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2.2.18. FREEZING POINT

The freezing point is the maximum temperature occurring during the solidification of a supercooled liquid.

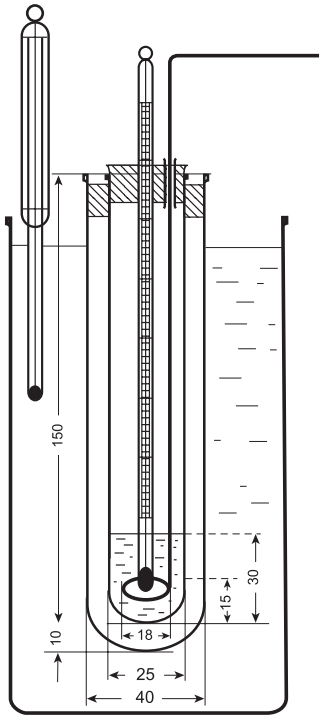

Figure 2.2.18.-1. – *Apparatus for the determination of freezing point*

Dimensions in millimetres

Apparatus. The apparatus (see Figure 2.2.18.-1) consists of a test-tube about 25 mm in diameter and 150 mm long placed inside a test-tube about 40 mm in diameter and 160 mm long. The inner tube is closed by a stopper which carries a thermometer about 175 mm long and graduated in 0.2 °C fixed so that the bulb is about 15 mm above the bottom of the tube. The stopper has a hole allowing the passage of the stem of a stirrer made from a glass rod or other suitable material formed at one end into a loop of about 18 mm overall diameter at right angles to the rod. The inner tube with its jacket is supported centrally in a 1 litre beaker containing a suitable cooling liquid to within 20 mm of the top. A thermometer is supported in the cooling bath.

Method. Place in the inner tube sufficient quantity of the liquid or previously melted substance to be examined, to cover the thermometer bulb and determine the approximate freezing point by cooling rapidly. Place the inner tube in a bath about 5 °C above the approximate freezing point until all but the last traces of crystals are melted. Fill the beaker with water or a saturated solution of sodium chloride, at a temperature about 5 °C lower than the expected freezing point, insert the inner tube into the outer tube, ensuring that some seed crystals are present, and stir thoroughly until solidification takes place. Note the highest temperature observed during solidification.

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2.2.19. AMPEROMETRIC TITRATION

In amperometric titration the end-point is determined by following the variation of the current measured between 2 electrodes (either one indicator electrode and one reference electrode or 2 indicator electrodes) immersed in the solution to be examined and maintained at a constant potential difference as a function of the quantity of titrant added.

The potential of the measuring electrode is sufficient to ensure a diffusion current for the electroactive substance.

Apparatus. The apparatus comprises an adjustable voltage source and a sensitive microammeter; the detection system generally consists of an indicator electrode (for example, a platinum electrode, a dropping-mercury electrode, a rotating-disc electrode or a carbon electrode) and a reference electrode (for example, a calomel electrode or a silver-silver chloride electrode).

A three-electrode apparatus is sometimes used, consisting of an indicator electrode, a reference electrode and a polarised auxiliary electrode.

Method. Set the potential of the indicator electrode as prescribed and plot a graph of the initial current and the values obtained during the titration as functions of the quantity of titrant added. Add the titrant in not fewer than 3 successive quantities equal to a total of about 80 per cent of the theoretical volume corresponding to the presumed equivalence point. The 3 values must fall on a straight line. Continue adding the titrant beyond the presumed equivalence point in not fewer than 3 successive quantities. The values obtained must fall on a straight line. The point of intersection of the 2 lines represents the end-point of the titration.

For amperometric titration with 2 indicator electrodes, the whole titration curve is recorded and used to determine the end-point.

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2.2.20. POTENTIOMETRIC TITRATION

In a potentiometric titration the end-point of the titration is determined by following the variation of the potential difference between 2 electrodes (either one indicator electrode and one reference electrode or 2 indicator electrodes) immersed in the solution to be examined as a function of the quantity of titrant added.

The potential is usually measured at zero or practically zero current.

Apparatus. The apparatus used (a simple potentiometer or electronic device) comprises a voltmeter allowing readings to the nearest millivolt.

The indicator electrode to be used depends on the substance to be determined and may be a glass or metal electrode (for example, platinum, gold, silver or mercury). The reference electrode is generally a calomel or a silver-silver chloride electrode.

For acid-base titrations and unless otherwise prescribed, a glass-calomel or glass-silver-silver chloride electrode combination is used.

Method. The solvent mixture is neutralised, if necessary, before dissolution of the substance to be examined. Plot a graph of the variation of potential difference as a function of the quantity of the titrant added, continuing the addition of the titrant beyond the presumed equivalence point. The end-point corresponds to a sharp variation of potential difference.