15. Liquid-in-Glass Thermometry

Even though the liquid-in-glass thermometer is used much less frequently today than formerly, it is still a very commonly used device. Although it is normally an instrument of only moderate accuracy, the very best of them, when used with sufficient attention to detail, have millikelvin capability over a narrow temperature range. Amongst its advantages are easy portability, independence of auxiliary equipment, low cost, compatibility with most environments, moderate ruggedness, and wide range (it has been used to measure temperatures as low as 70 K and as high as 1000 °C, but its most frequent use is within the range -40 °C to 250 °C). Disadvantages include a large sensing element, impossibility for continuous or automatic readout, long time constant, awkward dimensions, secular changes, and hysteresis (except for special types).

The components of a ypical liquid-in-glass thermometer are shown in Fig. 15.1. These include:

Bulb: The reservoir for containing most of the thermometric liquid.

Stem: The glass tube having a capillary bore along which the liquid moves with changes in temperature.

Auxiliary Scale: A narrow-temperature-range scale for reading a reference temperature (usually the ice point). It should be marked as for the main scale (below). If the main scale range includes the reference temperature no auxiliary scale is supplied.

Contraction Chamber: An enlargement of the capillary bore between the auxiliary and main scales, or between the reservoir and the main scale, to limit the length of the capillary (and hence the thermometer).

Immersion Line: A line marking the depth to which a partial-immersion thermometer should be immersed.

Main Scale: An engraved, etched, or otherwise permanently attached scale with well-defined, narrow graduation lines against which the height of the liquid in the capillary is measured. There may be a colored backing material for better visibility of the lines. The main scale is graduated in fractions or multiples of degrees Celsius. If its range incorporates the reference temperature, it is the only scale.
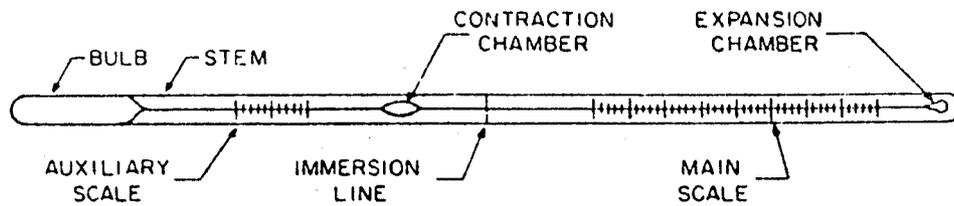
Fig. 15.1: Principal features of a solid-stem liquid-in-glass thermometer [after Wise (1976)].
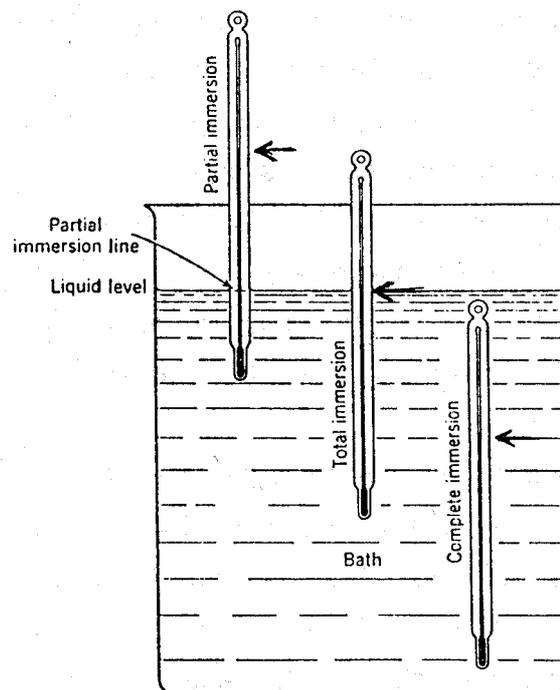

Fig. 15.2: Illustrating the proper immersion techniques for the three types of liquid-in-glass thermometers. The arrow shows the location of the meniscus in each case.

Expansion Chamber: An enlargement at the top of the capillary into which the liquid can flow if the thermometer temperature exceeds the scale limit. It is undesirable for liquid to enter the expansion chamber, however, so it is much better to ensure that there is no overheating of the thermometer. The expansion chamber also prevents excessive gas pressure when the thermometer is used near the top of its range, especially in high-temperature pressurized thermometers.

The range of a liquid-in-glass thermometer is limited by the liquid, by the glass, and by the construction. The commonest and best liquid is mercury. The recommended range of use is from near the mercury freezing point (-38 °C) to about 350 °C with soda-lime glasses; higher temperatures require borosilicate or other special glasses. The capillary above the mercury is filled with a dry gas (frequently nitrogen) to prevent separation of the column and to inhibit distillation of the mercury; in the higher-temperature models, substantial gas pressures are required to raise the mercury boiling point above the range of the thermometer. Air is not a good filling gas because it may lead to oxidation of the mercury and consequent sticking of the latter in the capillary. A eutectic alloy of mercury containing 8.5 weight percent of thallium is used to extend the lower temperature limit to -56 °C; commonly the upper limit is at or a little above 0 °C to allow for ice-point reference checks. Organic liquids are used in thermometers for lower temperatures (alcohol, toluene, pentane, butane), in some cases down to -200 °C. These lower-temperature thermometers suffer from drainage problems associated with the low surface tension of the liquids and from vaporization; they are less reliable than mercury thermometers where the latter can be used.

Thermometers are designed and calibrated for vertical immersion of the bulb and stem to the top of the liquid column (*total immersion*), of the bulb and stem to the immersion line (*partial immersion*), or of the whole thermometer (*complete immersion*). These three types are illustrated in Fig. 15.2. The total-immersion type is the most accurate and is recommended wherever possible; the complete-immersion type is the least common.

For calibration, the ice (or other reference) point is always taken first, but not before the thermometer has been at least 72 h at room temperature. Suitable preparation of an ice bath is described in Supplementary Information. The thermometer must be allowed to attain thermal equilibrium with the ice and should be *gently* tapped with the fingernail or a pencil to ensure a non-sticking meniscus before reading.

For a thermometer graduated above 300 °C, a requisite quality check is to raise its temperature to the highest point on the scale immediately after taking the ice point, then to allow a rest period of three days at room temperature and to take a second ice point. If the agreement between the first and second ice points is not within the stated accuracy limit of the thermometer, the thermometer should be discarded. Following the ice-point checks, the thermometer is calibrated from the lowest to the highest temperature against a laboratory standard in a suitable bath. Readings may be taken with the bath temperature slowly increasing to ensure that the meniscus is fully convex (less than one scale division per five minutes is recommended to ensure that the exposed stem remains in thermal equilibrium) or with the bath stabilized at the calibration temperature. In the latter case, bath-temperature excursions should be smaller than the precision of reading and the thermometer should be tapped before reading. After calibration at the highest temperature, the ice point should be retaken after the thermometer has had time (in hours, approximately $t_{max}/100$) to relax back to its static condition.

Calibration temperatures should be approximately equally spaced, their number depending upon the thermometer range, the accuracy required and the scale graduation interval. Calibration every 50 to 100 scale divisions should give an accuracy within one-half of one division. For linear interpolation between calibration points on a plot of scale correction versus temperature, the uncertainty is about one-half the largest discrepancy found by extrapolating each linear segment to the next calibration point.

A thermometer calibration applies as long as the ice-point reading remains the same as during calibration. Subsequent changes in the ice-point reading will result from small changes in the glass of the thermometer bulb which affect its volume. Volume changes in the capillary are minimal by comparison and, as a result, changes in the ice-point reading of the thermometer (taken after not less than 3 days at room temperature) will be accompanied by similar changes in readings at each point along the scale. The ice point should be taken periodically, and scale corrections adjusted as necessary. If the ice point change is too large, the thermometer must be recalibrated. How large a change is "too large" depends upon the application and the type of thermometer .

Parallax errors of many tenths of a division may easily occur in reading a liquid-in-glass thermometer. To avoid them one must view the thermometer from exactly the same angle as was used for calibration, virtually always perpendicular to the liquid column. One of the better ways of avoiding parallax and at the same time obtaining a precise reading is to view the thermometer through a telescope which is aligned at the proper angle, or through a magnifying lens attached to the thermometer. In the latter case, lack of parallax is indicated by a straight (as opposed to curved) image of the graduation mark. In

the former case, a cross-hair can be centered by eye very accurately at the midpoint between the scale lines; if this is done, a good scale can be read to better than 1/20 division. For this reason it is recommended not to use too sensitive a thermometer; any attendant gain in sensitivity is outweighed by lack of stability, lack of linearity, increased fragility, and smaller temperature range of use. Similarly, it is recommended not to use a thermometer with graduations smaller than 1/10 °C, even if it is desired to measure temperatures to within a few hundredths oC.

With a partial-immersion thermometer, the average temperature (t_c) of the emergent stem (that part of the stem between the point of immersion and the top of the liquid column) during calibration should be stated. In subsequent use the average emergent-stem temperature (t_s) should be measured [Wise (1976)] and an additional correction (Δt) added to the reading, where Δt is given by

$$\Delta t = k\, n(t_c - t_s) \quad . \tag{15.1}$$

In Eq. (15.1) n is the equivalent number of degrees of the emergent stem and k is the differential coefficient of thermal expansion of the thermometer liquid relative to the thermometer glass. For mercury in pyrex for example, $k = 1.6 \times 10^{-4}/°C$; for organic liquids $k \approx 10^{-3}/°C$. Variations of coefficient of expansion among glasses are negligible in this connection.

A similar correction applies if a total-immersion thermometer is used at partial immersion, where now for t_c in Eq. (15.1) the temperature of the thermometer bulb is used.

The readings of a liquid-in-glass thermometer change with changes in both internal and external pressure: the former include change in bulb pressure resulting from the head of mercury in the capillary and from change of temperature of the gas above the mercury; the latter are usually due to variations in atmospheric pressure and in depths of immersion. Since there are approximately "6000 °C of mercury" contained in the bulb, obviously a small change in bulb volume can cause a large change in reading. The external pressure coefficient of a mercury-in-glass thermometer depends upon the internal and external bulb radii, and is usually about 1×10^{-6} °C/Pa. The internal pressure coefficient is about 10% larger.

Changes in bulb volume also occur because of both irreversible (secular) and reversible (temporary depression) structural changes in the glass that are influenced by time and heat treatment respectively. The secular change is almost always a slow contraction of the bulb, producing an increased thermometer reading. The rate of secular

rise decreases with time but increases with exposure of the thermometer to high temperatures. The maximum secular rise is unlikely to exceed 0.1 °C over several years in well-constructed thermometers provided the glass is not heated beyond its exposure limit. The reversible changes appear as a hysteresis on thermal cycling. The bulb expands on exposure to high temperatures and does not return to its original volume immediately on cooling, resulting in a depression of the ice-point reading (and all other readings). Recovery may not be complete for 24 to 72 hours or, if the thermometer is cooled very slowly, no depression may occur. It is to monitor and correct for these changes in bulb volume that ice points are taken before and after calibration, as described earlier. In a good thermometer the temporary depression is small.

For a variety of reasons the mercury in the capillary tube may become separated, leading to spurious readings until the separation is removed. Methods for doing this are described by Ween (1968); among these are centrifuging, shaking, rejoining in the contraction chamber or in the bulb, and (a very slow process) distillation. Ice-point checks are an easy way of detecting abnormal thermometer behaviour: a substantial increase in ice-point reading frequently indicates a separated column; a substantial decrease may mean that mercury is trapped in the expansion chamber or that the thermometer has been overheated. A small amount of mercury trapped in the expansion chamber can be detected by careful visual observation.

More detailed discussion of the calibration and use of liquid-in-glass thermometers is given by Wise (1976), ASTM (1985a), Ween (1968), Thompson (1968), and BS (1985).