

DETERMINATION OF BOILING POINTS OF VERY SMALL QUANTITIES OF LIQUIDS.

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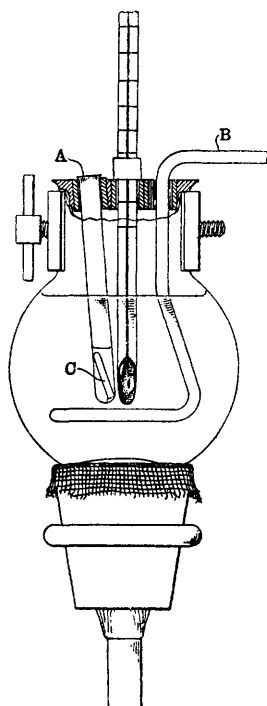
The determination of boiling points of very small quantities of liquids by distillation is by no means satisfactory, because in the first place considerable loss in the already small quantity of liquid may take place, and it is difficult to actually arrive at the boiling point owing to the time necessary to heat the thermometer up so that it may show the correct temperature, and the liquid often all distils over before this happens. Various methods have at one time or another been suggested for determining boiling points for very small quantities of liquids, but few of these have been accurate and reliable. Of course it is no use trying to ascertain the boiling point of very small quantities of liquid which is not pure, but it often happens in chemical research that one obtains very small quantities of pure products, and for purposes of identification or even simply to ascertain the boiling point of an unknown substance some reliable method is necessary.

In some textbooks a method is described which, if it gave reliable results, would be very satisfactory. A small glass tube about 6 cm. long and about $\frac{3}{4}$ cm. in diameter, closed at one end, is fastened by means of a piece of platinum wire against a thermometer, and the thermometer and tube are fixed by means of a clamp into a beaker containing sulphuric acid or other liquid of high boiling point. The beaker is fitted with a stirrer in the ordinary way. The determination of the boiling point is made by placing 1 cm. of the liquid into this little test-tube; then a capillary tube, which is sealed together about 1 c.c. from its end, is also placed into it so that the liquid reaches about up to the sealed part of the capillary. The directions for taking the boiling points are as follows :—

The liquid in the beaker is heated by means of a burner, and in order to insure the steady rise of temperature it is agitated by means of the stirrer. When the liquid in the test-tube has nearly reached its boiling point bubbles of air commence to rise up through the liquid from the end of the capillary. The burner is now removed from below the beaker and the liquid thoroughly agitated so that the temperature may be uniform. It is then again replaced for a short time and again removed, these operations being repeated so that the rise of the temperature may be easily noted from degree to degree. As the boiling point is neared bubbles of air rise more rapidly, until when the liquid is just boiling they are given off in a continuous chain. At this point the thermometer is read, and by repeating the operation two or three times, each time putting a fresh capillary in, it is said to be possible to obtain close results. We very carefully tried this method but found it to be anything but accurate.

With moderately low boiling substances the temperature might be ascertained within two or three degrees. With very low boiling substances it is

quite inaccurate, and with high boiling substances it was also not to be depended upon. We then tried various methods of modifying this process in order to see whether it might be possible to make it accurate. For example, a piece of platinum wire was fused through the end to the small test-tube, and an improvement was undoubtedly obtained, but even yet the results were by no means accurate. Finally, we devised the following process, which gives results leaving very little to be desired. The apparatus is depicted in the diagram. A flask *A* which holds about



100–110 c.c. of fluid is placed upon a wire gauze fastened over an inverted cone, such as is used to prevent Bunsen burners from flickering. The object of using this kind of chimney is that the heat may be evenly distributed upon the bottom of the flask. The flask has a very wide neck, about 4 cm. in diameter, which is fitted with a cork having three holes bored in it. Through the central hole a thermometer is passed, and through *B* a small thin-walled test-tube, about 7–8 cm. long, and having a diameter of $\frac{3}{4}$ cm. This tube, however, is not passed directly through the cork but passed through a piece of glass tubing which is fitted into a cork so that it may be inserted and withdrawn without any difficulty. And, furthermore, if it happens to be moist with sulphuric acid, should this be the heated liquid employed, the cork will not be charred. In order to prevent the tube from slipping through into the flask the top of it is slightly widened out, so as to act as a collar. The thermometer also passes through a similar tube, and to prevent it dropping down too low a piece of rubber tubing *C* is placed round it to act as a support. The stirrer *D* of glass rod fits loosely through another tube, so that the air, as it expands upon heating, shall not set up a pressure.

About $\frac{1}{2}$ c.c. of liquid, the boiling point of which is to be determined, is placed into the tube, and then a capillary tube, sealed at one end, and about 1-1 $\frac{1}{2}$ cm. long, is dropped into the liquid in such a way that the open end is to the bottom. The determination is then carried out as follows :—

The temperature is raised by means of a Bunsen burner, the liquid being gently stirred in the meanwhile. The temperature is raised fairly quickly at first until a continuous stream of bubbles is given off from the bottom of the capillary tube. The source of heat is then removed and the temperature allowed to drop, the heating liquid being thoroughly stirred while it cools. As the temperature drops the bubbles begin to be given off less rapidly, and finally stop altogether. At the moment the bubbles cease to be given off—that is, when the pressure of the vapour within the tube is equal to the atmospheric pressure—the thermometer is read off and this is the boiling point of the liquid. A second determination can be made by at once again rapidly rising the temperature before the liquid is sucked back into the capillary tube. The stream of bubbles is again obtained, and on cooling down a second reading may be taken as before. It is found that by proceeding in this manner, and being careful to stir, absolutely accurate results may be obtained. If the liquid is not stirred the results are by no means accurate. This is, we think, due to the condensed vapour which has risen up in the tube *B*, which, being cooler than the heating bath, runs down to the liquid and stops it boiling. This, however, does not affect the thermometer sufficiently rapidly to drop the mercury, consequently the liquid ceases boiling inside the tube *B* and too high a boiling point is registered by the thermometer.

We append a table of boiling points obtained by this apparatus.

Column 1 gives the actual boiling point, those marked in asterisk having been obtained by previous distillation with the same thermometer, the others being the known boiling points of the substances taken from the literature.

Column 2 gives the boiling point obtained with this apparatus when stirrer was used.

Column 3 gives the results when no stirrer was employed.

	Mean Experimental Boiling Point.		
	Actual Boiling Point.	With Stirrer.	Without.
Ether	*35-36°	35°75'	—
Acetone	*56°5-57°	56°8'	—
Hexane	*67°	67°0'	—
Distilled Water	100°	—	100°0'
Ethyl propionate... ..	*98°0'	98°2'	99°5'
Anisole	155°	—	154°5'
Aniline	184°0'	—	184°0'
Nitrobenzene	*206°	206°0'	209°0'
Safrol	*231-231°5'	231°2'	234°0'

It is obvious that, with efficient stirring during cooling, the closeness with which the temperature of the inner liquid keeps to that of the outer depends on the rate of cooling, and this in turn depends upon the volume of the outer liquid. If, therefore, great accuracy is required, it is only necessary to employ a standard thermometer, a large flask to contain the heating liquid, and, perhaps, a mechanical stirrer. Now, as the rate of cooling at any time depends upon the difference of temperature between the liquid and the air

the same amount of accuracy can be obtained for low temperatures by using a much smaller flask than would be necessary for high temperatures, because the cooling is slower when the temperature approaches that of the atmosphere. It is also an all-important feature that the small test-tube should dip well into the heating liquid to ensure thorough heating of the condensed liquid within the tube, because this runs back down the sides and would otherwise stop the boiling. And, finally, the thermometer should be read when the inner liquid ceases to give off vapour—that is, when the last bubble stops increasing in size. Under these circumstances, all errors due to thickness of glass, &c., may be neglected. After being in use for some little time the sulphuric acid becomes dark in colour. This can be prevented and the acid again be rendered colourless by the addition of a few small crystals of potassium nitrate, which are easily dropped in by removing the small tube.