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STUDIES IN VAPOR PRESSURE: I. A METHOD FOR DETERMINING UNDER CONSTANT CONDITIONS THE BOILING POINTS OF EVEN MINUTE QUANTITIES OF LIQUIDS AND OF NON-FUSING SOLIDS.[1]

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For solids which do not melt, no method of determining the boiling point ("vaporizing point") that is at once simple and accurate is available. The chemist, when he encounters such a material, is thus deprived of both of his favorite methods for the characterization of substances. The crude plan of heating the substance in a deep crucible, placed in a draft cupboard, and taking the temperature of the vaporizing solid[2] is highly inconvenient, is very wasteful of material and, as we shall see, is not accurate.

The measurement of the boiling point of a liquid, as usually made by means of a distilling flask and thermometer, is open to several objections. One of these is that, even if the whole of the mercury thread of the thermometer is immersed in the vapor, the apparatus is not such that the other conditions can be exactly specified and constantly fulfilled. Varying results are therefore obtainable with the same substance by different observers, or even by the same observer. Thus, it is a familiar fact that use of a larger flame will raise the apparent boiling point. Again, use of a sand bath, a metal bath, or a wire gauze may cause superheating of the thermometer by radiation.

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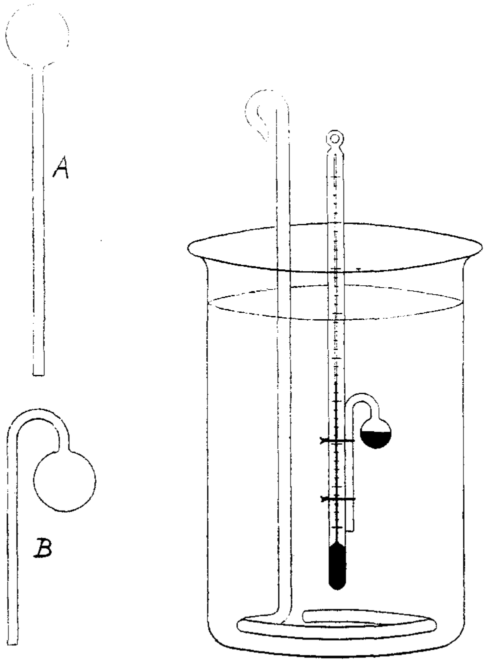
[1] Read before the American Chemical Society, Dec. 30, 1909.

[2] V. Meyer and Harris, *Ber.*, 27, 1482.

On the other hand, many liquids are easily superheated, and boil irregularly in consequence.

When the liquid boils regularly, use of a small flame, playing on the naked bulb of the flask and touching the latter only below the level of the surface of the liquid, gives the most constant and easily reproducible results. But trial will show that at least five minutes' continuous boiling is required before the thermometer reaches the true temperature. Unless the liquid is distilling over very slowly during this time, a considerable supply of the material is thus required, and must be prepared. Even if the boiling point were to be determined in a vessel attached to a reflux condenser, at least 10–20 cc. of the liquid would be required to wet the condenser and leave a sufficient amount of the liquid to cover the flame.

Surrounding the bulb of the thermometer with cotton[1] may protect the instrument from contact with superheated vapor arising from a "bumping" liquid, and so overcome one of these objections. But cotton is a bad conductor, and the air it contains is very slowly expelled, so that its use will be found to triple the time elapsing before the thermometer reading reaches the true boiling point. Its employment involves the provision of a slightly larger supply of the substance than would ordinarily be required.



Use of the apparatus here described enables one to avoid all these objections. The method automatically provides that constancy of conditions required for securing unvarying results. It enables one, also, to determine the boiling point of a solid as easily as that of a liquid. The whole operation takes no more time, and but little more of the substance than the measurement of a melting point, made with a like degree of accuracy.

The Apparatus.—A small bulb, with a wide capillary tube 3–4 cm. long and not less than 1 mm. in width

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[1] Sydney Young, Stoichiometry (London, 1908), 141.

(figure, A) is prepared as for organic combustion of a liquid. The capillary is bent close to the bulb (figure, B), and a small amount (0.03-0.1 g.) of the liquid, or of the pulverized solid, is introduced (the latter most easily before bending). To exclude moisture, liquids may be distilled directly into a crucible or small test tube placed in a Brühl receiver, suitably desiccated. The bulblet stands stem downwards in, or hangs on the edge of, thec rucible. When the receiver is partially exhausted, and air is again admitted, the liquid enters the bulb. The bulblet, after being charged, is attached with thread or asbestos cord above the bulb of the thermometer. Use of wire is apt to cause breakage of the latter. The whole is then fixed in a beaker (preferably of tall form) filled with a transparent liquid, and provided with a glass stirrer, all just as for a melting-point determination (figure).

The Bath Liquid.—For substances boiling below 100°, the beaker may usually be filled with water, or a strong solution of calcium chloride. For substances boiling below 200°, sulphuric acid, and for those boiling as high as 280–300° melted paraffin wax (m. p. about 53°) may be employed. With substances boiling between 220° and 450° (or higher) we have used a eutectic mixture of potassium and sodium nitrates.[1] To extend the range downwards (to 120°), lithium nitrate may be added, but above 250° the lithium nitrate damages the thermometer and beaker by slowly attacking the glass and rendering it opaque. The composition of the mixtures is as follows:

$NaNO_3$.	KNO_3.	$LiNO_3$.	M. p.
18.18	54.54	27.27	120°
45.5	54.5	...	218°

When the nitrate baths are used, the melt is poured into an iron or porcelain dish and not allowed to solidify in the glass beaker. To secure a transparent liquid from a formerly turbid one, the outside of the solidified mass may be washed before being again used. The whole apparatus stands over a metal tray (*e. g.*, a "drip-pan"), which, in case of accidental breakage, catches the molten salts.

The Manipulation.—The apparatus being in order, the bath is heated and, as the boiling point is approached, is stirred vigorously. At first, a few bubbles of air are expelled in consequence of expansion. When the boiling point is reached, all the air in the submerged bulblet is quickly displaced and, provided the substance is not soluble in the bath liquid, bubbles of the vapor of the substance rise to the surface in a rapid and regular stream. On removing the flame, a fall in temperature by a small fraction of a degree interrupts the stream sharply, and a re-elevation by the same amount restores it. Since all solids have air and moisture adhering to their surfaces, and liquids are likely to contain oxygen and

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[1] Carveth, *J. Physic. Chem.*, **2**, 207; see also Scudder, THIS JOURNAL, **25**, 161.

nitrogen and traces of water dissolved in them, a gentle stream of bubbles is allowed to pass off for a few moments before the temperature is allowed to fall preliminary to the final temperature reading. This reading is taken when, with very slowly falling temperature, accompanied by vigorous stirring, the stream of bubbles ceases. This applies only to the case of mutual insolubility of the substance and bath liquid: the procedure in the contrary case will be described presently.

The whole process should be repeated until constant readings are secured. To prevent the entrance into the bulb of the liquid from the bath, the thermometer and bulblet are finally raised out of the liquid. The barometric height (reduced to mercury at 0°) is recorded, as usual, along with the observed temperature. A necessary correction will be discussed later.

If the substance is soluble in the bath liquid, the temperature at which vapor ceases to issue cannot be observed sharply. The temperature reading is therefore taken when the bath liquid has ascended the capillary to a predetermined point, 5–10 mm. from the opening. The position of this point may be fixed by noting some mark on the thermometer or binding threads. When the substance is very soluble in the bath liquid, as alcohol is in water, the bubbles of vapor dissolve, instead of rising to the surface, and only the few bubbles of air are seen. When, in such a case, the flame is removed, and the bath liquid enters the capillary, the section of the latter is so small that the surface layer of the liquid within it quickly becomes saturated with the vapor of the substance. Hence the vapor cannot any longer dissolve nearly as fast as fresh vapor can be evolved from the substance in the bulblet. The level reached in the capillary is therefore unaffected by the tendency to absorb the vapor, and is fixed solely by the vapor pressure of the substance, which is slowly diminishing as the temperature falls.

The fact that the bath liquid may have considerable vapor pressure of its own—as, for example, when the boiling point of benzene is being determined with water as the bath liquid—has no influence on the observed boiling point. Such an influence would be observed only if the vapor of the water were able to diffuse up the capillary so as to reach the surface of the substance contained in the bulblet, and this it has no opportunity to do when the methods are used as directed. In particular the second method, involving ascent of the bath liquid into the capillary, should not be used with insoluble vapors. When thus no process of solution is occurring, the vapor of the substance is stationary and very slowly condensing. A little of the vapor of the bath liquid, if the latter has any appreciable vapor pressure, may then diffuse backwards into the bulblet. When, in such circumstances, the reading is made too deliberately, the dilution of the vapor in the bulb may lead to the reading of a temperature 0.05–0.1° too low.

Even when the vapor of the substance interacts chemically with the material in the bath, the boiling point will usually be still determinable. Thus, we have obtained serviceable boiling points of calomel with a bath of melted nitrates, although the vapor causes a slow precipitation of mercuric oxide; and of ammonium chloride, although the vapor interacts with the nitrates, giving rise to a continuous formation of nitrous oxide. In the latter instance, the temperature at the point of minimum gas-evolution was taken.

Correction for Immersed Depth.—Since the pressure, due to the height of the liquid in the beaker over the opening of the capillary in the first method, or over the point to which the liquid ascends in the capillary in the second, will raise the boiling point above that shown in an open flask, a correction of the barometric reading for this effect is required. The depth from the surface to the end of the capillary, or to the mark opposite the point to which the liquid ascended, is measured by means of a scale held in front of the beaker. This distance (in mm.) is multiplied by the specific gravity of the liquid at the temperature used and divided by the specific gravity of mercury at 0° (13.59). The result is added to the barometric reading. For ordinary purposes this distance and the specific gravity of the liquid do not need to be known with great accuracy. An error even remotely approaching 0.2 mm. of mercury in the pressure, representing an error of 2.7 mm. in the measurement of immersed depth when water is the bath liquid, could not possibly be

Sulphuric acid (92.75%).		Paraffin (M. p. 53°).		Two nitrates (Na and K).		Three nitrates (Na, K and Li).	
30°	1.818	60°	0.778	230°	1.968	120°	2.002
40	1.809	70	0.772	240	1.961	130	1.993
50	1.799	80	0.767	250	1.954	140	1.985
60	1.790	90	0.761	260	1.947	150	1.977
70	1.781	100	0.755	270	1.940	160	1.969
80	1.771	110	0.749	280	1.933	170	1.962
90	1.762	120	0.743	290	1.926	180	1.954
100	1.753	130	0.737	300	1.918	190	1.946
110	1.744	140	0.730	310	1.911	200	1.939
120	1.735	150	0.724	320	1.903	210	1.931
130	1.726	160	0.718	330	1.896	220	1.924
140	1.717	170	0.712	340	1.888	230	1.917
150	1.708	180	0.706	350	1.880	240	1.910
160	1.699	190	0.699	360	1.872	250	1.903
170	1.690	200	0.693	370	1.865	260	1.896
180	1.682	210	0.687	380	1.857	270	1.890
190	1.673	220	0.680	390	1.848	280	1.883
200	1.664	230	0.674	400	...	290	1.877
..	...	..	...	..	...	300	1.870

made. Yet such an inconceivable error would usually involve a difference of only 0.01° in the boiling point.

The above table of specific gravities[1] may be used in making the correction. For intermediate temperatures, the value is obtained by linear interpolation.

Precautions for Special Accuracy: *Stirring, Thermometry, Capillarity.* —(1) It is necessary that temperature changes near the boiling point should proceed very slowly, and that uniform distribution of temperature be secured by violent stirring.

(2) The thermometer must be accurate, or its errors known. The usual correction for exposed thread must be made. Use of short thermometers, with a range of only 50–60° each, and of a deep beaker, will permit complete immersion of the whole thread and render this correction unnecessary. The accuracy of the readings is ordinarily limited only by the accuracy of the thermometers used.

(3) Since the tendency to capillary rise in the narrow tube contributes an added pressure, and slightly elevates the boiling point, a capillary less than 1 mm. in diameter should not be employed.

It might be expected that this pressure, due to capillary ascension, would involve an appreciable error, but this is not the case. It is true that water has an exceptionally high capillary constant—at 0° nearly 31 mm. for a tube 1 mm. in diameter, and at 100° about 25 mm. In the single case, therefore, in which the substance and the bath liquid are both pure water, this pressure amounts to 1.7 mm. of mercury, and raises the boiling point 0.06°. But the capillary constants of other liquids are usually much smaller. Thus, the ascents in a tube 1 mm. in diameter are: paraffin oil (at 100°) 10.8 mm. (= 0.6 mm. Hg), sulphuric acid (at 100° 9.8 mm. (= 1.3 mm Hg). With the nitrates, however, *when pure*, the ascent is very high. Thus the ascent of the two nitrates in a tube 1 mm. in diameter is 23.4 mm. at 270° (= 3.3 mm. Hg). When water is the bath liquid, and some other substance is contained in the bulb, then the capillary ascension of the water contaminated with the distillate is not that of water alone, but very nearly that of the substance. Thus, when the substance is one miscible with water, such as alcohol, the capillary ascent, assuming 50 per cent. alcohol within the capillary, is 10.4 mm. (= 0.7 mm. Hg). When the substance is one immiscible

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[1] These specific gravities were determined in this laboratory by Mr. F. B. Plummer, to whom we desire to express our indebtedness. The values are accurate to within one unit in the third place of decimals. The following formulas summarize the results, and give values correct to the second decimal place within the limits of temperature specified:

Sulphuric acid (92.75%, 30–200°), 1.818–0.000906 (t — 30).
Paraffin (m. p. 53°, 60–230°), 0.778–0.000612 (t — 60).
Two nitrates (230–390°), 1.968–0.00075 (t — 230).

with water, the ascent, as is well known, is greatly reduced by the oily matter in the liquid and the tube. In the case of benzene and water, for example, at 0°, it is only about 14 mm. (= 0.9 mm. of Hg). The ascent of the nitrates is likewise reduced. Thus, when the tube is wet with an organic substance which does not mix with the salts, the elevation is of the order of the smallest of the foregoing values. Thus the correction, if any be made on this account, represents only about 1 mm. of mercury, which would raise the boiling point on an average about 0.04°. The temperature readings must therefore be accurate to less than 0.04° to justify the use of this correction. When correction on this account is desired, the capillary rise may be measured to the nearest mm. by severing the bulb from the capillary tube, wetting the interior of the latter with the substance, and dipping the tube in the bath liquid.

Examples.—The following sample boiling points (not corrected for capillarity) show: (1) that the correspondence of the results given by the submerged bulblet method (column 6) with those given by the distilling flask method[1] (col. 7), both obtained with the same thermometer, is satisfactory; (2) that this correspondence is as good whether the substance is very soluble or is insoluble in the bath liquid (col. 2); (3) that the correspondence is equally good whether the bath liquid has itself a high or a low vapor pressure at the temperature concerned; (4) that the correspondence in the case of solids is also satisfactory so far as data for comparison are obtainable:

Substance.	Bath liq.	Immersed depth.	Density of bath liq.	V. p. increase for 1°.	B. p. subm. bulblet.	B. p. dist. flask.
Benzene..............	Water	113	0.97	24	79.01°	79.00°
"	H_2SO_4	104	1.77	..	79.04	79.00
"	Min. oil	60	0.9	..	79.35[2]	79.33[2]
Ether................	$CaCl_2$ sol.	70	1.47	27	33.87	33.85
"	Water	73	0.99	..	33.91	33.85
Alcohol..............	Water	60	0.97	31	77.56	77.55
Camphor..............	Paraffin	45	0.69	20	208.00	207.65
Naphthalene...........	3 Nitrates	68	1.93	17	217.68	217.73
Calomel..............	2 Nitrates	59	1.85	..	383.2	[382.5]
Com. am. carbonate.....	Olive oil	57	0.88	..	58.5	[58.5]

For the sake of comparison, the results for liquids by the submerged bulblet (col. 6), being obtained under greater pressure than those in the open flask (col. 7), are reduced to the existing atmospheric pressure by means of the known vapor pressure changes for 1° (col. 5).

The value for calomel in col. 7 is taken from vapor pressure measurements made by ourselves, using a platinum resistance thermometer.

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[1] Naked flask, flame below the level of the liquid, and boiling continued to constant reading.

[2] These observations were made at a different barometric pressure from the preceding ones.

Since a mercury thermometer, even when nitrogen-filled under pressure, and calibrated by comparison with a resistance thermometer, is accurate only ±1° at temperatures above 300°, this correspondence is satisfactory. V. Meyer (*loc. cit.*), using an open crucible, found the temperature of the vapor 357° (corr.), the error by his method being therefore 25.5°.

The vaporizing temperature of commercial ammonium carbonate is necessarily variable, since the substance is not of constant composition. The value in col. 7 is the mean of two values (59.6° and 57.6°, respectively) taken from Naumann's[1] and Isambert's[2] measurements of the vapor pressures of ammonium carbamate, and is therefore not strictly comparable.

Probably because the liquid is heated equally from all sides, and not merely from below, no tendency to "bumping" was observed.

Impure and Decomposing Liquids.—The submerged bulblet method will not only give the boiling point of a pure liquid, but has, in addition, the advantage of showing promptly when a mixture, and not a pure liquid, is being handled. If a second reading, following a second brief period of boiling for the removal of the volatile substances possibly present, shows a divergence from the first reading, the boiling or distilling operation can be repeated again and again. Since at most only two drops of material have been taken, as much as half of the sample can be boiled away in two or three minutes, and another observation made. If a continuously changing series of boiling points is observed, then the substance is impure (either originally, or in consequence of rapid decomposition). These operations are essentially fractionations, involving, however, only minute amounts of material and an insignificant expenditure of time.

To illustrate the behavior of a mixture, equal volumes of benzene and commercial toluene were taken, and 0.03 cc. of this mixture was used. The successive boiling points, with sulphuric acid as bath liquid, were 91.1°, 92.7°, 94.0°, 96.1°, 98.7°. After five observations, about half the contents of the bulblet still remained.

Characteristics of the Submerged Bulblet Method.—The chief features of the method are:

(1) That it is applicable to non-fusing solids, for the determination of the boiling points of which no simple and accurate method has been known.

(2) That a minimum of material[3] (at most 0.1 g.), and a minimum of time are consumed.

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[1] *Ber.*, **4**, 782.

[2] *Compt. rend.*, **97**, 1212.

[3] For other methods requiring but little material cf. Sivolobov, *Ber.*, **19**, 765; Mulliken, "Identification of Pure Organic Compounds," Vol. I, p. 282 (1904); Schleiermacher, *Ber.*, **24**, 944.

(3) That the conditions are definite and easily reproducible with exactness, and that, in particular, it is impossible for the liquid, the vapor, and the thermometer to differ in temperature. The boiling points ascertained are therefore more accurate, and more exactly comparable than are those obtained by the usual method.

(4) That with impure or decomposing liquids a fractional distillation in miniature may quickly be carried out and the impureness recognized.

(5) That when the dissolved or occluded gases, or volatile substances which are always present, can be removed by boiling, the removal may be accomplished and a satisfactory boiling point secured.

(6) That by taking the boiling point of a mixture of the two, the identity or non-identity of two liquids of almost identical boiling points may often be ascertained without sacrifice of an appreciable amount of material. This method will apply, however, only when the two substances are of chemically dissimilar natures, and not usually to very similar substances.[1]

(7) That the method may be adapted to finding boiling points at normal pressure (760 mm.), and under reduced pressure (see next two papers).

[Communication from the Laboratories of General and Physical Chemistry of the University of Chicago.]

A COMMON THERMOMETRIC ERROR IN THE DETERMINATION OF BOILING POINTS UNDER REDUCED PRESSURE.

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In very accurate work, when the thermometer is immersed in a bath of liquid, a correction is introduced on account of the apparent elevation of the temperature, due to compression of the bulb. The converse effect, namely, a dilatation of the bulb, causing an apparent lowering in the temperature, when the thermometer bulb is immersed in a vapor under reduced pressure, may be equally well known. Having had occasion, however, to study a large part of the literature of boiling points and vapor pressures, we have not happened to observe any mention of this source of error, or any case in which a correction was applied on account of it.[2] This source of error would appear therefore to be neglected by many chemists. Yet in the magnitude of its effects it usually far exceeds the correction for compression, since evacuation involves the removal of a pressure equivalent to a head of about 30 feet of water, while the compression involves usually the addition of only a few inches. The following observations show that, in point of fact, the effect cannot be ignored in any but the roughest work.

[1] Young, Stoichiometry (London), 1908), 264.

[2] Since the above was written, a single, inconspicuous instance has been noticed.