Temperature. Degrees.	Vapor pressure. Mm.	Temperature. Degrees.	Vapor pressure. Mm.
50	2.154	75	11.21
55	3.069	80	15.09
60	4.285	85	20.21
65	5.962	90	26.78
70	8.196	95	35.24

2. These results together with those obtained by Baxter, Hickey and Holmes between 0° and 50° may be expressed very closely by either of the two formulas

$$\log p = -106.3930 + 46.611 \log T - 0.031677\, T$$
$$\log p = 9.7522 - 2863.54/(T - 19).$$

3. The average molecular heat of sublimation of iodine at these temperatures is calculated to be 14.7 kilogram calories or 61.6 kilojoules.

A portion of the apparatus and materials used were provided through the generous assistance of the Carnegie Institution of Washington.

CAMBRIDGE, MASS.

ON FRACTIONAL DISTILLATION WITH REGULATED STILLHEADS.

[SECOND COMMUNICATION.]

DISTILLATION OF TERNARY MIXTURES.

BY M. A. ROSANOFF, JOHN F. W. SCHULZE AND R. A. DUNPHY.

Received January 18, 1915.

On the basis of an interesting series of experiments, F. D. Brown[1] describes the distillation of mixtures through a regulated stillhead in terms of the following law, or rule: "In distillations with a stillhead maintained at a constant temperature, *the composition of the distillate is constant*, and is identical with that of the vapor evolved by a mixture whose boiling point equals the temperature of the stillhead." Sometime ago this rule was examined by Rosanoff and Bacon in connection with mixtures whose boiling-point curve passes through a maximum or a minimum,[2] and it was shown that in a case of this type two different distillates may be expected at certain temperatures, depending upon the composition of the liquid originally introduced into the still; but that, whichever of the two possible distillates is produced, the distillation proceeds in conformity with Brown's law, in as far as the composition of the distillate is constant, and is identical with that of the vapor evolved by a mixture whose boiling point equals the temperature of the stillhead.

But both Brown's experiments and those just mentioned dealt exclusively

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[1] Brown, *J. Chem. Soc.*, **37**, 59 (1880); *Ibid.*, **39**, 521 (1881).

[2] Rosanoff and Bacon, first communication of the present series, THIS JOURNAL, **37**, 301 (1915).

with binary mixtures. And yet the possibilities[1] that the regulated stillhead may have, expecially in the industries, would mostly be in connection, not with simple binary mixtures, but with mixtures of three components or more. It seemed highly desirable, therefore, to investigate the working of the regulated stillhead in the case of a typical set of ternary mixtures, with a view to discovering the general principle involved.

The three substances chosen for the experiments were toluene, carbon tetrachloride, and ethylene bromide: their binary boiling-point curves and their ternary boiling-point surface show, as expected, neither maximum nor minimum, and therefore the case may be considered as of the simpler type. Further, the substances differ considerably in their physical properties, and thus we could expect to be able to analyze our distillates accurately by a rapid physico-chemical method.

And first the analytical method was worked out by one of us,[2] the work including a determination of the boiling-point surface. Then, in order to know what vapors might be expected to issue from the stillhead uncondensed, we determined[3] the composition of the vapors evolved by various mixtures boiling at the temperatures: 83°, 91°, 99°, 107°, and 115°. After these preliminary steps had been taken, we were able to attack our main problem.

The powerful metallic stillhead which had been employed in the study of binary mixtures with maxima and minima in the boiling-point curves[4] was again made use of in the present investigation. The liquids—toluene, carbon tetrachloride, and ethylene bromide—were the identical ones that Schulze had used in working out the analytical method, and a re-statement of the method of their purification is unnecessary. Each experiment consisted in fixing the temperature of the stillhead at one of the points for which we had previously determined the ternary partial pressures (composition of the vapors); then introducing into the still a mixture boiling at a somewhat higher temperature than that of the stillhead, and collecting for analysis a number of fractions sufficient to indicate the character of the distillate at every instant, and its variation—if any. Then a new run would be made, with the stillhead at the same temperature as before, but this time with a different mixture initially in the still. Thus two runs were made with the stillhead kept at 83°, and three runs at each of the remaining four temperatures. The results of the fourteen runs are reproduced in the tables below. In addition, six further runs were made

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[1] Warren, *Memoirs of the American Academy*, New Series, **9**, 121 (1864), and Liebig's *Ann.*, **4** (Supplementband), 51 (1865); Brown, *J. Chem. Soc.*, **37**, 59 (1880); Young and Thomas, *Ibid.*, **71**, 440 (1897); Lord Rayleigh, *Phil. Mag.*, [6] **4**, 535 (1902); and also Young, "Fractional Distillation" (London, **1903**), p. 189.

[2] Schulze, THIS JOURNAL, **36**, 498 (1914).

[3] Rosanoff, Schulze and Dunphy, *Ibid.*, **36**, 2480 (1914).

[4] See Rosanoff and Bacon, *Loc. cit.*, Fig. 2.

by way of a check on results that appeared somewhat doubtful; but as these additional results were practically identical with those obtained at first, their reproduction here would be superfluous.

Throughout the experiments it was important to maintain the same atmospheric pressure, *viz.*, 749.0 mm., under which the boiling points of the various ternary mixtures had been determined by Schulze;[1] for under a changed atmospheric pressure the set of liquids boiling at the temperature of the stillhead would have been different from the set previously employed in studying the composition of the ternary vapors, and consequently we should not have known what vapors to expect. The required external pressure was established, and maintained constant, with the aid of a 100 liter manostat tank connected by sufficiently wide tubing with our receiver.

The volume of liquid mixture introduced into the still amounted each time to about 400 cc. The volume of each fraction of distillate was from 15 to 20 cc., and the distillates were "analyzed" by determining their refractive indices and their densities, both at 25°. All percentages given below are by weight.

The theoretical question before us was, whether Brown's law is applicable to mixtures of more than two substances. That in part the law must hold true whatever the number of components, might be confidently expected: namely, the composition of the vapor issuing from the stillhead at any instant must quite generally be "identical with that of the vapor evolved by a liquid whose boiling point equals the temperature of the stillhead." For what issues from the stillhead, is a vapor that is saturated at the temperature of the stillhead, and therefore one that would be evolved by a liquid boiling at the temperature of the stillhead. The question whether the issuing vapor will have a constant composition is more involved. In the case of binary mixtures with neither maximum nor minimum in the boiling-point curve, there is only one mixture boiling at the temperature of the stillhead, and therefore the escaping vapor can also have but one composition. Binary mixtures with a maximum or a minimum in the boiling-point curve must still follow Brown's law and yield a vapor of constant composition, although here, as stated before, one of two different vapors may be expected at certain stillhead temperatures. The addition of a third component introduces a new degree of freedom: a given set of three substances may be mixed in an infinity of proportions to give mixtures boiling at one and the same temperature, but each mixture will evolve its own vapor. While, therefore, with the stillhead kept at the common boiling temperature of these mixtures, the escaping saturated vapor will at every instant be identical with that evolved by one of the infinity of mixtures in question, its composition will by no

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[1] Schulze, *Loc. cit.*

means be determined by the stillhead temperature alone, as in the case of binary mixtures. The composition of the vapor must certainly depend also on that of the mixture originally introduced into the still. But given a certain definite mixture in the still to start with, it would not be easy to foretell whether during a single distillation (the distillation of that particular mixture) the issuing vapor would have a constant composition or not.

TABLE I.

STILLHEAD, 83°. ORIGINAL MIXTURE: 67.8% CCl_4 + 16.4% $C_6H_5CH_3$ + 15.8% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
91.4	5.5	3.1
91.4	5.4	3.2
91.4	5.4	3.2
91.5	5.5	3.0
91.5	5.5	3.0
91.5	5.5	3.0
91.5	5.5	3.0
91.4	5.6	3.0
91.4	5.6	3.0
91.4	5.6	3.0
91.4	5.5	3.1
91.4	5.5	3.1
91.4	5.8	2.8
91.4	5.7	2.9

TABLE II.

STILLHEAD, 83°. ORIGINAL MIXTURE: 58.4% CCl_4 + 7.7% $C_6H_5CH_3$ + 33.9% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$
90.9	2.7	6.4
90.8	2.7	6.5
91.0	2.7	6.3
91.0	2.7	6.3
91.0	2.7	6.3
90.6	2.9	6.5
91.1	2.8	6.1
91.1	2.8	6.1
91.1	3.1	5.8
91.1	3.1	5.8
91.0	3.2	5.8
91.0	3.1	5.9
90.8	3.2	6.0

TABLE III.

STILLHEAD, 91°. ORIGINAL MIXTURE: 48.3% CCl_4 + 46.0% $C_6H_5CH_3$ + 5.7% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
78.0	20.9	1.1
78.0	20.9	1.1
78.0	20.9	1.1
78.0	21.1	0.9
78.0	21.2	0.8
78.0	21.1	0.9
78.0	21.2	0.8
78.0	21.4	0.6
77.8	21.4	0.8
77.7	21.8	0.5

TABLE IV.

STILLHEAD, 91°. ORIGINAL MIXTURE: 47.0% CCl_4 + 25.0% $C_6H_5CH_3$ + 28.0% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
78.7	13.3	8.0
78.7	13.5	7.8
78.7	13.6	7.7
78.7	13.7	7.6
78.5	14.0	7.5
78.7	14.0	7.3
78.7	14.2	7.1
78.7	14.3	7.0
78.7	14.6	6.7
78.5	14.9	6.6

TABLE V.

STILLHEAD, 91°. ORIGINAL MIXTURE: 45.0% CCl_4 + 10.2% $C_6H_5CH_3$ + 44.8% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
79.0	5.8	15.2
79.0	5.9	15.1
79.0	6.1	14.9
79.0	6.1	14.9
78.9	6.3	14.8
79.0	6.4	14.6
78.9	6.6	14.5
79.0	6.6	14.4
79.0	6.9	14.1
79.0	7.0	14.0
79.0	7.3	13.7
79.0	7.5	13.5

TABLE VI.

STILLHEAD, 90°. ORIGINAL MIXTURE: 28.4% CCl_4 + 54.8% $C_6H_5CH_3$ + 16.8% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
58.2	35.8	6.0
57.9	36.3	5.8
57.8	36.7	5.5
57.8	36.8	5.4
57.7	37.1	5.2
57.6	37.3	5.1
57.6	37.4	5.0
57.4	37.8	4.8
57.2	38.4	4.4

TABLE VII.

STILLHEAD, 99°. ORIGINAL MIXTURE: 27.2% CCl_4 + 29.3% $C_6H_5CH_3$ + 43.5% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_4CH_3$.	%$C_2H_4Br_2$.
62.6	21.0	16.4
62.1	21.6	16.3
62.0	22.0	16.0
61.8	22.4	15.8
61.9	22.8	15.3
61.8	23.7	14.5
61.5	24.3	14.2
61.6	24.7	13.7

TABLE VIII.

STILLHEAD, 99°. ORIGINAL MIXTURE: 25.0% CCl_4 + 13.9% $C_6H_5CH_3$ + 61.1% $C_2H_4Br_2$.

Composition of distillates.

%CCl_2.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
65.2	10.9	23.9
64.3	11.5	24.2
64.0	12.0	24.0
63.7	12.3	24.0
63.9	12.8	23.3
63.6	13.5	22.9
63.9	14.4	21.7
63.7	15.6	20.7

TABLE IX.

STILLHEAD, 107°. ORIGINAL MIXTURE: 10.0% CCl_4 + 70.0% $C_6H_5CH_3$ + 20.0% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
26.4	63.8	9.8
25.8	64.8	9.4
25.4	65.7	8.9
25.2	66.4	8.4
25.1	66.7	8.2
24.8	67.4	7.8
24.6	68.0	7.4
24.3	68.9	6.8

TABLE X.

STILLHEAD, 107°. ORIGINAL MIXTURE: 14.3% CCl_4 + 34.5% $C_6H_5CH_3$ + 51.2% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_8H_4Br_2$.
38.8	33.6	27.6
38.4	34.5	27.1
38.0	35.4	26.6
37.7	36.2	26.1
37.2	37.3	25.5
36.8	38.5	74.7
36.2	40.2	23.6
35.6	42.1	22.3

TABLE XI.

STILLHEAD, 107°. ORIGINAL MIXTURE: 15.0% CCl_4 + 15.7% $C_6H_5CH_3$ + 69.3% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
45.1	16.9	38.0
45.3	17.3	37.4
45.2	17.8	37.0
44.8	18.7	36.5
44.5	19.6	35.9
44.0	20.7	35.3
43.3	22.4	34.3
42.0	24.2	33.8

TABLE XII.

STILLHEAD, 115°. ORIGINAL MIXTURE: 2.0% CCl_4 + 32.9% $C_6H_5CH_3$ + 64.1% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
8.1	47.6	44.3
7.7	48.3	44.0
7.2	49.2	43.6
6.6	50.6	42.8
6.0	51.7	42.3
5.2	53.1	41.7
4.5	53.6	40.9

TABLE XIII.

STILLHEAD, 115°. ORIGINAL MIXTURE: 4.8% CCl_4 + 26.8% $C_6H_5CH_3$ + 68.4% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
16.8	35.0	48.2
16.2	36.0	47.8
15.6	37.0	47.4
14.8	38.3	46.9
14.0	39.6	46.4
13.1	41.3	45.6

TABLE XIV.

STILLHEAD, 115°. ORIGINAL MIXTURE: 8.2% CCl_4 + 9.2% $C_6H_5CH_3$ + 82.6% $C_2H_4Br_2$.

Composition of distillates.

%CCl_4.	%$C_6H_5CH_3$.	%$C_2H_4Br_2$.
30.0	12.9	57.1
29.5	13.7	56.8
29.1	14.3	56.6
28.4	15.3	56.3
27.7	16.4	55.9
26.4	18.3	55.3

It appeared plausible to expect that a vapor of constant composition would be produced only in those cases where the ratio of the amounts of the two less volatile components is the same in the vapors as in the liquids in equilibrium with them; but that usually, even during a single distillation, the vapors issuing from the regulated stillhead would not be uniform. We thought it best, however, to submit the question to direct experiment, and our results are tabulated above.

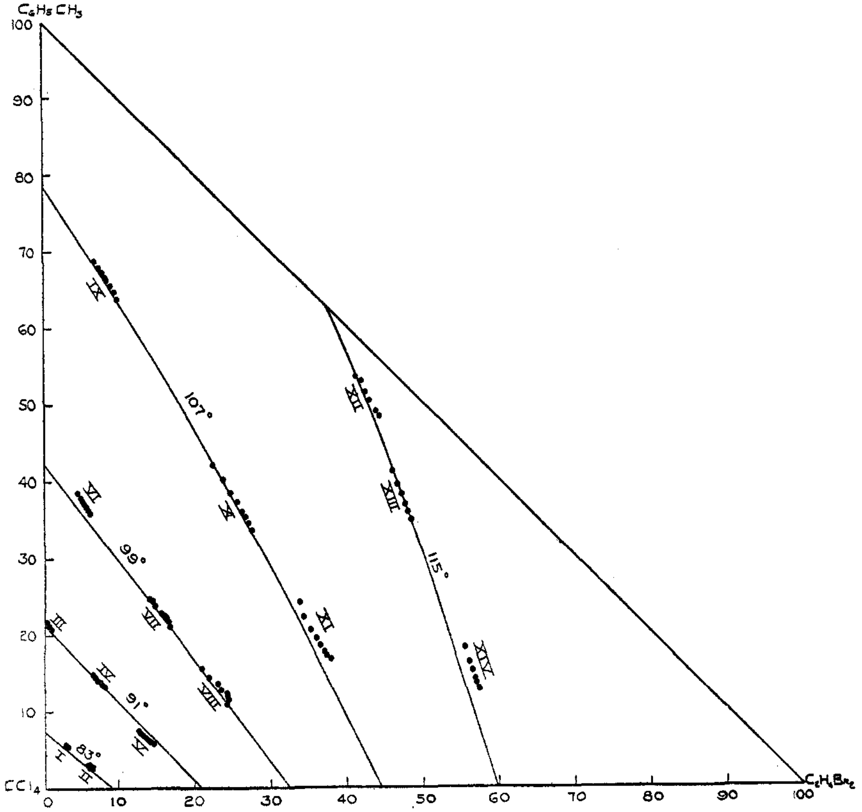

Fig. 1.

In the accompanying figure the curves represent the composition of the vapors evolved by the various liquid mixtures boiling at the stated temperatures.[1] The composition of the vapors yielded by the regulated stillhead are indicated by the several sets of points (the number near each set of points being that of the table, the results of which the set represents).

Conclusions.

Our tables and the figure answer plainly the questions under investigation.

(1) We had expected that at each stillhead temperature the distillates would have the same composition as vapors evolved by liquid mixtures boiling at the temperature of the stillhead; in other words, that the points

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[1] See Rosanoff, Schulze and Dunphy, This Journal, 36, 2480 (1914).

(by which we represent the composition of the distillates) would lie, in the diagram, *on the curves* which represent the composition of such vapors. As a matter of fact, the points are almost on the curves, the distance between each point and the curve to which it belongs representing in most cases only a fraction of one per cent.

(2) The different sets of points corresponding to each curve are widely separated, which shows that in the case of mixtures of three or more substances different distillates will be yielded by a regulated stillhead, if different mixtures are introduced into the still to begin with.

(3) The points of each separate set do not coincide, which shows that even during a single distillation the composition of the distillate does not remain constant.

(4) What is, however, of the greatest importance practically, is that this variation of the distillate during a single distillation is comparatively slight, as shown by the points of each set being close together. Moreover, the nearer the temperature of the stillhead is to the boiling point of the most volatile component, the more nearly constant is the composition of the distillate. Thus, as the diagram shows, for a stillhead temperature 7° above the boiling point of carbon tetrachloride, the separate points of each set can scarcely be distinguished; likewise, of course, the composition of the distillates as numerically expressed in Tables I and II is very nearly constant. *Practically the regulated stillhead can thus be used to obtain a uniform distillate from poly-component as well as from simple binary mixtures.*

(5) On the basis of the results obtained by Brown, of those of the first communication of the present series, and of those of this present communication, the working of the regulated stillhead may now be summed up in terms of the following general rule: *In distillations with a stillhead maintained at a constant temperature, the composition of the distillate is at every instant identical with that of a vapor evolved by a mixture whose boiling point equals the temperature of the stillhead. If the mixture is binary, the composition of the distillate is, in the course of a single distillation, constant. In those cases in which the binary boiling-point curve passes through a maximum or a minimum, the composition of the distillate depends on that of the mixture originally placed in the still. If the number of substances in the mixture is three or more, the composition of the distillate not only depends on that of the original mixture, but varies in the course of a single distillation. This variation, however, is moderate, and the nearer the constant temperature of the stillhead is to the boiling point of the most volatile component, the more nearly constant is the composition of the distillate.* An important limitation of this rule will be demonstrated in our next communication.

In conclusion it is a duty to recall that the cost of the apparatus used in this study was defrayed out of a grant from the Rumford Fund of the

American Academy, for which we here again cordially thank the Rumford Committee of the Academy.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH,
UNIVERSITY OF PITTSBURGH.

[CONTRIBUTION FROM THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE, LABORATORY OF CLINICAL RESEARCH, RUSH MEDICAL COLLEGE.]

A NEW METHOD OF PREPARATION AND SOME INTERESTING TRANSFORMATIONS OF COLLOIDAL MANGANESE DIOXIDE.

BY EDGAR J. WITZEMANN.

Received February 22, 1915.

Within the last few years several papers on the formation of colloidal manganese dioxide have appeared. Thus far, however, the intermediate formation of colloidal manganese dioxide in the ordinary oxidations of organic compounds with potassium permanganate has not been reported. The following paper is a report of some observations on this subject. In the course of the experiments it was found that the gelatinous form of colloidal manganese dioxide first obtained is slowly and automatically converted into a limpid colloidal solution. This transformation was studied somewhat more in detail and was found to be readily influenced (1) by the temperature at which the gel form was prepared, (2) by the concentration of the reacting solutions, (3) by the temperature to which the gel was subjected during the transformation, and (4) by the variations in the small concentrations of alkali necessary to cause the oxidation to take place rapidly.

The unusual chemical properties of manganese dioxide have for a long time occupied the attention of chemists, so that its existence as a colloid did not escape observation very long. Georgeu[1] boiled pure finely powdered Mn_3O_4 repeatedly with concentrated nitric acid and then washed the residue with water. When the wash waters were no longer acid the hydrated manganese dioxide went into solution, giving a brown liquid. He observed that the manganese dioxide is easily precipitated by the addition of very small amounts of nitric, sulfuric, or hydrochloric acids, ammonia, potassium or barium hydroxides and other compounds. Swiontkowski[2] found that on reducing a solution of potassium permanganate with pure neutral hydrogen peroxide a coffee-colored solution of colloidal manganese dioxide was obtained. This colloid was not obtained if the hydrogen peroxide was not neutral and was readily precipitated by the addition of very small quantities of acids and salts. Spring[3] and Spring

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[1] *Ann. chim. phys.*, [3] **66**, 154 (1862); *Jahresberichte*, **1862**, 155.

[2] *Ann. Chem. Pharm.*, **141**, 205 (1867).

[3] *Ber.*, **16**, 1142 (1883).