1.2 Determination of melting temperature, melting range, congealing point, boiling point, and boiling range

The thermodynamically true melting point of a substance (the triple point) is a physical constant that is indicative of the identity and purity of the material. It is defined as the temperature at which the solid, liquid, and gaseous phases of the substance are in equilibrium in an evacuated, closed system. Under normal atmospheric pressure the solid and liquid phases of a substance are in equilibrium at a temperature that differs somewhat from the triple point but, since pressure effects on the solid-liquid transition temperature are minimal, this difference does not, in general, exceed a few hundredths of a degree Celsius.

Methods for the determination of equilibrium melting points are laborious and require complicated equipment. The usual practice is, therefore, to estimate melting points by dynamic rather than equilibrium methods. The melting points thus determined usually differ significantly from the corresponding triple points. The magnitude of the deviation varies with the particular method employed, with the criterion adopted as the "melting point", and possibly with the substance under examination. Melting points determined by the capillary method of the *International Pharmacopoeia* are typically about one degree higher than the thermodynamically true melting points.

Determination of melting points (called subsequently melting temperatures) is used in pharmacopoeial specifications primarily for identification of the substance concerned. The validity of the identification is greatly enhanced if the so-called mixed-melting point procedure is applied. This involves an additional determination to demonstrate that the substance being examined and a mixture prepared of equal parts of this substance and an authentic specimen (reference substance) of the substance melt at the same temperature. If the two substances are not identical the mixture normally melts at a significantly lower temperature than the substance being examined, and the melting range is relatively broad.

The presence of impurities in a substance results in a more or less pronounced lowering of its melting point. Even more significant is that impurities present in the substance may cause its melting range to be extended. In most cases where melting behaviour is used as a criterion of purity the *International Pharmacopoeia,* therefore, prescribes determination of the melting range rather than the melting point.

Similarly for liquids, determinations of boiling point and boiling range give information that contributes to the identification and purity estimation of liquid compounds. Practical considerations again dictate the use of methods that yield apparent constants that may differ from the thermodynamically true values. However, if the prescribed experimental conditions are closely adhered to, the results obtained are of sufficient reproducibility.