

3. Specialized Fixed Points

A temperature fixed point is a calibration point for thermometers that differs from a comparison calibration point in that its temperature value is not measured, during the calibration process, by another already calibrated thermometer, but has been previously established either by definition (if it is a defining point of the ITS-90) or by previous experiments (if it is a secondary reference point) [Bedford et al. (1984)]. Whether measured or assigned, the temperature value is associated with a thermodynamic state of a substance; how closely that state is approximated during the calibration depends upon the stringency of the specifications on it (e.g. requirements on purity, isotopic compositions, annealing, ...) and upon the experimental uncertainty of the measurements.

The ITS-90 can be approximated not only by simplified interpolation with primary or non-primary thermometers (as will be discussed in the next sections of this monograph), but also by relaxing the fixed point specifications or by using the fixed points in different ways. In this chapter we describe a number of specialized fixed points and unconventional ways of realizing conventional fixed points, with indications of the accuracies that may be attained. Methods for highly accurate fixed point realizations are described in detail in "Supplementary Information for the ITS-90" [CCT (1990)] and will not be repeated here.

3.1 Fixed Points Below 0 °C

3.1.1 Superconductive Fixed Points

3.1.1.1 General Remarks

Superconductive transitions are solid state phase changes of second order in contrast to most fixed points used in thermometry which are first-order phase changes. Second order phase changes are distinguished by the absence of an associated latent heat. Essential peculiarities of the superconductive transitions are the larger influence on them of impurities, crystal defects, and physical strain which affect both the transition widths and temperatures (T^C). This does not prevent their application as thermometric fixed points, however, if special sample preparation techniques and special methods for the detection of the superconductive transitions are used.

With the promulgation of the EPT-76 [CCT (1979)], superconductive transition temperatures (ST -temperatures) were officially used as fixed points for the realization of an international temperature scale. However, connected with the peculiarities mentioned above, the definition of the EPT -76 was based only upon the superconductive fixed-point

device SRM 767 [Schooley et al. (1980) and Schooley and Soulen (1982)], so that the ST - temperatures were only used officially in the sense of a reference material (see Sec. 3.1.2). Furthermore, ST-temperatures are not used as fixed points in the definition of the ITS-90. Metrological investigations of SRM 767 fixed-point samples [El Samahy et al. (1982)] verified that T^C values are reproducible within about 1 mK. Efforts towards improvement have shown that a reduction of the non-uniformity of the TC values well below 1 mK is possible by carefully annealing all samples and by selecting them on the basis of maximum allowed transition widths [Schooley (1984)].

3.1.1.2 Requirements for Superconductive Fixed Points

Problems in, and possibilities for, the realization of superconductive transitions as true thermometric reference points are reviewed for the metals Cd, In, Al, Sn, Pb, and Nb by Fellmuth and Maas (1987). This review shows that modern sample preparation and handling techniques, in conjunction with convenient material characterization methods, are sufficient to guarantee an accuracy and stability of the ST-temperatures of these elements within about 1 mK if definite specifications concerning sample parameters are fulfilled.

The main difficulty in realizing a superconductive fixed point is the influence of impurities and crystal defects on the ST-temperature. The influence of impurities is of the same order of magnitude as for metal freezing points: typically ($|dT^C/dc| \approx 1$ mK per ppm^{*}, where c is the impurity content). The residual resistance is an excellent indicator of this influence except in the few cases where localized magnetic moments exist; in this latter case dTC/dc can be much larger so the concentration of the magnetic impurities must be determined separately. The effect of crystal defects can be reduced to a few tenths of a millikelvin by using suitable preparation techniques, which may differ for different elements. For checking the magnitude of this effect it is important that the transition width be always smaller than the change in the ST-temperature due to the defects. Hence, for the realization of superconductive reference points, detailed information concerning both the physical properties of the materials and the preparation and characterization methods is necessary. Such information is given for the six metals listed above in the review of Fellmuth and Maas (1987) and, for niobium, by Fellmuth et al. (1985), (1987).

* The abbreviation ppm is used to mean an impurity content of one solute atom per 10^6 solvent atoms.

3.1.1.3 Realization of Superconductive Fixed Points

In Table 3.1 the ST-temperatures on the ITS-90 of the six metals Cd, In, Al, In, Pb, and Nb are listed*. The uncertainties given include the temperature measurement uncertainties assigned for the available experimental data, the non-uniqueness of the EPT-76, the differences of the T_{76}^C values published for high-quality samples of different origin and different parameters, and the effect on the ST-temperatures of the various factors that can be expected to influence the parameters of the investigated samples. In the application of superconductive fixed points the dependence of the ST-temperature on detection techniques has to be taken into consideration [Nara (1984)]. The mutual inductive technique is most effective because of its relative ease of application, the minimum stress transmitted to the sample, and the negligible sample contamination [Soulen and Colwell (1971)]. Thermal anchoring of the samples and of the electrical leads is critical for the observation of non-hysteretic and reproducible transitions [Schooley et al. (1980) and Schooley and Soulen (1982)]. Because of the absence of latent heat, a high-quality adiabatic cryostat is necessary for accurate T^C measurements. To check that the thermal conditions are adequate, the difference between the ST-temperature values obtained with increasing and decreasing the temperature of the sample through the transition range should always be measured. The temperature should then be stabilized at the mid-point of the transition before thermometer calibrations are carried out. Furthermore, external magnetic fields (earth's magnetic field and measuring field) can have an influence of a few mK on the ST-temperatures; the effect can be corrected for, or, more comfortably, compensated for.

3.1.2 Standard Reference Materials

In contrast to the foregoing fixed point definition, the temperature value assigned to a standard reference material (SRM) is a *device*-temperature, i.e. the device reproduces precisely a temperature value which has been determined by calibration but which, within stated limits, is characteristic only of the individual device. The boundary between a SRM and a fixed point may be ill-defined as the specifications of a SRM can be so strict that the value assigned is the same as that of the physical state, within a comparable uncertainty. For example, below 10 K, several superconductive transitions may be used as fixed points.

* Note that the temperatures in Table 3.1 are slightly different from those used with the reference material NBS-SRM 767; the latter are given in Table 3.2.

Table 3.1 : Current Best Estimates of Superconductive Transition Temperatures and of the Total Uncertainties of the Estimate [Fellmuth and Maas (1987)] ,

Element	TC90/ K
Cd	0.5200 ± 0.0030
Zn	0.8500 ± 0.0030
Al	1.1810 ± 0.0025
In	3.4145 ± 0.0025
Pb	7.1997 ± 0.0025
Nb	9.2880 ± 0.0025

Table 3.2: Temperatures Assigned to Superconductive Fixed Points in the NBS (now NIST) Fixed-Point Devices

*T ^C (K)	Substance	Width (mK)	Reproducibility (1 standard deviation) (mK)
0.0160	°W	0.7	± 0.2
0.0230	°Be	0.2	0.1
0.0990	°Ir	0.8	0.1
0.1605	°AuAl ₂	0.3	0.1
0.2065	°AuIn ₂	0.4	0.15
0.5190	+Cd	0.5-8.0	0.3
0.8510	+Zn	2.5-10	0.4
1.1796	+Al	1.5-4.0	0.4
3.4145	+In	0.5-2.5	0.2
7.1996	+Pb	0.6-2.0	0.2

°SRM 768 [Schooley and Soulen (1982)]

+SRM 767 [Schooley et al. (1980)] * T₉₀ above 0.5 K.

For these, there exist two SRMs issued by the National Institute of Standards and Technology: SRM 767 [Schooley and Soulen (1972), El Samahy et al. (1982)] and SRM 768* [Schooley and Soulen (1982)], each of which includes five metals with specified superconductive transition temperatures (Table 3.2). Within 1 mK, the devices can be considered to reproduce the temperature values of the physical states, though they are supplied calibrated. For the niobium transition near 9.3 K, another calibrated device is now available [Fellmuth et al. (1985)].

Above 14 K, the fixed points are triple and boiling points obtained from condensing gases; the reliability of bottled gases as SRMs is questionable as their use involves manipulation and consequent risk of contamination. However, the technique of sealing gaseous samples in metal cells makes it possible to obtain both reference fixed points [CCT (1983), Pavese et al. (1984)] and reference materials [Pavese (1980)]. Examples of sealed cells as SRMs as opposed to fixed points are the deuterium triple point when using gas obtained by hydrolysis of heavy water because of the high HD content, and the oxygen triple point when using gas distilled from air because of the unknown remaining contamination by argon. Most of the fixed points listed as second- or third-quality by Bedford et al. (1984) could still be used as SRMs in sealed cells.

3.1.3 Vapour Pressure Thermometers

Vapour pressure scales may be considered as giving a continuous set of fixed points, some of which are used also as defining points of the ITS-90 (the hydrogen boiling points and the helium vapour pressure scales). A realization of the ITS-90 that involves vapour pressure points, however, is complex and must include purity-effect analysis. Even without such analysis, any point of the vapour pressure curve can be used to obtain in a simple way and with an accuracy that depends upon the gas purity (see Chapter 6), a temperature value from the relationship to pressure and so to calibrate thermometers fitted into the same bulb. The use of vapour pressure thermometers is fully described in Chapter 6.

The requirements for the cryostat are essentially the same as for thermometer calibration in a comparison copper block, except that a bulb and sensing tube must be provided. Often the regulation is by control of the pressure rather than of the temperature. At the higher temperatures (for example, in a hypsometer for the steam point or for a sulphur boiling point) the boiler and comparison chamber are connected to a large ballast volume to ensure good stability.

* SRM 768 provides fixed points below the lower limit of the ITS-90.

The widely-used, but not very reliable, method of taking advantage of an open bath of a boiling cryogen (oxygen, nitrogen, helium, rarely hydrogen or argon) is a very simplified way to do vapour pressure thermometry at a single point at atmospheric pressure. The bath should be stirred or other precautions taken to reduce temperature gradients, for example by lagging the comparison block.

The sensitivities of some fluids commonly used in vapour pressure thermometers are given in Table 3.3.

3.1.4 Sealed Cells

Though possible [Pavese (1981), Bonhoure and Pello (1983)], pressure measurement is generally not convenient with sealed samples, so the sealed-cell method is best used only for triple points. A general discussion is given elsewhere [CCT (1990), Pavese et al. (1984)]. Some thermal parameters of thermometric substances that are relevant to the design of sealed cells are given in Table 3.4; a detailed tabulation of all parameters is available in, for example, L'Air Liquide (1976). To approximate the ITS-90, solid-solid transitions can also be measured although, in general, they are of lower precision. Compared with triple or boiling points, they are at a disadvantage in that there is less self-stabilization of the cell because of the lower heat of transition and the less effective thermal coupling with the condensed sample. Such a self-stabilization is largely due to the presence of the liquid phase, especially when it is kept in thin layers. In solid-solid transitions, on the contrary, the solid has poor thermal contact with the cell and also a much lower vapour pressure. Additionally, the diffusion of the transition is generally a slow process.

The self-stabilization effect can be better understood from Table 3.4 where the enthalpy change in melting of the sample is compared with the heat capacity of the cell. Any small perturbation of the temperature due to stray heat exchanges with the cryostat can be compensated by melting or freezing of a small fraction of the sample. For this reason, any of the cryostats shown in Chapter 2 are satisfactory, and their performances are much less critical than in comparison, or vapour pressure, measurements. Values for temperature error versus heat leak are as low as 10 $\mu\text{K}/\text{mW}$ above 20 K, increasing to 500 $\mu\text{K}/\text{mW}$ at 14 K. Examples of thermal analyses are given by Seifert and Fellmuth (1989), Seifert (1982), and Bonnier and Hermier (1982). This self-stabilization is also beneficial for simplifying the use of sealed cells. Firstly, the cell can become the reference for an inexpensive differential temperature regulation of the isothermal shield of the cryostat, thus eliminating costly and critical absolute-temperature controllers. Secondly, a cell acts as an almost ideal temperature-generator, able to drive a large thermal load. It may be

Table 3.3: Sensitivities of some Fluids Commonly Used in Vapour Pressure Thermometers

Fluid	Practical Range of Use (K)	Pressure					
		13.3 kPa		100 kPa		133 kPa	
		T/K	$\frac{dP}{dT}$ (kPa/K)	T/K	$\frac{dP}{dT}$ (kPa/K)	T/K	$\frac{dP}{dT}$ (kPa/K)
⁴ He	1 to 5.22	2.63	24	4.2	96	4.52	115.6
	63.2 to 84	63.5	2.3	77.35	11.7	79.9	14.7
	70 to 98	74.5	2.1	90.18	10.7	92.9	12.7
CH ₄	90 to 170	92	1	141	9.5	180	14
		0.25 kPa				4 000 kPa	
C ₂ H ₆ O	160 to 400	255	0.04	250	4.3	380	80
						3 500 kPa	
CCl ₂ F ₂ (Fréon 12)	220 to 380			240	6	373	120
						13 300 kPa	
H ₂ O	280 to 640	324	0.6	373	3.6	600	1 700
		550 kPa				6 600 kPa	
CO ₂	220 to 300	218	9			300	148

Table 3.4: Relevant Parameters for Some Cryogenic Thermometric Substances at their Triple Points.

Gas	T_{tp} (K)	P_{tp} (kPa)	H_f (J/mol)	d_{tp}/d_{NTP}	λ (mW/cm K)	$X=H_f/c_p^*$ (kg K/mol)
e-Hydrogen	13.8033	7.034	117	1040	1.03	90
e-Deuterium	18.689	17.079	197	1040	1.23	110
Neon	24.5561	43.379	335	1728	1.17	33
Oxygen	54.3584	0.1464	444	980	1.96	4.4
Nitrogen	63.1504	12.526	720	814	1.61	4.8
Argon	83.8058	68.892	1189	980	1.25	6
Krypton	115.776	73.0	1500	812		6
Xenon	161.404	81.681	3100	647		10
Carbon Dioxide	216.589	518	8400	825	1.58	28

T_{tp} = triple point temperature (T_{90}); P_{tp} = triple point pressure; H_f = melting enthalpy; d_{tp}/d_{NTP} = density ratio between the liquid at T_{tp} and the gas at 20 °C; λ = thermal conductivity of the liquid at the triple point; X = "driving" capability (see text, page 25; c_p = copper specific heat).

* The table uses the example of a copper cell.

designed not only for thermometers fitted internally (Fig. 3.1a), but also so as to thermostat an experiment fitted to the cell [Pavese (1987)] or to a large external comparison block. On the block, more than one cell can be fitted, performing a multiple reference-point arrangement (Fig. 3.1 b). As an alternative, the cell itself may be designed with many compartments for different substances, giving a compact multi-reference device (Fig. 3.1c) [Bonnier and Hermier (1982)]. Another, and a novel, design (from the Physical Technical and Radio Technical Measurements Institute, Moscow) for a multi-reference cell is shown in Fig. 3.1 d. A "sealed" cell with a removable sealing screw to allow for refilling [Ancsin (1982)] is shown in Fig. 3.1 e.

A high accuracy with melting plateaux in sealed cells is still available when using such simplified methods of operation. The slope of the plateau (on a plot of temperature versus

fraction of sample melted) can give information regarding impurities in the melting substance (see Section 6.3.6). In addition, the lifetimes of these fixed points is at least of the order of decades; no changes of the reproduced temperatures have yet been observed in about a dozen years.

Sealed cells offer many advantages for disseminating and approximating the ITS-90. They provide the possibility of a whole set of defining and secondary fixed points spanning a wide temperature range, instead of just the triple point of water, for checking the stability of thermometers. For small changes in thermometer calibration, they allow retrieval of a calibration. Furthermore, calibration procedures can be simplified and still maintain good accuracy. The cells also allow dissemination of fixed points (rather than calibrated thermometers) for ITS-90 maintenance.

The sealed cell is well adapted to the cryogenic range and hence, in particular, to the calibration of capsule-type thermometers in adiabatic cryostats. However, the technique has also been applied to the calibration of long-stem SPRTs in the range from the triple point of argon to the triple point of indium [Bonnier (1975), Bonnier and Moser (1983), Ancsin and Phillips (1984)] under heat-flow conditions. Apparatuses that have been used successfully are illustrated in Figs. 3.2a, b.

Sealed cells are also commonly used for calibrations of resistance thermometers or thermocouples at metal freezing points to temperatures as high as the freezing point of copper (1085 °C). The crucibles used are essentially the same as those for non-sealed operation [CCT (1990)]. A national standardizing laboratory usually constructs its own sealed cells, but the procedure is moderately difficult; they are also available commercially. The sealed cell usually consists of enclosing the crucible in a purged, sealed, silica envelope having a re-entrant well close-fitted within the crucible well. Care should be taken to ensure that the pressure of the inert gas filling is such as to give closely one atmosphere pressure during the melting or freezing transition. A typical sealed cell (for the copper freezing point [Crovini et al. (1987)]) is shown in Fig. 3.3. (See also Sections 3.2 and 3.3; see, for example, [Bonnier and Moser (1983)] for discussion of general techniques and especially for filling of the crucible.)

3.2 Fixed Points -50 °C to 630 °C

3.2.1 Ice Point (0 °C)

For many measurements with platinum resistance thermometers and for all measurements with thermocouples (or with liquid-in-glass thermometers) an ice point, rather than a water triple point, is sufficiently accurate [Thomas (1934)].

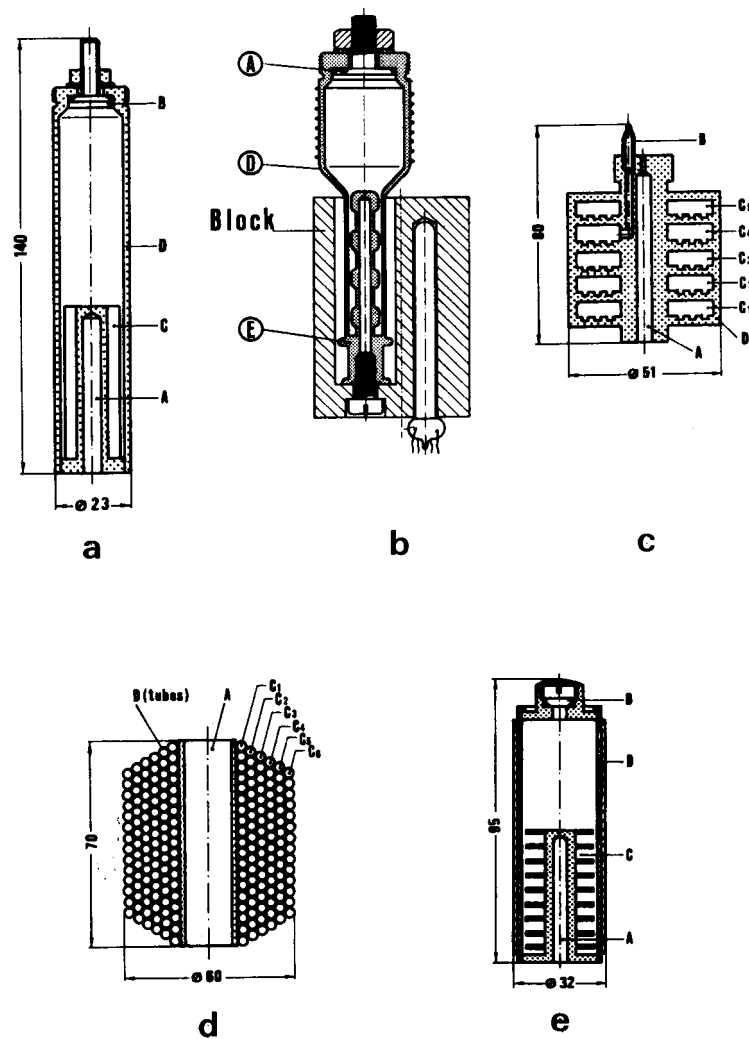


Fig. 3.1: Different approaches with sealed cells: a) thermometers inserted in a well A of the block C protruding inside the cell D [IMGC design, see Pavese et al. (1984)]; b) thermometers inserted in a block C, where one or more cells D (each containing a different substance) can be screwed on at E [Pavese (1987)]; c) thermometers inserted as in a), but the cell itself has many compartments, each containing a different substance (B is the sealing system of the cell: indium gasket or pinch-weld tube) [Bonnier and Hermier (1982)]; d) another multicompartment cell with sample chambers ($C_1 - C_6$) of copper coils surrounding the thermometer well [PAMI design, see Pavese et al. (1984)]; e) as in a) but with a screw seal to allow for refilling and with thin horizontal copper baffles in the sample chamber to improve thermal contact between thermometer and sample [Ancsin (1982)].

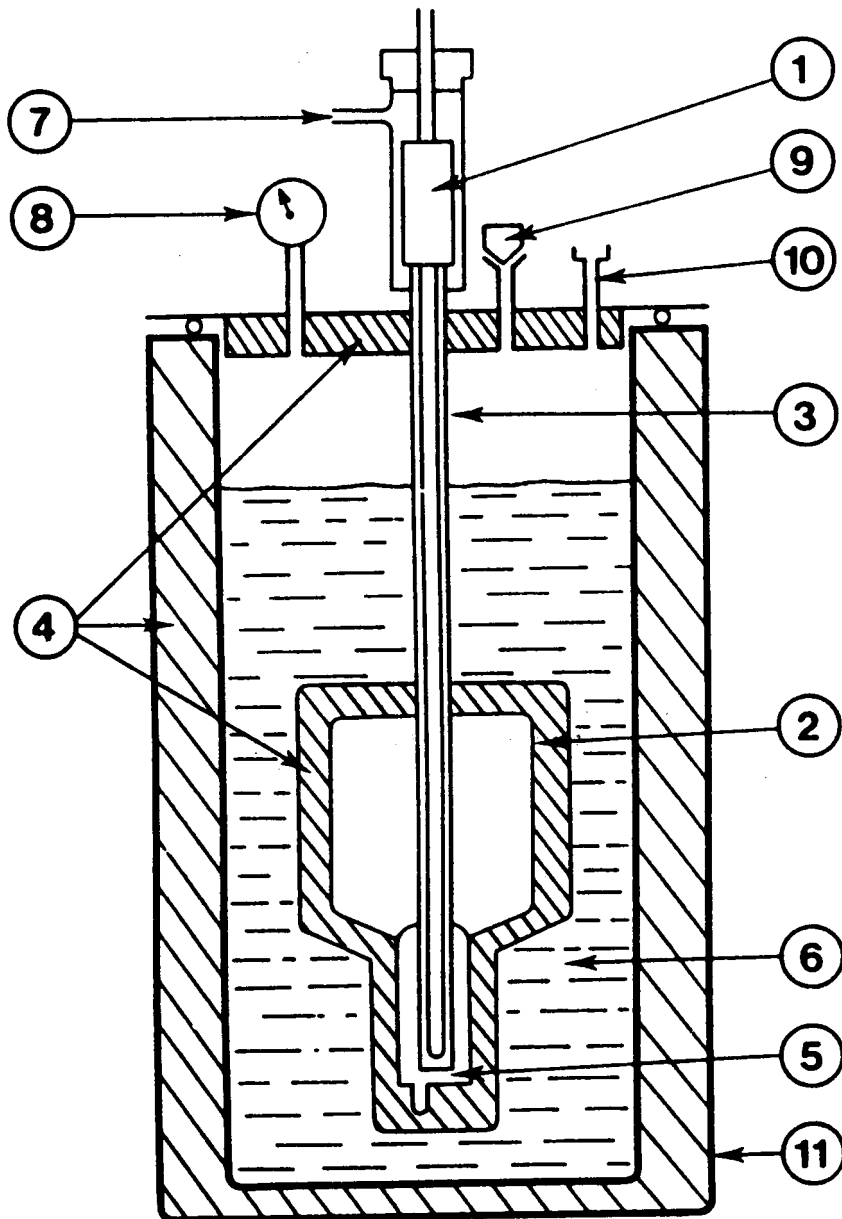


Fig. 3.2a: Apparatus for the calibration of long-stem platinum resistance thermometers at the argon triple point using a sealed cell: 1, long-stem platinum resistance thermometer; 2, stainless-steel body of cell; 3, thermometer tube; 4, polyurethane foam; 5, solid-liquid argon; 6, bath of liquid nitrogen; 7, helium gas inlet; 8, manometer; 9, valve; 10, filling tube for liquid nitrogen; 11, cryostat [Bonnier and Moser (1983)];

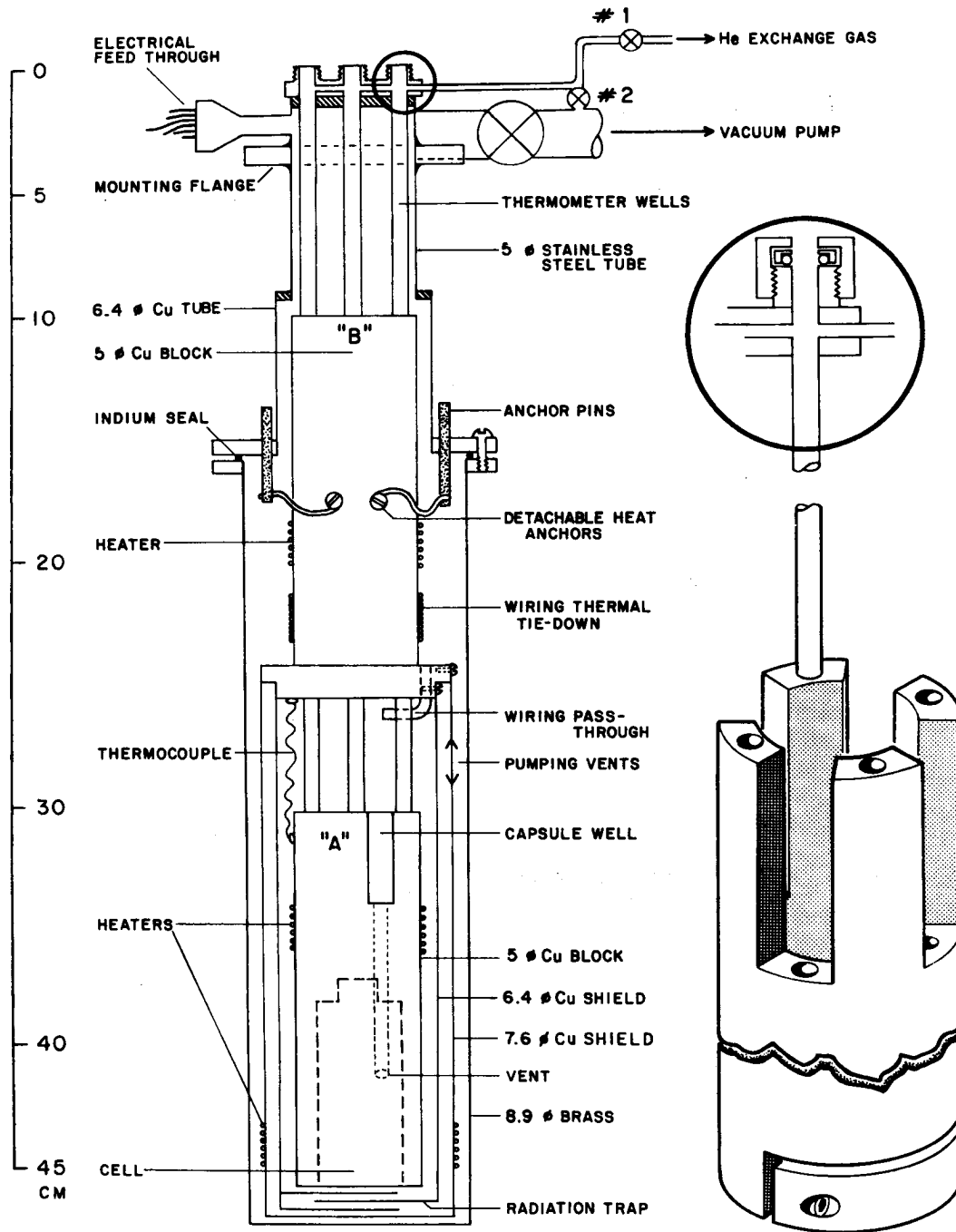


Fig. 3.2b: Apparatus for the calibration and comparison of long-stem and capsule platinum resistance thermometers from the triple point of argon to the triple point of indium [Ancsin and Phillips (1984)].

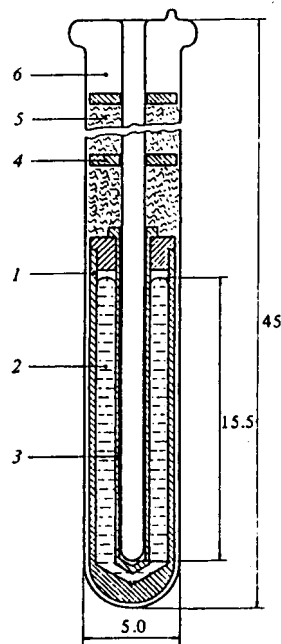


Fig. 3.3: Sealed cell for realization of the copper freezing or melting point (dimensions are in centimetres): 1, graphite crucible; 2, copper; 3, graphite; 4, graphite disk shields; 5, pure silica wool; 6, shielding argon atmosphere [Crovini et al. (1987)].

The equilibrium between ice and water does not require that there be a large amount of water present; the flushing action arising from the melting of surface ice is sufficient when measurements are required only to about 1 mK. However, in such cases an ice point bath must contain enough water to provide good thermal coupling between the ice-water interface and the thermometer. If the ice is melted away from a cooling thermometer it must be carefully repacked when the temperature is nearly stable. A relatively water-free ice bath should routinely provide an uncertainty in the temperature approaching 1 mK if the thermometer immersion is not less than 300 mm; the uncertainty may well be some tens of millikelvins for immersions of the order of 100 mm.

Thermoelectrically-operated ice-point devices are available for use in less accurate thermometry (e.g., with thermocouples).

3.2.1.1 Preparation of the Ice Point

The equipment required for preparing an ice point of high accuracy consists of a wide-mouth dewar flask about 70 or 80 mm inner diameter and long enough to hold the

thermometer; a large dewar of about 150 mm inner diameter; a source of clean and pure shaved ice; a clean container to hold the ice; some pure water either distilled or, at least, de-ionized; and an aluminium or stainless-steel stirrer.

The ice is best made in an ice machine that does not freeze all of the water since the freezing process helps in the purification by concentrating the impurities in the unfrozen liquid. If an uncertainty smaller than 1 mK is required the machine should be supplied with distilled water. With commercial ice that is frozen in large blocks, the center of the block, which freezes last, should not be used; rather one should use only the clear outer layers, after the surface has been carefully washed to remove contamination. The ice should always be transferred with a clean scoop and never touched by the hands.

The procedure for the preparation of an ice point of the highest quality is as follows:

All the utensils, the stirrer and the thermometer are carefully cleaned with mild detergent solution then rinsed two or three times with ordinary water at room temperature. A final wash should be given with distilled water. The large dewar is $2/3$ filled with distilled water, and shaved ice is added (by picking it up on the stirrer or with the clean scoop) with strong stirring until there is a water-ice slush thin enough for the stirrer to pass through easily, yet sufficiently thick to allow some of it to be picked up on the stirrer if it is lifted out slowly. The slush is then transferred to fill the smaller dewar and aerated distilled water, precooled by ice, is added to fill it almost to the top, but preferably not enough actually to float the ice.

As an alternative procedure to the above, the ice point may be made up in a dewar or a vessel deep enough to accommodate the longest expected thermometer immersion with the 0 °C mark near the top of the stem. This dewar should be fitted with a syphon or drain cock to permit removal of free water from below the ice water mix. The ice water mix can be flushed with aerated distilled water at 0 °C and the excess water removed by the syphon or drain.

3.2.1.2 Operating Conditions

The precooled thermometer is gently pushed into the centre of the ice mixture. Liquid-in-glass thermometers are immersed so that the ice point marking is just above the lip of the dewar; for thermocouples and resistance thermometers the depth of immersion should be about 300 mm. If there is any doubt as to whether the immersion is sufficient, the thermometer should be read a second time at about 50 mm less immersion to ensure that the reading is truly independent of immersion depth. However, the sensing element must not go beyond the bottom of the ice since very pronounced temperature layering exists in water below the ice level.

Final readings of the thermometer should not be taken until temperature equilibrium has been achieved as indicated by a constant reading over several minutes. A useful check against possible contamination introduced with the thermometer is to withdraw the thermometer and reinsert it immediately in a different location - then go through the reading procedure a second time. In very precise work, or when immersion is limited, a clean aluminium foil over the top of the ice should be used to prevent transmitted radiation from affecting the temperature of the sensing element.

If all of the precautions described above are taken, an ice bath should be capable of providing the conditions for the realization of the ice point to an accuracy within about 0.3 mK. However, at this level of accuracy the triple point of water is preferable: the triple-point cell is simpler to use, less prone to errors, and may be maintained for a longer time without attention.

3.3 Fixed Points above 630 °C

Except for the very highest temperatures, all of the fixed points in this region are metal freezing or melting points. For calibrations to very high accuracy, the metal is contained in a (usually) graphite crucible in such a way that a continuous liquid/solid interface encloses (as nearly as is practical) the sensing element of the thermometer. For resistance-thermometer calibrations, two such interfaces are generally induced. The outer one forms a solid shell that surrounds the liquid phase and the inner one, whose temperature is measured by the thermometer, surrounds the thermometer well. The techniques required in the generation of these interfaces, the crucible assemblies, suitable furnaces, and methods for checking the quality of the results are described in detail in "Supplementary Information for the ITS-90" [CCT (1990)]. Variations of the techniques suitable for resistance thermometer, thermocouple, or optical pyrometer calibrations are included there. Above 630 °C the metals to which the methods apply are Sb (630.633 °C), Al, Ag, Au, and Cu. The methods can also be used for the melting point of the eutectic alloy Cu 71.9% Ag 28.1% (779.91 °C), but because of the nature of eutectic phase transitions the accuracy is limited to about ± 0.03 °C, even with resistance thermometers. Remarks on the eutectic point are given in Sec. 3.3.1. Sealed cells (Sec. 3.1.4) can often be used for the realization of these metal freezing or melting points.

At higher temperatures the most-used fixed points are the melting or freezing points of Pd and Pt, to which the above methods are applicable only with considerable difficulty because the extreme temperatures require different and more complicated furnace construction, different crucible materials, and so on. In any case, above 1100 °C a much lower accuracy is tolerable with fixed-point calibrations and so specialized techniques have

been developed. Also, below 1100 °C, much simpler and less costly but less accurate techniques are possible. These various special procedures are discussed in Secs. 3.3.2 - 3.3.3.

3.3.1 Copper 28.1% Silver 71.9% Eutectic Alloy

It is unfortunate that no pure metal has a freezing temperature in the approximately 300 kelvin interval between the freezing points of aluminium and silver - a strategic interval for both thermocouple and resistance thermometry. The melting point of the eutectic alloy Cu 28.1% Ag 71.9 % (Cu/Ag) at 779.91 °C is ideally placed but, even when realized according to the same stringent procedures as for the pure metals, it is reliable to at best ± 30 mK in contrast to ± 1 mK for the pure metals. Nevertheless, the point can be useful in connection with thermocouple calibrations. Studies of it with resistance thermometers are described by Bongiovanni et al. (1972) and McAllan (1982), with thermocouples by Itoh (1983), and with optical pyrometers and thermocouples by Bedford and Ma (1982), all with techniques comparable to the foregoing.

The eutectic freezing point is not a good reference point because its temperature value is freezing-rate dependent. This is so because, during freezing, the components in the liquid have to separate by diffusion to form the two different solid eutectic phases, and because the temperature also depends upon the details of nucleation. Consequently, the eutectic melting point is recommended as the reference. It is much more reproducible, and is not strongly dependent on the overall composition. Itoh (1983) found that changing the relative compositions by $\pm 2\%$ from the exact eutectic composition had no significant effect on the observed melting temperature.

The eutectic freezing temperature is always lower than the melting temperature and can vary over several tenths of a kelvin depending largely upon the rate of freezing. Because the rate of freezing also affects the slope of the subsequent melting curve, it is recommended that each melting point determination be preceded by a very slow (several hours) freeze. Also, since even under optimum conditions the melting curve has a more pronounced slope than for a pure metal, some consistent criterion for choosing the melting temperature is required. McAllan (1982) suggests that the most reliable estimate for the equilibrium eutectic temperature is given by the intersection of the extrapolation of the region of the melting curve just before the commencement of the rapid rise with the 100%-melted axis. Alternatively, the maximum in a histogram that shows percentage of time spent in consecutive temperature intervals can be taken as the melting temperature. An extension of this latter method when the histogram has several peaks indicating segregation of impurities is to use the centroid rather than the maximum. These three

temperatures differ (usually) systematically from each other, the extrapolated value being the highest and the centroid the lowest. The largest difference is seldom more than 20 mK.

3.3.2 Melting Points of Gold (1064 °C), Palladium (1555 °C), and Platinum (1768 °C) by the Wire-Bridge Method

For noble-metal thermocouple calibrations not requiring the highest accuracy, the wire method or wire-bridge method is sufficient. With this technique the temperature of melting of a small piece of metal (wire, disk, or rod) that is fastened (welded, or mechanically clamped) to the thermocouple tip or between the thermocouple legs is measured. The method is simple, rapid, inexpensive, and adequately accurate.

This calibration technique is most commonly used at the gold, palladium, and platinum points. It is also sometimes used at the silver point, but this is not recommended because of the danger of the melting temperature being affected by solution of silver oxide. It is necessary to protect the internal chamber of the furnace from contamination by the fixed-point material by using a protective recrystallized alumina tube. This alumina furnace tube should be kept extremely clean and used only in the calibration of noble-metal thermocouples. To apply the method, a small piece (typical weight < 0.1 g) of metal or short length (5 to 10 mm) of 0.5 mm diameter wire of high purity (at least 99.99%) is used to form the junction between the two elements of the thermocouple by mechanically fastening, wrapping, or welding. Various ways of completing the junction are described by Bedford (1964) and by Bongiovanni and Perissi (1984). For welding, a microtorch with an oxygen-hydrogen gas mixture is convenient. With welding, however, there is risk of contaminating the metal with Pt or Rh. Pre-cleaning of the metal link in cool, dilute nitric acid has been recommended. The thermocouple is then slowly inserted into a furnace maintained several degrees below the melting point of the fixed-point material. When equilibrium is reached, the furnace power is increased by a predetermined amount (a heating rate of 0.3 K/min will yield long and flat melting plateaux) and the thermocouple output recorded as the temperature passes through the melting point. Sometimes, but not usually, the metal bridge breaks on melting, interrupting the thermocouple output. During the melt an increase in emf of 2 to 10 μV is typical (smallest with Au, largest with Pt), with the melting lasting 2 to 8 minutes and with a momentary stabilization (0.5 to 2 min) just before completion of melting. Which emf to assign to the fixed point is somewhat ambiguous; the sudden rise from the melting plateau indicating the completion of melting was considered by Bedford (1964) as the most reproducible index, whereas Crovini et al. (1987) recommend using the median of the plateau. It is advisable to test the reliability

with a repeat calibration after clipping about 1 cm of wire from the hot junction to avoid effects of contamination.

Reliable freezing points cannot be obtained with this method because some material from the thermoelements dissolves in the molten bridge, changing its freezing temperature by an indeterminate amount and producing a freezing transition with a rapidly changing temperature.

The melting temperature of palladium is influenced by dissolved oxygen; in an oxygen-free atmosphere the melting temperature is 1554.8 °C and in air is about 1553.5 °C [Jones and Hall (1979), Coates et al. (1983), Bedford (1972a), Jones (1988)]. With a platinum bridge on a thermocouple with a pure platinum thermoelement, either the bridge frequently breaks or the platinum thermoelement melts near, and before, the bridge itself, depending upon the degree of temperature uniformity. The platinum point is best used with double alloy noble metal thermocouples or with refractory metal thermocouples.

The accuracy of the procedure is mainly limited by the contamination of the metal bridge by the thermocouple wire, and by the furnace's tendency to raise the temperature of the thermocouple legs, weakly opposed by the latent heat absorbed by the melting bridge, above the melting point. With Pt10Rh/Pt thermocouples it is possible to obtain a reproducibility (1 standard deviation) of about $\pm 2 \mu\text{V}$ between two test runs at the gold point, about $\pm 4 \mu\text{V}$ at the palladium point, and about $\pm 8 \mu\text{V}$ at the platinum point. A detailed description of the use of the wire-bridge method in an interlaboratory intercomparison is given by Crovini et al. (1987).

3.3.3 Miniature Fixed Points for Thermocouple Calibrations

Tischler and Koremlit (1982) have devised a modification of metal-fixed-point-calibrations for thermocouples using miniature ingots that has some of the advantages of both regular fixed points and the wire-bridge method. It can provide calibrations that in many cases are as accurate as the thermocouples themselves and can also provide the possibility of in-situ calibration. The technique has been applied successfully with In, Sn, Cd, Pb, In, Sb, Al, Ag, Au, Cu. A small crucible (volume - 0.1 cm³, mass - 0.3 g) machined from 6 mm diameter graphite rod to the shape shown in Fig. 3.4 is filled with a pure metal ingot (mass of metal from 0.5 to 2 g). A hole is drilled through the graphite below the ingot chamber and another through the graphite lid. One leg of the thermocouple can be inserted into each hole without touching the metal ingot. This completes the electric circuit, prevents contamination of the metal ingot, and permits repeated use of the crucible with the same thermocouple or the exchange of thermocouples.

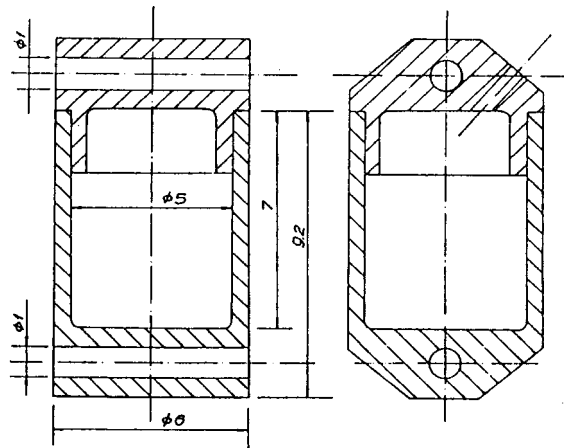


Fig. 3.4: Cross sectional drawing of a miniature graphite crucible for thermocouple calibrations (dimensions are in millimetres) [Tischler and Koremblit (1982)].

The tightly-fitting crucible lid has a small perforation to vent occluded gases that are released as the temperature is raised.

For calibration, the thermocouple with the crucible attached is placed in a small-diameter, fused-silica tube through which a slow flow of nitrogen is maintained to protect against oxidation of the graphite. The silica tube in turn is inserted into a conventional furnace at the appropriate temperature with the silica tube extending to room temperature. The furnace power is then increased so that the furnace equilibrium temperature will be slightly (typically 1 K to 5 K) higher than the melting temperature of the ingot and the melting transition is recorded. Following this, the furnace power is reduced so that the temperature will equilibrate at an equal amount *below* the transition temperature and the freezing transition is recorded. A typical transition plateau lasts about 20 min. Depending upon the rate of change of furnace temperature, and upon the difference between furnace temperature and transition temperature, the temperature of the freezing plateau will be significantly lower than that of the melting plateau because of the relatively small latent heats, large heat transfer, and effect of pressure on the ingot due to surface tension. Let V_P be the thermocouple emf at the temperature of the plateau, V_F the emf when the thermocouple has equilibrated at the furnace temperature following the transition, and V_T the emf at the true transition temperature. On a plot of V_F vs V_P , the intersection of a line joining the points corresponding to melting (V_{Pm}) and freezing (V_{Pf}) with the line $V_F = V_P$ gives the desired emf V_T , which is usually reproducible to about $\pm 1 \mu\text{V}$ and accurate to $\pm 0.3 \text{ K}$. It is likely almost as accurate to take for V_T the mean of the melt and freeze emfs.

With some deterioration in accuracy (± 0.5 K), a simpler method is not to stabilize the furnace temperature close to the transition temperature, but to let it pass through at a relatively high rate. For Cu, Sb, Pb, Sn, In take $V_T = V_{Pm}$ from the melt; the large amount of undercooling makes V_P from the freeze unreliable. For Au, Ag, In, and Cd take $V_T = (V_{Pm} + V_{Pf})/2$, or $V_T = V_{Pm}$, which will be almost the same. For Al it is necessary to take $V_T = (V_{Pm} + V_{Pf})/2$.

Variations of this technique are described by Tischler and Anteneodo (1986) where the freezing point is a permanent part of the thermocouple. Other workers are applying miniature fixed points for the calibration of standard-welded and metal-sheathed thermocouples.

3.4 Fixed Points for Pyrometry

3.4.1 Blackbody Furnaces

Infrared pyrometers (monochromatic or broad-band) must be calibrated against blackbodies. If modest accuracy is sufficient, it is possible to use semi-miniature furnaces as opposed to those recommended for highest accuracy [CCT (1990)]. Sakuma and Hattori (1982a) have designed furnaces of this sort that are in moderately wide use. A graphite blackbody crucible 4 cm diameter, 6.5 cm long, with a 1 cm aperture (Fig. 3.5) is encapsulated in a stainless-steel cylinder which carries the furnace heater, either embedded in grooves parallel to the axis or wound around the circumference. The steel cylinder extends beyond the blackbody aperture for better temperature uniformity, and includes a stainless-steel disk with a 6 mm aperture covering the front of the blackbody. Argon flows through the steel capsule to prevent oxidation of the graphite. This steel cylinder containing the crucible and furnace heater is mounted in an alumina tube that is surrounded by suitable radiation shields and thermal insulation (Fig. 3.6). The whole furnace is 10 cm diameter by 25 cm long, and is attached to a temperature-control unit consisting of a SCR power regulator, an on-off temperature controller, and indicators. A monitoring thermocouple is attached to the steel capsule. With the main power switch on and the regulator switch off, the furnace is maintained about 10°C above the freezing point of the metal in the blackbody. Then, with the regulator switch on, the crucible cools at a pre-determined rate through the freezing transition. The freezing plateau lasts about 10 min and is accurate to within about -0.1 ± 0.1 K. Such a furnace is available for each of the metals Cu, Ag, Al, Sb, and Zn.

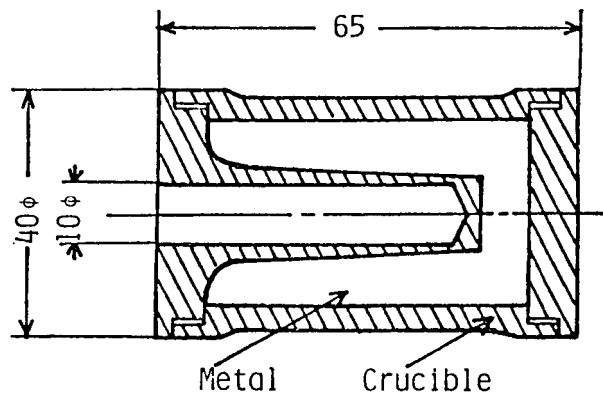


Fig. 3.5: Miniature graphite blackbody crucible for pyrometer calibrations (dimensions are in millimetres) [Sakuma and Hattori (1982a)].

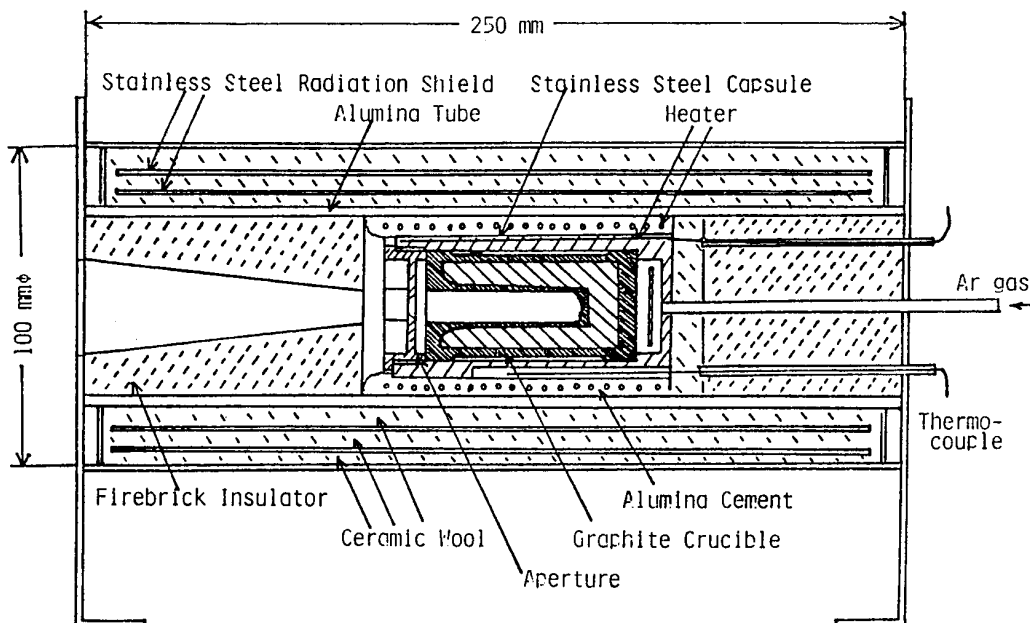


Fig. 3.6: Portable blackbody furnace for pyrometer calibrations [Sakuma and Hattori (1982a)].

3.4.2 Radiance Temperatures on Melting

For optical-pyrometer calibrations, especially at very high temperatures where conventional methods are difficult, the technique of measuring the radiance temperature at the melting point of selected pure metals offers a practical and moderately accurate alternative. In general, the method involves heating (in vacuum or inert atmosphere) a small specimen in the form of a strip or a tube through its melting point by passage of electric current. As used in conjunction with high-speed pyrometers, the specimen is heated from room temperature to the melting point in less than one second and the pyrometer focused on the specimen indicates a melting plateau lasting some tens of milliseconds. For use with conventional pyrometers, a technique would have to be devised to maintain a stable metallic surface for tens of seconds during the melting transition. Various experiments [for example, Cezairliyan et al. (1982)] have indicated that the radiance temperatures are reproducible to about ± 1 K and accurate to within a few kelvins. Bedford et al. (1984) list many such temperatures with their estimated accuracies. The radiance temperature is essentially independent of the initial surface condition of the solid specimen. The technique has the advantage that no emissivity correction is involved (it is, in essence, built into the radiance temperature), but it is important to note that the value of the radiance temperature applies only for the particular wavelength value listed. For widespread use a more comprehensive catalogue of radiance temperatures for more metals and at more wavelengths is required.