BOILING-POINT CURVES OF MIXED LIQUIDS

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The teacher of an elementary course in physical chemistry is confronted with the problem of picking out the most profitable laboratory experiments to be performed in the somewhat limited time available. The sort of course the writer has in mind is taken by undergraduates majoring in chemistry or related subjects during the senior or junior year and consists of lectures accompanied by one or two laboratory periods a week sometimes for a year but often for only one semester. Due to holidays, mid-year examinations, etc., there are usually available only about twenty-five periods for actual work.

Care must be taken not to spend more time on any topic than it is worth and in planning the course the instructor must have this in mind. It is desirable, of course, to strike a suitable balance between strictly quantitative experiments, semi-quantitative experiments and possibly some that are purely qualitative. Those finally chosen may give practice in the manipulation of special apparatus, such as a Beckmann thermometer or a constant temperature bath; they may make use of nothing more complicated than flasks or test tubes in illustrating physico-chemical principles or both points may be involved—namely, the use of special apparatus and its application in studying fundamental principles. As an example of this latter, mention might be made of the use of the Cottrell-Washburn apparatus in determining molecular weights or the use of a potentiometer in measuring pH values. Other things being equal it seems obvious that it is best to make use of apparatus as simple and inexpensive as possible and to carry out experiments that are the least time-consuming for the results obtained.

One of the most interesting chapters of physical chemistry has to do with liquid-vapor systems—boiling points, vapor pressures, distillation, and the like. Unfortunately, while of much practical importance, the theoretical treatment of the behavior of mixtures of completely miscible liquids is in a rather unsatisfactory state.

If it should happen (as is usually not the case) that the liquids form an ideal solution and we know the values of the vapor pressures at a series of temperatures for each, we can calculate the composition of the liquid at its boiling point and also the composition of the vapor. This is discussed quite clearly by Hildebrand[1] for the case of the presumably ideal solution formed by carbon tetrachloride and stannic chloride. Plotting mol fraction (or mol %) against boiling point, two curves are obtained (Fig. 1), the lower one showing the composition of the liquid and the upper one the composition of the distillate. An inspection of these curves shows

[1] "Solubility" (Chap. IV), A. C. S. Monograph, Chem. Cat. Co., **1924.**

that the distillate will always be richer in the more volatile liquid than the residue and it is upon this well-known fact that all fractional distillation is based. If the boiling-point curve has once been found by experiment and we know the vapor pressure-temperature relationships of the components, it is possible to work back and determine if the solution is an ideal one.

Mixtures which are met with in practice may approximate ideal solutions in their behavior, but frequently show wide variations, the complete explanation of which is not well understood. In many cases the curve shows a minimum while in others there may be a maximum. Ninety-
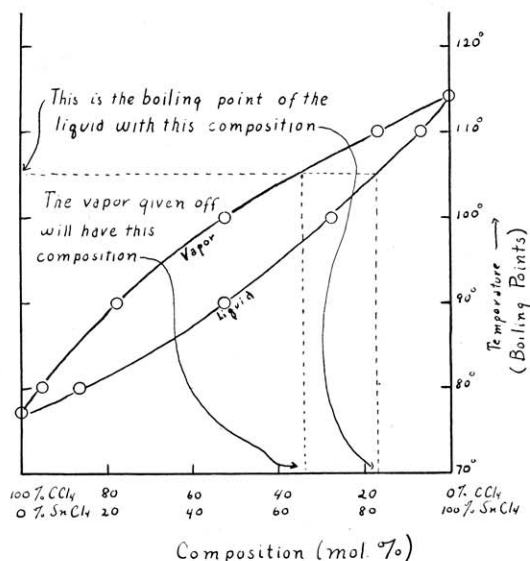

FIG. 1.—"IDEAL" BOILING POINT—COMPOSITION DIAGRAM

five per cent ethyl alcohol has a lower boiling temperature than the absolute and many other liquids behave in a similar way, although exact data is often lacking. The most familiar examples of the other extreme are mixtures of certain acids and water. The composition of the maximum boiling point hydrochloric acid has been studied by a number of investigators[2] and several laboratory manuals describe instructive experiments to show the gradual formation of this mixture when either dilute or concentrated hydrochloric acid is distilled. The distillate is at first richer in the more volatile component (water or gaseous hydrogen chloride) but as the distillation proceeds, the distillate and residue finally reach the same concentration after which no further change takes place.

[2] See, for example, Foulk and Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1220 (1923). Additional references are given in this article.

While it is in general impossible to predict what the behavior of an unknown pair of liquids will be[3] it is interesting as well as important to show experimentally the types which are possible. Certain manuals[4] give the experiment with hydrochloric acid outlined above and one to show a minimum boiling point. The ideal type is usually left to the course in organic chemistry where its relation to the others may not be emphasized. It would seem desirable to have all three types studied at the same time. Fairly pure materials are required for the work and the methods usually given require relatively large quantities. For classes of even moderate size it is rather time-consuming to prepare enough of the purified substances even if one follows the scheme[5] of having the student proceed from one distilling outfit to another. To follow the method of Davison and Van Klooster[6] special apparatus is required as is also the case with the more exact method given by Sherrill. The latter describes this as giving "reasonably good results when executed by careful students or with close supervision of the instructor but. . .not well suited for the use of large classes working under a limited time assignment."

It occurred to the writer that it might be possible to apply one of the boiling-point methods requiring only a small quantity of the liquid. These were developed for use with pure substances rather than mixtures and in one of them[7] the authors mention a change in boiling point taking place when successive determinations were made with impure liquids. The same error is, of course, inherent in the distillation methods also. Smith and Menzies "submerged bulblet" method, which is applicable to either liquids or solids, was tried out and, while it gave fairly good results, was dropped due to the difficulty in filling the bulbs without boiling away too much of the more volatile liquid before the actual determination was begun.

The method finally adopted is that of Siwoloboff[8] and consists in placing about 0.5 cc. of the liquid in a small fairly thin-walled tube which with a thermometer is immersed in a well-stirred bath of a suitable heating liquid. In the liquid under examination is placed a capillary tube about 2 cm. long and 1 mm. in diameter, open at the bottom and closed at the

[3] See, however, Appendix III of Robinson's "Elements of Fractional Distillation," McGraw-Hill, **1922.**

[4] For example, "Laboratory Experiments on Physico-Chemical Principles," Sherrill, Macmillan, **1923.**

"Laboratory Outlines in Physical Chemistry," Briggs, Ithaca, N. Y., **1926.**

"Laboratory Manual of Physical Chemistry," Davison and Van Klooster, John Wiley and Sons, Inc., **1922.**

[5] Sherrill, *loc. cit.*

[6] *Loc. cit.*

[7] Smith and Menzies, *J. Am. Chem. Soc.*, **32,** 897 (1910).

[8] *Ber.*, **19,** 795 (1886). See also O'Dowd and Perkin, *Trans. Faraday Soc.*, **4,** 95 (1908).

top. These are most easily made by drawing out tubing to a length of 6–8 cm., cutting the thin part out and melting it together in a small flame at a distance of 2 cm. from one end. The long part then serves as a handle. With the capillary in the liquid the bath is heated with constant stirring. Bubbles of air escape at first from the lower end of the capillary and when the boiling point of the liquid is slightly exceeded there will be a rapid stream of bubbles of vapor. The outer bath is then allowed to cool (constant stirring!) and when the bubbles cease and the liquid starts to suck back, the thermometer is read. This reading gives the temperature at which the total pressure inside the capillary is equal to the external pressure—in other words the boiling point. With a pure liquid the process may be repeated a number of times, but with mixtures this is inadvisable unless the superheating has been very slight. The reason for this is the change in composition of the mixture on boiling. It is often possible, however, to get two readings less than a degree apart.

The general set-up of the apparatus (Fig. 2) may be varied more or less. The writer prepared small tubes about 15 cm. long from ordinary 6 mm. "wash bottle" tubing, blowing a small bulb of fairly thin wall at one end to hold the liquid. One of these was fastened to the thermometer by rubber bands and immersed in the heating liquid (water or sulfuric acid) contained in a large Pyrex test tube. The bath contained a hand stirrer and was heated with a small burner. To make the
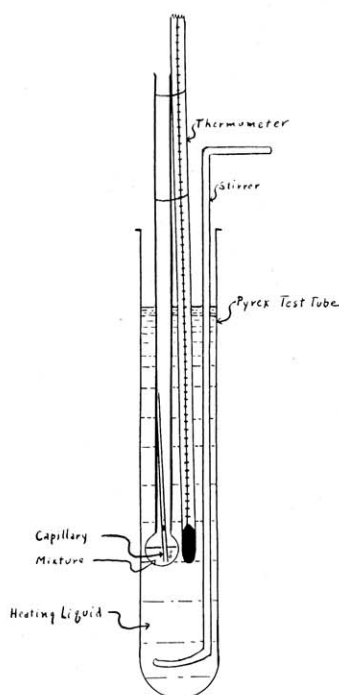

FIG. 2.—STUDENT BOILING-POINT APPARATUS

determination the liquid is added to the bulb tube and the capillary dropped in. The bath is then heated and allowed to cool as described above. After a determination is finished, the remaining liquid is shaken from the bulb and the latter placed in an oven where it will dry quite rapidly.

Efficient stirring is, of course, essential, particularly if such a small bath is used. A test tube was chosen merely to save time in making a determination as the liquid can be heated rapidly to the desired temperature. It was found to give satisfactory results with the mixtures used. To show a very small difference in boiling points, such as that between 95% and 100% ethyl alcohol (0.26°) a larger bath would be necessary.

The particular mixtures chosen for study were the following: benzene-toluene, ethyl alcohol-ethyl ether, chloroform-acetone, and methyl alcohol-chloroform. Starting with 5 cc. samples of one liquid (*e. g.*, benzene) mixtures containing 0, 20, 40, 60, 80, and 100 mol % of the other (toluene) were prepared. This requires only 25 cc. of benzene, less than 50 cc. of toluene and makes enough for about 10 students.

The mol % of toluene is given by the expression

$$\frac{(a)\ (0.86)\ (78)\ (100)}{(5)\ (92)\ (0.88) + (a)\ (78)\ (0.86)} \text{ or approximately } \frac{a}{6+a} \times 100$$

0.86 and 0.88 are the densities and 78 and 92 the molecular weights of the two liquids. "*a*" is the volume of toluene to be added to the 5 cc. of
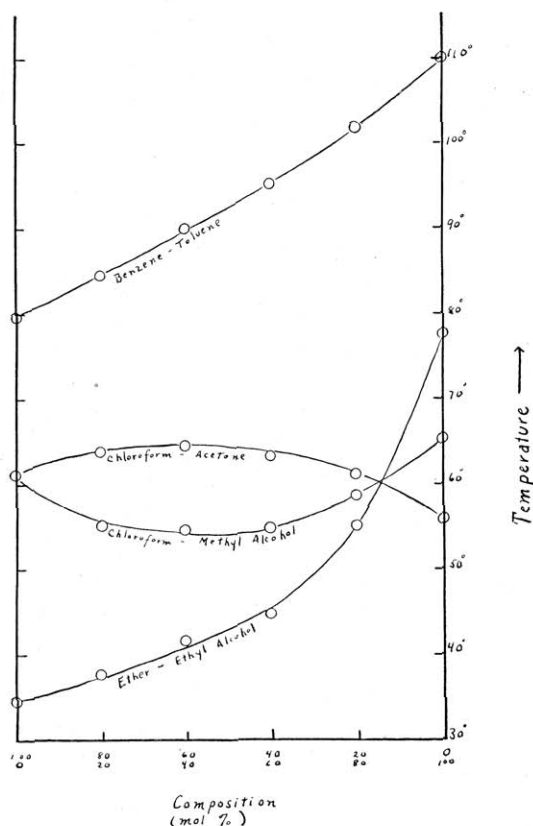

Fig. 3.—Characteristic Boiling-Point Curves

benzene. From this it is apparent that to make the 20% mixture, 1.5 cc. of toluene must be taken and 4, 9, and 24 cc., respectively, for the 40,

60, and 80% mixtures. The quantities of the other substances are determined by a similar method.

A class of eleven students was divided into four teams, each of which carried out the above calculations and prepared a set of mixtures for the use of all. Working individually each student then prepared at least some of the capillaries, assembled his own apparatus, and carried out the boiling-point determinations on two sets of liquids—twelve determinations in all. One laboratory period was found to be ample time for most students. The slower ones took somewhat longer.

Some experimental results are shown graphically in Figure 3. They agree well with the results obtained by distillation. Benzene-toluene and ethyl alcohol-ether are seen to approximate the ideal curve, while of the others, one shows a maximum and the other a minimum. It is evident that benzene and toluene or alcohol and ether could be separated by fractionation while the others would act like hydrochloric acid or an aqueous solution of ethyl alcohol. While no quantitative information is given regarding the composition of the distillate, it should theoretically be possible to separate the pure liquids from either the maximum or minimum boiling mixture. Practically this is possible only when there is a decided difference in their boiling points.

In addition to its simplicity and economy of materials several pedagogical features of this work may be mentioned. An experiment taking only one laboratory period illustrates the meaning of mol % and gives practice in making calculations regarding the same. It illustrates an important method of determining boiling points for both pure liquids and mixtures. It illustrates the relation between vapor pressure and external pressure when the liquid is at the boiling point and when superheated. It illustrates the difference between ideal solutions and others. It illustrates the behavior of the three types of binary mixtures of miscible liquids, at the same time giving data with which to prepare temperature-composition diagrams for such two-component systems.

Summary

The need is pointed out for a simple experiment illustrating the difference in behavior of the various types of mixed liquids from the viewpoint of the theory of distillation.

Such an experiment has been devised, use being made of the Siwoloboff boiling-point method, which is shown to give reasonably accurate results when applied to mixtures.

The pedagogical features of the proposed experiment are mentioned and a brief discussion of distillation in general is given.