6. Vapour Pressure Thermometry*

Vapour pressure thermometers are based on the saturated vapour pressure in a two-phase system in an enclosure. A boiling point is an example of a point on a vapour pressure curve; i.e. the techniques of vapour pressure thermometry described herein apply also to the special case of a boiling or a triple point determination. The behavior of a liquid-vapour system in equilibrium, for example, is describable by an equation P = f(T) (curve tC of Fig. 6.1). Along the curve for a pure substance, the pressure depends on the temperature and not on the quantity of substance enclosed or vaporized. The temperature range associated with vaporization is limited to temperatures between the critical point and the triple point of the substance. The range is even further reduced if the extreme pressures to be measured are outside the usable range of the pressure sensor.

For a given substance, the sensitivity of the thermometer increases approximately inversely with the temperature since u_v varies roughly as 1/P (curve tC in Fig. 6.1). According to the Clausius-Clapeyron equation, we have

$$\frac{dP}{dT} = \frac{L}{T(u_v - u_L)}$$

where L is the molar heat of vaporization which is temperature dependent, and u_v and u_L are the molar volumes of the saturated vapour and liquid respectively. Experimental tables giving P = f(T) have existed for a long time for commonly-used fluids and interpolation formulae have been internationally agreed upon for many of them [Bedford et al. (1984)]. It is therefore easy to obtain temperature from measurement of pressure.

The sublimation curve can be similarly used, but the range of measurable temperatures is then much smaller, limited on the high side by the triple point temperature and on the low side by the pressure becoming too low to be measured accurately enough. Here, the discussion emphasizes thermometers based on liquid-to-vapour

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* This chapter is written in more detail and contains rather more of the fundamentals of the theory than other chapters because no self-contained account of vapour pressure thermometry appears elsewhere, vapour pressure thermometry is one of the best means of approximating the ITS-90, and the techniques are moderately commonly used industrially.

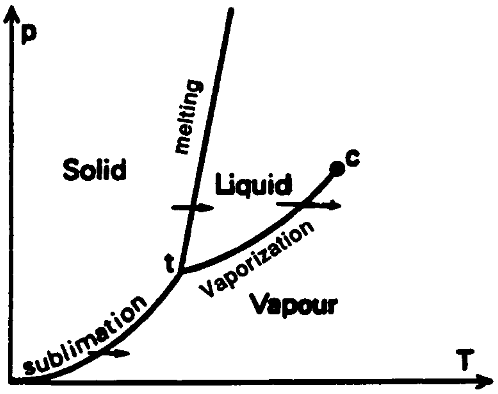

Fig. 6.1: Schematic phase diagram for a pure substance (t is the triple point and C the critical point.

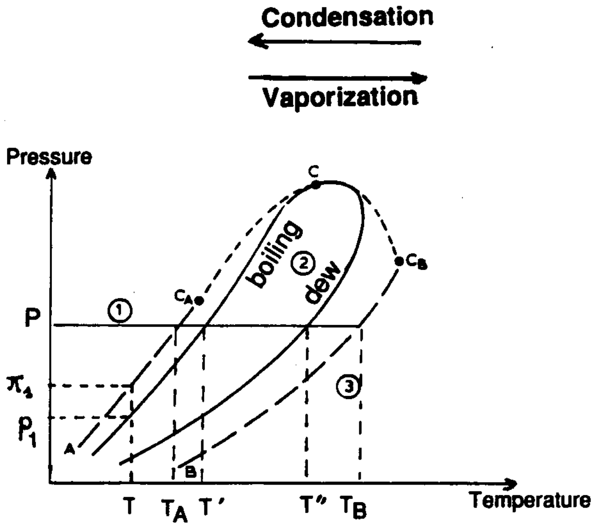

Fig. 6.2: Vaporization curve for a mixture of two pure substances: AC_A, saturated vapour pressure curve of pure substance A; BC_B, saturated vapour pressure curve of pure substance B; GC, critical point of the mixture; C_AC_B, locus of the critical points of the mixture as a function of overall composition.

transitions, but it could be applied also to those based on solid-to-vapour transitions (sublimation) with suitable changes.

6.1 Two-Phase Equilibrium

The number of parameters that can be arbitrarily imposed on a system is given by Gibb's phase rule:

$$v = c + 2 - \Phi$$

where c is the number of constituents of the system, Φ is the number of phases, and v is the number of degrees of freedom (or variance). For a pure substance with two phases ($c = 1$, $\Phi = 2$), $v = 1$. The data for the pressure therefore fix the value of the temperature at the intersection in Fig. 6.1 of a line T = constant with the curve tC; this is the measurement principle of the thermometers described here. In fact, the points of this curve are a series of equilibrium states that are distinguished by the distribution between the two phases of the total number of moles of the substance enclosed.

The equilibrium is regulated by the Gibbs-Duhem relationship, which holds in the simple case described here, by the simultaneous realization of three conditions:

$$P_L = P_v \qquad T_L = T_v \text{ and } \qquad \mu_L(T_L,P_L) = \mu_v(T_v,P_v) \quad ,$$

where the indices L and v refer to the liquid and vapour phases respectively; P and T are the pressure and temperature at the separation surface; and μ, the chemical potential, is identical for a pure substance to the free molar enthalpy. Any variation of one of the three quantities causes displacement of the equilibrium.

If the substance is not pure but contains soluble impurities, the variance of the system, becomes equal to the number of constituents present. Suppose that: each constituent is present at the same time in both liquid and vapour phases; the vapour phase is a mixture of perfect vapours; the surface-tension is negligible; the liquid phase is an ideal solution, that is to say, the substances mix without change of volume or enthalpy. This last assumption is realistic so long as the molar fractions x_i ($i = 2$ to n) of the ($n - 1$) impurities present (solutes) are very small with respect to that ($x_1 \sim 1$) of the pure substance (solvent) filling the thermometer. (Note that the respective concentrations denoted x_i^L and x_i^v ($i = 1$ to n) are generally not equal, as will be seen later.) Under these conditions, the deviation from an ideal solution is less than 1 % so long as the molar fractions of solutes are less than 10^{-3}.

The equilibrium of such a system must always satisfy the Gibbs-Duhem relation; that is, each constituent must have the same chemical potential in the two phases: $\mu_i v = \mu_i^L$ for i = 1 to n. The chemical potential is a function of pressure, temperature, and molar fractions of constituents.

The influence of the impurities present is as follows:

a) At temperature T, the pressure P above the liquid is different from the saturated vapour pressure Π_1 of the pure substance since it is equal to the sum of the partial pressures p_i of the various constituents (Dalton's Law): i.e.

$$P = \sum_{i=1}^{n} p_i = \sum_{i=1}^{n} x_i^v \cdot P$$

This can be used to determine the calibration errors of the apparatus.

b) At temperature T, the saturated vapour pressure Π_i of a pure substance is higher than the partial pressure p_i of this substance in the mixture:

$$p_i = x_i^L \, \Pi_i \qquad \text{(Raoult's Law)} .$$

For the solvent, for which $x_i^L \sim 1$, we can write:

$$p_1 = x_1{}^L \Pi_1 = \left(1 - \sum_{i=2}^{n} x_i{}^L\right) \Pi_1$$

For a weak concentration of solute ($x_i^L \to 0$) it is necessary to replace the above expression by

$$p_i = x_i^L \, k_i \qquad \text{(Henry's Law)} \quad ,$$

where k_i ($\neq \Pi_i$) is a constant that depends on the temperature and the nature of the constituents present.

As a result of the above, the quantity of every dissolved impurity is proportional to its own partial pressure. We can write

$$P = \Pi_1 - \sum_{i=2}^{n} x_i^L \left[\Pi_1 - k_i\right] \qquad ,$$

where the total pressure is a linear function of the concentrations of impurities in the liquid. The second term will be greater than or less than zero according as the impurities are more or less volatile than the solvent. The boiling temperature of a solution with a given concentration is not that of the pure substance at the same pressure.

In Fig. 6.2 showing a mixture of two components, the vaporization curve of pure substance A is AC_A and that of pure substance B is BC_B. The critical point of the mixture is somewhere on the dashed curve C_AC_B, depending upon the concentrations of the two components. If it is at C, the vaporization of the mixture takes place on the solid curve. Referring to Fig. 6.2, at the temperature T the pure substance boils at pressure Π_1. The solution boils at the partial pressure p_1, less than Π_1, since

$$\frac{\Pi_1 - p_1}{\Pi_1} = \sum_{i=2}^{2} x_i^L$$

Suppose the total pressure above the solution is P. At this pressure A would boil at T_A and B at T_B. If the solvent A is more volatile than the solute B, the solution begins to boil at $T' > T_A$. In the opposite case (solvent B less volatile than solute A), the closest the boiling temperature of the solution comes to T_B is T", obtained at the end of vaporization or the beginning of condensation (dew point).

c) The concentration of impurities is different in the two phases and changes during the course of vaporization. We can write:

$$x_i^v = \frac{p_i}{P} = \frac{x_i^L \Pi_i}{P}$$

(Π_i being replaced by k_i if $x_i \to 0$) ,

so that $$\frac{x_i^v}{x_1^v} = \frac{x_i^L}{x_1^L} \cdot \frac{\Pi_i}{\Pi_1} \qquad \text{for all } i = 2 \text{ to } n . \qquad (6.1)$$

Suppose again there are two constituents. If 1 is more volatile than 2, i.e. if

$$\Pi_1 > \Pi_2 \text{ , then } \frac{x_2^{\,v}}{x_1^{\,v}} < \frac{x_2^{\,L}}{x_2^{\,L}} \text{ , so that } x_1^{\,v} > x_1^{\,L} \text{ , and } x_2^{\,v} < x_2^{\,L} \text{ .}$$

Thus the vapour is always richer than the liquid in the more volatile constituent. A useful method to detect impurities is to compare the boiling temperatures for two different fillings of the bulb. If the total quantity of impurities is constant, the pressure for a given temperature will depend upon the level of liquid. The result deduced immediately following Eq. (6.1) may also be used for purifying a substance by withdrawing vapour during boiling. Conversely, if the impurity (constituent 1) is less volatile than the solvent (constituent 2), this procedure will increase the concentration of impurities in the solution.

For a given pressure P, we can trace figuratively the evolution of the system in Fig. 6.3a. For simplicity, suppose once more there is only one type of impurity ($x_2 = 1 - x_1$) . Two cases occur depending upon whether constituent 2 is more or less volatile than constituent 1. Let T_1 and T_2 be the boiling temperatures of pure substances 1 and 2 at pressure P. Suppose first $T_1 > T_2$ (i.e. impurity more volatile than solvent). If we cool a sample of vapour with concentration $x_2^v = x$, a drop of liquid will appear at temperature $T_A < T_1$ when the dew point is reached. The impurity concentration in this drop of liquid is $x_2^L = x' < x$, corresponding to point B. The temperature T_A obtained is the closest to T_1 that can be reached starting from the vapour concentration x_2^v. As the temperature continues to decrease, the condensation continues along the curve B → C until all the gas is liquified at point C with temperature $T_C < T_A$, and with a concentration $x_2^L = x$.

Conversely, with increasing temperature, the point C is attained first; the temperature the closest to T_1 is obtained at the end of the vaporization.

An analogous reasoning in the case of an impurity less volatile than the solvent shows that the temperature closest to T 1 will be obtained at the beginning of the vaporization (Fig. 6.3b).

If there are many types of impurities, some more volatile and others less volatile than the solvent, the reasoning becomes more complicated, and an experimental study is more profitable.

The above examples concern ideal solutions that can exist only if the constituents present have very similar properties. This approximation is made for a mixture of isotopes or for sufficiently dilute impurities. It becomes complicated for insoluble impurities that are present only in the vapour phase or for substances that have several stoichiometric forms with change of abundance ratios during vaporization. Moreover,

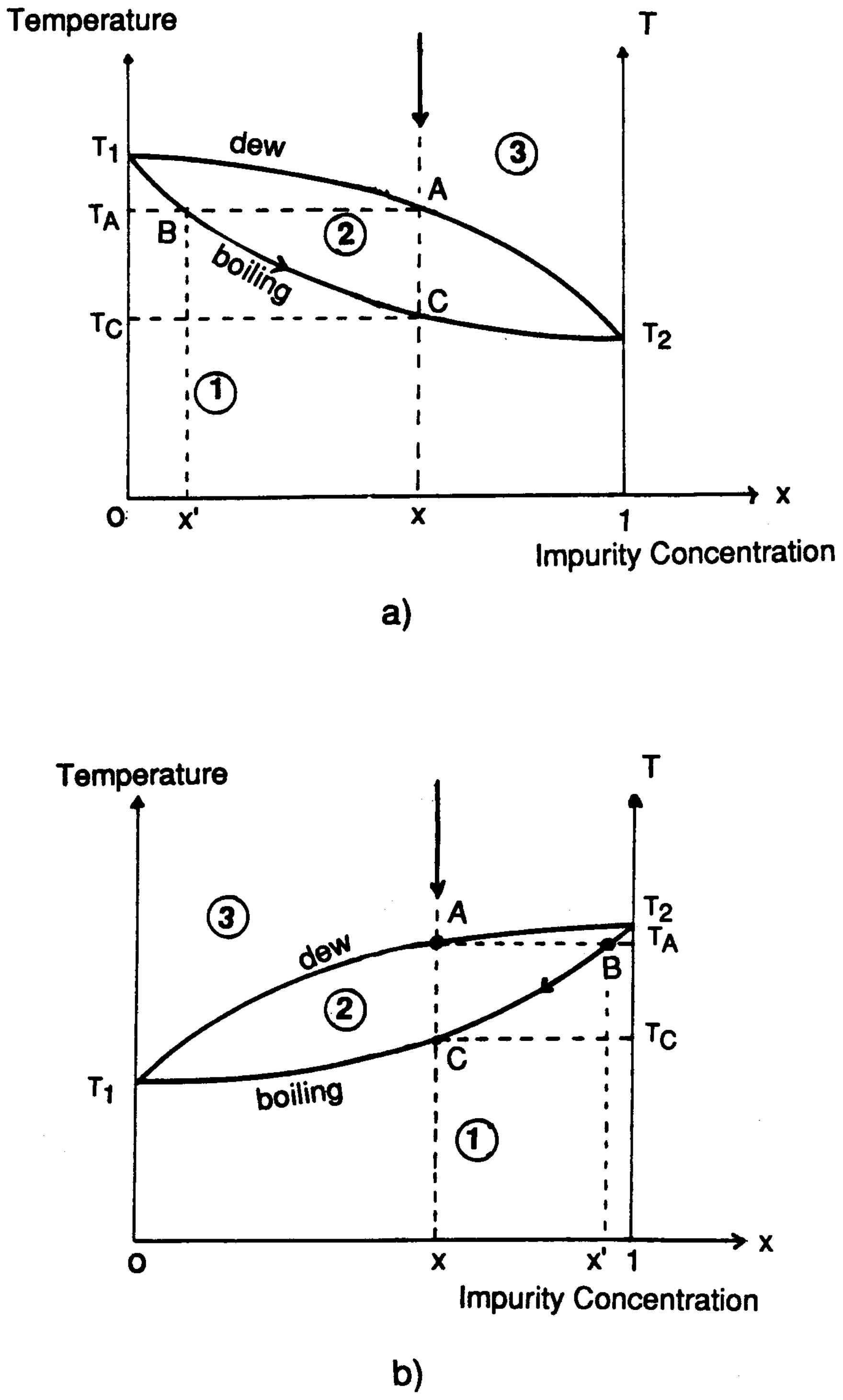

Fig. 6.3: Diagram at constant pressure of a two-phase mixture (1, liquid; 2, liquid-vapour; 3, vapour): (a) $T_1 > T_2$, impurity more volatile than solvent; (b) $T_2 > T_1$, impurity less volatile than solvent.

impurities with densities different from that of the pure substance can create concentration gradients in the liquid phase; the preceding reasoning is then valid only near the surface of separation.

This shows the necessity of selecting an easily purifiable substance for use as a vapour pressure thermometer.

6.2 Technical Details of Construction

A vapour pressure thermometer essentially consists of: a bulb containing the pure measuring substance in thermal equilibrium with the sample whose temperature is to be measured; a pressure sensor; a connecting tube long enough to connect the bulb to the pressure sensor; and a valve for filling (Fig. 6.4).

6.2.1 Bulb

The bulb can be very small depending upon the quantity of substance necessary to cover the required temperature range. It is necessary to ensure that at no time during temperature cycling the substance reassembles into a single phase. The maximum pressure that will occur determines the thickness of the walls of the bulb. The bulb is formed from a material that is a good heat conductor, is chemically neutral, and neither absorbs nor desorbs gases. It is thermally anchored into a copper block which also contains the sample whose temperature is to be measured. If the thermometer is intended to measure the temperature of a large body, the bulb is most often an elongated cylinder (for an industrial thermometer, typically 120 mm long by 15 mm diameter, giving a volume ~ 20 cm^3), but its shape can vary as required. For example, if it is intended to calibrate resistance thermometers, those sensors are located within the walls of the bulb.

The quantity of filling substance is determined by the necessity to ensure that the surface between the two phases be in the bulb and not in the connecting tube. Moreover, as we have seen, the temperature changes during boiling according to the nature of the impurities. Referring to Figs. 6.3a and 6.3b, we note that the bulb should contain relatively little substance if the impurities are more volatile than the solvent, and should be almost completely filled with liquid if the impurities are less volatile than the solvent.

The bulb's form is dictated by the necessity to take account of eventual concentration gradients caused by impurities in the liquid phase. If the enclosed substance is a poor conductor of heat in the condensed phase, e.g. non-superfluid helium, the interior of the bulb is so structured that no large thickness of the substance can become the centre of a temperature gradient. An example of a device used for calibration of germanium resistance thermometers is shown in Fig. 6.5 [after Moser and Bonnier (1972)].

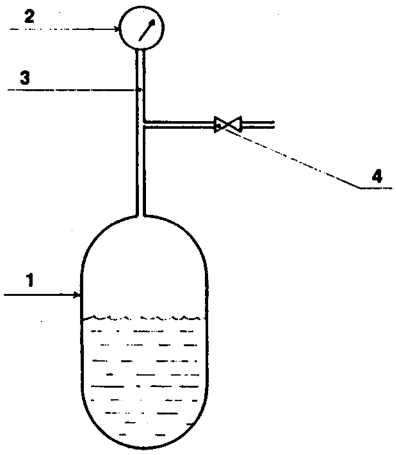

Fig. 6.4: Schematic construction of a saturated vapour pressure thermometer: 1, bulb containing two phases of a substance; 2, pressure sensor; 3, connecting tube; 4, filling system.

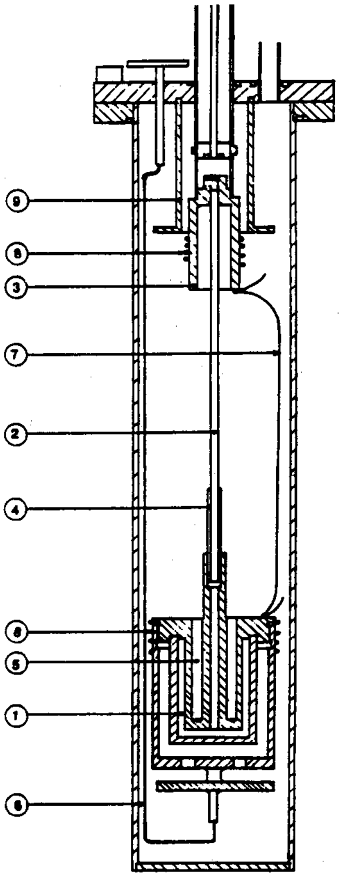

Fig. 6.5: Bulb of a helium vapour pressure thermometer [Moser and Bonnier (1972)]: 1, ^{4}He; 2, connecting tube; 3, radiation trap; 4, jacket; 5, thermometer well; 6, thermal leak; 7, differential thermocouple; 8, resistance heating; 9, conduction cooling.

6.2.2 Connecting Tube

Because the pressure sensor is usually at room temperature, the connecting tube must bea poor heat conductor; long enough to limit the contribution of heat due to the temperature gradient; equipped with a radiation trap to avoid direct radiation heating of the separation surface between the two phases; small enough that its volume is small compared to the volume of vapour in the bulb to prevent a large change in the liquid/vapour ratio; of cross section sufficient to limit thermomolecular effects and to avoid blocking. It is necessary to avoid creating a cold spot in the connecting tube where the enclosed substance can condense to form a drop of liquid that blocks the tube (although with helium such a cold spot does not form (it is self-quenching) [Ambler and Hudson (1956)] (see also Sec. 6.3.7)). Then the pressure measured would correspond to the temperature of the cold spot. This latter difficulty can be avoided by placing the connecting tube inside an evacuated tube (Fig. 6.6) and/or imposing a small heat flow along the connecting tube. The temperature gradient so created must be controlled (Fig. 6.5) and accounted for as a correction to the measurement results. For example, for a stainless steel connecting tube of 1 m length, internal diameter 2 mm, and external diameter 2.5 mm between 300 K and the helium temperature, the heat flux is about 6 mW (0.8 mW with glass), a heat leak which could produce a temperature difference of 3 mK between the bulb and the liquid helium.

The inner diameters used are generally 0.5 to 3 mm unless thermomolecular effects are likely to arise.

6.2.3 Pressure Sensor

The sensor is chosen according to the temperature range and the precision required. For an industrial thermometer it is most often a Bourdon gauge, or a mercury or oil (or any substance having small vapour pressure) manometer, used with a cathetometer. For high precision measurements, one can also use a Bourdon quartz spiral gauge periodically calibrated against a pressure balance. A diaphragm pressure transducer is also used, giving a signal that can be amplified and handled by a computer. It can be placed very close to the evaporation surface, which reduces many problems related to the connecting tube (Fig. 6.7), but then there are problems in calibrating it.

Whatever pressure sensor is chosen, its internal volume must be small (see Appendix D) and the metrological characteristics of the thermometer will be determined by the manometer. If the substance used in the thermometer is corrosive, the pressure can be transmitted across a membrane or incompressible liquid.

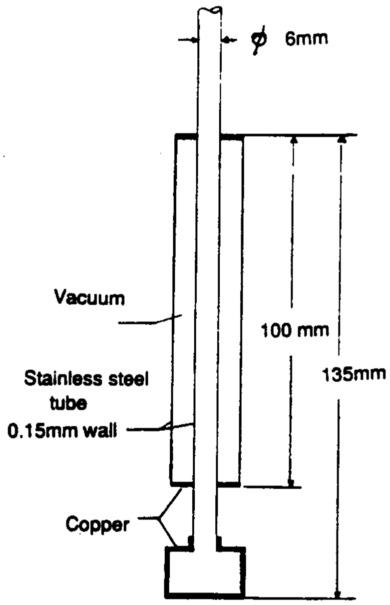

Fig. 6.6: Use of an evacuated jacket to avoid a cold spot in a helium vapour pressure thermometer [Cataland et al (1962)].

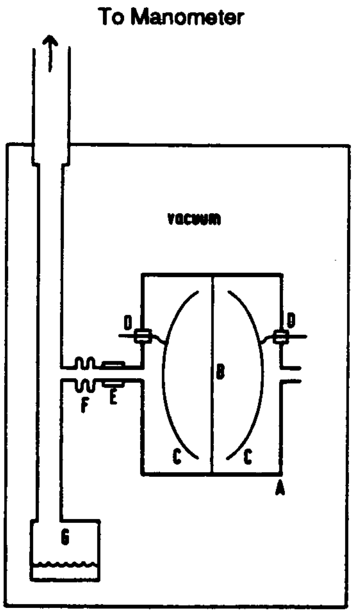

Fig. 6.7: Illustration of the use of a capacitive sensor with a vapour pressure thermometer [Gonano and Adams (1970)]: A, sensor sheet; B, diaphragm; C, capacitor plates; D, insulating feedthrough; E, insulating ceramic tube; F, bellows; G, bulb.

6.2.4 Filling the Thermometer

Before filling the bulb it is important to analyze the filling substance for the nature and quantity of impurities, to clean the enclosure with suitable chemicals or solvents, to bake it above 100 °C if possible, and to flush the enclosure several times with the filling substance to avoid contamination. When filling the thermometer, one must be certain that the volumes of the bulb, connecting tube, and manometer are compatible with the temperatures to be measured. To obtain the required quantity, it is necessary to include an extra reservoir (see Fig. 6.8); for example, one litre of liquid helium at normal pressure occupies 746 litres when it is transformed into the vapour phase at room temperature under normal pressure. The necessary details to determine the quantity of the substance at the pressure and temperature of filling are given in Appendix D.

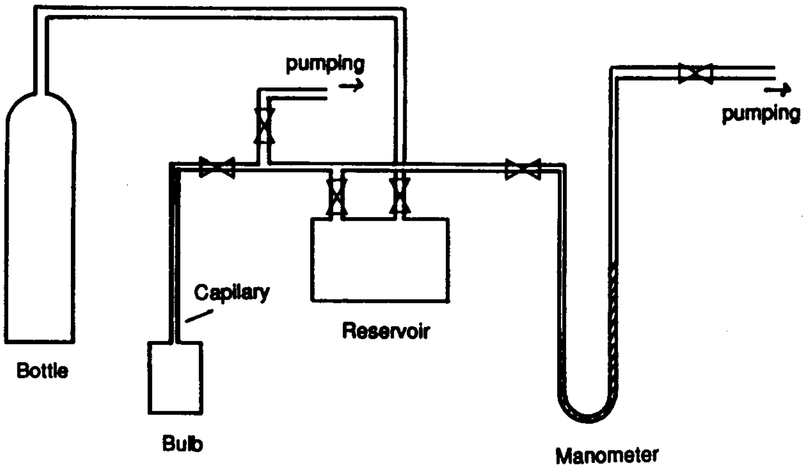

Fig. 6.8: Schematic drawing of an installation for filling a vapour pressure thermometer.

The filling proceeds as follows: after flushing and evacuating of the installation, the ensemble is filled under pressure P; on closing the inlet valve for the filling gas, the desired quantity is condensed into the bulb at temperature T_f and the pressure evolution followed until it reaches P_f. This can take a very long time because of the low thermal conductivities of the gas in the connecting tube and of the connecting tube itself [Van Mal (1969)]. The time is proportional to the length and diameter of the tube (30 min for a diameter of 5 mm and length of 50 cm for helium between 300 K and 4 K).

Following this, the connecting tube, bulb, and manometer are isolated from the remainder of the installation (see Fig. 6.8).

6.3 Metrological Characteristics and Measurement Corrections

6.3.1. Extent of Sensitivity and Measurement

Many substances could be used as a vapour pressure thermometer. The only constraint is to obtain a sufficient purity. The response curves P = f(T) of some substances are shown in Fig. 6.9. For each substance the temperature range is restricted. In the cryogenic domain, there are three temperature zones that are not covered: below 0.5 K (all pure substances have too low a vapour pressure), between 5.22 K and 13.81 K, and between 44.4 K and 63.15 K. These zones could be partially covered by sublimation vapour pressure thermometers. (Sublimation for nitrogen is possible between 56 K and 63.146 K [Bedford et al. (1984)] and for hydrogen between 10 K and 13.81 K). The response curve is usually an empirical relation of the form

$$\ln\frac{p}{p_0} = A - \frac{B}{T} + CT + \ldots \qquad \text{(with } p_0 = 101325 \text{ Pa)}$$

For ^{3}He and ^{4}He, vapour pressure equations were derived for the EPT -76 by Durieux et al. (1982) and Durieux and Rusby (1983). Inverted forms (T = f(P)) were subsequently produced by Rusby and Durieux (1984), and these are now included in the ITS -90. For other substances (H_2, Ne, N_2, Ar, O_2, S) the coefficients are given by Bedford et al. (1984).

The sensitivity of vapour pressure thermometers can be high, especially the higher the pressure, and this is one of their advantages.

6.3.2 Reproducibility and Accuracy

The reproducibility of a vapour pressure thermometer is essentially determined by the pressure sensor. The actual magnitude of the imprecision is dependent upon the particular manometer; as typical examples, for a mercury manometer between 233 000 Pa and 6 600 Pa, the imprecision can be ≤ 1.3 Pa; for an oil manometer with p < 6 600 Pa, the imprecision is 0.09 to 0.18 Pa.

The excellent intrinsic reproducibility (10^{-3} to 10^{-4} K for helium, 10^{-2} to 10^{-3} K for other cryogenic fluids) has led to vapour pressure thermometers being used to define some thermometric scales. In particular, ^{3}He and ^{4}He gave birth to T_{62} and T_{58} respectively [Sydoriak and Sherman (1964) and Brickwedde et al. (1960)]. Later, with

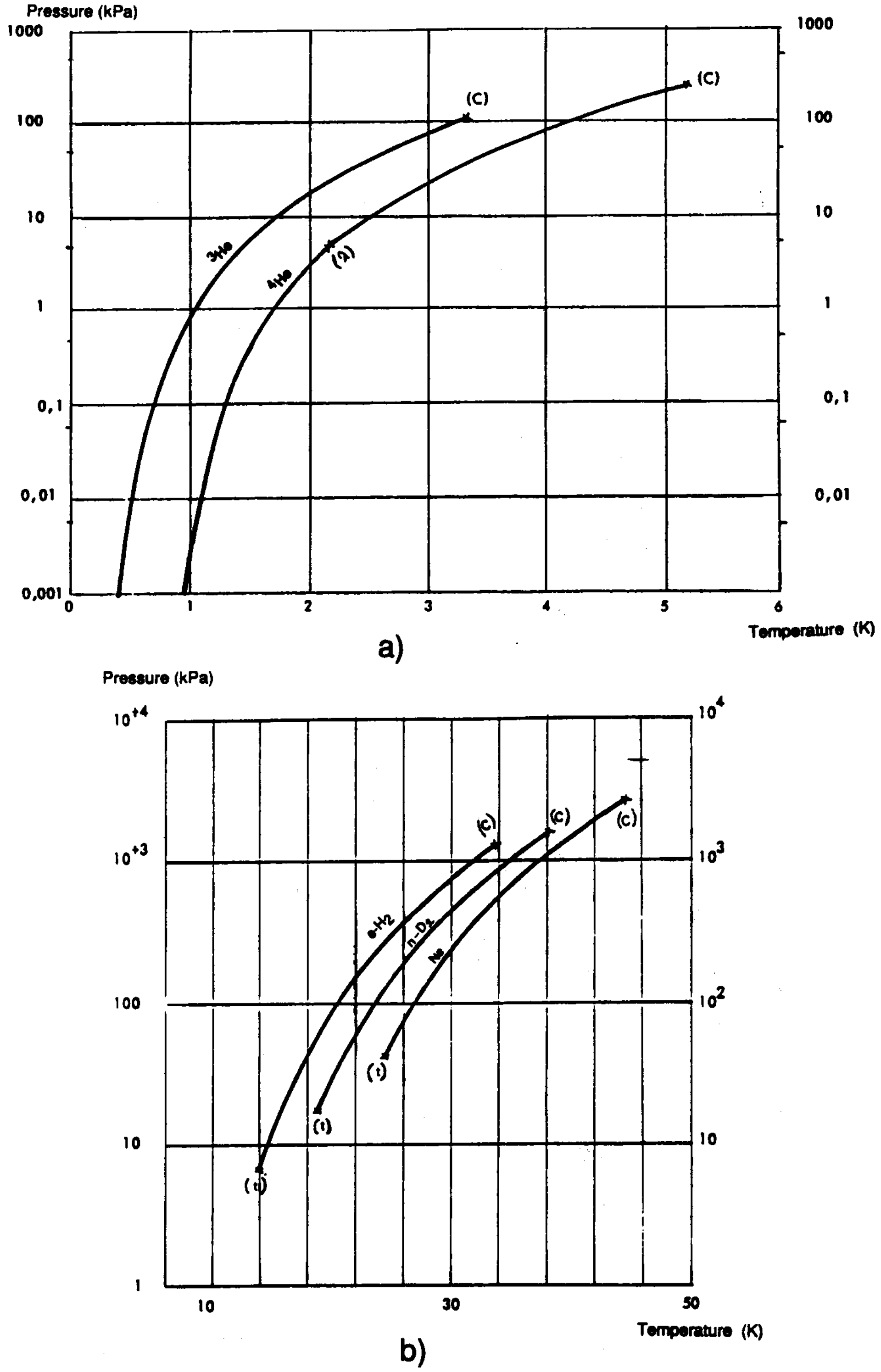

Fig. 6.9: Equilibrium vapour pressure curves for some substances used in saturated vapour pressure thermometers. The crosses on each curve are the triple point (lower) and the critical point (higher). (a) ^{3}He, ^{4}He; (b) normal H_2 and D_2 and Ne;

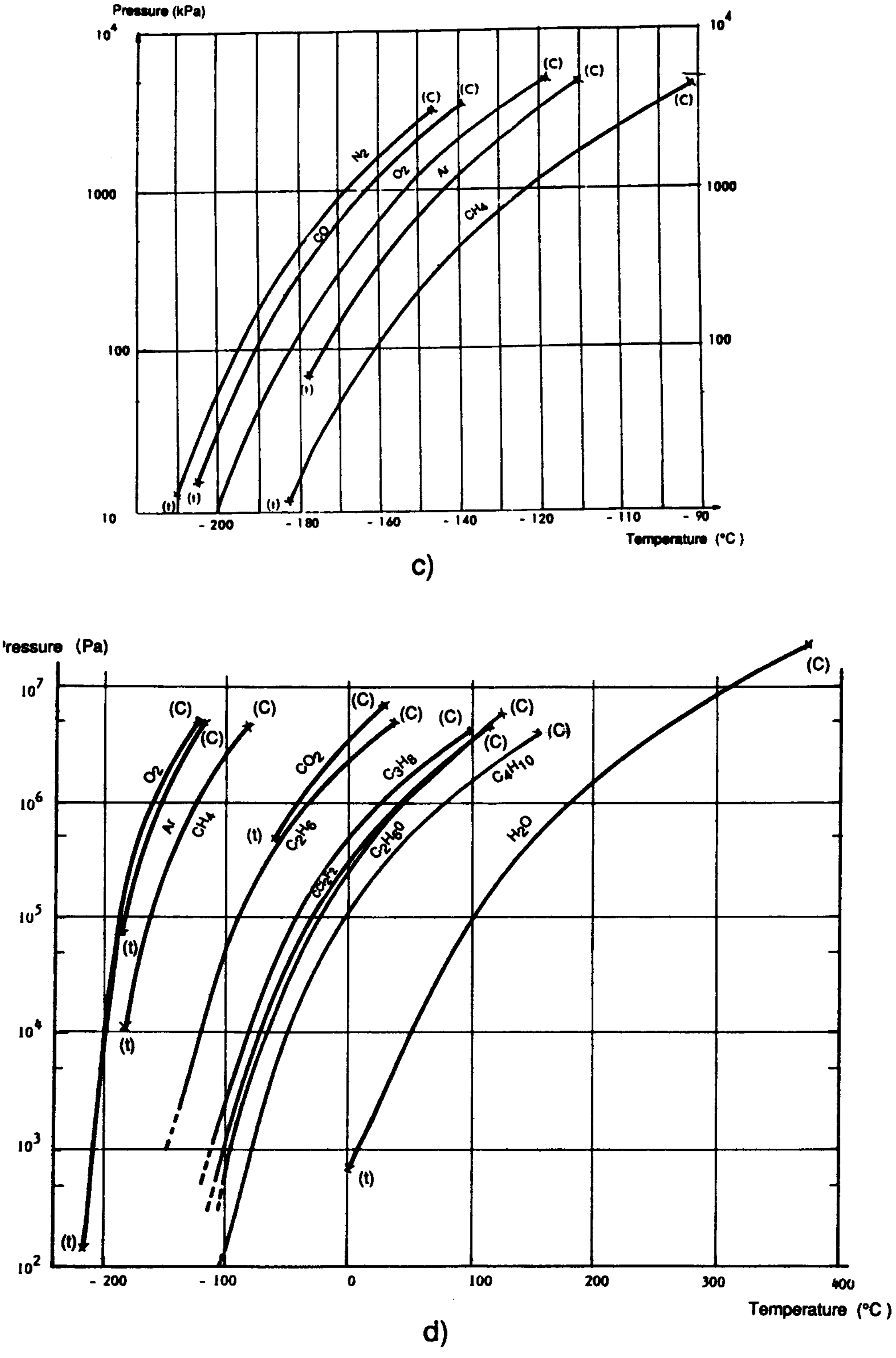

Fig. 6.9: (c) N_2, CO, Ar, O_2, CH_4; (d) Ar, O_2, CH_4, CO_2, C_2H_6, C_3H_8, CCl_2F_2, C_2H_6O, C4H10, H_2O.

some corrections, these scales served to extend the IPTS-68 to lower temperatures and to form part of the EPT-76 [Durieux et al. (1982)], and are now incorporated as part of the definition of the ITS-90.

Although the vapour pressure thermometer is an excellent secondary thermometer, it can only measure thermodynamic temperatures with many corrections and uncertainties and by using empirical values for the parameters.

6.3.3 Response Time

The time constant of a vapour pressure thermometer is essentially a function of that of the pressure sensor, of the thermal contact between the bulb and the object whose temperature is to be measured, and of the thermal diffusivity of the liquid. Certain particular configurations can make the time response very long.

6.3.4 Correction for Aerostatic Pressure

When the connecting tube is long, it is necessary to correct for the weight of the enclosed vertical vapour column. The correction requires a knowledge of the distribution of the temperatures because of the density variation in the connecting tube; it therefore depends upon the design and can be rather inaccurate (see Appendix E). The correction depends essentially on the part of the connecting tube which is close to the bulb.

For oxygen at the boiling point (~ 90 K) the pressure correction in a vacuum-jacketed sensing tube about 50 cm long is about 1 Pa, equivalent to a temperature correction of 1.3 mK. The uncertainty of the correction due to the inability to measure or predict the true temperature of the gas is at least 0.2 mK [Compton and Ward (1976), Kemp et al. (1976), Ancsin (1973a)]. For a 1 metre connecting tube containing helium joining room temperature to bulb temperature, Moser and Bonnier (1972) calculated corrections of 0.1 mK and 0.03 mK for bulb temperatures of 4.2 K and 2 K, respectively. The aerostatic correction may be determined with a 1 % uncertainty using an auxiliary tube [Klein et al. (1979)], but the procedure is difficult.

If possible, it is preferable to use a horizontal tube, or to pass the connecting tube through an isothermal enclosure, thus reducing the effects of a temperature gradient.

6.3.5 Thermomolecular Effect

There exists in the connecting tube a thermomolecular pressure gradient between the hot (higher pressure) and cold (lower pressure) extremities that is sizeable when the mean free path of the molecules is not much smaller than the tube diameter, e.g. for ^{4}He around 1 K. When the effect is not measured, one usually corrects for this gradient using the Weber-Schmidt equation [Weber et al. (1936)], although also the experimental tables of Roberts and Sydoriak (1956), or the calculation of Bennett and Tompkins (1957) can be used for the two helium isotopes. The Weber-Schmidt equation is

$$\ln\frac{P_1}{P_2}=\frac{1}{2}\ln\frac{T_1}{T_2}+0.18131\ln\frac{y_1+0.1878}{y_2+0.1878}+0.41284\ln\frac{y_1+1.8311}{y_2+1.8311}-0.15823\ln\frac{y_1+4.9930}{y_2+4.9930}$$

where $y=\frac{RP}{X(T/273.1)^{1+n}}$

$X = 1.8087$, $n = 0.147$ for helium,

$X = 1.1470$, $n = 0.195$ for hydrogen.

Index 1 indicates the hot end of the tube, index 2 the cold end; R designates the tube radius in cm, P the pressure in Pa, and T the temperature in K.

The trend of the effect is shown in Fig. 6.10 [Roberts and Sydoriak (1956), Durieux et al. (1982)].

Some temperature values for a vapour pressure thermometer using He or H_2 are shown in Table 6.1

With oxygen, the correction reaches 20 mK near 54 K (when P = 100 Pa), but it is already less than 0.05 mK at 64 K for an Inconel tube 1.6 mm in diameter [Tiggelman (1973)]. For neon near 20 K it is less than 1 mK [Tiggelman (1973)].

In general, these calculations can be 10% to 25% in error [McConville et al. (1966) and McConville (1972)], since the correction depends upon the material used for the tube and the physico-chemical conditions of its inner surface, which may also vary with time. They can be calculated [McConville et al. (1966)] as a function of the reflection coefficient of the tube but, unfortunately, the latter is never well known and may change after long exposure to the gas.

The thermomolecular effect can be measured with an additional tube [Berry (1979)]. Another solution, which eliminates the correction, is to use a diaphragm transducer located in the lower temperature region [Gonano and Adams (1970)] (see Fig. 6.7).

Current practice consists of using pressure tubes of the largest section possible compatible with keeping heat transfer losses reasonably small (and to include some means of blocking radiation (gains, not losses) and damping oscillations). If the calculated correction is to be realistic, it is indispensable to have a constant diameter in the parts of the tube where the temperature is ill-defined.

The two corrections from Secs. 6.3.4 and 6.3.5 are usually small and in many cases the only significant uncertainty is that due to the reading of the pressure.

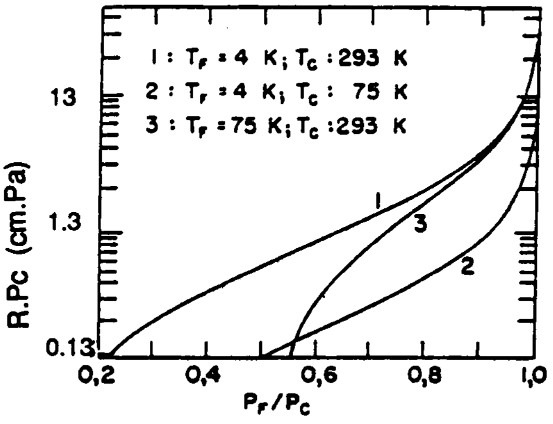

Fig. 6.10: Ratios of thermo molecular pressures for ^{3}He and ^{4}He (R, radius of tube in centimetres; p_F and p_C, pressure in Pa at the cold (T_F) and hot (T_C) extremities of the tube) [Roberts and Sydoriak (1956)].

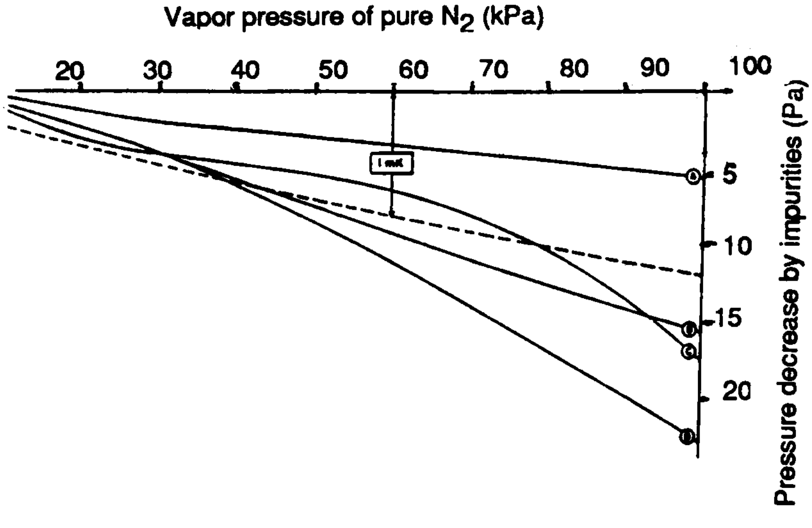

Fig. 6.11: The observed lowering of the vapour pressure of N_2 by nonvolatile impurities, as a function of the vapour pressure of pure N_2. Curve A, N_2:100 ppmv. CO; curve B, N_2:100 ppmv. Ar; curve C, N_2:100 ppmv. Kr; curve D, N_2:100 ppmv. O_2 [Ancsin (1974a)].

Table 6.1: Temperature values (K) at the cold extremity of the connecting tube of a vapour pressure thermometer using helium or hydrogen for various tube diameters, a hot extremity at room temperature, and thermomolecular effects of 10 mK and 1 mK.

Filling gas	Thermomolecular Effect	Tube Diameter (mm) 0.5	1	5	10
^{3}He:	dT = 10 mK	0.76	0.65	0.48	0.42 K
	dT= 1 mK	1.08	0.90	0.64	0.56 K
^{4}He:	dT = 10 mK	1.45	1.30	1.05	0.96 K
	dT= 1 mK	1.83	1.62	1.27	1.16 K
H_2:	dT = 10 mK	below 10 K			
	dT = 1 mK	below 10 K			

Table 6.2: Amounts by which small Concentrations of ^{3}He in liquid ^{4}He affect Vapour Pressure.

Concentration of ^{3}He (%)	Temperature (K)	Pressure Change (kPa)	Equivalent Temperature Change (K)
0.12	1.5	1.6	0.5
0.02	1.5	0.3	0.2
0.12	2.6	5.2	0.2
0.02	2.6	0.6	0.04

6.3.6 Corrections Due to Impurities

a. Helium (^{3}He, ^{4}He)

The only impurity problem with helium is isotopic since all other substances are solid at these temperatures and the solids are not soluble in liquid helium.

The presence of ^{4}He in liquid ^{3}He lowers the vapour pressure below that of pure ^{3}He. The concentration of ^{4}He in the vapour phase is much less important than in the liquid phase. For concentrations of ^{4}He in the liquid phase of < 10%, we can use [Sydoriak and Sherman (1964)] the approximate formula (derived from Raoult's Law)

$$\Pi - P_x = (1 - x)\frac{d(\ln P_x)}{dx}$$

In this expression x is the concentration of ^{3}He (> 90%); Π is the saturated vapour pressure of pure ^{3}He and P_x is the pressure of the mixture at temperature T; the derivative is taken for x = 1 at temperature T. One can obtain correction curves at the calculated temperatures according to this formula [Sydoriak and Sherman (1964)]. For 0.1 % of ^{4}He in the liquid phase, this gives a temperature correction of 0.02 mK at 0.4 K and of 0.71 mK at 3.2 K.

In ^{4}He, the only awkward impurity would be ^{3}He. Commercially supplied ^{4}He contains no ^{3}He, so the only risk of error would be from its accidental introduction from, e.g., poor manipulation of a dilution refrigerator. Not many measurements have been made, but they are confirmed by theoretical calculation. Even a small concentration of ^{3}He in ^{4}He causes a considerable increase in the vapour pressure, as shown in Table 6.2. The numerical values in the table concern the concentration of ^{3}He in the liquid phase of ^{4}He. The concentrations of ^{3}He in the vapour phase are even more important than in the liquid phase.

b. Hydrogen [Ancsin (1977)]

The only volatile impurity, He, seems not to be soluble in liquid hydrogen and is therefore not in contact with the separation surface. Other impurities are condensed and cause no problem except for Ne which can cause errors up to ΔP = 210 Pa (ΔT = 1 mK) at 19 K for a concentration of 410 ppm in volume.

Other errors can occur because the ortho-para conversion of hydrogen is not instantaneous and the proportion of these two states is a function of the temperature. At room temperature, normal hydrogen is 75% ortho and 25% para, while at 20 K equilibrium hydrogen is 0.21 % ortho and 99.79% para with a boiling point 0.12 K lower than that of normal hydrogen. To obtain reproducible results, one must introduce a catalyst into the bulb (hydrous ferric oxide). It should be enclosed in a metallic mesh to avoid its dispersing to the walls during boiling. The quantity of catalyst is not important (e.g. 0.15 g) but it is inefficient if it is not in good contact with the liquid phase.

There are similar problems with deuterium, which is more easily contaminated, and always contains some hydrogen deuteride (HD) even after the most careful preparation. HD will also be formed in measurable quantities (over 1%) from hydrogen atoms that diffuse from the bulk of the container or, more commonly, from exchange with H_2O if a hydrated catalyst is used. Errors of several hundredths of a kelvin may arise near 18.7 K [Pavese and McConville (1987)].

c. Neon [Ancsin (1978), Furukawa (1972), Tiggelman et al. (1972), Tiggelman (1973)]

The volatile impurities, H2 and He, are not soluble in the liquid phase and do not influence the vaporization curve. Their presence in the vapour phase causes a decrease in the boiling temperature of Ne. Their effect can be minimized by increasing the volume of the vapour phase [Ancsin (1978)].

Most of the possible nonvolatile impurities have small partial pressures below 27 K and are trapped somewhere in the tube. Only nitrogen has a notable influence. The limit of solubility of N_2 in Ne is 150 ppmv*. The triple point temperature of saturated Ne is 2.25 mK lower than for pure Ne. For a mixture with 1000 ppmv* of N_2, the vapour pressure is lowered by 100 to 300 Pa, giving a boiling temperature 6 to 10 mK higher than pure Ne between 24.562 K and 27.102 K.

It appears that the isotopic constitution of natural neon varies so little from one supplier to another that there is no need to be concerned with variations in it. Natural neon as described in "Supplementary Information for the ITS-90" [CCT (1990)] is composed of 90.5% of ^{20}Ne, 0.27% of ^{21}Ne, and 9.2% of ^{22}Ne. The ^{21}Ne is in too small a quantity to influence the results, but this is not the case for ^{22}Ne and ^{20}Ne which have different boiling and triple points: the latter are 24.546 K and 24.687 K respectively (corresponding to a pressure difference of 326 Pa). An increase of the concentration of ^{20}Ne by 0.1% increases the normal boiling point by 0.13 mK.

There also exists an isotopic composition difference between the liquid and vapour phases. The molar concentration of ^{22}Ne is higher in the liquid phase than in the vapour phase by 0.3% at the boiling point and 0.4% at the triple point [Furukawa (1972)]. This

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* The abbreviation ppmv is used to mean an impurity content of one part by volume of solute per 10^6 parts by volume of solvent.

creates an uncertainty of 0.4 mK in the value of the normal boiling point depending upon whether the ITS composition applies to the liquid or the vapour phase. In the absence of a precise analysis, the error can be minimized if the volume of the liquid phase is much larger than that of the vapour phase.

d. Nitrogen [Ancsin (1974a)]

For nitrogen in the liquid phase, volatile impurities such as He, H_2, and Ne, if present, stay entirely in the vapour phase and have no detectable effect on the temperature of the boiling liquid. Non-volatile impurities such as O_2 and Ar lower the triple point value, while CO and (especially) Kr raise it.

Impurities have a complex effect on the *whole* vapour pressure relationship, which cannot simply be represented as a shift proportional to the temperature changes at the triple and normal boiling points (Fig. 6.11). There is a consequent change of all the constants in the vapour pressure equation.

e. Argon [Ancsin (1973b)]

As impurities, He, Ne, and H_2 have no influence; N_2 (volatile) decreases the temperature of the dew point by more than 2 mK for 100 ppmv. Oxygen (nonvolatile) has no influence if the concentration is less than 200 ppmv, whereas CH_4 and Kr (nonvolatiles) increase the dew point temperature by approximately 2 mK for 100 ppmv.

f. Oxygen [Ancsin (1973a, 1974b), Tiggelman (1973), Compton and Ward (1976), Kemp et al. (1976)]

Since the principal impurities are volatile it is necessary to use a well-filled bulb. Helium and neon are not soluble in liquid oxygen. For a concentration of 1 ppmv, nitrogen decreases the boiling (condensation) point temperature by 19 μK; krypton increases it by 5.6 μK; argon decreases it by approximately 5 μK. The influence of H_2O and CO_2 is imperceptible up to a concentration of 100 ppmv.

As observed with nitrogen, the effect of the impurities on the *whole* vapour pressure curve is highly non-linear, and therefore distorts the whole vapour pressure equation (Fig. 6.12) [Ancsin (1974b)]. Some of the discrepancies observed in the literature between different vapour pressure scales can be attributed to this effect.

The isotopic effects in oxygen are perceptible only when the volume of residual liquid is small. The vapour pressure of pure ^{18}O is about 1.5% less than that of the "normal" mixture; the associated correction is about 11 μK at the boiling point for an isotopic composition of 0.210% instead of 0.204% [Tiggelman and Durieux (1972b)].

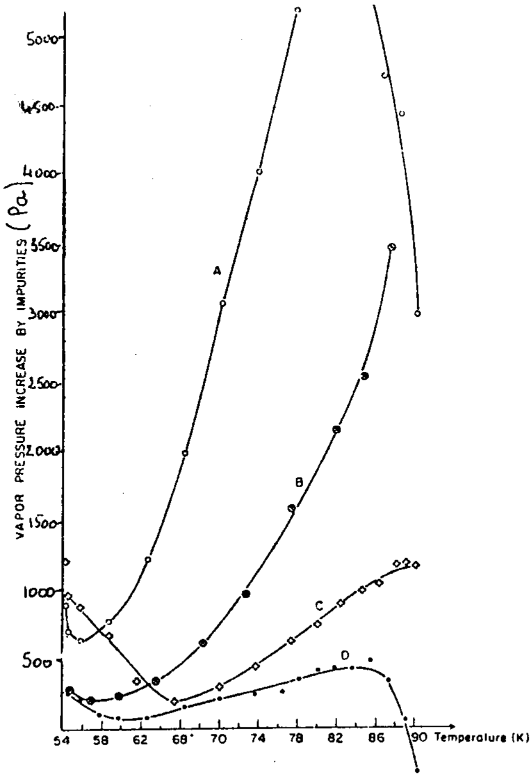

Fig. 6.12: Effect on the vapour pressure of oxygen due to the indicated volatile impurities as a function of temperature. Curve A, O_2:1000 ppmv. N_2 V (vapour phase) = 1.61; curve 8, O_2:1000 ppmv. Ar V (vapour phase) = 1.61; curve C, O_2:100 ppmv. N_2 V (vapour phase) = 0.41; curve D, O_2:100 ppmv. N_2 V (vapour phase) = 1.61 [Ancsin (1974b)].

6.3.7 Particular Problems with Helium [Cataland et al. (1962), Kerrik (1970), Montgomery and Pells (1963), Rusby and Swenson (1980)]

Information on the realization of helium vapour pressure scales is available in "Supplementary Information for the ITS-90" [CCT (1990)]. As for other substances, it is necessary to avoid the formation of cold spots which can cause an error in reading. In ^{4}He, such a cold spot can be at the same level as the liquid surface. In fact, He I above the λ-point (2.1768 K) has a very low thermal conductivity so temperature gradients can occur, especially near the surface if evaporation is taking place. Below the first 4 millimeters, the temperature variation under static (non-convective) conditions would be equal to that of the hydrostatic pressure (0.14 mK/cm at 4.2 K; 0.27 mK/cm at 3.34 K; 1 mK/cm at 2.2 K). Nearer the surface, the effect depends upon the cryostat design; at 4.2 K a temperature increase of up to 5 mK above the surface temperature in the first 4 mm has been observed [Durieux (1960)]. The vapour temperature above the surface is therefore lower by several mK than that of a body immersed just below the surface. The vertical gradient can cause an error of up to 20% of the measured temperature if the temperature of an immersed body is deduced from the pressure in the vapour phase and accounted for only with the hydrostatic correction. This temperature gradient, detectable by the appearance of bubbles in the center of the liquid, depends also on the rate of evaporation. It is necessary to use a well-insulated dewar and to fractionate the liquid mass with fins or massive braids to improve the thermal contact with the surface of the bulb (Fig. 6.5). Rather than measure the pressure just above the liquid in which the body whose temperature is required is immersed, one can also use a small auxiliary bulb in good thermal contact with it. The pressure tube must then cross the liquid-vapour surface in the dewar and it is there that there is a risk of a cold spot forming, although according to Ambler and Hudson (1956) this is unlikely (see also Sec. 6.2.2). A vacuum jacket around the capillary tube will suffice to avoid this cold spot but it must not reach to room temperature which would make thermal isolation difficult (Fig. 6.6). A heat flux along the wall of the internal tube must also be avoided; if it cannot be otherwise controlled, some copper foil in the bath and surrounding the capillary would prevent the formation of temperature gradients. In summary, large and unquantifiable temperature gradients can arise in bulk He I and therefore a bulb should be used.

Below 2.1768 K He II is an excellent thermal conductor so the temperature gradient does not exist. On the other hand, being a superfluid, He II climbs along the bulb walls, vaporizes, and returns to the liquid surface. This produces a heat input to the bulb by refluxing because the superfluid film does not carry away entropy, so the entropy density of the remaining liquid increases. The large Kapitza resistance is also troublesome. The temperature of the liquid can be many millikelvins higher than that of the walls (15 mK to 1.5 K). This phenomenon can be corrected for (but not reliably) by calculation, and can be reduced by increasing the surface of the bulb/liquid contact up to several hundreds of cm^2 (metal mesh or spirals of copper in the bulb). Furthermore, the viscosity of the return gas induces a pressure gradient in the capillary which can become important below 1 K.

Note that if these problems are not under control, the measured temperatures will be discontinuous at the λ-point. For precise measurements, the error due to the Kapitza effect (which can be about 4 mK at 1.5 K) is too important to ignore [Lounasmaa (1974) for temperatures below 1 K; Wilks (1967) for higher temperatures]. It can be calculated, or it can be avoided by using ^{3}He, which does not become superfluid, instead of ^{4}He in the temperature range where the two scales overlap; for ^{4}He one should always use a bulb above the λ -point, and always measure the bath pressure directly below the λ -point. Below the λ -point the refluxing and Kapitza effects can be avoided by measuring the vapour pressure a short distance up the pumping tube [Rusby and Swenson (1980)].

6.3.8 Other Corrections

Other corrections to be considered in pressure measurements include: expansion of the mercury of the manometer and variation of its density with the temperature; the shape of the meniscus; hydrostatic pressure correction (if we measure the temperature of a body immersed in the liquid). The latter can be uncertain but can usually be kept small because the depth of liquid is seldom large.

6.4 Conclusion

The vapour pressure thermometer can be used as a thermodynamic thermometer only within the limits of application of the Clausius-Clapeyron equation which result from lack of knowledge of several of the parameters. Otherwise it is an excellent practical thermometer based upon a physical property of a pure substance. Simple and practical, it allows a high measurement precision once the pressure-temperature relationship has been established. The bulb is simple to construct and can be very small. There are not many corrections to apply (a few for impurities possibly, but no dead space corrections as in the gas thermometer). The major inconveniences are its small working range (no pure substance covers a large temperature range) and its nonlinearity of response. The development of new pressure sensors may give renewed interest in vapour pressure thermometers.