where a fast-response instrument is required. They can often be used with an inexpensive, directly-calibrated meter and normally they do not need lead compensation as the resistance of the leads is small compared with that of the element.

Manufacturers have thermistor data sheets with considerable design detail for a variety of temperature measurement and control applications. Their resistance-temperature curve is of the form

$$R = a.T^c . e^{b/T}$$

where  $c$  is a small positive or negative number close to zero, so that to a good approximation the relation reduces to

$$R = a.e^{b/T}$$

and therefore the linear temperature coefficient is

$$a = 1/R . (dR/dT) = -b/T^2 .$$

Here  $b$  varies between 2000 and 6000 K, and a value of 3600 is equivalent to  $a = -4$  %/K at room temperature.

Manufacturers find it difficult to obtain reproducibility even within a batch of thermistors because the exponential term changes the characteristic so rapidly. It is possible to check a batch at several temperatures and to select pairs having almost identical response curves over a limited temperature region, so that simple and very precise difference measuring equipment can be used for heat flow measurement. Nevertheless, because thermistors are not interchangeable without careful calibration, they are not used a great deal for industrial temperature measurement. Their use is mainly as control sensors where the set point is determined by some other instrument, and in indicators where a warning light, "on-off" facility is all that is required.

Thermistors can be surprisingly stable. Many can cycle between -200 and +150°C without variations at the ice point of more than 0.01°C. When used over limited temperatures, differences of a few mK can be measured reliably. Because of their small size this makes them very useful as probes in agricultural and biological investigations.

Because of their small volume, small surface area and large resistance, heating by a measurement current produces very large errors in temperature unless very small currents are employed; whereas milliamp currents are used for wire elements, microamps are used for thermistors.

### Resistance Thermometry Above 450°C

Platinum resistance thermometers can be used in a straightforward fashion up to 450°C to improve on the precision obtained with thermocouples. In principle they could be used up to the melting point of platinum, but problems occur above 450°C and become increasingly severe as the temperature rises further, so that a practical limit is about 1000°C for laboratory standards and 700°C for industrial use. For most purposes the thermocouple is adequate, but improved accuracy and stability is needed in specialist areas, to monitor performance from 450 to 600°C in the electricity generating industry, for example.

When the platinum is at high temperatures impurities may diffuse from the insulators and the sheath. Usually this increases  $R_0$  and decreases  $\alpha$ , but the combined effect at high temperatures depends on the nature of the impurity and on the thermometer construction. If the impurity is oxidised it does not diffuse through the platinum, so the sheath is filled with dry air, or with an oxygen-argon mixture in some designs. Unfortunately platinum forms unstable oxides which can transport platinum from the wire to cooler parts of the sheath, especially if the thermometer undergoes thermal cycling. All these sources of instability are accentuated if the wire is very fine as it is in many 100  $\Omega$  thermometers.

To reduce movement of metal from the sheath it is good practice to oxidise the interior surface before assembly. High-nickel alloys produce stable oxide surfaces, whereas chromium has a volatile oxide which forms only at high temperatures. The resistance of platinum is affected much more by chromium than by nickel so high-chromium alloys like Inconel should be avoided. If the sheath is not adequately oxidised it may chemically combine with oxygen from the filling gas and aggravate the effects of contamination on platinum.

Electrical insulation degrades as temperature increases, shunting the element resistance. Adsorbed water can be retained by materials until they reach 200°C or more, and thermometers should be heated during assembly to at least this temperature to avoid this. Regions near the terminals may retain moisture and if this moisture moves when the temperature is cycled, anomalous resistance variations will occur.

Poor electrical insulation at high temperatures produces leakage between the furnace power supply and the thermometer and its measuring system. The effects of this depend on instrument design and in general the better the instrument is isolated from ground, the smaller is the effect. Insulation becomes more lossy as measuring frequency increases, so d.c. or low-frequency instruments are preferred and 400 Hz is the maximum frequency to be used. If a data acquisition system is attached it must not degrade the isolation of the measuring instrument.

When a thermometer is being progressively inserted into a furnace, for example to measure temperature profiles, the amount of hot insulation is progressively increased, causing shunting and producing an apparent temperature decrease. This is usually made larger by increased ground loop effects.

To reduce the effects of insulation shunting, low element resistances are used, especially for laboratory instruments. Instead of the usual

$R_0$  of 100 or 25.5  $\Omega$  , high-temperature thermometers use 10, 2.5 or 1  $\Omega$ . Lead resistance cannot be reduced because this could involve increased wire thickness and with it, thermal conduction. The lead resistance is therefore larger relative to that of the element, reducing sensitivity (except with some potentiometric measuring systems) and increasing the thermal noise. The latter can be reduced by suitable filtering, but only at the expense of longer measurement times.

Although many of these design problems must be considered for all resistance thermometers, they are especially severe for high-temperature applications. There is work in progress to develop superior methods for both laboratory standards and robust industrial thermometers for use at these temperatures.

