Microdetermination of the Boiling Temperature

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The literature gives various methods for the microdetermination of the so-called boiling point\(^1,3,4,8,9,13\). It may be pointed out that the boiling point is defined as the temperature at which the liquid phase is at equilibrium with vapor of 760.0 mm pressure, whereas one is able to observe only the boiling temperature with several of the methods in use.

The boiling point is determined by \textit{Swietoslawski}\(^3\) and \textit{Schleiermacher-Roth}\(^4\). The methods of \textit{Siwoloboff}\(^2\), \textit{Emich}\(^1\), and \textit{Kamm}\(^7\) determine the boiling temperature corresponding to the atmospheric pressure at the time of the observation. In this latter group, the first two have a certain popularity because of their simplicity and shall be considered in the following.

Contrary to quite common assumption, the usual practical problem is the determination of the boiling temperature of impure liquids or mixtures, rather than that of chemical individuals. Out of eleven substances of reagent grade, only one showed constancy of its boiling point on examination.

A cylindric heating block of aluminum, 60 mm in diameter, 90 mm high, with the necessary wells for thermometer (5 mm), apparatus (3 mm), and observation (3 mm) was used in all experiments. A Bunsen burner supplied the heat.

Method of Siwoloboff

A capillary of 0.2-mm inner diameter, about 9 cm long, and fused shut 3 mm above the lower end was placed into a micro test tube, 1.5- to 2-mm inner diameter and about 80 mm long, which contained the liquid to be tested.

Aside from the atmospheric pressure, the observed boiling temperature depends upon the signal adopted for indicator\(^2,5,6,8,9,12,15\), the procedure of heating\(^2,5,6,9,10\), the characteristics of the apparatus, and the amount
of sample. In addition it must be considered that three different objectives may be pursued: the determination of the boiling temperature of a pure liquid, the observation of the lowest boiling temperature of a mixture or its “representative boiling temperature”, and the determination of the boiling range of a mixture.

Since the moment at which the continuous flow of bubbles starts cannot be recognized with sufficient certainty, the entrance of the liquid into the boiling capillary was taken for the signal. The boiling capillary rested upon the bottom of the micro test tube. A preliminary determination of the boiling temperature was carried out, whereafter test tube and contents were centrifuged after cooling or a fresh sample was taken. The block was then heated to about 3°C below the boiling temperature found, whereupon the test tube with the sample was placed into the heating block. The temperature of the latter was raised at a rate of 2 degrees per minute just until bubbles started rising. The source of heat was removed, and the temperature was read when the liquid entered the boiling capillary. With a pure liquid, the determination may be repeated without limit by applying heat until the liquid is just expelled from the boiling capillary and again taking the temperature when it re-enters. By using the adopted procedure for preventing fractionation, several repetitions are even possible with impure substances and mixtures. In the instance of a pentanol, the boiling temperatures 118.0, 118.1, 118.2, and 118.2 were found in this manner. In continuing the experiment, an intense flow of bubbles was allowed to take place between observations, and the boiling temperatures increased to 122.0, 126.0, 128.1, 129.1, 129.9, 129.8, 130.2, 130.2, and 130.2.

It appears that the adopted procedure is not only suited for pure liquids, but is also able to give the initial or representative boiling temperature of impure liquids and mixtures. Emich’s method gave boiling temperatures from 113°C to 130°C with the same pentanol.

For the determination of the boiling range, it is preferable to suppress the amount of reflux by cutting off the test tube at the surface of the heating block. If, in addition, a small sample is used, the variability of the boiling temperature will be revealed by a smaller number of observations separated by periods of boiling. The following series of boiling temperatures have been observed with:

0.05 ml benzene, reagent grade: 77.6, 77.6, 78.0, 79.0, 79.5, 79.9, 80.0, 80.5, 80.7, 80.5, 80.9, 80.8, and 80.9.

0.3 ml benzene, reagent grade; test tube cut at the surface of the block: 80.0, 80.1, 80.1, 80.0, 80.0, and 80.1.

Anisol: 147.5, 150.0, 151.0, 151.5 (continued after removal of the condensate or cutting the tube at the surface of the block): 152.5, 153.0, 152.0, 153.5, 154.0, and 154.5.