

4. THE ^3He AND ^4He VAPOUR-PRESSURE SCALES AND PRESSURE MEASUREMENT

4.1 VAPOUR PRESSURES OF HELIUM (0,65 K to 5,0 K)

In the range 0,65 K to 5,0 K the ITS-90 is defined using equations relating the vapour pressures of ^3He and ^4He to T_{90} (see Equation 3 and Table 3 of the text of ITS-90). The techniques by which helium vapour pressures can be set up and measured are described in this section.

There are three principal requirements for any vapour pressure thermometer: to arrange for a volume of the pure liquid and vapour phases to come to thermal equilibrium; to measure absolutely the pressure at the (plane) interface; and to know the vapour pressure-temperature relationship. The following sections address these requirements.

4.2 VAPOUR PRESSURES RELATIONS FOR HELIUM

The vapour pressure relations for helium are of the form:

$$T_{90}/\text{K} = A_0 + \sum_{i=1}^9 A_i [(\ln(p/\text{Pa}) - B)/C]^i \quad (4.1)$$

Values of the constants A_0 , A_i , B and C are given in Table 3 of the text of the ITS-90 for the three ranges: 0,65 K to 3,2 K for ^3He ; 1,25 K to 2,1768 K for ^4He ($^4\text{He II}$)^{4.1}; and 2,1768 K to 5,0 K also for ^4He ($^4\text{He I}$)^{4.1}. The ^4He equations coincide at the lambda point (2,1768 K, 5041,8 Pa) with a first derivative $\text{dln}p/\text{d}T_{90}$ of $2,461 \text{ K}^{-1}$. In deriving these equations no constraints were placed on the second derivative, which physically is discontinuous at this point.

The upper temperature limits for the use of the two isotopes were chosen to be somewhat below the critical points, since the specification of the relationships and the measurement of vapour pressures become matters of some difficulty as the critical point is approached. The lower temperature limits are such that the vapour pressures are still not less than 100 Pa; at pressures below 100 Pa the inaccuracies of the vapour pressure thermometers are likely to be more than the $\pm 0,5 \text{ mK}$ which was

4.1 In the phase equilibrium diagram of ^4He the liquid phases of ^4He above and below the lambda line are distinguished by referring to them as to He I and He II respectively. The properties of $^4\text{He II}$ are very different from those of $^4\text{He I}$.

considered appropriate for the ITS-90, *see* Figure 4.1. It was also the intention to keep open the option of extending the scale to lower temperatures by other means.

The equations adopted in the ITS-90 are a restricted set of those derived by Rusby and Durieux (1984), which themselves were simplified forms of the equations of Durieux and Rusby (1983) that were approved by the CIPM (1982) following the introduction of the EPT-76 [BIPM (1979)]. The unrestricted forms are useful for those choosing to use them at temperatures close to the critical points or below 0,65 K.

4.3 HELIUM VAPOUR-PRESSURE THERMOMETRY

4.3.1 ^4He

In its simplest form a vapour-pressure thermometer consists of a vessel containing the liquid in equilibrium with its vapour.

For ^4He (both $^4\text{He I}$ and $^4\text{He II}$) the liquid is typically contained in a cryostat or storage vessel with appropriate precautions for reducing heat influx and hence the rate of evaporation. A schematic illustration of a cryostat for calibrating capsule thermometers is given in Figure 4.2a.

In this cryostat the refrigerating liquid is also the thermometer liquid. The manometer (not shown) senses the vapour pressure via a tube inserted into the vapour space and terminating close to the liquid surface. The pressure is usually regulated by means of a throttling valve in the pumping line. The pressure, and hence the temperature, is progressively reduced so as to prevent temperature stratification. An electrical heater at the bottom of the liquid (not shown) can be used for reheating and, at low power levels, will promote mixing.

The convection mechanism is a feeble one at these temperatures, and significant temperature gradients can be present in the liquid. Such gradients occur even when the temperature monotonically decreases with time, their magnitude being likely to increase as the temperature is lowered, perhaps becoming as high as 5 mK at the lambda point [Cataland *et al.* (1962)]. On re-heating, the temperature of the bulk liquid may respond only slowly if the pressure is allowed to rise, and gross gradients can then result.

Such difficulties can be avoided by mounting the artifacts in a copper block containing a vapour-pressure bulb (Figure 4.2b) that is independently supplied with helium so that a liquid-vapour interface is contained within it. In a closed system the liquid fraction will increase when the temperature is reduced, and the total mass of helium must be such that the bulb does not overflow. The supply tube (of stainless steel or another material of low thermal conductivity, and typically 2 mm in diameter) is also the pressure sensing tube, and where it passes through the surrounding liquid it must be insulated sufficiently well to avoid condensation within it. Light insulation is reported as being sufficient for this purpose, since cold spots tend to be self-stifling by virtue of the heat of condensation [Ambler and Hudson (1956)]; however, a stainless-steel vacuum jacket is often used and may extend up to room temperature. In addition, copper cladding or electrical heaters on the sensing tube can be used. These have the advantage of keeping the sensing tube and vapour within it relatively warm, only reaching the liquid temperature just above the bulb thereby reducing the aerostatic head correction. For an exposed tube and a bulb at 4,2 K this correction may be about 0,5 mK, compared with 0,1 to 0,2 mK that is typical for a vacuum-jacketed tube (for which, however, the temperature distribution needed for calculating the pressure head, can be difficult to ascertain). At the lower temperatures aerostatic head corrections are smaller in terms both of pressure and of the temperature equivalents because of the rapid decrease of vapour density with decrease in temperature.

No radiation trap is shown inside the pressure sensing tube of Figure 4.2b. If this is 2 mm in diameter the maximum radiative heat transfer down the tube (assuming that all the radiation emitted at room temperature is absorbed in the bulb) would be about 1,4 mW. The helium in the bulb is not likely to absorb much of this, while the copper block could easily do so without setting up significant temperature gradients. A trap could be included near the bottom of the tube, but it would need careful design. A simple bend in the tube is unlikely to be effective, while any other system must be so constructed that no liquid can be held at that point. Even with a straight tube it is possible for liquid to block the tube just above the bulb, leading to substantial measurement errors. A pressure pulse may dislodge such a block, but as a matter of design the portion of the tube exposed to low temperatures should be short, or the vacuum jacket can be extended right down to the bulb. In the latter case

the heat conducted down the sensing tube, perhaps 0,1 mW, can be readily absorbed in the block but a baffle must be included in the vacuum jacket to intercept the radiation from room temperature components of the jacket.

There will be some differential contraction between the sensing tube and the vacuum jacket. These must not touch, and an insulating spacer, which can also serve as the radiation trap, should be used to prevent this. Alternatively bellows or a sliding seal at the upper end of the tube can prevent touching.

While a vapour-pressure bulb is preferable for normal helium, He I, this is not the case for the superfluid He II. With He II in the bulb, a superfluid film would creep up the walls of the sensing tube, would evaporate at some higher temperature, and would then reflux back to the bulb. This action can result in a measurement error of several millikelvins [Sydoriak and Sherman (1964)] due in part to pressure gradients in the tube and in part to temperature gradients in the bulb. Continuity of measurements (thermometers calibrations or other) on passing through the lambda point is a good test of any design.

By contrast, the system of Figure 4.2a works well below the lambda point. In this system the superfluid film evaporates as part of the cooling process and never affects the pressure sensing. Furthermore, the phenomenal thermal diffusivity of He II ensures that no temperature gradients exist within the liquid. The only limitations are the ability of the pump to reduce the temperature as far as is required and, possibly, the appearance of thermomolecular effects at low pressures. The latter limitation is eliminated by use of a tube of diameter 10 mm or more equipped with appropriate radiation baffles. Clearly a dual system, in which both a vapour pressure bulb and a bath pressure-sensing tube are provided, would enable the complete ^4He range to be covered, and would also allow investigations of the differences between the two realizations to be made.

4.3.2. ^3He

Extensive vapour-pressure comparisons were carried out with ^3He by Sydoriak *et al.* (1964) prior to the derivation of the 1962 ^3He vapour-pressure scale and equation. Problems with ^3He are its high cost, of the order of 1000 times that of ^4He , and the need to take account of

contamination with ^4He (there is negligible natural occurrence of ^3He , so the reverse does not generally apply, and other impurities are frozen out).

Because of its cost, ^3He is usually kept in a closed system and repeatedly used. It is condensed into a small chamber (or pot) in the cryostat as needed for cooling, experimentation, or measurement. The vapour pressure can be measured using a second tube leading to the pot.

Condensation of, typically, up to 10 cm^3 of liquid ^3He is effected using a pumped ^4He pot (or bath of ^4He) at 1,5 K or below. The ^4He pot is then boiled dry (or the bath is isolated from the interior assembly), and further cooling is achieved by evaporation of ^3He . The heat of vaporisation of this is large compared with the amount of cooling typically required, so the lowest temperature reached will be limited by the pumping speed and heat leaks: 0,5 K can be readily achieved.

Sufficient heat-exchange area must be provided to ensure that the liquid is approximately isothermal and is in equilibrium with the experimental artifacts (including thermometers) despite the heat flows resulting from heat leaks into the pot and from the evaporation of the liquid.

A serious complication is that normal-grade ^3He may contain 0,1 % ^4He which would cause an error of as much as 0,6 mK at 3 K [Sydoriak *et al.* (1964)]. To overcome this, a second pot of perhaps 1 cm^3 using a small quantity of ^3He purified to about 0,01 % is often employed for the vapour-pressure measurement.

4.3.3 COMBINED ^4He , ^3He SYSTEM

A combined ^4He and ^3He vapour pressure cryostat, somewhat simpler than that of Sydoriak *et al.*, has been described by Rusby and Swenson (1980) and was used by them for the re-determination of the vapour-pressure relations, *see* Figure 4.3. The copper thermometer block containing the helium pots was suspended inside a vacuum jacket which was surrounded by liquid ^4He at 4,2 K. A single 50 cm^3 pot of ^4He was used for cooling and for sensing the vapour pressure. The problem of film flow was avoided by including an orifice of 0,6 mm diameter in the lid of the pot. Such film as flowed through this was soon evaporated (and thereby contributed to the cooling). The pressure sensing tube joined the 6 mm diameter pumping tube some 4 cm higher up and so was not affected by film refluxing. The pressure gradient across the orifice and

along this section of the tube was negligible at temperatures above 1,4 K. A larger orifice could have permitted accurate measurements to still lower temperatures. The ^4He pot contained a spiral of copper foil to promote temperature uniformity (*see* the authors' discussion of measurements above and below the lambda point).

A ^3He cooling chamber was provided, and measurements of ^3He vapour pressures were made with a small bulb and a sample of purified gas. Pumping tubes were about 20 mm in diameter between the ^4He bath and room temperature (with appropriate traps to intercept radiation). The vapour-pressure tubes were 2 mm in diameter at temperatures up to 4,2 K, and 6 mm (for ^4He) and 5 mm (for ^3He) above this. These dimensions give thermomolecular effects, calculated from the Weber-Schmidt equation (*see* Section 4.4.5), equivalent to 1 mK at 1,25 K and 0,65 K for ^4He and ^3He respectively, with the effects increasing rapidly at lower temperatures. Larger tubes may be desirable, especially for ^3He , though this would require a substantial quantity of gas to be available if ^3He vapour-pressure measurements are also to be made up to 3,2 K.

A way of reconciling the requirement for a small thermomolecular effect at lower pressures with the requirement that the amount of gas needed to fill the system at high pressures should not be too large is to increase the diameter of the tube some distance up the cryostat. The temperature of the junction must, of course, be known, but this is desirable in any case for the calculation of the aerostatic head effect. The vapour-pressure sensing tubes used by Rusby and Swenson passed through the ^4He bath and the aerostatic head was consequently quite large (equivalent to values as large as 0,6 mK). Steps also had to be taken to damp out thermal oscillations in the ^4He pumping tube (a woollen plug at room temperature, or an enlargement of the tube, usually suffices for this purpose). Cold spots were not evident in measurements at 4,2 K, but measurements of pressures above atmospheric were made only when the liquid level in the main helium bath had fallen below the top of the vacuum jacket, and with the bath pressurised to a maximum of 2 atmospheres (absolute).

In this or any similar system the tubing that is at room temperature but is open to the cryogenic area must be clean, as any desorbed vapours will diffuse into the cryostat and be re-adsorbed there. The pressure gradient due to this diffusion can be significant at low pressures.

4.4 PRESSURE MEASUREMENTS

Pressure measurements are required for the realization of the boiling points of hydrogen, the helium vapour pressure scales and the gas thermometer.

Table 4.1 summarises hydrogen and helium vapour pressure data and allows the measurement requirements to be calculated. It shows that in order to cover the complete range it is necessary to measure absolute pressures from 100 Pa to 200 000 Pa, with accuracies of 0,5 Pa to 75 Pa, respectively, to achieve 0,5 mK accuracy in T_{90} . The relative sensitivities (from column 4) are less wide ranging, varying from 0,03%/mK for hydrogen at 20,3 K to 0,9 %/mK for ^3He at 0,65 K. A measuring instrument with a constant relative uncertainty is thus more suitable than one with a constant absolute uncertainty.

For much of the range the requirements (in terms of room-temperature capability for pressure measurement) are not overly stringent. A mercury manometer of 10 Pa accuracy (achievable with simple optical aids) is sufficient to give 1 mK accuracy in T_{90} down to 2 K (with ^4He) or 1,2 K (with ^3He), and oil manometers with about 15 times greater sensitivity (though not accuracy) have often been used to lower temperatures.

Where 0,1 mK accuracy is sought, however, more sophisticated systems are needed. Superior mercury instruments are available but tend to be inconvenient to use. Quartz-spiral bourdon gauges and capacitance diaphragm gauges are adequately sensitive and convenient to use, but have constant pressure sensitivity and require comprehensive calibrations. Moreover, quartz is permeable to helium.

Pressure balances operated with air or helium in the 'absolute' mode, i.e. with the space above the assembly evacuated, are much more suitable. They retain essentially the same relative accuracy over their operating range, and this can be 20 parts in 10^6 (equivalent to less than 0,025 mK in the measurement of the vapour pressure of helium) without undue difficulty.

4.4.1 MERCURY MANOMETER

The classical method employs a cathetometer to determine the position of the mercury levels in a U-tube manometer, and has a limit of accuracy of about 3 Pa. For pressures up to 100 kPa higher accuracy can be attained if the levels are sensed by capacitive [Preston-Thomas and Kirby (1968), Guildner *et al.* (1970)] or interferometric [Bonhoure and Terrien (1967), Mitsui *et al.* (1972)] techniques: for pressures of the order of 1 standard atmosphere, such instruments can measure absolute pressures to about 3 in 10^6 or pressure ratios to about 1 in 10^6 .

At these levels of accuracy, uncertainties in length, density of mercury (which is pressure and temperature dependent), aerostatic head, mercury vapour pressure and capillary depression may become critical. For absolute pressure measurements (which are required for hydrogen vapour-pressure points and helium vapour pressure temperature measurements) a knowledge of the local value of the acceleration due to gravity (g) is required. However, for gas thermometry, in which pressure ratios only are measured, constant errors in the average density of the mercury or in the value of g cancel out.

The mean density of pure mercury at t_{90} in a barometric column supported by the pressure p being measured is given with sufficient accuracy, over the temperature range from 0 °C to 40 °C and for the pressures relevant to these measurements, by the relation

$$\rho\left(t_{90}, \frac{p}{2}\right) = \frac{\rho(20\text{ °C}, p_0)}{\left[1 + A(t_{90} - 20\text{ °C}) + B(t_{90} - 20\text{ °C})^2\right] \times \left[1 - \chi\left(\frac{p}{2} - p_0\right)\right]} \quad (4.2)$$

where $A = 1,8120 \times 10^{-4} \text{ °C}^{-1}$, $B = 8 \times 10^{-9} \text{ °C}^{-2}$, $\chi = 4 \times 10^{-11} \text{ Pa}^{-1}$, $p_0 = 101\,325 \text{ Pa}$ and $\rho(20\text{ °C}, p_0) = 13\,545,854 \text{ kg m}^{-3}$ [Ambrose (1990)]. A sufficiently accurate local value of g may be obtained by using the Réseau Gravimétrique International Unifié 1971 (IGSN-71) de l'Union Géodésique et Géophysique Internationale.

Corrections for the errors mentioned above are straightforward, except for the capillary depression of mercury surfaces of less than several centimetres diameter which remains a potential source of uncertainty in high-precision manometry [Brombacher *et al.* (1960)]. Tables for the capillary correction in terms of bore diameter and meniscus

height based upon experimental data are given by Kistemaker (1944-1946) and Cawood and Patterson (1933). Gould and Vickers (1952) computed similar tables for values of the coefficient of surface tension (σ), ranging from 0,4 to 0,5 Nm^{-1} ; within this range, for a given meniscus height, the capillary depression is practically linearly dependent on σ .

In practice, σ appears to vary from 0,4 to 0,58 Nm^{-1} depending upon the degree of surface cleanliness of the mercury and the surface conditions of the container; there is frequently a degree of hysteresis in the relation between meniscus height and pressure. The lack of a precise knowledge of σ is such that if an accuracy within 10 Pa is desired, a tube of diameter not less than 15 mm should be used. To achieve the highest levels of accuracy the diameter of the mercury surfaces should be so large (≥ 30 mm) that the uncertainty in the capillary depression will be negligible ($\leq 0,15$ Pa).

4.4.2 PRESSURE BALANCE

For this instrument the pressure is defined by the mass, the local value of g and the effective area of a piston freely rotating in a closely-fitting cylinder. Pressure settings for a given piston are changed by changing its mass, i.e. by adding additional weights [Dadson *et al.* (1982)].

The principal limitation here is the accuracy with which the effective area is known. This may be obtained from direct dimensional measurements or, more usually, by calibration against another pressure balance, or against a mercury instrument near standard atmospheric pressure (where this too has high relative accuracy). For stainless steel the temperature and pressure coefficients of the effective area amount to 2 to 3 $\times 10^{-5} \text{K}^{-1}$ and $-5 \times 10^{-6} \text{MPa}^{-1}$, respectively.

The calibration of the weights should not be a problem, even allowing for the need for buoyancy corrections (if the weighing is performed in air). The buoyancy of the floating member of the piston-cylinder assembly should be assessed carefully, however, as some parts may be made of aluminium, rather than stainless steel, to reduce the weight (which limits the lowest pressure at which the device can be operated). Some approximate means of measuring the temperature of the assembly should be included, as the temperature coefficient is likely to be more than 2 $\times 10^{-5} \text{K}^{-1}$.

In the measurement of absolute pressure (as required in vapour-pressure thermometers) the bell jar containing the piston assembly is evacuated and the local value of g must be known. Small corrections must be applied to take account of the effects of the gas streaming between the piston and the cylinder, and of the resulting residual pressure (which must therefore be measured) in the evacuated space above the piston. The gas head may vary by about 2 cm as the piston sinks in use, which (for argon) is equivalent to a few parts in 10^6 at standard atmospheric pressure.

Pressure balances are not so much *gauges* of pressure as *generators* of a series of pressures whose values are determined by the (fixed) effective area and the (variable) loading. The minimum value is that with the assembly unloaded. Since a continuum of pressures is not available, and because the assembly will need to be taken apart for occasional cleaning, it is usual to apply the generated pressure to the reference port of a differential capacitance-sensed diaphragm gauge (see Section 4.4.4). The vapour pressure to be measured is fed to the other port and the gauge output gives the difference between the two. The diaphragm gauge needs to be calibrated, and this can be done (at various line pressures) using two pressure balances, or one pressure balance and a temperature-controlled reference volume, or even with a temperature-controlled (or monitored) vapour pressure bath itself as the reference. The first is preferable, but in the measurement of helium vapour pressures the problem can be avoided by so adjusting the helium temperature that the diaphragm gauge reads zero - i.e. that the pressure to be measured exactly equals the pressure generated by the balance. The true zero of the diaphragm gauge can be simply checked by cross connecting the two sides of the diaphragm.

For measurements of ^4He vapour pressures it is convenient to operate the balance with helium, drawing gas from the vapour pressure system as needed. For ^3He , however, the cost of the gas usually precludes this, while ^4He should not be used for fear of contaminating the ^3He . Air, nitrogen or argon will be convenient, but once ^3He is admitted to the diaphragm gauge care must be taken not to allow air into the ^3He line. Cross-connection to check zero entails some wastage of gas and so for ^3He should preferably be carried out only immediately before and after a series of measurements, the minimum requirement.

As was mentioned earlier, the lower limit of operation of the pressure balance is that which supports just the unloaded floating member (which may be the piston or the cylinder, according to design). This can be reduced by choosing a light assembly with a large effective area, and a typical minimum pressure is 2 kPa.

The pressure balance can achieve an accuracy within 1 part in 10^5 and a resolution of 1 part in 10^6 between about 200 kPa and 2 kPa. Below the latter value an alternative device must be used.

Unless a gas-injection system is available, the measuring time available (≈ 5 min) is determined by the downward movement of the piston resulting from the inevitable gas loss through the annular gap between piston and cylinder. Elegant solutions to this problem are reported in the literature [Neubert (1977)].

4.4.3 QUARTZ PRESSURE GAUGE

The modern quartz bourdon-tube pressure gauge can be used as a pressure transfer and interpolating device. To avoid hysteresis, the pressure-sensing quartz element is restrained from making large excursions by a servo feedback system. The gas volume of such a gauge is very much smaller than that of a pressure balance; however, the quartz is highly permeable to helium, so care must be taken to prevent helium-rich gases for coming into contact with it. This type of gauge is usually calibrated directly against a pressure balance; regular checks are necessary although it may retain its calibration for very long periods. Accuracy can be within one part in 10^5 of full scale, the latter usually being somewhere in the range of 100 Pa to 100 kPa.

As in the case of the diaphragm gauge described in Section 4.4.4, the advantages are that the instrument has a direct read-out and that changes in pressure can readily be accommodated.

4.4.4 DIAPHRAGM AND CAPSULE PRESSURE TRANSDUCER

The diaphragm transducer consists of a thin, usually metal, membrane under tension located between two electrodes. Deflection of the membrane caused by a pressure difference across it can be accurately

detected by capacitance-bridge techniques. High accuracies require precise temperature control and isolation from vibrations. For absolute measurements diaphragm gauges are available with 0,1 kPa to 1 MPa ranges. Calibration can be readily carried out using a pressure balance and accuracies within 1 to 5 parts in 10^4 of full scale are possible provided periodic recalibrations of the instrument are carried out.

In the null mode, temperature and pressure dependence, hysteresis, and stability of the zero are the limiting factors; high linearity is desirable for ease of calibration but it is not essential. In this mode the resolution may approach 1 in 10^7 of 100 kPa and the temperature coefficient of the zero about 1 Pa/°C. Reproducibility is improved by prestressing the diaphragm in a given direction at a pressure corresponding to full scale deflection and taking care that afterwards the pressure never exceeds this value nor changes sign [Pavese (1981)].

As a null instrument the diaphragm gauge has found wide application in gas thermometry, where it is used primarily to isolate the gas bulb from the manometer system. This allows a large reduction of the dead space and its associated errors, and also a greater flexibility in the application of pressure-measuring systems. For example, a pressure balance can be employed despite its inevitable gas leak [Berry (1979)]. Using the diaphragm to measure residual pressure differences between the bulb and the pressure balance, rather than merely as a null instrument, compensates to some extent for the drawback that the balance can be operated only at discrete pressures.

In its absolute mode of operation (i.e., at zero backing pressure) the diaphragm gauge can fill the gap left by the conventional pressure balance below 2 kPa where it offers a high enough accuracy for low-temperature thermometry, such as the realization of the ^3He vapour pressure scale below 1 K. Finally, whenever the purity of a gas being used for thermometric purposes is a matter of concern - which is usually the case - it is worthwhile considering the use of an isolating diaphragm.

The capsule transducer consists of a gas-filled flexible capsule the moveable face of which can apply pressure to a quartz resonating crystal. The resonating frequency is a function of applied mechanical stress and hence of the pressure in the capsule. At about atmospheric pressure the accuracy of a calibrated capsule transducer can be about 10 Pa.

4.4.5 THERMOMOLECULAR PRESSURE DIFFERENCE

A thermomolecular pressure difference will result from a temperature gradient along a tube if the diameter of the tube is not large compared with the mean free path of the gas molecules.

The pressure at the higher-temperature end (frequently at room temperature) will be greater than the cryogenic bulb pressure due to the thermomolecular pressure difference. The magnitude of this pressure difference in a uniform diameter tube depends on the temperatures of the ends of the tube, on the tube diameter, on the pressure of the gas, and also on the accommodation coefficient of the surface which is a function of both the material and its surface state. Unfortunately, a straightforward and elementary discussion of these effects does not exist. Weber and Schmidt (1936) give an expression for the thermomolecular pressure difference which represents data for pyrex tubes. These calculations have been extended and generalized by McConville (1972) to represent data for both pyrex and stainless-steel tubes ; thermomolecular effects are reported to be 10 % to 15 % greater for stainless-steel than for pyrex, but note the effect of contact time mentioned below. McConville's differential equation can be simplified (to give the Weber-Schmidt relation) using a reasonable long mean free path approximation, and then can be integrated directly. The resulting equation is as complex and awkward to use as is that of Weber and Schmidt. However, the results can be approximated [Swenson (1989)] to within a few percent for pyrex by the relation

$$(p_H - p_L)/p_L = (2.10^{-9}) (Rp_L/m \cdot Pa)^{-1.99} [(T_H/K)^{2.27} - (T_L/K)^{2.27}] \quad (4.3)$$

where p_H , p_L , T_H and T_L refer to the pressures and temperatures at the high and low temperature extremities respectively of a tube of radius R .

Values calculated from equation (4.3) differ from those obtained using McConville's equation by less than 1 percent for $Rp_L \geq 2$ m·Pa, and by 4% for $Rp_L = 1,0$ m·Pa, for $T_H = 293$ K. According to McConville, the calculated pressure differences should be multiplied by roughly 1,1 if the pyrex is replaced by stainless steel. This difference may not be real, however, since there is evidence that the thermomolecular effect for these two surfaces become identical when the gas has remained in contact with the surface for an extended period of time, as is the case for a gas thermometry experiment for example. Equation (4.3), which refers to

pyrex, perhaps should be used for estimating the magnitude of these effects, but the design should be such that they need not be relied upon to better than about 10%.

Typical values for the thermomolecular pressure differences in a gas thermometer that meets the requirement of the ITS-90 are given in Tables 5.3 and 5.4 and are discussed in Section 5.5.2.

In the case of ^3He or ^4He vapour-pressure measurements, for a tube of constant diameter most (more than 90%) of the pressure difference occurs between 70 K and 300 K ; the magnitude of the effect can therefore be considerably reduced by employing a tube with two or more sections increasing in diameter from cold to hot [Sydoriak *et al.* (1964)]. However, in the extreme case of ^3He vapour-pressure measurements at 0,65 K the correction remains considerable: at this temperature, a uniform diameter of 5 mm would still necessitate a correction of about 1 mK.

TABLES, FIGURES AND REFERENCES

TABLE 4.1

Pressure and pressure sensitivity of some hydrogen and helium vapour pressure points that are used as defining fixed points or secondary reference points.

Substance	Temperature T_{90}/K	Pressure p/Pa	Sensitivity		
			$(dp/dT_{90})/\text{Pa K}^{-1}$	$(d\ln p/dT_{90})/\text{K}^{-1}$	
H_2	17,035	33 321,3	13 320	0,400	
	20,27	101 292	30 009	0,296	
^4He	1,25	114,73	757	6,598	
	1,5	471,54	2 289	4,854	
	2,0	3 129	9 200	2,939	
	2,176 8	5 041,8	12 408	2,461	
	2,5	10 227,8	20 062	1,962	
	3,0	24 046,4	36 018	1,498	
	3,5	47 045,4	56 773	1,207	
	4,0	81 616,2	82 330	1,009	
	4,222 1	101 325	95 329	0,941	
	4,5	130 260	113 235	0,869	
	5,0	196 016	151 189	0,771	
	^3He	0,65	115,91	1 081	9,325
		1,0	1 160,11	5 501	4,741
1,5		6 709,28	17 797	2,653	
2,0		19 999,2	36 348	1,817	
2,5		44 018,4	60 715	1,379	
3,0		81 825,7	91 831	1,122	
3,196 8		101 321	106 571	1,052	
3,2		101 662	106 826	1,051	

Figure 4.1 Examples of uncertainties in pressure measurements using a capacitance diaphragm pressure gauge below 1,3 kPa, and the equivalent uncertainties δT_3 and δT_4 in temperatures T_3 and T_4 for ^3He and ^4He vapour pressure measurements, respectively [Rusby and Swenson (1980)]. Section 4.2, 4.4.

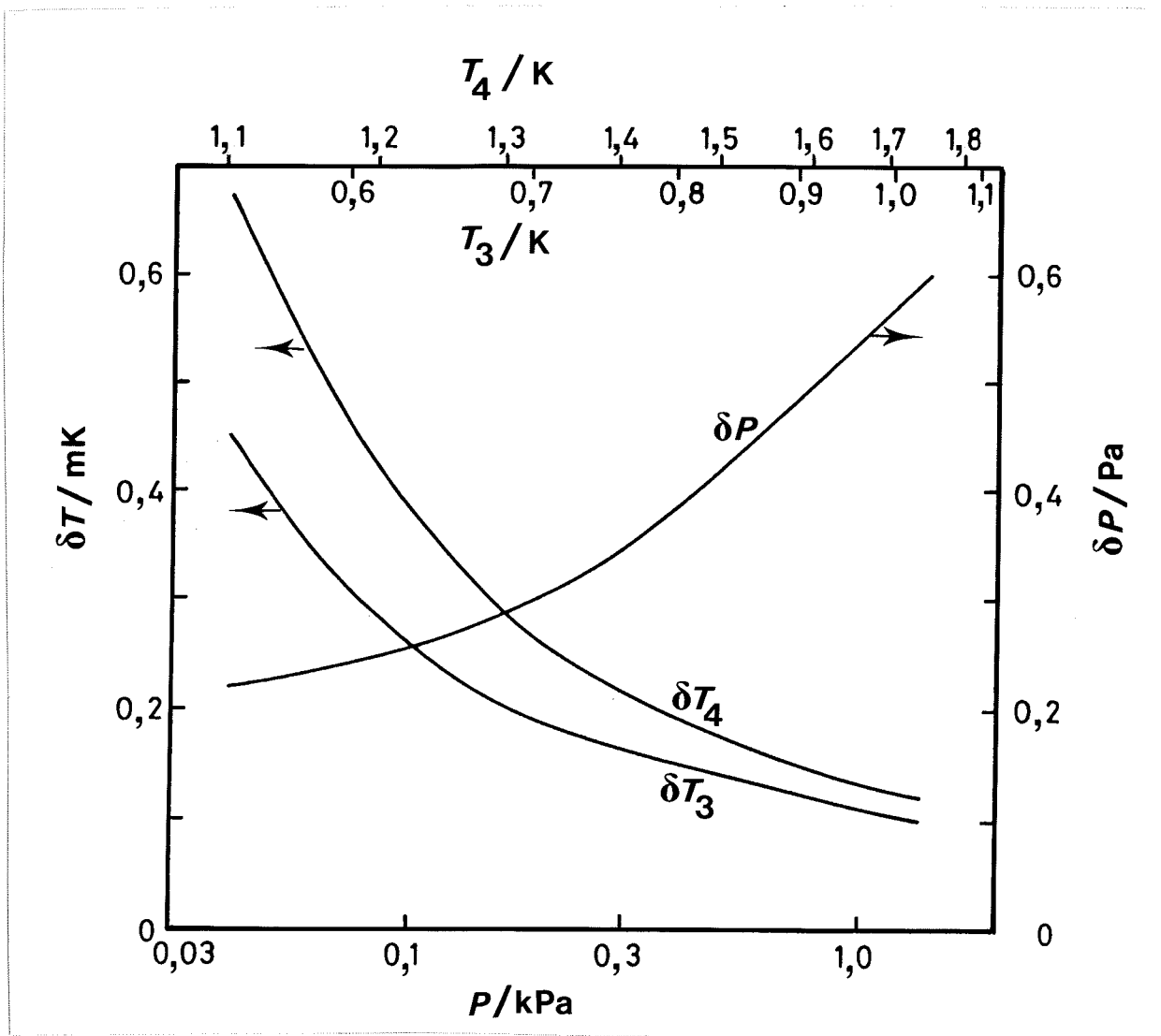


Figure 4.2 Schematic illustrations of systems for realizing ^4He vapour pressures: using a bath of liquid (a), suitable only for $^4\text{He II}$; and a bulb (b), for $^4\text{He I}$, unsuitable for $^4\text{He II}$. Thermal shields around the helium bath are not shown. Section 4.3.1.

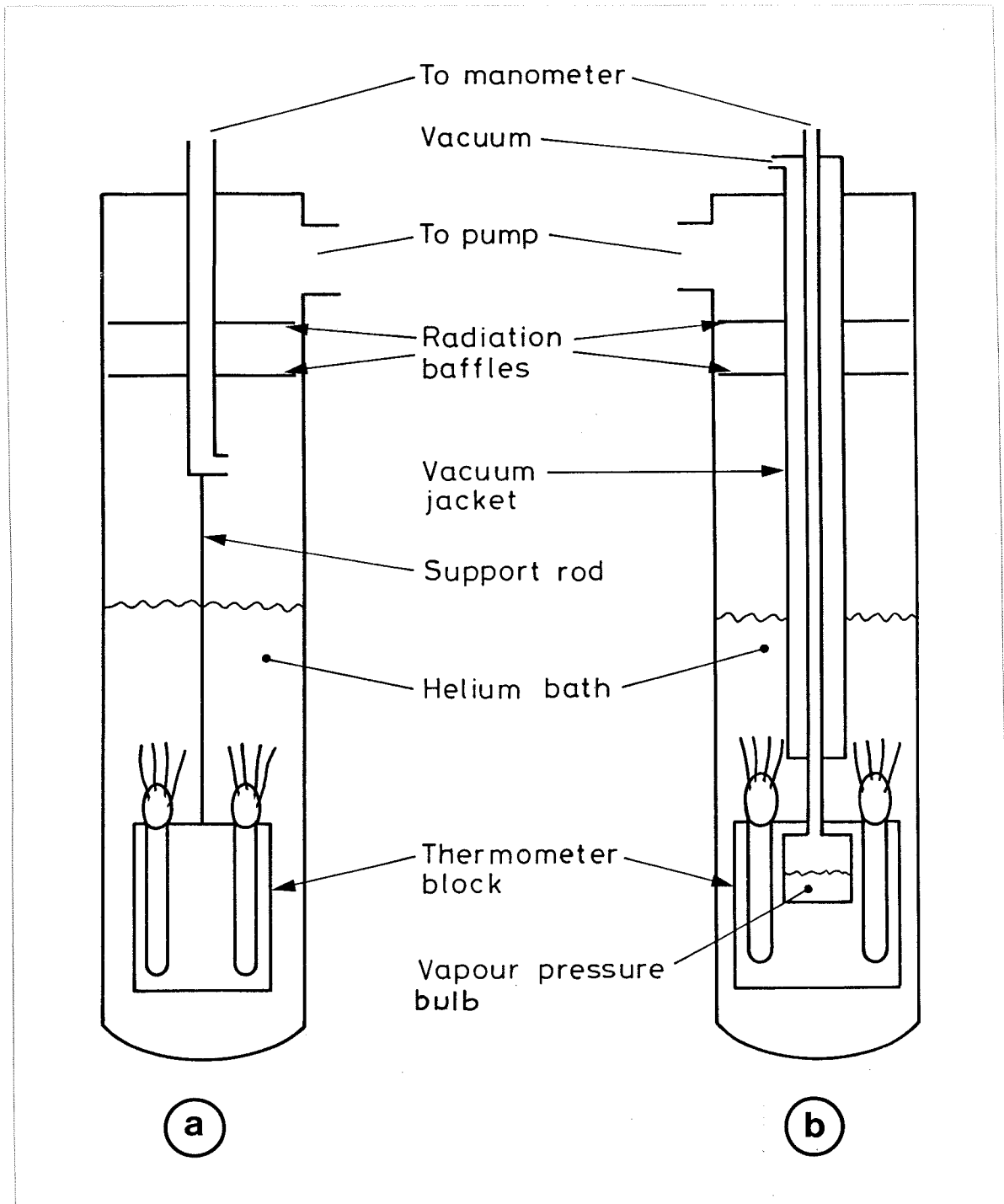
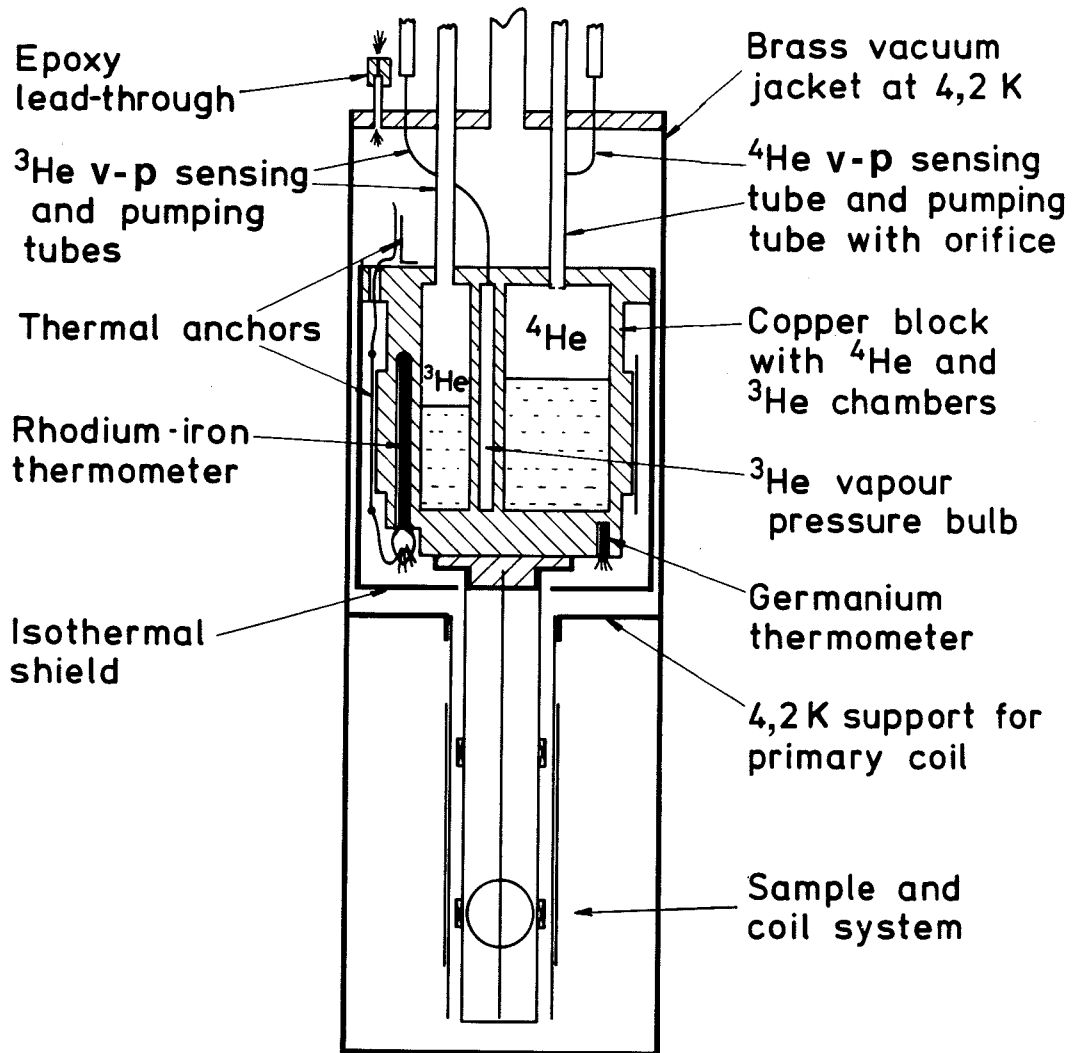


Figure 4.3 A schematic diagram of the cryostat used by Rusby and Swenson (1980) for CMN magnetic thermometry and for ^3He and ^4He I and ^4He II vapour-pressure measurements. Section 4.3.3.



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