paper that the results obtained by the chloride to silver ratio are more reliable than those obtained in former investigations by the oxide to chloride ratio in spite of the fact that they are farther from the accepted value. It has been found in this laboratory that some carbonate was still present in the oxides of erbium[1] and dysprosium[2] when ignited at 850° in platinum for several hours. This would tend to give high results in the oxide to chloride ratio. No attempt is made, however, to explain the reason of the higher results obtained in the present work over those obtained by the oxide to chloride ratio in the investigation of 1916.

Summary.

1. The chloride to silver ratio has been successfully tried on yttrium. The value 89.33 was obtained as the mean of 7 determinations.
2. The results obtained by the chloride to silver ratio seem more reliable than those obtained by the oxide to chloride ratio in a former investigation.

URBANA, ILLINOIS.

ON THE DETERMINATION OF BOILING POINTS OF SOLUTIONS.

BY F. G. COTTRELL.

Received February 17, 1919.

The method and apparatus here described were devised some 9 years ago and used with very satisfactory results in the undergraduate laboratory courses which the writer was then conducting in the University of California. It was the intention to subject them to a more rigorous test as regarded the ultimate accuracy attainable before publishing, but upon the author's leaving the University for the Government service a year later this program was interrupted.

A couple of years later Prof. E. W. Washburn kindly interested himself in the method and by adopting and further developing it incidentally to his own researches on the constitution of solutions, furnished the lacking data. At his request, the present account was prepared in March, 1913, to accompany his article and is now published in that connection[3] in the hope it will not only serve as a preface to his more important work on fundamental questions but also make the apparatus available in its simplest form for everyday use and be suggestive to others who may find opportunity to further develop and perfect it for still higher orders of accuracy.

The boiling-point determination for a pure liquid has always been one of the most accurate of temperature measurements, at the same time

---

[1] THIS JOURNAL, 40, 1618 (1918).

[2] *Ibid.*, 40, 609 (1918).

[3] Washburn and Read, THIS JOURNAL, 41, 729 (1919).

requiring only the simplest apparatus. Methods for determining the boiling point of a solution have on the contrary been most unsatisfactory and much complicated apparatus has been devised in attempted improvements. The fundamental difficulty lay in the fact that it was possible with the pure substance to place the thermometer above the boiling liquid and allow recondensation to give it a thin coating of liquid in contact with the vapor and thus guarantee ideal conditions for equilibrium. In the case of solutions, however, it does not seem to have occurred to anyone to produce these same mechanical conditions artificially, but instead the bulb of the thermometer has invariably been thrust under the mass of boiling liquid after which a vast amount of ingenuity has been expended in partially overcoming the obvious and very real difficulties of superheating within the liquid.

In this connection, it may not be out of place to call attention to the fact which seems often to have been overlooked that even if no real superheating occurred, the boiling point of most of our common solvents 3 or 4 cm. under the surface would still be approximately 0.1° higher than at the surface, solely because of the increase of pressure due to this column of liquid; consequently no matter how thoroughly equilibrium between vapor and liquid may be attained at any given point by the use of beads, platinum foil or even internal electric heating, what the thermometer really measures is merely the roughly averaged temperature throughout the liquid.

The novel feature of the method here described consists simply in placing the thermometer bulb in the gas phase as in the case of a pure liquid and making the boiling of the liquid itself pump some of the latter mechanically in a thin film over it, thus duplicating as far as possible the same relations of gas, liquid and thermometer which ordinarily obtain in boiling-point determinations of pure substances.

A simple and easily constructed form of apparatus for carrying this out is shown in Fig. 1*A*, in which A is a large test-tube; B a flat bottomed test tube or "specimen tube" in whose bottom two holes have been blown or ground. Through these holes pass loosely the Beckmann thermometer C, and the pump tube D, the thermometer as well as the tube B being entirely supported by the stopper J, while the tube D rests upon its shoulder K formed by simply softening the tube at this point in the blast lamp and pushing it slightly together from opposite ends. A moderate leak under the shoulder is of no consequence as an excess of liquid is pumped through B in any case. As an alternative to this shoulder a few turns of a stout, platinum wire helix fitting the tube snugly may be slipped over it at this point. This has the advantage of allowing adjustment of height at will and of permitting the removal of D from B at this end.

Another hole E is also provided in the side of B farthest from C to equilibrate gas pressure between A and B, and act as an overflow, thus defining the level of liquid in B. The water-jacket F secured by the rubber tubing G to the upper part of A forms with the latter the reflux condenser. Incidentally the manner of applying this tubing shown at G has the advantage of water cooling the tubing itself where it comes in contact with the hot glass.

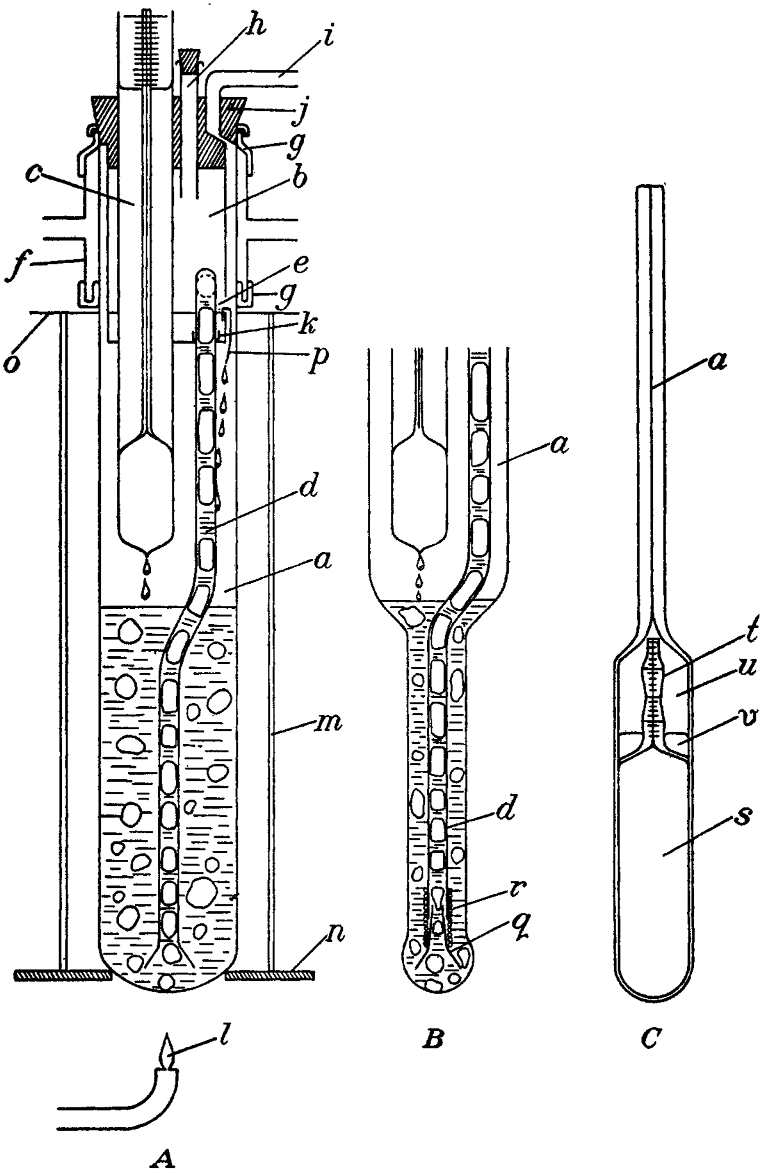

Fig. 1.

The tube H is for the introduction of the solute. The tube I connects through a number of radiating channels bored or burned through the stopper J with the annular condensing space between A and **B** and serves to equilibrate the pressure between the vapor space of the apparatus and the outside. When using hydroscopic solvents a drying tube is here attached and if it is desired to eliminate variations in barometric pressure or to work at other than atmospheric pressures, this is connected to a large volumed monostat as discussed below. Where these refinements are not necessary, a few grooves around the edge of the stopper may advantageously take the place of this tube I and these inner channels of the stopper. The liquid is boiled by direct application of a gas flame L of small diameter. The portion of the test-tube lying below the condenser may advantageously be protected from air currents by the wide glass tube M, resting on the asbestos plate N and closed above by the perforated mica plate O.

When the liquid in A is brought to boiling, part of the bubbles of vapor pass up the tube D carrying a broken stream of liquid with them into B exactly as in the operation of the well known air lift pumps. To prevent the squirting of liquid against the stopper J, the upper end of D is sealed and a hole blown in its side at this point. A short piece of small glass rod or piece of platinum wire P is hooked into the overflow hole E and allowed to extend slightly below the bottom of B to insure the overflow draining off at this point and not running back across the bottom to cause variations in the steady flow of that coming through the annular space between the thermometer and the slightly larger hole in B through which it passes.

The proper diameter of the pump tube D depends somewhat upon the solvent with which it is to be used. With liquids of small surface-tension such as ether and carbon disulfide, it may be as small as 2 mm., but for water, it works better at, say, 4 mm.

As the action of the pumping tube may be considered to be simply the balancing of the column of practically solid liquid in tube A against that of liquid and gas with correspondingly lower average density in tube D, it is evident that a considerable depth of liquid must be kept in A. In practice the length of D above the liquid should not be greater than the part immersed and preferably less. Where use of a large amount of solvent is objectionable, economy in this may be effected by constricting the bottom part of A as shown in Fig. 1*B*.

Figure 1*B* also shows the bell mouth of the tube D replaced by a separate funnel tube Q flexibly attached to D by a platinum wire helix R fitting snugly over both tubes, but allowing additional liquid to flow in between them. By adjusting the size and position of the outlet Q within **D** the efficiency and steadiness of the pumping may be somewhat increased over the form shown in Fig. 1*A*.

In either case the small flame L is so adjusted that enough of the bubbles of vapor pass up D to maintain a small overflow through E, the remainder of the bubbles bursting freely in A to supply the vapor phase about C.

The steadiness of the readings is notably enhanced by placing the whole apparatus in a small, glass case or hood about a foot square, as even with the above form of apparatus the effects of slight drafts are often very perceptible.

The thermometer must, of course, be frequently tapped; in fact some form of continuous mechanical tapper is almost indispensable for the best work. An ordinary electric bell with vibrator adjusted to as slow a stroke as possible and striking on a bit of cork cemented to the top of the thermometer serves very well. For refined measurements inconstancy of gas pressure feeding the heating flame must not be overlooked as a possible source of variation, although its effect is far less noticeable in this apparatus than in the older forms.

In practically all former types of apparatus which have come to the writer's attention, the residual errors, or at least uncertainties from superheating, were still so great or so highly dependent upon the personal skill and judgment of the operator that the other possible sources of error sank into comparative insignificance. In the apparatus here sketched, the dominance of this particular source of error is completely overcome; *i. e.*, it is now reduced to less importance than other variables to be expected. Comparison of the work of this apparatus with that of the best standard types in the hands of students have shown that at least 10 times the steadiness of reading can be expected with the new type. Variation in size of heating flame, drafts of air, height of liquid, etc., all have much less effect than in the older types.

In determinations with the standard forms of Beckmann apparatus (excluding possibly those of the Ladenburger type which require separate control of concentration) using ordinary care it is no uncommon thing to have the thermometer vary several hundredths of a degree in a very few minutes without apparent cause, while with the same degree of care, using the present apparatus, the variation is almost invariably less than as many thousandths. This naturally means that before it will be worth while carrying the line of improvements here developed any further, we must critically examine again the magnitude of all the remaining sources of error and direct our attack at the weakest points. The apparatus as here described is not therefore put forward as the form best adapted to investigations where ultimate precision is sought, but more as a simple type which will easily permit of bringing up everyday practice to an accuracy heretofore only attainable with elaborate precaution or long and special training. It is believed not to be overstating the case to say that this apparatus makes the boiling-point method for molecular weights as an everyday laboratory tool at least as accurate as the freezing-point method and considerably more convenient.

The next step should naturally be to further develop boiling-point methods for ultimate precision as they now open certain interesting possibilities not shared by cryoscopic methods.

Since, for the reasons mentioned at the outset, the writer sees no probability of his having opportunity to take up the further practical development of this work, the following points from the original program are set down in the hope that they may be at least suggestive to others undertaking the task.

The possible sources of error in the ordinary boiling-point method in somewhat the order of their probable seriousness may be stated as follows: 1. Superheating of the liquid and vapor. 2. Variations in atmospheric pressure during determinations. 3. Imperfections of the Beckmann thermometer; (*a*) uncertainty in effective length and average temperature of exposed thread; (*b*) mechanical friction in capillary thread; (*c*) mechanical and thermal hysteresis or lag of glass bulb; (*d*) effect of change in external pressure on bulb. 4. Changes in concentration due to amount of solvent in the vapor phase and as pure liquid returning from condenser. 5. Introduction of impurities from the stopper or through the air. 6. Radiation to or from thermometer bulb.

The improvements above described, it is believed have transferred superheating from the head to a position well down this list. The liquid in its long path through the pump tube, the chamber B, and down the thermometer stem continually in contact with vapor, has had a good opportunity of coming to temperature equilibrium before reaching the bulb of the thermometer. The vapor rising freely in A about the thermometer bulb may, however, still be somewhat superheated but the heat capacity of the amount that comes in contact with the liquid film is probably so much less than that of the latter as to produce errors of only a very low order. Even these might perhaps be further reduced in an analogous fashion, as for example by surrounding the thermometer bulb and stem below B with a concentric tubular bag of platinum wire screen leaving a few mm. of vapor space between and either dividing the present flow of liquid down the thermometer between the latter and the platinum screen or leaving this flow as it is and diverting the overflow from E down over the platinum. The platinum screen might even be replaced by a sheet platinum or glass tube with a discharge at the bottom so proportioned as to make the outflowing liquid suck through a steady current of vapor with it from the upper end, which would necessarily keep the same liquid and vapor in contact for establishment of equilibrium along the stem of the thermometer before reaching the bulb. Such envelopes would also guard against splashes of superheated liquid drops from A against the bulb, and if made of sheet platinum would incidentally protect the thermometer from possible errors due to radiation[1] if such indeed are at all appreciable.

The improvements already made and definitely tested have, however, brought the attainable accuracy up to a point where any further progress practically necessitates also improving the methods at present in use for measuring or controlling both pressure and temperature, *i. e.*, we are already down to the serious consideration of each thousandth of a degree, which with most solvents is equivalent to a pressure change of 0.03 mm. of mercury or less. If we stop to realize that this is about the change in pressure caused by the difference of 30 cm. in altitude above sea level and that a change of a quarter of a degree in the temperature of mercury in the barometer column would make an equivalent effect in its apparent reading, it becomes evident what a high order of accuracy in gas pressure we must deal with. This, however, depends upon a technique which has already been worked out and standardized by the physicist to a degree of accuracy amply sufficient for the needs of the present problems and it would be superfluous to discuss this phase of the work here.

In cases where this degree of accuracy is sought, it will probably be expedient to eliminate the natural variations of atmospheric pressure entirely by closing the boiling-point apparatus and the manometer system from the air of the room and connecting them instead to a large closed vessel in which the pressure is immediately under the observer's control.[2] This has the further advantage of permitting determinations of boiling-point elevation starting at different initial temperatures with the same solvent, thus opening the way to a direct study of the effect of temperature on the solute. What is perhaps even a more important advantage of this arrangement lies in the possibility of thus applying the principles and advantages of the ebullioscopic method to the direct isothermal measurement of vapor pressures by so varying the pressure as to bring the boiling point of the solution after each addition of solute back to that initially observed for the pure solvent. Not only are the data of these isothermal measurements usually better suited to accurate theoretical treatment, but the actual thermometric measurements are simplified to the mere reestablishment of a single fixed temperature, *i. e.*, we have a zero method as regards temperature and can correspondingly simplify our thermometer, thus eliminating the weakest points still outstanding from the older methods and apparatus as indicated in the outline of sources of error given above.

To illustrate this, compare the possibilities of the Beckmann thermometer

---

[1] H. C. Jones, *Am. Chem. J.*, 17, 581 (1897).

[2] Cf. also Washburn's method with two thermometers, THIS JOURNAL, 41, 731 (1919).

with those of a thermoscope, as it may be termed, such as shown in Fig. 1*C*. This is simply a very short-stemmed thermometer with a single graduation (or at most, a very few for aid in interpolating the pressure readings). The bulb S filled with mercury communicates through the capillary T with the evacuated overflow chamber U. By heating up the instrument to slightly above the temperature to which its zero point is to be adjusted, the excess of mercury is forced out of S collecting at V. When it is desired to readjust for a lower temperature, it is inverted to bring the top of T under the mercury V and S is cooled, V, if necessary, being gently warmed so that the vapor tension of its mercury may help drive the latter into S. The long stem W after facilitating evacuation and sealing permits of rigid support through the stopper and application of the mechanical tapper during observation in the usual way. Since when in use all the mercury of the instrument is within the vapor chamber, the errors of exposed thread disappear. These uncertainties arising from the variable and illy defined temperature of the "exposed thread" are often larger than would at first seem probable, especially as in many ordinary Beckmann thermometers the capillary below the scale will be found several times larger in the internal cross section than the graduated portion. The capillary of the new form being very short may be made of even smaller bore than the ordinary Beckmann without unduly increasing friction and may, if desired, be made distinctly conical or may be drawn down for a few mm. near its middle to provide for differences of sensitiveness depending upon which point is selected for the zero line to which temperature is to be held in any particular set of determinations. The simplicity of construction and elimination of the necessity for a long, uniform capillary easily permit of making the whole instrument of fused quartz thus practically eliminating the thermal and mechanical hystereses which are still quite appreciable even in the best Jena thermometer glass. The great mechanical rigidity of quartz will probably also reduce the effect of varying pressure on the volume of the bulb but this is a factor which can be experimentally determined. It will probably prove inappreciable for the ranges of pressure between pure solvent and solution usually encountered.

The form of condenser shown in Fig. 1 is not only more compact but reduces to a minimum the vapor space and amount of returning condensed liquid and also avoids to a great extent the danger of contamination of the solution from solvent condensing and acting upon the stopper. Even if ground joints and mercury seals replace cork or rubber stoppers, the prevention of condensation and retention of solvent in the joints is, of course, highly desirable.

In conclusion, I wish to express my thanks and obligations to Messrs. L. B. Shipley and R. Tavener, former students in my classes for their particularly effective work in connection with the development and testing of the above apparatus.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. PUBLICATION NO. 34.]

THE LAWS OF "CONCENTRATED" SOLUTIONS. VI. THE GENERAL BOILING-POINT LAW.

BY EDWARD W. WASHBURN AND JOHN W. READ.

Received February 17, 1919.

CONTENTS.—1. Purpose of the Investigation. 2. Purification of Materials. 3. The Boiling-Point Apparatus. 4. Experimental Procedure. 5. Analysis of the Solutions. 6. Calculation of the Results. 7. The Results. 8. The Boiling-Point Law for Ideal Solutions. 9. Boiling-Point Elevation and Barometric Pressure. 10. The Determination of Molecular Weights by the Boiling-Point Method.

1. Purpose of the Investigation.

This investigation was undertaken: (1) for the purpose of developing an apparatus and method for measuring the boiling-point elevation of solutions, based upon the determination of the composition of the liquid phase which at a definite determinable temperature and pressure is in equilibrium with the vapor phase; and (2) to secure an experimental demonstration of the validity of the theoretical boiling-point law for ideal solutions, for much higher concentrations than have previously been investigated. Benzene was chosen as the "solvent" to be employed and the two substances diphenyl and naphthalene were selected as the "solutes," since previous studies[1] of the freezing-point curves for these systems had demonstrated that they behaved as ideal solutions.

2. Purification of Materials.

(*a*) **Benzene.**—Kahlbaum's "thiophen frei" benzene was allowed to stand 4 weeks in contact with pure sulfuric acid with frequent shaking. The acid always acquired a distinctly brown coloration after this treatment, due probably to presence of thiophene in the benzene. The benzene thus treated was then distilled from pure sulfuric acid and collected for preservation in a distilling flask containing metallic calcium. When benzene was desired for use this distilling flask was directly connected to the condenser of the boiling-point apparatus (Fig. 1) and the benzene distilled directly into the apparatus. The benzene obtained in this manner had a melting point of 5.43° (corr.).

(*b*) **Diphenyl.**—Kahlbaum's diphenyl was first recrystallized twice from absolute alcohol and dried. It was then twice distilled from metallic calcium under a pressure of about 22 millimeters, the distillate coming over at approximately 145°. The product obtained in this manner had a constant melting point of 68.95° (corr.).

---

[1] Washburn and Read, *Proc. Nat. Acad. Sci.*, 1, 191 (1915).