

jectionable since CuSO_4 in the presence of KMnO_4 liberates all the Br from KBr .¹

The following tests show the reliability of the method:

TABLE V.

No.	Mg. Br.	Mg. CNS.	Mg. CN.	Mg. $\text{Fe}(\text{CN})_6^{4-}$.	Results.
1	0.0	250	Absolutely no color
2-5	1.0	250	Negative
6-7	1.5	250	Fair
8-16	2.0-3.0	250	Good
17-20	4.0-10.0	250	Strong color
21-25	2.0	500	Good
26	4.0	500	Excellent
27	1.0	...	500	...	Negative
28-30	2.0	...	500	...	Excellent
31	1.0	500	Negative
32-34	2.0	500	Excellent
35	2.0	200	150	150	Good
36	2.0	300	100	100	Good
37	2.0	100	200	200	Good
38	2.0	400	50	50	Good

The average time required for the completion of a test was 15 min.

Summary.

1. Attention has been called to the interference of thiocyanates, cyanides and ferrocyanides in the detection of bromides by the ordinary methods.
2. The interference offered by each of these substances has been determined.
3. A rapid method has been devised which is capable of detecting 2 mg. of bromine in the presence of 500 mg. of each of the interfering substances.
4. Numerous test experiments show the method to be trustworthy.

NEW YORK, N. Y.

ON FRACTIONAL DISTILLATION WITH REGULATED STILLHEADS.

[FIRST COMMUNICATION.]

CASES IN WHICH THE BOILING-POINT CURVE PASSES THROUGH A MAXIMUM OR A MINIMUM.

By M. A. ROSANOFF AND C. W. BACON.

Received December 31, 1914.

Section I. Introductory.

A recent joint communication² outlined a theory of fractional distillation based on a new relationship between the slopes of the total pressure curve and the relative compositions of the liquid mixtures and the corresponding vapors. In the mathematical treatment it was assumed that

¹ Prescott and Johnson's "Qualitative Analysis," p. 346.

² Rosanoff, Bacon, and Schulze, *THIS JOURNAL*, 36, 1993 (1914).

the process involved no reflux condensation whatever, that is, that the vapors escaped without any part of them undergoing liquefaction on the way and returning to the still. This is the simplest thinkable type of distillation, and, therefore, of unquestionable interest theoretically. As an actual means of separating the constituents of liquid mixtures, whether for scientific or industrial purposes, it is not used. For hundreds of years¹ chemists have purposely employed partial reflux condensation to produce as wide a difference between the distillate and the residue in the still as can be conveniently brought about in a single operation, and thus increase the efficiency of fractional distillation.

F. D. Brown² differentiates two processes by which partial reflux condensation is brought about in the various forms of apparatus in general use. To quote from Brown's own statement: "Though differing much in detail, they [the various apparatus] are all designed to subject the mixed vapors to one or both of two well-defined processes, which may be termed respectively *washing* and *cooling*. In the process of *washing*, the mixed vapors issuing from the still are made to pass through several layers of liquid obtained by their own partial condensation, they are thus *washed* by these successive layers, and it is supposed that the vapor of the liquid of highest boiling point is partially removed by this process, which results, therefore, in a distillate containing more of the liquid of lower boiling point than would be obtained by simple distillation In the process of *cooling*, the mixed vapors are partially condensed, either by allowing radiation to take place, or by passing them through a coil kept at a given temperature; the liquid of highest boiling point suffers, of course, the most condensation, and runs back into the still, a better distillate being thus obtained With a view to learning whether these two processes of *washing* and *cooling* really differ in their effects, I have made the experiments now to be described."

In the present state of knowledge no experiments would be necessary to prove that partial condensation by washing and partial condensation by cooling are different processes. Thus numberless cases might be specified in which a colder mixed vapor would be partially condensed by passing through a *hotter* mixed liquid. In such cases "cooling" is out of the question, yet partial condensation would take place, due to what Brown calls the "washing" of the vapor. Brown demonstrated the difference between washing and cooling by fractionating mixtures of carbon disulfide and benzene under suitably varied experimental conditions. The results are summed up by his statement (p. 56): "These distillations prove conclusively that the processes of *washing* and of *cooling* are not identical."

¹ See Young, "Fractional Distillation" (London, 1903), p. 154.

² Brown, *Trans. Chem. Soc.*, 37, 49, 50 and 56 (1880).

In the stillheads or columns generally used, the processes of washing and cooling are more or less intimately combined, for the ascending vapor is not only washed, but also cooled, by the reflux condensate. Nevertheless, it is certain that the main process by which the efficiency of such apparatus is determined, is washing; and a vast majority of the patented improvements consist in the introduction of ingenious "traps" in which the vapors are thoroughly washed in pools of the reflux condensate. Where cooling devices proper are employed at all, they play a decidedly subordinate role.

That distillation depending principally, almost exclusively on *cooling*, may have important possibilities of its own, has long been suspected, and attempts have been made to rationalize fractional distillation by the use of a non-washing stillhead kept at a constant temperature. The first to employ such a stillhead practically (in the fractionation of petroleum, coal tar, and other mixtures) was C. M. Warren, of Boston, who believed that the method promised results of great value.¹ The first to investigate the working of a regulated stillhead systematically was F. D. Brown,² who improved Warren's stillhead and made extensive observations on the effect of cooling a saturated binary vapor to a given constant temperature. Brown sums up his results in the following important statement: "*In distillation with a stillhead maintained at a constant temperature the composition of the distillate is constant, and is identical with that of the vapour evolved by a mixture whose boiling point equals the temperature of the stillhead.*"

An attempt to utilize the regulated stillhead was also made by Lord Rayleigh.³ On the other hand, Carveth⁴ experimented with a combination of the washing and the cooling processes by filling a tin pipe condenser with intercepts and maintaining the pipe at a constant temperature.⁵ Finally, Sydney Young and Thomas⁶ obtained valuable results by connecting in series a dephlegmator (washing column) and a regulated temperature stillhead, as is frequently done in the industries. But these studies have thrown no new light upon the regulated stillhead theoretically.

In course of the past five years, the working of the regulated stillhead has been fully reinvestigated by one of us with several collaborators. It was found that Brown's law requires serious modification, and that only in its true form can it serve as the basis of a rational, almost ideal, process of fractional distillation, such as the previous investigators have searched for in vain. The modified law, and the process of distillation based upon

¹ Warren, "Memoirs of the American Academy," New Series, 9, 121 (1864), and *Ann.*, 4 (*Supplementband*), 51 (1865).

² Brown, *J. Chem. Soc.*, 37, 49 (1880), and especially *Ibid.*, 39, 517 (1881).

³ Lord Rayleigh, *Phil. Mag.*, [VI] 4, 535 (1902).

⁴ Carveth, *J. Phys. Chem.*, 6, 253 (1902).

⁵ An arrangement similar in principle had already been employed by Perrier.

⁶ Young and Thomas, *J. Chem. Soc.*, 71, 440 (1897).

it, will be discussed in a series of communications to which the present paper may serve as an introduction.

The main object of this present communication is to point out how the regulated stillhead should be expected to function in those numerous cases in which the boiling-point curve passes through a maximum or a minimum; in which, therefore, there may be *two* mixtures boiling at one and the same temperature: in the words of Brown's law, *two* mixtures "whose boiling point equals the temperature of the stillhead."

Section II. Brown's Law in the Cases under Consideration.

Let us assume for the present that Brown's law is true in its original form, as expressed above. And considering a simple case, like that of carbon disulfide and carbon tetrachloride, where the boiling points of all mixtures are intermediate between those of the isolated components, let the temperature of a regulated stillhead be made equal to the boiling point of the more volatile component. Then, by the original Brown law, no matter what the composition of the mixture boiling in the still, the escaping vapor should consist almost entirely of that component.

On the other hand, suppose we are dealing with a pair of substances whose boiling-point curve passes through a minimum. And, while any given mixture of the two is boiling in the still, let the stillhead, originally cold, be heated to the boiling temperature of the most volatile mixture (*i. e.*, the one having the minimum boiling point). The vapor from such a mixture has the same composition as the mixture itself, and, therefore, if Brown's law is correct, that should also be the composition of the escaping vapor, no matter what mixture is at any given instant boiling in the still. But next let us still further raise the temperature of the stillhead, and fix it at the boiling point of the more volatile component. Now the stillhead temperature is really equal to the boiling point of two different liquids: the more volatile component pure and a certain mixture. The vapors given off by the two liquids are, of course, different: in one case a single substance, in the other a mixture. Which of the two vapors will be escaping from the stillhead?

Brown's experiments with the pairs carbon disulfide-alcohol and carbon disulfide-ethyl acetate taught him that it is the *mixed* vapor that is produced invariably.¹ In the case of carbon disulfide and alcohol, keeping the stillhead at the boiling point of pure carbon disulfide, Brown obtained a uniform distillate containing about 87.3% of carbon disulfide. In the case of carbon disulfide and ethyl acetate, with the stillhead at the boiling point of pure carbon disulfide, he obtained a uniform distillate containing about 72.6% of carbon disulfide.

Brown says nothing as to the effect of keeping the stillhead at temperatures *intermediate* between the boiling point of the most volatile mixture

¹ Brown, *J. Chem. Soc.*, 39, 529 (1881).

and that of the isolated more volatile component—temperatures at which two different mixed vapors should be expected according to his law. Nor does he refer at all to those cases in which the boiling-point curve passes through a maximum, and in which, therefore, two different mixed vapors might be expected at any stillhead temperature intermediate between the boiling point of the least volatile mixture and that of the isolated less volatile component. He evidently felt that an experimental elucidation of the subject would be of value; for he expresses the hope of returning to the problem in a future communication. This he never did. Nor is the subject at all mentioned in the more recent monograph literature on heterogeneous equilibria or fractional distillation.

At the present time, especially if we employ the form of diagram (see Fig. 1) in which both the boiling-point curve and the dew curve (vapor-composition curve) are plotted with respect to abscissae representing the composition of liquid mixtures, the question as to which of the two possible

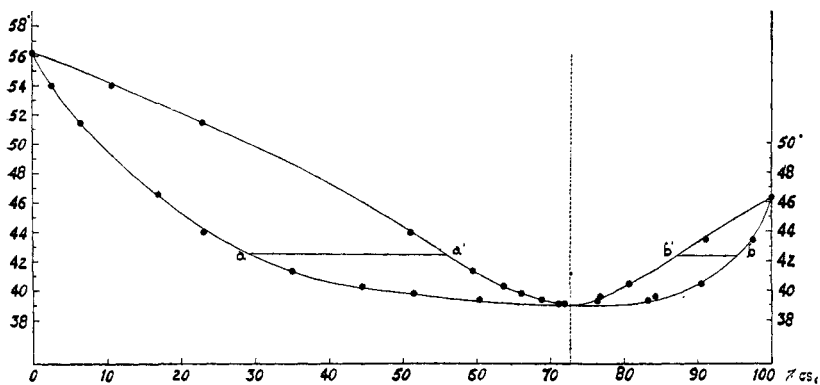


Fig. 1.

mixed vapors should be expected in accordance with Brown's law, presents no real difficulty. Since distillation with a regulated stillhead cannot affect the composition of a mixture of maximum or minimum boiling point, it is almost obvious that in all cases of the type in question the diagram should be divided into two parts by a straight line perpendicular to the composition-axis and passing through the maximum, or the minimum, of the boiling-point curve, and each part should be considered as an independent diagram by itself. The composition of the resulting vapor would then appear to depend upon whether the composition of the liquid in the still is comprised in the right-hand or the left-hand part of the diagram. For example, in our Fig. 1, which pictures the case of carbon disulfide and acetone, let the stillhead temperature be at the height of the lines aa' , $b'b$. Then it is obvious in the first place that the stillhead will have no effect at all if the liquid in the still corresponds to any point

lying between a and b ; for any such liquid would boil below the temperature of the stillhead, and a hot stillhead cannot condense a cold vapor. But further we should expect that if the composition of the liquid boiling in the still is represented by a point lying to the left of a , the stillhead will deliver a uniform vapor of the composition a' ; if the liquid boiling in the still has a composition lying to the right of b , then the stillhead, *at the same temperature as before*, will yield a uniform vapor of the composition b' .

Trustworthy as these theoretical expectations appear, it nevertheless seemed desirable to carry out a series of experiments, to obtain a practical demonstration of their correctness. The results are reproduced below.

Section III. The Apparatus.

Our apparatus (Fig. 2) was similar in principle to the one employed, in a former study, by Rosanoff, Lamb, and Breithut.¹ It consisted of a large double-walled cylinder of tinned copper, without top or bottom, fastened within a cylindrical tank full of water. The closed annular space between the walls of the copper cylinder was connected with the still below by a brass pipe passing through the bottom of the outside tank, near the rim. A similar pipe, serving as a delivery tube, and passing through the side of the outside tank, near the top, connected the annular space with a condenser. The lower edge of the double-walled cylinder was in a plane slanting downward toward the still, to permit any condensate within the annular space to flow back without forming a pool at the bottom. The water in which the double-walled cylinder was immersed was kept in vigorous motion by a pair of horizontally revolving fans whose diameter was little less than the internal diameter of the copper cylinder, and which acted with the effect of an Archimedes screw. In this manner uniform temperature was secured throughout the tank, an electric regulator maintaining the temperature of the bath constant within $\pm 0.02^\circ$. The greatest height of the double-walled cylinder was 76 cm.; its smallest height was 70 cm.; the mean diameter was 25 cm.; and the annular space between the walls was 0.95 cm. wide. It may be positively stated that a stillhead of this form is greatly superior to the coil condensers used by previous investigators.

The substances used were purified, and our consecutive distillates were analyzed, in the manner described in a former communication.²

And first of all, the efficiency of our regulated stillhead was subjected to test in the case of carbon disulfide-carbon tetrachloride, which is not complicated by either a maximum or a minimum in the boiling-point curve. A mixture containing slightly over 26% of carbon disulfide was introduced

¹ Rosanoff, Lamb, and Breithut, *THIS JOURNAL*, 31, 454 (1909); *Z. physik. Chem.*, 66, 356 (1909).

² Rosanoff, Bacon and White, *THIS JOURNAL*, 36, 1803 (1914).

into the still, and the temperature of the stillhead was maintained constant at $59.82^{\circ} \pm 0.02^{\circ}$. Theoretically, *i. e.*, according to Brown's law, the

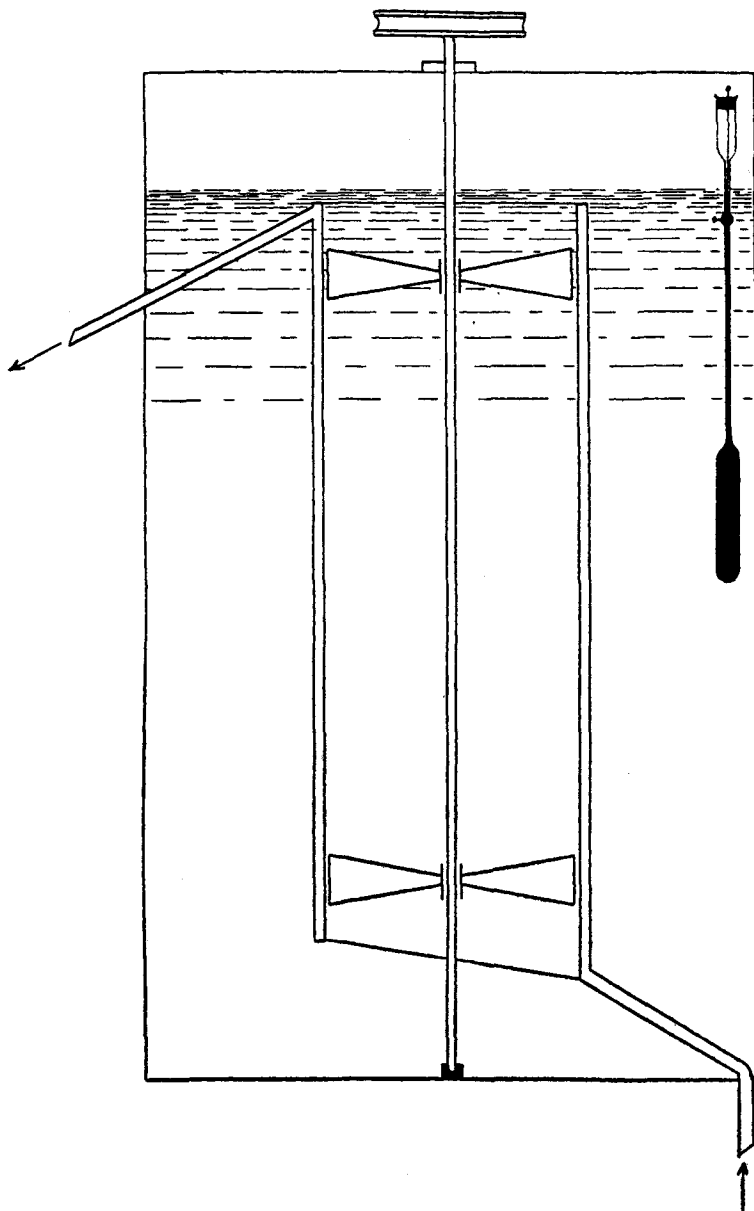


Fig. 2.

distillates were expected to contain 60.8% CS_2 . Seven consecutive fractions were actually found to contain 60.8, 60.7, 60.7, 60.5, 60.7, 60.5,

60.7, 60.7, and 60.7% of carbon disulfide, respectively. The reliability of the apparatus was thus demonstrated.

Section IV. Results.

Case 1. Carbon Disulfide and Acetone.—In this case the boiling-point curve passes through a *minimum*.¹

In a first experiment a mixture containing only a small percentage of acetone was introduced into the still. The temperature of the stillhead was kept constant at $40.02^\circ \pm 0.01^\circ$. Seven consecutive fractions of the distillate contained: 75.2, 75.2, 75.1, 75.1, 75.1, 75.1, and 75.1 molar per cent. of carbon disulfide, respectively.

In a second experiment, we introduced into the still a mixture containing only 29% CS_2 (a composition lying within the left-hand part of the diagram). The temperature of the stillhead was again kept at $40.02^\circ \pm 0.01^\circ$. Yet this time fifteen consecutive fractions of the distillate were found to contain, respectively, 55.4, 55.3, 55.4, 55.4, 55.4, 55.3, 55.4, 55.4, 55.4, 55.4, 55.4, 55.2, 55.4, 55.3, and 55.3 molar per cent. of carbon disulfide.

Case 2. Ethyl Iodide and Ethyl Acetate.—In this case again the boiling point passes through a *minimum*.

In a first experiment a mixture containing only a small percentage of ethyl acetate was introduced into the still, and the temperature of the stillhead was fixed at $71.22^\circ \pm 0.02^\circ$. Four consecutive fractions of the distillate contained 89.9, 89.3, 89.2, and 89.1 molar per cent. of ethyl iodide, respectively.

In a second experiment a mixture of roughly equal parts of the two components was introduced into the still. The temperature of the stillhead was the same as in the first experiment. But this time four consecutive fractions of the distillate were found to contain, respectively, 49.4, 49.3, 48.9, and 48.9 molar per cent. of ethyl iodide. In this case the uniformity of the distillates was not as perfect as before. Nevertheless the two experiments illustrate the question involved sufficiently well.

Case 3. Chloroform and Acetone.—In this case the boiling-point curve passes through a *maximum*.

Two experiments again were performed. In the first, a mixture containing roughly 6% of acetone (a composition lying to the right of the maximum) was introduced into the still. The temperature of the stillhead was fixed at $62.02^\circ \pm 0.01^\circ$. Six consecutive fractions of the distillate were found to contain, respectively, 92.4, 92.4, 92.4, 92.5, 92.3, and 92.3 molar per cent. of chloroform.

In the second experiment the mixture originally introduced into the still contained something over 40% CHCl_3 (a composition lying to the left of the maximum). The temperature of the stillhead was again maintained

¹ This case is illustrated by Fig. 1, in which, however, the abscissae represent *weight per cents*.

at 62°. This time, however, six fractions of the distillate were found to contain, respectively, 30.8, 30.8, 30.9, 30.8, 30.9, and 30.9 molar per cent. of chloroform.

As already stated, changes in Brown's law itself will be proposed in communications to follow. Here we would again express our thanks to the Rumford Committee of the American Academy for a grant in aid of our researches.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. NO. 19.]

THE MEASUREMENT OF VAPOR PRESSURE LOWERING BY THE AIR SATURATION METHOD.¹

BY EDWARD W. WASHBURN AND EDWARD O. HEUSE.

Received December 16, 1914.

I. Introduction.

The importance of having a reasonably accurate method for investigating the molecular character of aqueous solutions over a considerable concentration range and at a constant temperature led to an attempt to improve the vapor pressure method so that it might be employed for this purpose. The experimental work in connection with the problem was begun in 1909 by Mr. H. B. Gordon. He was able to show that the method could be made to give the desired accuracy and in addition to building and testing the apparatus he also measured the vapor pressure lowering of several aqueous solutions. The results of his work together with a comparative discussion of previous investigations in the same field were printed and distributed in 1912 in the form of a Doctor's Thesis,² but were not formally published. In September 1912 the experimental work was taken up by Mr. E. O. Heuse and is being carried on by him at the present time. A description of the theory of the method together with some of the results obtained was presented at the Chicago meeting of the American Physical Society, November, 1914, and published in abstract in the *Physical Review*.

The appearance of a recent paper by Frazer and Lovelace³ on an improved *static* apparatus for measuring vapor pressure lowering seems to make it worth while to publish a description of our apparatus and method at this time, for purposes of comparison, postponing until later

¹ This paper is an abstract of a thesis presented to the Graduate Faculty of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1914.

² H. B. Gordon, Univ. of Ill. Theses, 1912.

³ Frazer and Lovelace, THIS JOURNAL, 26, 2439 (1914).